Photoactive Supramolecular Cyclodextrin Assemblies

Muath Atmeh

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Photoactive Supramolecular Cyclodextrin Assemblies

By

Muath Atmeh

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF DUBLIN INSTITUTE OF TECHNOLOGY IN FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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SCHOOL OF CHEMISTRY AND PHARMACEUTICAL SCIENCES

DUBLIN INSTITUTE OF TECHNOLOGY
June 2008
Ligands with a macrocyclic host unit attached to a photoactive metal core are of interest across a range of applications from luminescent or electrochemical sensors, light harvesting and energy-collection purposes. Their versatile properties and possibility of associating cyclodextrins with other molecules both covalently and non-covalently mean that these macrocyclic ligands can be employed in the design and the formation of supramolecular complexes.

A particularly attractive proposition is to combine the selective inclusion capabilities of CD with luminophores which may act as reporters of binding or other interactions at the cyclodextrin cavity. Ruthenium, osmium, and iridium polypyridyl complexes are particularly attractive reporters in this regard because of their visible emission and their useful redox properties. Their long lived excited states are particularly attractive providing significant scope for interaction with an included species compared with organic fluorphores, which can be very insensitive to their environments due to their fast radiative decays.

In this thesis, we exploited the properties of CD and ruthenium polypyridyl complexes in designing photoactive metallocyclodextrin where 5-amino-1,10-phenanthroline has been attached to the primary side of β-cyclodextrin. This ligand, β-CD-aphen has been used to design [Ru(bpy)\(_2\)(aphen-CD)]. [Ru(bpy)\(_2\)(aphen-CD) ][PF\(_6\)]\(_2\) exhibits an intense luminescence ascribed to a \(^3\)MLCT state at room temperature in DMF and water with \(\lambda_{\text{max}}\) at 618 nm, a lifetime of approximately 1 \(\mu\)s and quantum yield of \(\phi = 0.013\) in deaerated solution. The secondary side of cyclodextrin is still available. We exploited the idea that metals like Copper and Zinc can be coordinated to the secondary side in constructing of molecular assembly where the donor and acceptor are held together via covalent link through a bridge. We have designed a trinuclear metallocyclodextrin-based donor-acceptor complex where the dicopper (II) sites are hydroxo bridged to the secondary side of β-CD in [Ru(bpy)\(_2\)(aphen-CD)].
The donor and acceptor in our system are linked via a β-Cyclodextrin On the account of their relatively hydrophobic interiors; CDs have the ability to form inclusion complexes with wide range of Substrates. This idea has been exploited to bring the donor and the acceptor in a close proximity and study the energy and/or electron transfer in these novel supramolecular assemblies. The effect of anthraquinone and anthraquinoncarboxyclic on the luminescence of ruthenium was investigated in chapter three. In addition we demonstrate, for the first time, that the luminescence quantum yield and lifetime of Ru (II) polypyridyl center shows remarkable sensitivity to pH and we present detailed pH titrations for luminescence intensity and lifetime. The range of pH response is extremely broad, from pH 1 to pH 13 and alterations to luminescence quantum yield of greater than 60% are observed. In chapter 6 we have examined photoinduced transfer process between Ru and Ir metal centers in water mediated by non-covalent interactions through a cyclodextrin cavity. On the basis of the inclusion ability of β-CD and the redox properties of pyrene we have studied Ru-Ir interaction in trimer [Ir-(RuCD)$_2$] in aqueous solution. Formation of the Ru-Py-Ir trimer through cyclodextrins induces significant changes in the photophysical behavior of both pyrene and appended Ruthenium. We couldn't detect a significant change in the photophysical of Iridium metal centre. This means that communication between the two metal centers is very weak. This behavior may be attributed to the presence of pyrene moiety which blocks the interaction between the two metal centers. In [Ir-(RuCD)$_2$] pyrene acts as a store for the energy instead of mediating the transfer process. Future work on these complexes will include further studies on the nature of the electron transfer process. This will include, for example, more detailed transient absorption spectroscopy to discern the direction of transfer either Ir→Ru or Py→Ru or both.

We then extended our work to make homonuclear photoactive cyclodextrins dimers. These dimers comprised of two photoactive metal centers covalently attached to the primary side of γ-cyclodextrin.
In chapter 5, we exploit the inclusion ability to design a tetrameric metallocyclodextrins containing photoactive Ru(II) polypyridyl units covalently bonded to γ-CD. Then the cyclodextrin complexes were self-assembled with a fullerene moiety in 2:1 ratio to produce the tetramer. The synthesis and characterization of the complexes and in particular their spectroscopic electrochemical and photophysical properties described. We provide evidence for photoinduced processes and discuss the possibility of electron and energy transfers in these novel supramolecular assemblies.
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possible. Special thanks go to my family in Jordan for giving me the support and prayer.
**Abbreviations**

In figure legends, $b = \beta$, $g = \gamma$, $\text{Mn}2 = \text{Mn}_2$ and $\text{C}60 = \text{C}_{60}$

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>A</td>
<td>Acceptor</td>
</tr>
<tr>
<td>ANCD</td>
<td>Cyclodextrin-appended Anthracene</td>
</tr>
<tr>
<td>AQC</td>
<td>Anthraquinone-2-Carboxylic acid</td>
</tr>
<tr>
<td>BET</td>
<td>Back electron transfer</td>
</tr>
<tr>
<td>Bpy</td>
<td>Bipyridine</td>
</tr>
<tr>
<td>AQ</td>
<td>Anthraquinone</td>
</tr>
<tr>
<td>C</td>
<td>Chromophore</td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>Buckminsterfullerene</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled device</td>
</tr>
<tr>
<td>CD</td>
<td>Cyclodextrin</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlated spectroscopy</td>
</tr>
<tr>
<td>CS</td>
<td>Charge separation</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>Cys</td>
<td>Cysteine</td>
</tr>
<tr>
<td>CcO</td>
<td>Cytochrome c Oxidase</td>
</tr>
<tr>
<td>D</td>
<td>Donor</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DMF</td>
<td>N, N-Dimethylformamide</td>
</tr>
<tr>
<td>DPV</td>
<td>Differential pulse voltammetry</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>Fc/Fc$^+$</td>
<td>Ferrocene/ferrocenium ion</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infra red</td>
</tr>
<tr>
<td>FMS</td>
<td>Fluorescent Molecular Sensors</td>
</tr>
<tr>
<td>FRET</td>
<td>Fluorescence Resonance Energy Transfer</td>
</tr>
<tr>
<td>G</td>
<td>Guest</td>
</tr>
<tr>
<td>GCD</td>
<td>Guanidinocycloheptaamylose (Guanidinyl$\beta$-cyclodextrin)</td>
</tr>
<tr>
<td>His</td>
<td>Histidine</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HPLC</td>
<td>High pressure liquid chromatography</td>
</tr>
<tr>
<td>ic</td>
<td>Internal conversion</td>
</tr>
<tr>
<td>ILCT</td>
<td>Inter ligand charge transfer</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-red</td>
</tr>
<tr>
<td>IRF</td>
<td>Instrument response function</td>
</tr>
<tr>
<td>isc</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>LC</td>
<td>Ligand centred</td>
</tr>
<tr>
<td>LC/MS</td>
<td>Liquid chromatography/Mass spectroscopy</td>
</tr>
<tr>
<td>LiClO₄</td>
<td>Lithium perchlorate</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>LLCT</td>
<td>Ligand to ligand charge transfer</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand to metal charge transfer</td>
</tr>
<tr>
<td>M</td>
<td>Multiplicity</td>
</tr>
<tr>
<td>M*</td>
<td>Excited molecule</td>
</tr>
<tr>
<td>MC</td>
<td>Metal centred</td>
</tr>
<tr>
<td>MCA</td>
<td>Multichannel Analyzer</td>
</tr>
<tr>
<td>M.S.B</td>
<td>Magnetic susceptibility balance</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal to ligand charge transfer</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NBu₄BF₄</td>
<td>Tetrabutylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>N₂OR</td>
<td>Nitrous Oxide Reductase</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal hydrogen electrode</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOESY</td>
<td>Nuclear Overhauser effect spectroscopy</td>
</tr>
<tr>
<td>ODA</td>
<td>4, 4’ –Oxydianiline</td>
</tr>
<tr>
<td>OTs</td>
<td>Toslyate group</td>
</tr>
<tr>
<td>OTE</td>
<td>Optical Transparent Electrode</td>
</tr>
<tr>
<td>OTTLE</td>
<td>Optical Transparent Thin-layer Electrode</td>
</tr>
<tr>
<td>Aphen</td>
<td>5-Amino-1,10-Phenanthroline</td>
</tr>
<tr>
<td>PET</td>
<td>Photoinduced Electron Transfer</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene Glycol</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PMDA</td>
<td>Pyromellitic dianhydride</td>
</tr>
<tr>
<td>PMDI</td>
<td>Pyromellitic dimide</td>
</tr>
<tr>
<td>PMMO</td>
<td>Particulate methane oxidase monooxygenase</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
</tr>
<tr>
<td>PI</td>
<td>Photoinduced</td>
</tr>
<tr>
<td>Py</td>
<td>Pyridine</td>
</tr>
<tr>
<td>RR</td>
<td>Resonance Raman</td>
</tr>
<tr>
<td>Q</td>
<td>Quencher</td>
</tr>
<tr>
<td>S</td>
<td>Spin quantum number / Singlet state</td>
</tr>
<tr>
<td>SEC</td>
<td>Spectroelectrochemistry</td>
</tr>
<tr>
<td>SOD</td>
<td>Superoxide Dismutase</td>
</tr>
<tr>
<td>T</td>
<td>Triplet state</td>
</tr>
<tr>
<td>TAC</td>
<td>Time-to-amplitude converter</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time correlated single photon counting</td>
</tr>
<tr>
<td>TICT</td>
<td>Twisted Internal Charge Transfer</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Z</td>
<td>Atomic number / Collision frequency</td>
</tr>
<tr>
<td>Y&lt;sub&gt;z&lt;/sub&gt;</td>
<td>Thyrosine</td>
</tr>
</tbody>
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Chapter 1
General Introduction
1.1 Supramolecular chemistry

Supramolecular chemistry has been defined as the "the chemistry of molecular assemblies and intermolecular bond". It can be described as the study of systems, which contain more than one molecule, and it aims to understand the structure, function, and properties of these assemblies.

Traditional chemistry deals with the construction of individual molecules from atoms, whereas supramolecular chemistry deals with the construction of organized molecular "arrays". In Molecular chemistry, the unit is the molecule which consists of atoms linked strong association forces such as covalent and ionic bonds. In supramolecular assemblies different molecular arrays are linked together by weaker forces (non-covalent interactions). These non-covalent interactions are H-bonding, polar attractions, Vander-Waals and hydrophilic-hydrophobic interactions. The properties of the supramolecular system are greater than the sum of the properties the contributing parts. In the filed of supramolecular photochemistry the definition of a supramolecular compound is that of as "a group of molecular components that contribute properties that each component posses individually to the whole assembly (covalent or noncovalent)".

The key feature that distinguishes a supermolecule from a large molecule is the ability to split the supermolecule into individual molecular subunits, each with their own intrinsic properties. The properties of the subunits generally experience perturbation upon formation of supermolecule. This might lead to new approaches such as:

i- Intercomponent energy and electron transfer.

ii- Co i operative effect, for example the complexation of other species by two or more components.

The supermolecule may have new properties that are distinct from the properties of the subunits. The components of the supermolecule may have distinct spectroscopic, photophysical, photochemical and redox properties that govern the behaviors of the supermolecule. The essence of the difference between the supermolecule versus large molecule lies in the degree of the interaction between the electronic subsystems of the component units.
1.1.1 Host-Guest Chemistry

A ‘host-guest’ guest or supramolecule is formed when a molecule (host) binds another molecule (guest) by intermolecular forces. The relations with the resulting host-guest in supramolecular chemistry describes complexes that are composed of two or more molecules or ions held together in unique structural relationships by hydrogen bonding, ion–pairing, Vander Waals forces and/or hydrophobic interactions rather than those of covalent bonds. The host normally is a large molecule or aggregate such as an enzyme or synthetic cyclic compound with a suitable size hole or cavity. The guest may be a monoatomic species, a simple inorganic anion, or neutral molecule. The host is defined as “the molecular entity possessing convergent binding site”, (e.g. Lewis basic donor atoms, hydrogen donors etc.). The guest is defined as “the molecular entity possessing divergent binding sites”, (e.g. a spherical, Lewis acidic metal cation or hydrogen bond acceptor halide anion). Host cavities can include suitable guests, and thereby act as the building blocks for large functional architectures. The molecular recognition properties of the hosts for inclusion appropriate guest can be utilized in designing sensors, switches and nanoscale components. The popular hosts which have been studied include are cyclodextrins, calixarenes, cucurbiturils, porphorins, and crown ethers.

1.2.1 Calixarenes

Calixarenes are a popular and versatile class of macrocycle formed from the condensation from p-substituted phenol with formaldehyde. Since they contain bridged aromatic rings, they are members of the cyclophane family. The most common cyclic tetramer with p-t-butyl substituents termed p-t-butyl-calix[4]arene. The calixarenes are extremely versatile host frameworks and may act as hosts for cations, anions and neutral molecules. Calixarenes serves as a simultaneous receptor for cations and neutral molecules; the phenolic oxygen atoms at the calixarene lower rim act as a host for cations and the calixarene hydrophobic cavity also hosts a neutral guests as shown in Figure 1.1.
1.2.2 Crown ethers

The crown ethers are among the simplest and most appealing macrocyclic ligands, and are ubiquitous in supramolecular chemistry as hosts for both cations and neutral molecules as shown in Figure 1.2. They consist of a cyclic array of ether oxygen atoms linked by organic spacers, typically $-\text{CH}_2\text{CH}_2-$ groups. Their metal binding ability is higher than those of unidentate ethers such as diethyl ether due to the chelate and macrocyclic effects.

**Figure 1.1.** Conformations of calixarenes.
1.1.2 Cyclodextrins

Cyclodextrins (CDs), as they are known today, were called cellosin when first described by Villers. Soon after Shardinger identified the three naturally occurring cyclodextrins $\alpha, \beta, \gamma$. By the mid of 1970’s, each of natural cyclodextrins had been structurally and chemically characterized. Structurally, the most common cyclodextrins consist of 6, 7, or 8 $\alpha, \beta, \gamma$ respectively. D-glucosepyranosyl units connected by alpha 1, 4-glycosidic linkages. The most stable three dimensional molecular configuration for these non-reducing cyclic oligosaccharides takes the form of a toroid with the upper (larger) and lower smaller opening of the toroid presenting secondary and primary hydroxyl groups, respectively, to the solvent environment. The interior of the toroid is hydrophobic as a result of hydrogen atoms and the glycosidic oxygen atoms.

The structure of $\beta$-cyclodextrin (Mwt=1134.98 g/mol) is shown in Figure 1.3.
The structure of the glucose units with secondary hydroxyl in 2-position and 3-postion and primary hydroxyls in 6-position are shown in Figure 1.3. The chemical and physical properties of cyclodextrin are presented in Table 1.1. α, β, and γ CDs are water soluble due to their hydrophilic exterior with their solubilities 14.5, 1.85, and 23.2 g/100 mL for α, β, γ-cyclodextrins, respectively. The β-Cyclodextrin has the lowest water solubility of all CDs. This is thought to be due to hydrogen bonding between C-2-OH, and C-3-OH which form a secondary belt which makes the β-CD a very rigid structure.
Table 1.1 Chemical and physical properties of Cyclodextrins

<table>
<thead>
<tr>
<th>Cyclodextrin Type</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Glucose Units</td>
<td>6</td>
<td>7</td>
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<tr>
<td>Bulk Density, g/cm³</td>
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<td>0.4 – 0.7</td>
<td>0.4 – 0.7</td>
</tr>
<tr>
<td>Water Solubility (25 °C), g/100 mL</td>
<td>14.5</td>
<td>1.8</td>
<td>23.2</td>
</tr>
<tr>
<td>Water</td>
<td>&lt;10%</td>
<td>&lt;14%</td>
<td>&lt;11%</td>
</tr>
</tbody>
</table>

As a consequence of the $^4C_1$ conformations of the glycopyranose units, all secondary hydroxyls are situated on the wide rim of the cone, whereas all primary hydroxyls are placed at the narrow rim. The CD structure is generally described as a truncated cone. As described the hydrogen atoms and glycosidic oxygen bridges line the cavity.
Figure 1.4. Molecular dimensions of cyclodextrins.

Cyclodextrins undergo minimal hydrolysis in the presence of weak acids and hydrolyze to yield a mixture of oligosaccharides. These oligosaccharides range from an open ring to fragmented glucose units. The rate of hydrolysis is dependent on the concentration of an acid and the temperature. No detectable hydrolysis takes place in the presence of strong base. Under normal experimental conditions at pH higher than 3.5 and temperature lower than 60 °C, CDs are stable.

In addition to the three common types of cyclodextrins shown in Figure 1.4 with their molecular dimensions, the nine-membered δ-cyclodextrin was isolated from the commercially available CD conversion mixture by chromatography.

The solubility of δ-cyclodextrin is greater than β-cyclodextrin but less than that of α-, γ-cyclodextrin. δ-cyclodextrin is the most stable of CDs. The larger CDs do not have a regular cylinder shaped structure. They are collapsed, so their real cavity is in fact smaller than that of γ-CD as shown in Figure 1.5. Their molecular inclusion ability is restricted due to the weaker driving force for complex formation.
1.1.3 CD-Inclusion complexes:

On account of their relatively hydrophobic interiors, CDs have the ability to form inclusion complexes with a wide range of hydrophobic substrates. Studies involving the inclusion of solute into cyclodextrin are important due to the resulting improvement of the aqueous solubility, enhanced stability against chemical and photochemical degradation and the possibility of controlled drug release, which are the key applications in drug formulations. In addition, the solute inclusion can lead to many other interesting phenomena such as enzyme biomimics, in catalysis, and for the separation of isomers (chiral recognition) among others. In the host-guest complexes of cyclodextrin, a guest molecule is held within the cavity of the cyclodextrin as shown in Figure 1.6. Complex formation is due to dimensional fit between host cavity and guest molecule. No covalent bonds are broken or formed during formation of the inclusion complexes.
Figure 1.6. Forming an inclusion complex involves multiple interactions between active, solvent and cyclodextrin.\textsuperscript{18}

The main driving force of the complex formation is the release of the enthalpy-rich water molecules from the cavity. Water molecules are displaced by more hydrophobic guest molecules present in the solution to obtain apolar-apolar association and the decrease of cyclodextrin ring strain resulting in a more stable state.\textsuperscript{19}

The binding of guest molecules within the host cyclodextrin is not fixed or permanent, but rather is a dynamic equilibrium process, which can be illustrated in the following equation.\textsuperscript{20}

\[
\text{CD} + \text{G} \rightleftharpoons \text{CD-G}
\]

CD-G is the inclusion complex between CD (cyclodextrin) and a guest (G).

The stability of CD-G complex can be expressed in terms of a formation constant ($K_f$) or the dissociation constant ($K_d$).

\[
K_f = \frac{[\text{CD-G}]}{[\text{CD}][\text{G}]}
\quad \text{Equation 1.1}
\]

\[
K_d = \frac{1}{K_f}
\quad \text{Equation 1.2}
\]
The affinity of a host for a particular receptor over that of another host can be estimated from the ratio of the binding constant of the two prospective guests:

$$\text{Selectivity} = \frac{K_{\text{Guest}_1}}{K_{\text{Guest}_2}}$$  \hspace{1cm} \text{Equation 1.3}

The binding constant may be estimated by any experimental technique that can yield information about the concentration of the complex [CD-G], with changing concentration of G. In practice the methods that are used in common are potentiometric titration, nuclear magnetic resonance, fluorescence titration and calorimetric titration. Only fluorescence titration will be discussed in detail here, as it was the method employed in this thesis.

In a fluorescence titration the measurements are based on the magnitude of fluorescence intensity in relation to fluorophore concentration (Guest, G). For 1:1 complex with host, CD, with stability constant is given as:

$$K_S = \frac{[\text{CD-G}]}{[\text{CD}][G]}$$  \hspace{1cm} \text{Equation 1.4}

The fluorescence intensity \(I\) is given by:

$$I = k_G [G] + K_{11} [\text{CD-G}]$$  \hspace{1cm} \text{Equation 1.5}

Where \(k_G\) and \(K_S\) represent proportionality constants for guest and the 1:1 host-guest complex respectively.

In the absence of the host the fluorescence intensity \(I_0\) is given by:

$$I_0 = k_G^0 G_t$$  \hspace{1cm} \text{Equation 1.6}

Where \(G_t = [G] + [\text{CD-G}]\)

Combining the two relationships gives the following equation:

$$\frac{I}{I_0} = \frac{k_G / k_G^0 + (K_{11} / k_G^0)K_S[H]}{1 + K_S[H]}$$  \hspace{1cm} \text{Equation 1.7}

Equation 1.7 provides the basis of most fluorometric methods for stability constant \(K_S\) determination. The equation is simplified when host-guest complex is non-fluorescent, \(k_G = k_G^0\) and \(K_{11} = 0\), to give:

$$\frac{I_0}{I_t} = 1 + K_S[CD]$$  \hspace{1cm} \text{Equation 1.8}
A simple plot of $\frac{I_0}{I_f}$ against [CD] from the titration of a quenching host solution into a guest solution should yield a straight line of slope $K_S$. This form of the equation is the same as that of Stern-Volmer see equation 1.21.

The binding constant was found to be temperature dependent. This was obtained from experiments on the inclusion complexes of chlorophenols with $\beta$-CD.\textsuperscript{21}

The 1:1 and 1:2 guest/host inclusion complexes have been widely reported in the literature depending on the relative size of host and guest.\textsuperscript{22}

Significant changes in the luminescence of the guest may result upon inclusion in the cavity.\textsuperscript{23} These changes can be attributed largely to the fact that the structural conformation of the cyclodextrin protects the analyte from external quenching agents. Ru(II) and Re(I)-polypyridine which possess phenyl-substituted ligands exhibit significant interaction with cyclodextrin as shown in Figure 1.7. CD binding interaction resulted in the enhancement of fluorescent intensity due to protection of the complex from oxygen quenching.

\textbf{Figure 1.7.} Schematic of $\beta$-CD binding to the anchor ligand, a 4-alkylpyridine.  \textsuperscript{23}
The cyclodextrin cavity provides the included chromophores with altered microenvironment of the guest changing quantum efficiencies and hence the intensities of the luminescence. Another impact of inclusion may be the reduction of degrees of freedom of the motion of the guest, for example, rotation of the guest may be hindered inside the cavity, which results in a decrease in the vibrational deactivation of the excited state.

Inclusion complexes of the anesthetic 2-(diethylamino) ethyl-p-amino-benzoate (Novocain) under several circumstances have been investigated. Novocain is a tertiary amine, which shows characteristic fluorescence intensity upon inclusion in the β-cyclodextrin. The fluorescence intensity was enhanced in both acidic and basic medium. The emission of the novociane originates from the twisted internal charge transfer (TICT). TICT emission depends on the polarity of the medium; as the polarity decreases the emission shifts to a shorter wavelength. Inclusion of novociane in the cavity results in a strong increase of fluorescence emission, since the resulting induced molecular rigidity of the fluorophore thus reducing the radiationless decay via molecular relaxation of the TICT state.

The detection limit of many analytes can be increased upon inclusion in the cavity where fluorescence intensity is increased. For example retinal is insoluble in water and is non-fluorescent in solution at room temperature. Upon inclusion in the β-, γ-cyclodextrin, Retinal emits luminescence at 450 nm even in deoxygenated aqueous solution.

The ability of CDs to include part of an organometallic complex in their internal hydrophobic cavities has been investigated for a number of complexes. The inclusion generally modifies the chemical, electrochemical, and photochemical properties of organometallic compounds.

1.1.4 Larger Arrays built on CD Host-Guest Interaction:

On the basis of simple inclusion, complexation of CDs (receptors) and target molecules (substrates), many nanometer-sized supramolecular aggregates have been constructed
and their properties as molecular devices, machines and other functional materials explored. Mechanically interlocked molecules such as rotaxanes and catenanes are suitable candidates for the construction of molecular machines. Many kinds of molecular components can be used to construct molecular-level machines. Crown ethers, cyclophanes, calixarenes, and cyclodextrins have extensively been used as cyclic components in the construction of the supramolecular structures.

Cyclodextrins offer several advantages compared to other ring molecules due to the characteristics mentioned above. Rotaxanes consist of a long, approximately linear molecule threaded through a macrocyclic ring. Rotaxanes are examples of mechanically interlocked molecules. Typically they consist of one or more rings and one or more molecular axes Figure 1.8. Because they have a rotor and axle, rotaxanes are prototypes of molecular machine. CDs spontaneously incorporate guest molecules, a necessary requisite for rotaxane formation. Cyclodextrin rotaxanes were first reported in 1978, using α-cyclodextrin as the rotor of rotaxane, metal complexes were used as stoppers. The stoppers should be a little bigger than the diameter of the CD cavity to guarantee stability of the rotaxane.

![Figure 1.8. Ring-slide on cyclodextrin polyrotaxane.](image)

---

26. [Reference]
27. [Reference]
28. [Reference]
29. [Reference]
Despite of the non-covalent interaction between axes and rings, rotaxanes are stable entities due to high free energy of dissociation, $\Delta G_{\text{diss}}$. Threading of the axis through the ring is a necessary requirement for the synthesis of a rotoxane. The template synthesis has proven to be an efficient method for preparing rotaxanes because it leads to high rotaxane yields. The template method involves the host-guest interaction between the axis and the ring. Threading many CD rings onto a polymer chain, Figure 1.8, forms a linear CD polyrotaxane, which were first reported by A. Harada. Polyethylene glycol (PEG) has been widely used as a linker in the formation of polyrotaxanes. An example of polypseudorotaxanes is shown in Figure 1.9. In this system a nano-scaled functional molecular assembly was formed by the reaction of cyclodextrin-based complexes of $\alpha$-, $\beta$-, $\gamma$-cyclodextrins and 4,4'-dipyridine with Ni(II) or Cu(II) ions in aqueous solution.

Figure 1.9. Polypseudorotaxanes constructed by the coordination linkage of Cu(II) with $\gamma$-cyclodextrins and 4,4'-dipyridine inclusion complex.

The results showed that these polypseudorotaxanes existed as individual linear arrays at a low concentration but tended to form polymeric rod-like fibers at a relatively high concentration. Harada et al. prepared tens of CD-based polypseudorotaxanes and polyrotaxanes by threading many CD units onto a polymer chain and then extended them to form molecular tubes through the covalent cross-linking of adjacent CD units in a polyrotaxane. Stoddart et al. prepared polyrotaxanes and reviewed a number of CD-containing aggregates formed by host-guest complexation, which exhibited significant chemical and biological functions. Li and McGown reported the ability of $\beta$- and $\gamma$-CDs to construct molecular nanometer-scale tubes using diphenylhexatrienes as
linkers.\textsuperscript{35} Moreover, molecular semiconductors and nanoengineered devices at supramolecular level have also been prepared by threading a charge-transport macromolecule.\textsuperscript{36}

Molecular shuttles have been prepared by exploiting the movement of the cyclodextrin along the polymer chain in the polyrotoxanes.\textsuperscript{37} A molecular shuttle was designed from \(\alpha\)-cyclodextrin as a ring, two polymethylene chains as stations, 4,4'-bipyridinium units as linkers, and dinitrophenyl groups as stoppers, Figure 1.9. In this molecular shuttle the cyclodextrin moves back and forth along the chain. Shuttling behaviour of the molecular shuttle is solvent- and temperature sensitive and could be controlled by double interactions: hydrophobic interaction between a cyclodextrin ring and a station and a repulsive interaction between a cyclodextrin ring and a linker. This is a new method to control the mobility of a bead in a molecular shuttle.
Figure 1.10. (a) Chemical structure of methylated polyrotaxane. (b) Stimuli (temperature)-induced change in distribution of methylated CDs in a polyrotaxane.

A novel sol-gel transition at elevated temperature based on polyrotaxane was reported, Figure 1.10. The mechanism postulated was the sliding behavior of the methylated α-cyclodextrins along the PEG chains. The authors simply controlled the number of cyclodextrins threaded to each PEG chain so that there were free spaces for sliding, and adamantanyl groups behaved as stopper to prevent de-threading of the cyclodextrin at elevated temperature. The cyclodextrins can only closely pack with each other at the chain end to form a block and crystallize into crosslinking points. Hence, gelation thus occurs.
A molecular wire was recently reported using a polyrotaxane as an orientational control molecule shown in Figure 1.11.\(^{39}\)

For application to molecular electronics, the wire is a very important component because it can be used as an interconnection between a metal electrode and other functional molecules, such as a molecular diode or transistor, to create complex molecular circuits. It is also important that the conducting part of a molecular wire should have metallic characteristics. For these reasons, conducting polymers are very attractive materials among the different candidates for molecular wires. Their electrical conductivity can be controlled over the full range from insulator to metal by chemical or electrochemical doping. They can be synthesized with highly controlled lengths and can be integrated in complex circuits by chemically bonding with other functional molecules without changing their electronic properties. In order to prevent the possible interaction between different molecular wires it would be better if a single polymer chain were to be encapsulated into a bulky insulated structure and hence forming a molecular enamel wire. According to the "molecular enamel wire" concept, the insulators are placed around a conducting centre. It has been also suggested that the "molecular enamel wire" would be one of the key concepts for realizing a high performance molecular supercomputer.

The molecular wire in Figure 1.11 was designed using a self-organized interconnect method. This method requires three kinds of molecules: interface control molecule (4-iodobenzenthiol), orientation control molecule (polyrotoxane), and a function control molecule (stilbene, diarylethene). Firstly, the interface molecules are bound to two gold nanoelectrodes. Secondly, the orientation control molecules are attached to the interface control molecules. This π-system is covered with α-cyclodextrin to keep the molecular structure straight and to control the growth direction of the molecules along
the electrode spacing. The third step is to connect both modified electrodes using a function control molecule which leads to the formation of a molecular wire.

### 1.2 Chemically Modification of cyclodextrins

Many different chemical moieties may be introduced onto the cyclodextrin molecule by reaction with hydroxyl groups. Modification of cyclodextrins have been the focus of much research for example, in attempts to mimic the catalytic activity of enzymes and the binding ability of antibodies.

Key synthetic challenges in selective modification of CD are provided by the presence of the hydrophobic cavity and the large number of hydroxyl groups. Three hydroxyls present in the cyclodextrins are available for modification. Those at the 6-position are the most basic, and those at the 2-position are the most acidic, and those at 3-position the most inaccessible. Thus reactive reagents will not only react with hydroxyl groups at the 6-positions but also with those on the secondary side; whereas less reactive reagents will react more selectively with the 6-position hydroxyl groups. Since hydroxyl groups present at 2-, 3-, 6-positions compete for reagent and making selective modification extremely difficult. Another problem can arise where the cavity may complex the reagent depending on reagent properties. To avoid this complication protection of one side is first achieved, then formation of the incoming electrophile to hydroxyl groups at 6-positions. The most popular method for the monomodifications at 6-position is by nucleophilic attack of a reagent containing an appropriate group. 6-Tosylcyclodextrins are the most important precursors for a variety of modified cyclodextrins because this nucleophile can selectively attack the electrophilic carbon atom at 6-position to produce a corresponding functionality.

A nucleophilic displacement of the tosyl group by suitable nucleophiles such as iodide, azide, thioacetate, hydroxylamine, alkyl or polyalkylamines and bromide afford monoiodo-, azido, thio, hydroxylamine, or alkylaminocyclodextrins. This strategy has been exploited in synthesis of metallo-cyclodextrins. Di, Tri, and multisubstitution have been also achieved. Persulfonates are generally prepared from cyclodextrins and large excess of sulfonylchloride in pyridine.
Per-6-deoxy-6-substituted cyclodextrins are easily obtained by displacing the 6 sulfonate groups with suitable nucleophiles such as halides, azides, or thiolates. Perbromocyclodextrins can be obtained by the reaction of cyclodextrins with methanesulfonylbromide in DMF at high temperature. Another report has shown in detail the synthesis of per-bromocyclodextrins by the reaction of cyclodextrins with Vilemeier-Haack reagent [(CH$_3$)$_2$NCHBr]$^+$ Br$^-$.  

A series of modified γ-cyclodextrins with flexible or rigid caps were used as a chiral supramolecular host for mediating the enantiodifferentiating photocyclodimerization of 2-anthracenecarboxylic.  

Another interesting example is the synthesis of two derivatives of β-cyclodextrin, shown in Figure 1.12. Both of which have been shown to act as nanomachines having a photochemical on/off switch. The molecular machine is illustrated in Figure 1.12.

**Figure 1.12.** A molecular pump based on modified β-cyclodextrin.

Here, this molecular pump comprises of a piston; aryl substituent attached to cyclodextrin, a cylinder, the cyclodextrin, and a pump fuel, which is the 1-adamantanol. The operation of on/off switch depends on the conformations of the aryl substituents upon inclusion of the 1-adamantanol in the cavity. β-cyclodextrin modified with cholic acid and deoxycholic acid was recently prepared. These derivatives have the ability to act as anion recognition probes.
1.3 Molecular Photochemistry and photophysics:

The term photochemistry is the chemistry that deals with the excited electronic state, while the thermal or ordinary chemistry deals with the electronic ground state. Along with photophysics, photochemistry is combined to describe the excited state processes. The term photophysics refers to physical mechanism and deactivation of an excited state, shown in the Jablonski Diagram Figure 1.13. According to the Born-oppenhiemer approximation each electronic state is represented by a curve showing potential energy plotted against intermolecular distance. Horizontal lines indicate the vibrational states. The equilibrium bond distances and the shapes of potential-energy curves vary for different electronic states of a molecule, and the spacing of the vibrational levels is therefore different. Figure 1.14 shows two electronic states of a diatomic molecule.

Each electronic state can be described mathematically by a multidimensional Morse potential, with vibrational and rotational levels within it. The energy well associated with the ground state of the molecule lies lower in energy than the wells associated with the excited states. The structure of the excited state is different from the ground state, since the distribution of electrons around the nuclei is different in different states of the molecule.

At room temperature the majority of the molecules will be in the \( v = 0 \) vibrational level of the ground state. Before transition, the molecules who are in the ground vibrational state \( v = 0 \) at the most probable position (the center of the line). According to Frank-Condon principle, Figure 1.14, the transition is so fast that there is no chance for intermolecular distance to change. The transition must be a vertical transition from the ground state to the positions above it on the curve representing the excited electronic state.

An electron can move from the ground state energy level of a molecule to a higher level (i.e. an unoccupied orbital of higher energy) if appropriate energy is supplied, \( E = h \nu \).

In almost all photochemical reactions, a molecule absorbs one quantum (\( h \nu \)) of the radiation to induce reaction.

Absorption of one quantum of light by molecule A gives the excited state \( A^* \)
\[ A + h\nu \rightarrow A^* \]

Photochemistry is typically initiated by visible or UV photons, which have enough energy to strongly effect chemical bonds.

After the absorption, the photon energy \( h\nu \) is degraded in a variety of processes that induce chemical or physical changes:

1. \( A^* \) can undergo a chemical reaction to form another species, \( K_{\text{chemical}} \).
2. \( A^* \) can decay to the ground state with the emission of photon \( K_{\text{radiative}} \).
3. \( A^* \) can decay to the ground state without emission \( K_{\text{nonradiative}} \).

**Figure 1.13.** Modified *Jablonski* diagram, the electronic states of the excited singlet and triplet states in addition to the ground electronic states.

The photophysical processes, which occur between the absorption and emission of light, are summarized by *Jablonski* diagram Figure 1.13. In most organic molecules, all electrons in the ground state are spin paired. A molecule in which all spins are paired is a singlet (S), while one in which two unpaired electrons have the same spin is called a triplet (T). The singlet electronic states are denoted \( S_0 \) (Ground state), the lowest excited state is called \( S_1 \), the next is called \( S_2 \) ... etc, and triplet states are similarly labeled \( T_1, T_2, T_3 \), etc.
Transitions from the ground state to an excited state having the same spin multiplicity value are allowed and generally give an intense band, whereas transitions to excited states of different spin multiplicity values are forbidden and cannot normally be observed in the absorption spectra or are very weak.

Figure 1.14. Top: Potential energy diagrams with vertical transitions (Frank-Condon principle). Bottom, shape of the absorption bands; the vertical broken lines represent the absorption lines observed for a vapor, whereas broadening of the spectra is expected in solution (solid lines).\textsuperscript{53}

Following light absorption, several processes usually occur in which excited states can be deactivated either radiative (i.e. with emission of a photon) or non-radiative processes, these processes are:
1.3.1 **Internal Conversion:**
This process is a non-radiative transition between electronic states of the same spin multiplicity. The time-scale of this process is $10^{-13} - 10^{-11}$ s, and it competes effectively with fluorescence and intersystem crossing.

1.3.2 **Fluorescence:**

Emission of photon accompanying the $S_1 \rightarrow S_0$ relaxation is called fluorescence. This spin allowed radiative transition is usually fast (of the order of $10^{-9} - 10^{-8}$ s).

1.3.3 **Intersystem Crossing (ISC):**

ISC is a non-radiative transition between two isoenergetic vibrational levels belonging to electronic state of different multiplicities. ISC may be fast enough ($10^{-7} - 10^{-9}$ s) to compete with other pathways such as fluorescence and internal conversion ($S \rightarrow T$). Crossing is forbidden process because it occurs between states of different multiplicities, but it becomes possible due to spin-orbit coupling which relaxes the formal assignment of singlet and triplet.

1.3.4 **Phosphorescence:**

Spin forbidden radiative transitions can also be observed as a luminescence, which is called phosphorescence. Phosphorescence is the $T_1 \rightarrow S_0$ transition. But because of very slow rate on the order $10^{-3} - 10^1$, for typical organic molecules at room temperature in fluid solutions, non-radiative routes of deactivation through phosphorescence are almost impossible to observe. The process is forbidden but it can be observed due to spin orbit coupling. Molecules containing heavy atoms such as bromine and iodine or metals facilitate ISC and thus enhance phosphorescence quantum yields. Phosphorescence spectrum occurs at wavelengths longer than fluorescence in a given molecule because the energy level of the lowest vibrational level of the triplet state $T_1$ is lower than that rate of the single state $S_1$.  

24
Relaxation through ISC or IC to the ground state typically occurs to a higher vibrational ground-state level, which then quickly reaches thermal equilibrium. Therefore, the emission spectrum is always typically a mirror image of the absorption of the $S_0 \rightarrow S_1$. According to the Jablonski diagram the energy of the emission is less that of the absorption. Therefore, the fluorescence spectrum is located at lower energy than the absorption spectrum, called Stokes shift as shown in Figure 1.15. Fluorescence emission in fluid solution occurs from $S_1$ and therefore their characteristics do not depend on the excitation wavelength. The 0-0 transition is usually the same for absorption and fluorescence. For organic molecules the emission of $S_1 \rightarrow S_0$ is a typically mirror image of the absorption spectrum of the $S_0 \rightarrow S_1$ transition. This similarity occurs because electronic excitation does not greatly alter the nuclear geometry.

![Stokes shift](image)

**Figure 1.15.** Absorption (A) and Fluorescence (F) spectra and the Stoks shift

### 1.4 The fluorescence lifetimes and quantum yield:

#### 1.4.1 Lifetimes
The luminescent lifetime and quantum yield are key measurable characteristics of a fluorophore. The lifetime indicates the time available for the fluorophore to interact or diffuse in its environment, and hence the quantity of information available from its emission. The lifetime of the excited state is defined as ‘the average time the molecule spends in the excited state prior to return to the ground state’.

The rate constants for key photophysical processes outlined in Jablonski diagram can be written as follows:

For de-excitation from $S_1$:

- $k^s$: The rate constant for fluorescence.
- $k^s_{ic}$: The constant for internal conversion.
- $k^s_{isc}$: The rate constant of the intersystem crossing.

For deactivation from $T_1$:

- $k^T_r$: Rate constant for radiative deactivation (phosphorescence).
- $k^T_{nr}$: Rate constant for non-radiative deactivation (ISC).

The rate constant of the non-radiative pathways is given by:

$$k^s_{nr} = k^s_{isc} + k^s_{ic}$$  \hspace{1cm} \text{Equation 1.9}

The overall rate constant of the deactivations pathways from the $S_1$ is given as:

$$k_{\text{decay}} = k^s_r + k^s_{nr}$$  \hspace{1cm} \text{Equation 1.10}

The lifetime of the singlet excited state, $\tau_s$, is given by the inverse of $k_{\text{decay}}$:

$$\tau_s = \frac{1}{k^s_r + k^s_{nr}}$$  \hspace{1cm} \text{Equation 1.11}

If fluorescence is the only pathway of deactivation from the singlet state then the lifetime will be:

$$\tau_s = \frac{1}{k^s_r}$$  \hspace{1cm} \text{Equation 1.12}
\( \tau_s \) is called the radiative lifetime.

The lifetime decays exponentially from the triplet state with a time constant \( \tau_T \), which is given by:

\[
\tau_T = \frac{1}{k_r^T + k_{nr}^T}
\]

Equation 1.13

### 1.4.2 Quantum yields

The quantum yield of fluorescence, \( \Phi_F \), is the number of emitted photons relative to the number of the absorbed photons i.e the fraction of excited molecules that return to the ground state \( S_0 \) with emission of fluorescence. The process is governed by the rate constants \( k_r^S \) and \( k_{nr}^S \) which depopulate the excited state. The quantum yield, \( \Phi_F \) is related to the radiative and non-radiative rate constants by:

\[
\phi_F = \frac{k_c}{k_r^S + k_{nr}^S} \text{or } \phi_F = k_r^S \tau_s
\]

Equation 1.14

The quantum yields of intersystem crossing (\( \Phi_{isc} \)) and phosphorescence (\( \Phi_P \)) are given by:

\[
\phi_{isc} = \frac{k_r}{k_r^S + k_{nr}^S} = k_{isc} \tau_s
\]

Equation 1.15

\[
\phi_P = \frac{k_r}{k_r^T + k_{nr}^T} \phi_{isc}
\]

Equation 1.16

A photochemical quantum yield of 0.1 is significant and means that the molecule is quite emissive. A radiative quantum yield as low as \( \text{ca.} 10^{-4} \) or so can be detected by human eye.
1.5 Quenching of the excited state of a metal complex:

As mentioned excited states return to the ground state via radiative and non-radiative deactivation pathways. On the interaction with another chemical species, the emission of an excited state may decrease or be eliminated completely i.e. the emission has been quenched. Quenching is a non-radiative deactivation of an excited molecule A* by a quencher molecule. Quenching involves an energy or electron transfer between the excited state of one molecule (excited state A*) and the ground state of another molecule (the quencher, Q). The quenching can lead to a chemical reaction between the donor and the acceptor, or quenching can involve energy transfer where no new chemical species are formed.

The emission characteristics such as decay time and/or emission quantum yield of A* is affected by the presence of Q.

Excitation of a molecule by light pulse in the presence of quencher (Q) reduces the excited-state of A* population and consequently the fluorescence intensity which decreases more rapidly than in the absence of Q.

Quenching occurs in cases where donor and acceptor present in solution (intermolecular) or are covalently linked to each others (intramolecular).

In an intermolecular process there are two mechanisms which can account for the quenching of the excited A* by quencher Q. Those two mechanisms are known as static or dynamic quenching

a) If the quenching occurs through a diffusional motion with encounters between the fluorophore (M) and quencher (Q) during the excited-state lifetime, then the quenching is called dynamic quenching.

The fluorescence decay in the presence of quencher Q is:

\[ \tau = \frac{1}{(1/\tau_0 + k_q[Q])} \]  

Equation 1.17

Hence:-

\[ \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] \]  

Equation 1.18
The fluorescence quantum yield in the presence of quencher is

\[ \Phi = \frac{K_r}{(K_r + K_{nr} + k_q[Q])} = \frac{k_r}{1/\tau_0 + k_q[Q]} \]  

Equation 1.19

Whereas in the absence of quencher it’s given by

\[ \Phi_0 = k_r \tau_0 \]  

Equation 1.20

Therefore

\[ \frac{\Phi_0}{\Phi} = \frac{I_0}{I} = 1 + k_q \tau_0[Q] = 1 + K_{sv}[Q] \]  

Equation 1.21

Where \( I_0, I \) are the steady state fluorescence intensities in the absence and in the presence of the quencher, respectively; \( K_{sv} \) is the Stern-Volmer constant which is given by \( K_{sv} = k_q \tau_0 \). If the quenching is known to be static \( K_{sv} \) will be simply \( K_D \). Otherwise this constant will be described as \( K_{sv} \). Because the linear dependence of \( I_0/I \) on the quencher \( [Q] \), the quenching data are usually presented by a plot of \( I_0/I \) against \( [Q] \) which is called Stern-Volmer plot. The y-intercept of Stern-Volmer plot equals to one and the slope is \( K_{sv} \) or \( K_D \). We can obtain information from the plot that helps to define the mechanism of quenching. If the plot is linear this can confirm the presence of one class of fluorophore that is available for the quencher. Deviation of Stern-Volmer Plot from linearity to x-axis may indicate the presence of two classes of fluorophores one of them is inaccessible to quencher. Linear Stern-Volmer does not confirm that the collisional quenching has occurred, as static quenching also shows a linear Stern-Volmer plot.

b) Static quenching occurs either if \( Q \) is in a large excess or in rigid matrix where \( A^* \) and \( Q \) cannot diffuse so there is a high probability that \( A^* \) and \( Q \) will be in a close contact at the time of excitation, so that the interaction is significant or upon formation of a non-fluorescent complex between \( A \) and \( Q \).

The term Static quenching implies either the existence of a sphere of effective quenching or the formation of a ground state non-fluorescent complex. The dependence of the fluorescence intensity on quencher concentration in static quenching can be derive the association constant for the complex formation.
In Perrin “action volume” model, usually applied in circumstances where donor/acceptor cannot diffuse as polymer matrix, of static quenching; each excited molecule is surrounded by a sphere is called the sphere of effective quenching. If one (or several ) quenchers $Q$ are located inside this sphere ($V_q$) the quenching is assumed to be complete.

But if there is no quencher $Q$ in the range of action volume, then $A^*$ emits as if there is no quencher. In the case where $Q$ and $A$ form 1:1 non-fluorescent complex the excited-state lifetime of uncomplexed fluorophore remains constant, in contrast to dynamic quenching, but the fluorescence intensity decreases according to the following equation:

$$I_0/I = 1 + k_s [Q] \quad \text{but } \tau_0/\tau \text{ is constant}$$

Equation 1.22

The relation between $I_0/I$ and $[Q]$ is linear; $K_s$ is the association constant of the non-fluorescent complex.

The lifetime measurements can be used to distinguish between static and dynamic quenching. In both cases a linear relationship is thus obtained from a Stern-Volmer plot, but in the case of static quenching there is no change in the excited state lifetimes, whereas in the case of dynamic the ratio $I_0/I$ is proportional to the ratio of $\tau_0/\tau$ of the lifetimes.

In many cases both static and dynamic quenching can occur simultaneously. In this case upward curvature of Stern-Volmer plot is observed. Therefore, equation 1.19 was modified to account for upward curvature when both static and dynamic occur for the same fluorophore. The equation is given as:

$$I_0/I = 1 + (K_D + K_S) [Q] + K_D K_S [Q]^2$$

Equation 1.23

### 1.6 Photophysics Ru(II), Os(II), and Ir(III) polypyridine complexes:

$\text{Ru}^{2+}$ is a $d^6$ system and the polypyridine ligands most commonly applied in photoactive Ru complexes are colorless molecules possessing $\sigma$-donor orbitals localized on the
nitrogen atoms and π-donor and π* acceptor orbitals delocalised on the aromatic rings. The electronic configuration of the d⁶ metal complex is shown in Figure 1.16.

![Figure 1.16. Electronic configuration of metal complexes.](image)

Promotion of an electron from the Highest Occupied Molecular Orbital (HOMO) πₗ orbital to the Lowest Unoccupied Molecular Orbital (LUMO) π*ₗ ligand orbitals give rise to metal-to-ligand charge transfer (MLCT) excited states, whereas the promotion of an electron from πₗ to σ*ₗ gives rise to metal centered (MC) excited states. Ligand centered excited states can be obtained by promoting an electron from πₗ to π*ₗ. All these excited states may have singlet or triplet multiplicity, although spin-orbit coupling causes singlet to triplet mixing in MC and MLCT excited states. Ru(bpy)₃²⁺, as well as the other Ru(LL)₃²⁺ complexes (LL=is one bidentate polypyridine ligand ), exhibits a D₃ symmetry.⁵⁵
The highest filled molecular orbitals are $\pi_m a_1(d)$ and $\pi_m e(d)$, which are predominantly localized on the metal; whereas the lowest unfilled molecular orbitals $\pi^*_L a_2(\Psi)$ and $\pi^*_L e(\Psi)$ are predominantly localized on the ligand.

The ground state of the complex is singlet, derived from the $\pi_m e(\Psi)^4 \pi_m e(\Psi)^2$ electronic configurations. The high energy excited states of transition metal complexes undergo fast radiationless deactivation. Thus the lowest excited state and upper states that can populate on the basis of Boltzmann equilibrium may play a role in the luminescence emission and bimolecular processes. The metal centered excited states of $d^6$ octahedral complexes are strongly displaced with respect to the ground-state geometry along metal-ligand vibration coordinates as shown in Figure 1.17. Therefore, when the lowest excited state is $^1MC$ as in [Ru(tpy)$_3$]$^{2+}$, the lifetime is very short, and no luminescence can be observed. This occurs because $^1MC$ states undergo fast radiationless deactivation to the ground state and/or ligand dissociation reaction. However, when $^3LC$ and $^3MLCT$ are the lowest excited states thus luminescence can be generally observed. The rate constant of the radiative deactivation of $^3MLCT$ is higher than that of $^3LC$ due to the spin-orbit coupling effect. Therefore, generally the $^3LC$ of excited states are longer lived at low temperature and in a rigid matrix such as [Ru(bpy)$_3$]$^{2+}$. The $^3MLCT$ excited states exhibit luminescence at room temperature.
MC states of the metal are also important; indeed the possibility to populate such states by thermal deactivation is one of the main radiationless deactivation paths of the luminescence excited state. Bidentate N-N ligands like bpy and phen (bpy, 2,2'-bipyridine; phen, 1,10-phenanthroline) are much better chelating units than tridentate species like tpy (tpy, 2,2':6',2''-terpyridine) for Ru(II) because of the bite angle of the chelating sites. As a consequence, at room temperature in fluid solution $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Ru(phen)}_3]^{2+}$ exhibit strong and long-lived luminescence ($\tau$ of the order of $10^2$–$10^3$ ns) whereas $[\text{Ru(tpy)}_2]^{2+}$ is very weakly luminescent ($\tau$ ca. 0.25 ns) because of the low energy of the MC states, which are thermally populated from the luminescent $^3\text{MLCT}$ state, Figure 1.17. The spectroscopic properties of Ru-tpy complexes have been improved by appending suitable groups at the 4'-position of the tpy ligand. According to the above discussion the positions of the MC, MLCT, and LC states depend on the ligand field strength, the redox properties of metal and ligands, and the intrinsic properties of the ligands, respectively. Thus, the excited state properties of a complex can be tuned by suitable choice of the ligands.

1.6.1 The absorption spectra of Ru and Os polypyridyl complexes:
Figure 1.18. UV-Vis of [Ru(bpy)_3]^{2+} in water.

The absorption spectrum of [Ru(bpy)_3]^{2+} is shown in Figure 1.18, along with the proposed assignments. The bands at 185 nm and 285 nm are assigned to spin-allowed LC (π-π*) transitions. Two intense bands at 240 nm and 450 nm are assigned to d-π* (1MLCT) transitions. The shoulders at 322 nm and 344 nm may be assigned to MC transitions.

Like [Ru(bpy)_3]^{2+}, [Os(bpy)_3]^{2+} is a coordinately saturated d^6, however instead of being a second row transition metal like Ru, Os is a third-row transition metal. The difference between the two complexes is that the ligand field splitting Δ for Os is expected to be 40% larger than that of Ru complexes.

For Os polypyridyl complexes the absorption maximum of the spin-allowed MLCT band in the visible region lies similar wavelength as the of Ru(II). The spin-forbidden MLCT band (λ_{max} = 657 nm) though is also observed for Os and is quite intense, as expected because of the large spin coupling caused by the heavy Os atom.

1.6.2 The excited state of the Ru(II) and Os(II) polypyridyl complexes:

The luminescence of [Ru(bpy)_3]^{2+} is temperature dependent. Detailed studies have
shown that luminescence originates from a set of three closely spaced energy levels in thermal equilibrium. The energy separation between these levels was found to be 10, and 61 cm$^{-1}$. Excitation with visible light leads the formation of the singlet MLCT excited state, which, within a few hundred fs, is transformed into the lowest triplet MLCT excited state via intersystem crossing ($k_{isc}$).

The $^3$MLCT excited state return to the ground state via three major pathways as shown in the *Jablonski diagram* in Figure 1.19. The radiative ($k_r$) and non-radiative ($k_{nr}$) pathways from $^3$MLCT to the ground state. The third pathway, crossover ($k_{dd}$) to the nearby MC which decays radiationless to the ground state.

The luminescence lifetime of the [Ru(bpy)$_3$]$^{2+}$ is ~ 5 μs and the emission quantum yield is ~ 0.4 at 77 K. In addition, the emission spectrum exhibits a vibrational structure, which assigned to the vibrational progression. The luminescence quantum yield and
lifetime decreases with increasing the temperature. At room temperature the emission lifetime of \([\text{Ru(bpy)}_3]^{2+}\) is 0.6 \(\mu\)s and the quantum yield of emission is 0.04 in deaerated water.

The temperature dependent behaviour is described by the stepwise term \(B\) and two Arrhenius terms in the following equation:

\[
\frac{1}{\tau} = k_0 + \frac{B}{1 + \exp(1/T - 1/T_B)} + A_1 \exp(-\Delta_1/RT) + A_2 \exp(-\Delta_2/RT) \quad \text{Equation 1.24}
\]

The value of the parameters involve in this equation was found to be solvent dependent. \(k_0\) includes both radiative and non-radiative rate constants at 84 K. \(B\) is a function term due to the melting of the matrix (100-150 K) and is ascribed to the vibrations capable of facilitating the radiationless deactivation. The first Arrhenius term \(A_1\) corresponds to the thermal equilibration with a level which slightly higher in energy than \(3\text{MLCT}\) and with electronic nature as the \(3\text{MLCT}\). So, this level would be a fourth MLCT state with singlet character.

The second Arrhenius term corresponds to the thermal population of the upper-lying \(3\text{MC}\) level, which undergoes fast deactivation because of its large distortion. In polypolypyridine complexes, Os(II) is easier to oxidize than Ru(II), and therefore in Os(II) complexes the \(3\text{MLCT}\) level is lower than the analogous Ru complex while the \(3\text{MC}\) level is higher than that of Ru(II) due to the stronger ligand field.

1.7 Redox properties of Ru(II) and Os(II) Polypyridine complexes in the ground state:

The complexes of Ru(II) polypyridine family are particularly interesting as excited state reactants or products in electron transfer processes and as mediators of electron transfer reactions involving lights due to the stability of the oxidized and reduced forms.

The electrochemical behavior of Ruthenium polypyridine complexes in the ground state has been the focus of extensive studies. Cyclic voltammetry is the most common electrochemical method that used to determine the redox properties and hence the energies of different redox states. Generally speaking, the oxidation of \([M^{II}(N, N)_3]^{3+}\) is metal-localized, occurring at 0.85 and 0.42 V vs SCE for Ru and Os, respectively. \(^{50}\)
All six reductions of $[M^{III}(N,N)_3]^{3+}$ are ligand–localized. Most Ru complexes show the first potential between $-1.0$ and $-2.0$. The reduction potential of the ligand depends on electron repulsion, on interligand interaction energy, and on solvation energy. For example the most electron accepting ligand is reduced first. Here we discuss the cyclic voltammetry of $[\text{Ru(bpy)}_3]^{2+}$, comparable electrochemical behavior is seen for Os polypyridyl complexes.

Figure 1.20 shows one oxidation and three reductions processes; all one electronic and reversible can be observed. Oxidation of Ru(II) polypyridine complexes usually involves a metal centered ($\pi_M t_{2g}$) orbital in octahedral symmetry, with the formation of Ru(III) complexes (low spin $4d^5$ configuration which are inert to ligand substitution.

The oxidation process can be described as:

$$[\text{Ru}^{2+}(\text{LL})_3]^{2+} \rightarrow [\text{Ru}(\text{LL})_3]^{3+} + e^-$$

The oxidation potential of $\text{Ru(bpy)}_3^{2+}$ occurs at fairly positive potential around $+1.3V$ vs. Ag/Ag+. Reduction of Ru(II) polypyridine complexes may involve a ligand–centered orbital, depending on the reactive energy ordering.
Figure 1.20. Cyclic voltammetry of [Ru(bpy)$_3$]$^{3+2}$ in acetonitrile, using glassy carbon as a working electrode, Ag/Ag$^+$ and platinum wire as a counter electrode with 0.1 M TBABF$_6$ as a supporting electrolyte.

The reduced form, keeping its low-spin 4d$^6$ configuration, is usually quite inert and the reduction process is reversible:

$$[\text{Ru}^{2+}(\text{LL})_3]^{2+} + e^- \leftrightarrow [\text{Ru}(\text{LL})^{+2}(\text{LL})]^{+}$$

The added electron appears to be localized on a single ligand.

Several reductions steps can be observed in common potential range windows.

In the t$_2$g$^6$ system, a one-electron reduced species, the $\pi^*_L$ and $\sigma^*_M$ orbitals involved in the reduction processes (redox orbitals) are the same orbitals, which are involved in the MLCT or MC transition, respectively (spectroscopic orbitals). Thus reversibility of the first reduction step, indicating a ligand centered LUMO, also implies that the lowest
oxidation potential of Ru(II) can be altered by changing the $\sigma$ and $\pi$ properties of the ligand.\textsuperscript{60}

The excited state of $[\text{Ru(bpy)}_3]^{2+}$ is $[\text{Ru(bpy)}_2(\text{bpy})^{-1}]^{2+}$, which is a $^3\text{MLCT}$ state, the ruthenium is oxidized and one ligand is reduced. The redox potentials of the excited state can be calculated according to Eq 1.22, Eq 1.23.

\[
E^*(\text{Ru}^{3+}/\text{Ru}^{2+}) = E(\text{Ru}^{3+}/\text{Ru}^{2+}) - E^{0-0}\quad \text{Equation 1.25}
\]

\[
E^*(\text{Ru}^{2+}/\text{Ru}^{+1}) = E(\text{Ru}^{2+}/\text{Ru}^{+1}) - E^{0-0}\quad \text{Equation 1.26}
\]

Where $E(\text{Ru}^{3+}/\text{Ru}^{2+})$ and $E(\text{Ru}^{2+}/\text{Ru}^{+1})$ are the potentials for the ground state oxidation and reduction respectively and $E^{0-0}$ is the zero-zero excitation energy.

Thus by changing the ground state redox potentials and/or the excited state energy, the excited state potentials can be controlled.\textsuperscript{61}

\textbf{1.8 Photoinduced electron transfer:}

A photoinduced electron transfer from the donor (D) to the acceptor (A) results in the formation of a charge separated state which consists of the corresponding radical cation and anion, and the process is in direct competition with the radiative and nonradiative processes that are present in the excited state of A (or D). Electron transfer can be regarded as another deactivation pathway of the locally excited (singlet) state that can exist in addition to internal conversion (IC), inter system crossing (ISC) to the triplet manifold and emission as shown in Figure 1.21. So, photoinduced electron transfer (PET) is often responsible for fluorescence quenching.\textsuperscript{62}
The PET process is involved in many organic photochemical reactions. It plays a major role in photosynthesis and in artificial systems for the conversion of solar energy based on photo charge separation. Fluorescence quenching experiments provide a useful insight into electron transfer processes occurring in these systems.

An excited molecule is generally both a better reductant and oxidant than its ground state analogue. Photoinduced oxidative and reductive electron transfer processes occur according to the following reactions:

$$^1D^* + A \rightarrow D^+ + A^-$$  Oxidative electron transfer
$$^1A^* + D \rightarrow A^- + D^+$$  Reductive electron transfer

These can be illustrated in the following Scheme1.1. 53

Electron transfer depends on the redox potentials of the donor ($E^0_D$) and acceptor ($E^0_A$) together with the excitation energy $E^0_0$ i.e. the difference in the energy between the lowest vibrational levels of the excited state and the ground state. The variations in
standard free energy $\Delta G^0$ for the above reactions can be expressed using the redox potentials $E^0$ and the excitation energy

$$\Delta G^0 = E^0_{D^+/D} - E^0_{A^+/A} = E^0_{D^+/D} - E^0_{A^+/A}$$

Equation 1.27

$$\Delta G^0 = E^0_{D^+/D} - E^0_{A^+/A^-} = E^0_{D^+/D} - E^0_{A^+/A^-}$$

Equation 1.28

**Scheme 1.1.** Reductive and Oxidative electron transfer

These equations are called Rehm-Veller equations and were originally solved for the gas phase reactions. To apply these equations in solution the solvation effect (enthalpic
term $\Delta H_{\text{solv.}}$) and coulombic energy of the ion pair formed should be added to these equations.

\[
\Delta G^0 = E^0_{D,+/-D} - E^0_{A/A^-} - \Delta E^0(D) - \Delta H_{\text{solv}} - e^2/4\pi\varepsilon r
\]  
Equation 1.29

\[
\Delta G^0 = E^0_{D,+/-D} - E^0_{A/A^-} - \Delta E^0(A) - \Delta H_{\text{solv}} - e^2/4\pi\varepsilon r
\]  
Equation 1.30

Where $e$ is the electron charge, $\varepsilon$ is the dielectric constant of the solvent and $r$ is the distance between two ions, however for solvents of high dielectric constant these terms can be neglected.

Marcus theory of electron transfer predicts a quadratic dependence of the activation energy $\Delta G^*$ versus $\Delta G^0$ (standard free energy) of electron transfer reaction.\textsuperscript{65}

\[
\Delta G^* = (\Delta G^0 + \lambda / 4\lambda)^2
\]  
Equation 1.31

In this equation $\lambda$ is the total reorganization energy given by:

\[
\lambda = \lambda_{\text{in}} + \lambda_s
\]  
Equation 1.32

where $\lambda_{\text{in}}$ is the contribution due to changes in the intramolecular bond length and bond angle in the donor and acceptor during the electron transfer, and $\lambda_s$ the contribution of the solvent reorganization. In the case of collision theory, $k_{ET}$ can be evaluated by the following relation:

\[
k_{ET} = Z \exp(-\Delta G^*/RT)
\]  
Equation 1.33

Where $Z$ is the frequency of collisions and $\Delta G^*$ is the free energy of activation for the ET process.

The free energies of the of the reactant state (D-A) before and after electron transfer (D$^+$-A$^-$) are illustrated according to classical model as simple parabolas as a function of the reaction coordinates, Figure 1.23. These parabolas are employed since the Marcus theory assumes that reactants and products behave according to simple harmonic oscillator model. Two factors can influence the rate of electron transfer the first one is Franck-Condon principle which states that there is no change in nuclear configuration.
during electron transfers. The other factor is that the energy must be conserved during electron transfer according to the first law of thermodynamics. These two factors are fulfilled if the crossover occurs at the point where the two parabolas intersect, Figure 1.22.

**Figure 1.22.** Representation of the potential energy curves used in electron transfer theory. The barrier to charge separation ($\Delta G^*$), the overall Gibbs free energy change ($\Delta G$) and the total reorganization energy ($\lambda$) are indicated.

The variation in $\ln k_{ET}$ versus $\Delta G^0$ expected to be a parabola whose maximum corresponds to $\Delta G^0=0$, beyond the maximum $\Delta G^0>0$, Figure 1.23, $k_{ET}$ decreases when $\Delta G^0$ increases (normal region), whereas below the maximum $\Delta G^0<0$, the inverse is expected (Marcus inverse region), Figure 1.23.

The inverse region hasn't been observed for intermolecular electron transfer, because when $\Delta G^0<<0$, $K_{ET}$ is large that the reaction is diffusion limited.
The Marcus theory implies that electron transfer occurs if $\lambda = -\Delta G_{\text{CS}}$, Figure 1.24. This is called the optimal region. If $\lambda > -\Delta G_{\text{CS}}$ the electron transfer rate increases with larger driving forces. However, in the Marcus inverted region, $\lambda < -\Delta G_{\text{CS}}$, the rate decreases with larger driving forces. The barrier is very thin in the inverted region. This facilitates nuclear tunnelling and thus, in processes in the inverted region (charge recombination is often an inverted region process) the observed rates are higher than expected from the classical Marcus theory.
Nevertheless, the inverse region has been observed in supramolecular systems where the electron donor and electron acceptor are held apart by a bridge\textsuperscript{64}. Solution phase studies on these systems have shown that the bridge has an influence on the rate of electron transfer. In systems where the donor and acceptor are connected to each other through a bridge the hole and electron transfers are bridged-mediated, and may occur via super-exchange or hopping mechanisms. The distinction between hole and electron transfers is illustrated in Scheme 1.2.

In photoinduced electron transfer the process involves interaction between the LUMO of the donor with the HOMO of the acceptor or direct orbital overlap between them or is mediated through bridges. The bridges which have $\pi$ or $\pi^*$ LUMO orbitals mediate electron transfer between the donor and acceptor by accepting and transferring an electron. Studies showed that aromatic bridges support faster electron transfer. Similar results were observed on $\sigma$-bond or H-bonding linked donor and acceptor systems.
The rate of electron transfer for systems in which the donor and the acceptor are held together at a fixed distance and orientation, as a function of temperature $T$ is given as:

$$k_{ET} = \sqrt{\frac{4\pi^3}{\hbar^2\lambda k_B T}} \left( \frac{H_{AB}^2}{k_B T} \right) \exp \left( -\frac{\Delta G^*}{k_B T} \right)$$

Equation 1.34

$k_B$ is the Boltzmann constant, $\Delta G^*$ is the activation free energy, $\lambda$ is the nuclear reorganisation parameter, $H_{AB}$ is the electronic coupling matrix element, and $\hbar$ is Planck’s constant.

The rate of electron transfer can be estimated using time-resolved emission measurements. The total rate of decay of a supramolecular system is the sum of the normal decay of the excited state and the rate of forward electron transfer $k_{PET}$.

$$k_d = k_{PET} + k^0_d$$

Equation 1.35

Then

$$K_{PET} = 1/\tau_{D-A} - 1/\tau_{MODEL}$$

Equation 1.36
Where $\tau_{D-A}$ represents the luminescent lifetime of the donor-acceptor system, and $\tau_{\text{model}}$ represents lifetime of the model complex in absence of any photoinduced process.

### 1.9 Photoinduced energy transfer:

Non-radiative energy transfer of excitation energy requires some interaction between donor and acceptor molecules, and it can occur if there is overlap between the emission spectrum of the donor and absorption spectrum of the acceptor, so that energy of vibronic transitions in the donor is equal to those transitions in the acceptor. Such transitions are coupled i.e. are in resonance.

Energy transfer can result from difficult interaction mechanisms:

(a) Coulombic interaction (Förster mechanism).

(b) Intermolecular orbital overlap (Dexter mechanism).

The coulombic interactions consist of long-range dipole-dipole interactions (Förster mechanism). The exchange mechanism (Dexter’s mechanism) requires intermolecular orbital overlap, which include electron exchange.

In fluorescence resonance in energy transfer (FRET) the donor molecules emit at a shorter wavelengths, which overlap with the absorption spectrum of the acceptor. The distance at which FRET is 50% efficient, called the Förster distance, is typically in the range of 20-60 Å. The rate of energy transfer from the donor to the acceptor ($k_T$) is given by

$$k_T = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6$$

Equation 1.37

Where $\tau_D$ is the decay time of the donor in the absence of the acceptor, $R_0$ is the Förster distance, and $r$ is the donor-to-acceptor (D-A) distance.

To obtain structural information about the macromolecule, we can use the extent of energy transfer between the donor and the acceptor to calculate the distance between them using the following equation:
$R_0 = 0.211[\kappa^2 \eta^{-4} \Phi_D \ J(\lambda)]^{1/6}$  

Equation 1.38

Where $\Phi_D$ is the donor quantum yield in the absence of the acceptor; $\eta$ is the refractive index of the medium; $J(\lambda)$ is the overlap integral which expresses the degree of spectral overlap between the donor emission and the acceptor absorption; $\kappa^2$ is a factor describing the relative orientation in space of the transition dipoles of the donor and acceptor and is usually assumed to be equal to 2/3, which is appropriate for dynamic random averaging of the donor and acceptor. The efficiency of energy transfer ($E$) is the fraction of photons absorbed by the donor that are transferred to the acceptor. The transfer energy is typically measured using fluorescence intensity of the donor, in the absence ($F_D$) and in the presence ($F_{DA}$) of the acceptor:

$$E = 1 - \frac{F_{DA}}{F_D}$$  

Equation 1.39

The coulombic term corresponds to the energy transfer process in which the initially excited electron on the donor returns to the ground state orbital on D, while simultaneously an electron on the acceptor A is promoted to the excited state.

The exchange term corresponds to an energy transfer process associated with an exchange of two electrons between D and A, Scheme 1.3.\textsuperscript{54}

Exchange mechanism is operative only at short distances < 10\textsuperscript{9}A because it requires orbitals overlap of the molecules. In contrast, the columbic mechanism can still be effective at large distances (up to 80 - 100\textsuperscript{9}A).

Electron exchange mechanisms leading to collisional energy transfer (Dexter type). As the name suggests, this requires bimolecular collision between the reactants and can be visualised as an exchange of electrons which can take place when there is simultaneous and favourable overlap of the approximate orbitals. Therefore, the range of effectiveness of these mechanisms is usually restricted to distances ≤ 10 A. The diagram in scheme 1.3 depicts electron and energy transfer mechanisms.
The objectives of this thesis:

The objective of this study is to construct supramolecular assemblies that combine both the photophysical properties of a metal complex and the properties of cyclodextrins and to exploit these assemblies in useful applications. In Chapter 3, a ruthenium metal complex was covalently linked to the primary rim of β-cyclodextrin. The synthesis and characterization of this complex was described in detail in this chapter. Then we have conducted detailed photophysical studies on the luminescent host [Ru(bpy)$_2$(phen-
The complex exhibits a strong pH dependent luminescence, which is attributed to protonation/deprotonation of the secondary amine bridge linking the CD and ruthenium polypyridyl centre. The ability of cyclodextrin to include apolar compounds has been investigated in detail. This property of cyclodextrin was exploited to study electron transfer between the donor/acceptor included in the cavity and donor/acceptor covalently linked to cyclodextrin. In chapter 4, the same complex prepared in chapter 3 was used to design a new supramolecular system in which the donor and the acceptor were both covalently linked to cyclodextrin. A novel supramolecular donor acceptor system incorporating a ruthenium polypyridyl functionalized β-cyclodextrin moiety with an hydroxo-bridged Cu(II) dimer is described in Chapter 4.

Efficient photoinduced electron transfer from the copper centre to the pendant ruthenium polypyridyl centre is evident. This work suggests that luminescently labelled CDs may have value in metal sensing provided the luminophore is sufficiently long lived. In chapter 6, heterometallic ruthenium-iridium supramolecular assembly was described. The electron transfer process between Ru and Ir through included pyrene was investigated. In Chapter 5, dimers of ruthenium and osmium functionalized γ-cyclodextrin were prepared. C₆₀ tetramers of the dimers were also prepared and electron transfer between Ru and Os via C₆₀ was investigated.
1.10 References:


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Chapter 2

Experimental Approaches and Instrumentation
2.1 Experimental

2.1.1 Chemicals
β-Cyclodextrin (Aldrich), 5-nitro-1,10-phenanthroline (Aldrich), 2,2’bipyridine(Aldrich), 
RuCl$_3$.3H$_2$O (Aldrich), DMF (Aldrich) and NMP (Aldrich), Britton-Robinson buffer tablets
(BDH Chemicals Ltd.), were used as received. All reagents employed were analytical
grade. Water was purified using a Milli-Qplus 185 Millipore installation. Chemicals
purchased from Aldrich were used without further purification.

2.1.2 NMR Spectroscopy:
$^1$H NMR and COSY spectra were recorded on a 400 MHz Bruker Advance series NMR
spectrometer. Chemical shifts are reported relative to the solvent reference [D$_6$] DMSO
2.49ppm.

2.1.3 Mass Spectroscopy
Mass spectra were obtained using a Bruker LC/MS Esquire Series mass spectrometer
at Dublin City University (DCU). Electrospray ionisation with positive ion polarity was
used.

2.1.4 Electronic Spectroscopy

Electronic absorption spectra were measured on a Shimadzu 3500 UV-VIS/NIR
spectrophotometer in all cases; the spectroscopic grade solvent used to dissolve the
compound was used as a reference. Molar extinction coefficients ($\varepsilon$) were calculated
using the Beer Lambert relationship: 

$$ A = \varepsilon c l. $$

2.1.5 Electrochemistry

Cyclic voltammetry was carried out using a CH instrument Model 660 electrochemical
work station. A conventional three-electrode cell was used, consisting of glassy
carbon (3 mm dia.) as a working electrode, Ag/AgCl as a reference electrode and
Platinum wire as a counter. The cyclic voltammetry of Cu$_2$CDRu obtained using
platinum microelectrode (50 μm dia.) that was polished and electrochemically cleaned as described previously. Compounds were dissolved in DMF with 0.1 tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The working electrode was polished using 0.05Mm Alumina. The solution was degassed for 30 minutes with N₂ and gas blanket was maintained over the solution surface during all experiments. The solution was sonicated between each experiment.

2.1.6 Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra were recorded by using a Perkin Elmer FT-IR system, Spectrum GX. Samples were contained as fused KBr disks (typical constitution, 5% sample 95% KBr). Backgrounds were obtained of the pure KBr disks and were automatically subtracted from sample spectra to minimise interference with sample spectra.

2.1.7 Photophysical Measurements:

Steady-state emission spectra were recorded on a Cary Eclipse Fluorescence spectrophotometer, and luminescence lifetimes were obtained using a Picoquant Fluotime 100 TCSPC system exciting at 470 nm and detecting at 600 nm. In order to capture short lived species (≤ 10 ns) higher resolution and sensitivity than possible with the Edinburgh Instruments SPC is required. Therefore in the case of short τ measurements, a PicoQuant Fluotime 100 instrument was used, Figure 2.1. This instrument is designed to operate with a sub-nanosecond pulsed laser (PLS 370 or PLS 450) and can measure decay in a pico-second time scale. Focusing and collecting optics are used to achieve ultimate sensitivity. For spectral filtering of the emission light, cut-off filters are used for high light throughput. A fast and reliable PMT detector allows detection with an Instrument Response Function (IRF) of about 300 ps. The PicoQuant TimeHarp board acquires lifetime data and τ is calculated using 'FluoFit' fluorescence decay data analysis software. The program implements an iterative reconvolution of the instrument response with non-linear least squares, error minimisation based on the Levenberg-Marquardt and Simplex algorithms.
Figure 2. Schematic diagram of the PicoQuant - FluoTime 100 SPC instrument.³

2.1.8 Emission Quantum Yields:
Quantum yields were measured using a comparative method.⁴ In quenching studies, all spectra were corrected for dilution.

2.1.8 Elemental Analysis
Elemental analysis for carbon, hydrogen and nitrogen was performed at University College Dublin (UCD) microanalytical laboratories.

2.1.9 HPLC
HPLC involved the use of a LC-10AT Shimadzu Liquid Chromatograph in conjunction with a Walters 2487 Dual λ Absorbance detector. Typically, a C18 2915, Hichrom reverse phase column was used.
2.1.10 Magnetic Susceptibility

Magnetic moments were determined via the Evans method on a Bruker 80 MHz instrument (model AW 80) using coaxial tubes.

2.1.12 Raman Spectroscopy:
Raman spectroscopy was conducted on a Dilor. Jobinývon. Spex HRLabram, the set-up is shown in Figure 2.2. The exciting, Ar ion laser (514.5, 488 nm) laser was focused on the sample using a 10x objective lens. Focusing was confirmed by using an imaging video camera. A spectral resolution of 0.5 cm\(^{-1}\) per pixel was achieved using grating of 1800 lines mm\(^{-1}\), and the x-axis was calibrated against silicon. Steady-state emission spectra were recorded employing a Varian Cary Eclipse luminescence spectrophotometer. 1 cm quartz cuvettes were used with spectroscopic grade Dimethylformamide (DMF) as solvent (unless otherwise stated).

![Figure 2.2. Typical Raman set-up.](image)

2.1.11 Laser Flash Photolysis:
Luminescence lifetimes were measured using the third harmonic (355nm, 30mJ/pulse) of a continuum surelite Q-switched ND: YAG laser for excitation, emission was detected in a right–angled configuration to the laser using Andor Model M20 gated intensified CCD coupled to an Oriel Model MS125 spectrograph. This configuration allows a complete emission spectrum (spectral range 250nm) to be obtained within times as short as 10ns. The gate width i.e. the exposure time of the CCD was never more than 5% of the excited state lifetime the step size, i.e., the time between the acquisition of discrete spectra was typically 5% of the excited half-life. Time–resolved absorption spectra were collected using the instrumentation in absorption mode with an Oriel 300 W Xe arc lamp acting as a monitoring source. In this instance, spectra were typically recorded using the average of 25 laser shots. The gate width, i.e., the exposure time of the CCD, was never more than 10% of the excited state lifetime.

2.1.13 Transient Absorption Spectroscopy:

Time resolved transient absorption spectra were collected using the same instrumentation as for laser flash photolysis in absorption mode with an Oriel 300 W Xe arc lamp acting as the monitoring source. Spectra were typically recorded using the average of 25 laser shots. The gate-width, i.e., the exposure time of the CCD, was never more than 10% of the excited state lifetime.

2.2 Theoretical background of techniques

2.2.1 Time-Resolved Spectroscopy

2.2.1.1 Transient- Absorption spectroscopy

Transient absorption spectroscopy is a method, for monitoring the dynamics of extremely fast events in real time. The time resolution of the experiment is determined by the laser pulse duration. Today it is possible routinely to produce pulses as short as
10 fs. The principle of the transient absorption experiment is rather simple. An intensive pulse, called the pump pulse, perturbs the system, Figure 2.3. This perturbation may lead to energy or electron redistribution inside the molecule or may initiate a reaction such as isomerization or dissociation. Then the second pulse, called a probe pulse, passes the sample and the intensity of the probe is monitored as a function of time delay with respect to the pump pulse. As the absorption spectrum of the sample is a signature of the species present in the sample, modifications in the absorption of the sample after the excitation, i.e. after the pump pulse, reflect pump pulse induced changes in the sample. The absorption of the sample may increase or it may decrease or completely new absorptions may be born indicating formation of the photochemical products. By changing the time delay between the pump and the probe it is possible to follow temporal behaviour of these spectral features. The pulses travel at the speed of light and one may then calculate that 10 fs time difference between the pulses corresponds to 3 μm difference in path.

\[ \Delta \text{Abs} = \text{Abs. after} - \text{Abs. before} \]  

Equation 2.1

Figure 2.3. Schematic representation of the pump and probe technique.

The detected signal in the transient absorption measurement is the change in absorption, ΔAbs with time. Where ΔAbs is the difference between the absorption after and before the excitation is given as:

\[ \Delta \text{Abs} = \text{Abs. after} - \text{Abs. before} \]  

Equation 2.1
After excitation of a sample with appropriate wavelength one can follow population dynamics at the given wavelength by varying $\Delta t$ with time resolution determined by the pulse duration (Fig. 2.4). On the other hand, one may measure transient spectrum of the sample at the given time delay after the excitation pulse. Measurement of the transient spectrum may be helpful in assignment of different absorbing species. In both cases one has to know the spectral characteristics of the studied molecule, which can be obtained for example from steady state spectrum using spectroelectrochemistry if a radical species is involved.

**Figure 2.4.** Schematic diagram showing (a) formation and subsequent decay of the excited state absorbance following photo-excitation of a sample ($h\nu'$) and (b) corresponding depletion and reoccurrence of the ground state absorbance.\(^7\)
2.2.1.2 Time-Correlated Single Photon Counting (TCSPC):

Time-correlated single photon counting is a very powerful time-resolved technique for determining excited state luminescent lifetimes. Acquisition of fluorescence decay curves by means of TCSPC is done by histogramming of arrival times of individual photons over many excitation/emission cycles as shown in Figure 2.5. The arrival times recorded in the histogram are relative times between laser excitation and corresponding fluorescence photon arrival (start-stop-times) ideally resolved down to few picoseconds. Due to the photon counting statistics it requires a large number of cycles to collect the histogram to such a degree of signal-noise-ratio, that a fluorescent lifetime can be calculated. In fluorescence decay experiments the light being analysed is a pulse that start out bright and then rapidly decays in intensity.

![Figure 2.5. Schematic diagram showing the basic working principle of a TCSPC.][1]

The source in this technique is high repetition rate laser is used to excite the sample. The detector is a photomultiplier tube (PMT). Part of the excitation light is directed into a photodiode using a beam splitter, and triggers an electronic device called time-to-amplitude converter (TAC). This pulse initiates a voltage ramp in the TAC that increases steadily from zero at certain rate. The second PM, which is very sensitive and capable of detecting a single photon, is positioned after the sample and detects the emission at the emission at the right angles to the excitation light. When the second PM detects an emitted photon, it sends a signal to the TAC that will stop the increase of the voltage.

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[1]: /content/mathml.png
The time difference between the excitation and detection of emission is then converted into a voltage. A multichannel analyzer (MCA) connected to the time-amplitude converter that divides the ramp into several channels. Each channel counts the number of times a specific voltage level is obtained and by repeating the cycle many times per second a complete spectrum is produced in the memory of the MCA. The probability that an emitted photon will be detected within a given time interval, which corresponds to a single channel on the MCA, decreases with increasing time. This decay profile can give very precise estimates of radiative lifetimes ranging from a time scale of a few nanoseconds to milliseconds.

2.2.2 Vibrational Spectroscopy.

Vibrational spectra are ordinarily measured by two very different techniques infrared and Raman spectroscopy.

2.2.2.1 Infrared (ir) spectroscopy

In Infrared spectroscopy light of all different frequencies is passed through a sample and the intensity of the transmitted light is measured at each frequency. At frequencies corresponding to vibrational energies of the sample, some light is absorbed and less light is transmitted than at frequencies which don't correspond to vibrational energies of the molecule. In order to compensate for absorption and scattering of the light by the solvent and sample cell, the incident light is split into two beams, one of which goes through the sample and the other is passed through a reference usually consisting of pure solvent in a cell identical to the sample or referenced against air. Transmittance is then defined as $I_s / I_r$, where $I_s$ is the intensity of light passing through the sample cell and $I_r$ is the intensity of light passing through the reference cell.

2.2.2.1 Raman Spectroscopy

In Raman spectroscopy we do not observe transmitted but light scattered by the sample. The scattered light may be observed from any convenient direction with respect to the incident light. Light of a single frequency, monochromatic light, must be
used for a Raman experiment. If the incident light of frequency $\nu_0$ passed through the sample, some of the light (about 1/1000 of the incident intensity) is scattered in all directions. This phenomenon is called Rayleigh scattering. A very small fraction of the scattered does not have a frequency $\nu_0$. Instead, this light has frequencies $\nu_i$ such that:

$$\Delta E = h|\nu_0 - \nu_i|$$  \hspace{1cm} \text{Equation 2.2}$$

Equation 2.1 corresponds to the energies that are absorbed by the sample. The frequency $\nu_0$ may be in any region of the spectrum, with visible light being the most typical, but the difference $|\nu_0 - \nu_i|$, in an infrared (vibrational) frequency. The which produces light of frequency other than $\nu_0$ is called Raman scattering. $\nu_i$ may be greater or less than $\nu_0$, but the amount of light with frequency $\nu_i < \nu_0$, is much greater or less than that with frequency $\nu_i > \nu_0$. The former, Raman scattered radiation, is called Stockes radiation, and the latter is called anti-Stockes radiation. The scattering event occurs in $10^{-14}$ seconds or less. The virtual state description of scattering is shown in Figure 2.6. The energy difference between the incident and scattered photons is represented by the arrows of different lengths in Figure 2.6. Numerically, the energy difference between the initial and final vibrational levels, $\tilde{\nu}$, or Raman shift in wave numbers (cm$^{-1}$), is calculated through equation 2.2

$$\tilde{\nu} = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}}$$  \hspace{1cm} \text{Equation 2.3}$$

in which $\lambda_{\text{incident}}$ and $\lambda_{\text{scattered}}$ are the wavelengths (in cm) of the incident and Raman scattered photons, respectively. The vibrational energy is ultimately dissipated as heat. Because of the low intensity of Raman scattering, the heat dissipation does not cause a measurable temperature rise in a material. At room temperature the thermal population of vibrational excited states is low, although not zero. Therefore, the initial state is the ground state, and the scattered photon will have lower energy (longer wavelength) than the exciting photon. This Stokes shifted scatter is what is usually observed in Raman spectroscopy. Figure 2.6 depicts Raman Stokes scattering.
Figure 2.6. Energy level diagram for Raman scattering; (a) Stokes Raman scattering (b) anti-Stokes Raman scattering.

A small fraction of the molecules are in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the ground state. The scattered photon appears at higher energy. This anti-Stokes-shifted Raman spectrum is always weaker than the Stokes-shifted spectrum, but at room temperature it is strong enough to be useful for vibrational frequencies less than about 1500 cm\(^{-1}\). The Stokes and anti-Stokes spectra contain the same frequency information. The ratio of anti-Stokes to Stokes intensity at any vibrational frequency is a measure of temperature. Anti-Stokes Raman scattering is used for contactless thermometry. The anti-Stokes spectrum is also used when the Stokes spectrum is not directly observable, for example because of poor detector response or spectrograph efficiency.

2.2.2.1 Raman Selection Rules and Intensities

The physical basis for selection rules for fundamental transitions. A vibrational transition is ir active if the dipole moment of the molecule changes during the vibration. A molecule with zero dipole moment can have ir active vibrational modes. A transition is Raman active if the polarizability of the molecule changes during the vibration. A simple classical electromagnetic field description of Raman spectroscopy can be used to explain many of the important features of Raman band intensities. The dipole moment, \( P \), induced in a molecule by an external electric field, \( E \) is proportional to the field as shown in equation 2.3.\(^{10} \)
\[ P = \alpha E \quad \text{Equation 2.4} \]

The proportionality constant \( \alpha \) is the polarizability of the molecule. The polarizability measures the ease with which the electron cloud around a molecule can be distorted. The induced dipole emits or scatters light at the optical frequency of the incident light wave.

Raman scattering occurs because a molecular vibration can change the polarizability. The change is described by the polarizability derivative, \( \frac{d\alpha}{dQ} \), where \( Q \) is the normal coordinate of the vibration. The selection rule for a Raman-active vibration, that there is a change in polarizability during the vibration, is given in equation 2.4.

\[ \frac{d\alpha}{dQ} \neq 0 \quad \text{Equation 2.5} \]

The Raman selection rule is analogous to the more familiar selection rule for an infrared-active vibration, which states that there must be a net change in permanent dipole moment during the vibration. From group theory it is straightforward to show that if a molecule has a centre of symmetry, vibrations, which are Raman-active, will be silent in the infrared, and vice versa.

Scattering intensity is proportional to the square of the induced dipole moment, which is to the square of the polarizability derivative, \( \left( \frac{d\alpha}{dQ} \right)^2 \). If a vibration does not greatly change the polarizability, then the polarizability derivative will be near zero, and the intensity of the Raman band will be low. The vibration of modes of a highly polar moiety, such as the O-H bond, are weak scatterers. An external electric field cannot induce a large change in the dipole moment and stretching or bending the bond does not change this.

Typical strong Raman scatterers are moieties with distributed electron clouds, such as carbon-carbon double bonds. The \( \pi \)-electron cloud of the double bond is easily distorted in an external electric field. Bending or stretching the bond changes the
distribution of electron density substantially, and causes a large change in induced
dipole moment.

Chemists generally prefer a quantum-mechanical approach to Raman scattering theory,
which relates scattering frequencies and intensities to vibrational and electronic energy
states of the molecule. The standard perturbation theory treatment assumes that the
frequency of the incident light is low compared to the frequency of the first electronic
excited state. The small changes in the ground state wave function are described in
terms of the sum of all possible excited vibronic states of the molecule.

2.2.2.2 Polarization Effects

Raman scatter is partially polarized, even for molecules in a gas or liquid, where the
individual molecules are randomly oriented. The effect is most easily seen with an
exciting source which is plane polarized. In isotropic media polarization arises because
the induced electric dipole has components, which vary spatially with respect to the
coordinates of the molecule. Raman scatter from totally symmetric modes will be
strongly polarized parallel to the plane of polarization of the incident light. The scattered
intensity from non-totally symmetric vibrations is \( \geq 3/4 \) as strong in the plane
perpendicular to the plane of polarization of the incident light as in the plane parallel to
it. The situation is more complicated in a crystalline material. In that case the orientation
of the crystal is fixed in the optical system. The polarization components depend on the
orientation of the crystal axes with respect to the plane of polarization of the input light,
as well as on the relative polarization of the input and the observing polarizer.

2.2.2.3 Resonance-Enhanced Raman Scattering

Raman spectroscopy is conventionally performed with green, red or near-infrared
lasers. The wavelengths are below the first electronic transitions of most molecules, as
assumed by scattering theory. The situation changes if the wavelength of the exciting
laser within the electronic spectrum of a molecule. In that case the intensity of some
Raman-active vibrations increases by a factor of \( 10^2 \text{--} 10^4 \). This resonance enhancement
or resonance Raman effect can be quite useful.
The resonance Raman effect is of potential value in biology for the study of colored metalloproteins and other colored macromolecules. Since the emission intensity is greatly enhanced, the enables very low concentrations of macromolecules to be observed. Furthermore, the resonance Raman spectrum is generally associated with the region of the molecule responsible for the electronic absorption band. For this reason the immediate environment of transition metal ions in complexes may be especially amenable to study by resonance Raman spectroscopy. This allows the physical biochemist to probe the chromophoric site (often the active site) without spectral interference from the surrounding protein. Resonance Raman spectroscopy is also a major probe of the chemistry of fullerenes, polydiacetylenes and other "exotic" molecules which strongly absorb in the visible. Although many more molecules absorb in the ultraviolet, the high cost of lasers and optics for this spectral region have limited UV resonance Raman spectroscopy to a small number of specialists.

The vibrations whose Raman bands are resonance enhanced fall into two or three general classes. The most common case is Franck-Condon enhancement, in which a component of the normal coordinate of the vibration is in a direction in which the molecule expands during an electronic excitation. The more the molecule expands along this axis when it absorbs light, the larger the enhancement factor. The easily visualized ring breathing (in-plane expansion) modes of porphyrins fall into this class. Vibrations which couple two electronic excited states are also resonance enhanced. This mechanism is called vibronic enhancement. In both cases enhancement factors roughly follow the intensities of the absorption spectrum. The theory of resonance enhancement is beyond the scope of this thesis.

Resonance enhancement does not begin at a sharply defined wavelength. In fact, enhancement of 5X-10X is commonly observed if the exciting laser is even within a few hundred wave numbers below the electronic transition wavelength of a molecule. This pre-resonance enhancement can be experimentally useful.
2.2.3 Electrochemistry:

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reaction. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, the kinetics of the heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. A cyclic voltammogram is recorded by cycling the potential of the working electrode; In this case the voltage is swept between two values (see below) at a fixed rate, Figure 2.7, however when the voltage reaches \( V_2 \) the scan is reversed and the voltage is swept back to \( V_1 \) then the resulting current is detected. This gives the potentials at which charge transfer reactions take place and indicates if they reversible or not. Figure 2.7 shows how the potential is varied together with a voltammogram for a reversible redox couple.

![Voltage vs Time Graph](image)

**Figure 2.7.** Voltage sweeping in cyclic voltammetry between \( V_1 \) and \( V_2 \).

The appearance of a cyclic voltammogram reflects the reaction occurring at the electrode surface as the potential cycled. The equilibrium established on the electrode surface can be described according to Nernst's equation,
\[ E = E^0 + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} \]  
\text{Equation 2.6}

where \( E \) is the electrode potential; \( E^0 \), formal redox potential; \([Ox]\) and \([Red]\) are the concentration of the redox couple at equilibrium, \( n \) is the number of electrons transferred in the electron transfer process; \( F \), is the Farady’s constant.

According to Nernst’s equation, the ratio of \( \frac{[Ox]}{[Red]} \) will change when the potential on the working electrode is changed. Thus, when the potential is scanned towards positive values, an oxidation reaction, \( \text{Red} \rightarrow \text{Ox} + n\text{e}^- \), will occur as the potential approaches the formal potential \( E^0 \). This will give rise to an anodic current \( (i_{an}) \) that increases until the amount of the Red-form at the electrode surface is depleted which will cause at the current to decrease, resulting in a peak in the anodic region. When the potential is scanned in the other direction, i.e. towards negative values, the opposite will occur. Approaching \( E^0 \), a reduction will occur at the surface, \( \text{Ox} + n\text{e}^- \rightarrow \text{Red} \), that gives the cathodic current \( (i_{cat}) \).

The peak current for a reversible couple at 25° C, is given by the Randles-Sevcik equation 2.6:

\[ i_p = (2.69 \times 10^5)n^{3/2} ACD^{1/2} \nu^{1/2} \]  
\text{Equation 2.7}

Where \( A \) is the electrode area (in cm²), \( C \) the concentration (in mol/cm³), \( D \) the diffusion coefficient (in cm²/s) and \( \nu \) the scan rate (V/s). Accordingly, the current is directly proportional to concentration and increases with the square root of the scan rate. The ratio of the reverse –to-forward peak currents, \( i_{p,c}/i_{p,a} \), equal to 1 for a simple reversible couple. The current peaks are commonly measured by extrapolating the preceding baseline current as shown in Figure 2.8. The position of the peaks on the potential axis \( (E_p) \) is related to the formal potential of the redox process. The formal potential for a reversible couple is centered between the \( E_{pa} \) and \( E_{pc} \) according to Equation 2.7:

\[ E^0 = \frac{(E_{pa} + E_{pc})}{2} \]  
\text{Equation 2.8}

The separation between the peak potentials (for a reversible couple) is given by:
\[ \Delta E = E_{pa} - E_{pc} = 59 \text{ mV/n} \]  

Equation 2.9

The peak separation can be used to determine the number of electrons transferred. A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in Figure 2.8. The solution contains only a single electrochemical reactant.

**Figure 2.8.** Typical cyclic voltammogram for a single electrochemical reactant showing \( i_p \) and \( E_p \).

### 2.2.4 Spectroelectrochemistry (SEC):

Spectroelectrochemical methods provide the opportunity to spectroscopically probe the chemical species that are generated in situ during redox reactions at electrode surfaces. In many cases electrochemistry yields synthetically inaccessible oxidation states, and therefore spectroelectrochemistry offers new windows for exploring novel chemical pathways.
The major challenge for the development of a spectroelectrochemical method is to design an electrochemical cell that is mutually compatible with the desired spectroscopic technique. Numerous cell designs and optically transparent electrodes (OTEs) for a wide range of spectroscopic techniques are described in the literature, but in general have been developed for a specific application. An exception to this is the optically transparent thin-layer electrode (OTTLE), which has been routinely used for transmission spectroelectrochemistry. The OTTLE cell has been implemented for numerous UV-visible spectroelectrochemical studies under a variety of experimental conditions due to ease of construction, the need for only small sample volumes, and the capability for rapid electrolysis. SEC combines the techniques of electrochemistry and spectroscopy. In a specially designed electrochemical cell, a redox active compound is oxidised or reduced. The products of the redox transformation or following chemical reactions are monitored in situ by spectroscopic techniques. UV-vis SEC monitors changes in the UV or visible spectra as potentials are applied to the working electrode in the cell. The diagram below (Figure 2.9) is representative of SEC cell used for UV-vis spectroelectrochemistry in this study. It is designed to be easily contained within the sample compartment of a UV-vis spectrometer. The electrochemical cell is coupled to a quartz cell in which bulk electrolysis is performed. Changes in the UV-Vis spectrum of the redox species are monitored as the sample is electrolysed.

Figure 2.9. Spectroelectrochemical Cell. RE, WE and AE are reference, working and auxiliary electrodes respectively. Platinum gauze is used as WE.
2.2.5 Magnetochemistry

Selwood (1943) defined Magnetochemistry as "the application of magnetic susceptibilities and of closely related quantities to the solution of chemical problems". Nowadays, Magnetochemistry is the study of the magnetic properties of materials and optimization of these properties to design new materials with improved performance. Magnetism arises from the response of elementary current loops to the applied magnetic field, which tends to orient their associated magnetic moments in its direction. In a material which does not have a current present, there are still magnetic interactions. Atoms are made of charged particles (protons and electrons) which are moving constantly. The processes which create magnetic fields in an atom are:

I. **Nuclear spin.** Some nuclei, such as a hydrogen atom, have a net spin which creates a magnetic field.

II. **Electron spin.** An electron has two intrinsic spin states which we call up and down or alpha and beta.

III. **Electron orbital motion.** There is a magnetic field due to the electron moving around the nucleus.

Each of these magnetic fields interacts with one another and with external magnetic fields. However, some of these interactions are strong and others are negligible. Measurement of interactions with nuclear spins is used to analyze compounds in nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopy. The interaction between an electron's intrinsic spin and its orbital motion is called spin-orbit coupling. Spin-orbit coupling has a significant effect on the energy levels of the orbitals in many inorganic compounds.

The magnetisation (M) is defined as the magnetic dipole moment per unit volume acquired by a substance when subjected to a magnetic field, and having therefore the units \([M]=\text{A m}^{-1}\). The magnetisation can be expressed as:

\[
M = \mu_0^{-1} \chi_m B \quad \text{Equation 2.10}
\]
Where $\mu_0$ is the vacuum permeability and $\chi_m$ is the magnetic susceptibility, the magnetisation induced by unit applied magnetic field $B$.

Magnetic susceptibilities were measured using a modification of Evans of the Gouy method mass susceptibility balance (M. S. B). The Evans method uses the same configuration as the Gouy method but, instead of measuring the force which a magnet exerts on the sample, the equal and opposite force which the sample exerts on a suspended permanent magnet is observed. The M. S. B. works on the basis of a stationary sample and moving magnets. The pairs of magnets are placed at opposite ends of a beam so placing the system in balance. Introduction of the sample between the poles of one pair of magnets produces a deflection of the beam which is registered by means of phototransistors. A current is made to pass through a coil mounted between the poles of the other pair of magnets, producing a force restoring the system to balance. At the position of equilibrium, the current through the coil is proportional to the force exerted by the sample, and can be measured as a voltage drop.

The following expression for mass susceptibility $\chi_g$ in c.g.s units may be derived in the same manner as for the traditional Gouy method 13:

$$\chi_g = \frac{1}{m} \left[ c(R - R_0) + A \chi_{\text{air}} \right]$$

Equation 2.11

where:
- $c$ = constant of proportionality
- $R$ = reading obtained for tube plus sample
- $R_0$ = the empty tube reading
- $l$ = sample length (cm)
- $m$ = sample mass (g)
- $A$ = the cross sectional area of the tube (cm$^2$)
- $\chi_{\text{air}}$ = volume susceptibility of the displaced air

For powdered samples the air correction term may be normally be ignored.

$C$, the constant of proportionality is related to the calibration of a given balance by the formula:

$$C = \frac{C_{\text{bal}}}{10^7}$$
The molar susceptibility, $\chi_m$, can then be calculated by multiplying the mass susceptibility, $\chi_g$, by the molecular weight of the substance being measured. For diamagnetic compounds, $\chi_m$ is negative, whereas it is positive for paramagnetic compounds.

For compounds containing a paramagnetic ion, $\chi_m$ must be corrected for the diamagnetic contribution of the other groups or ligands present. Since the magnetic moments are additive, $\chi_m^{\text{corr}}$ can be obtained from $\chi_m$ by the addition of the appropriate corrections ($\chi_{\text{dia}}$) as calculated from Pascals' values.$^{14}$

$\chi_m^{\text{corr}}$ is related to the magnetic moment, $\mu_{\text{eff}}$ in Bohr Magnetons by the expression.$^{14}$

$$\mu_{\text{eff}} = \sqrt{\frac{3kT\chi_m^{\text{corr}}}{N\beta^2}} = 2.828\sqrt{\chi_m^{\text{corr}}} T$$

Equation 2.12

Where: $N =$ Avogadro’s number, $\beta =$ The Bohr magneton, $k =$ Boltzmann’s constant and $T =$ absolute temperature (K)

The orbital contribution to the magnetic moment is effectively absent for metal complexes with A or E type ground states. Complexes having T type ground states do show some (~10%) contribution. Hence, for complexes of the first transitional series the orbital contribution to the magnetic moment is almost completely quenched by the ligand field so that only the spin angular momentum of the electrons is effective in forming the elementary magnetic dipole. Therefore, a very simple expression can be given for $\mu_{\text{eff}}$ which is known as the ‘spin only’ formula:

$$\mu_{\text{spin only}} = \sqrt{4S(S+1)} \quad \text{(B. M.)}$$

Equation 2.13

Here $S$ is the quantum number specifying the total spin angular momentum of the ion. Since $S = n \ (1/2)$, where $n$ is the number of unpaired electrons in the unfilled shell, Equation 2.10 can be re-written as:

$$\mu_{\text{spin only}} = \sqrt{n(n+2)} \quad \text{(B. M.)}$$

Equation 2.14

Equation 2.13 can be used to calculate the approximate values for the magnetic moment.
References:

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6 www.future-fab.com
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9 http://www.picoquant.com
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Chapter 3

The photophysics of a luminescent ruthenium polypyridyl complex with pendant β-cyclodextrin; pH modulation of lifetime and photoinduced electron transfer
3.1 Introduction:

3.1.1 Molecular Sensing:

Designing photochemical devices that have applications in sensing, energy transport or storage, or directional electron transfer have attracted a lot of attention.¹ These devices have applications in switches, molecular wires or energy conversion systems. The design of fluorescent sensors is of major importance because of the high demand in analytical chemistry, clinical biochemistry, medicine, the environment etc. There is a need for sensors even though there is already a wide choice of fluorescent molecular sensors (FMS) for particular applications and many of them are commercially available. Most of these supramolecular systems that function as sensors consist of a molecular receptor, a linker, and a fluorophore. The fluorophore is the signalling unit i.e. it acts as a signal transducer that converts the information, the presence of analyte, into an optical signal expressed as the changes in the photophysical characteristics of the fluorophore. There are three classes of FMS, these classes are:

Class A: the fluorophores are quenched by collision with the analyte, e.g. O₂, Cl⁻

Class B: the fluorophore is quenched by reversibly bind the analyte, e.g. fluorescent pH indicator is often used if the analyte is proton.

Class C: the fluorophore is connected to a receptor via a spacer or without spacer. This type of sensors based on molecular or ion recognition by a receptor. The receptors are very important in such functional systems. The receptors can be modified for selective binding of differently sized molecules. In this class of sensors also the fluorescence can be quenched or enhanced. The mechanism of quenching can be either photoinduced electron or energy transfer. Many examples have been designed based on Photoinduced Electron Transfer (PET). Crown Containing PET sensors, Cryptand-based PET sensors, Podand-Based and chelating PET sensors, and Calixarenes-based PET sensors. All these sensors have been used for sensing cations. The same supermolecules previously reported have been used to design fluorescent photoinduced
charge transfer cation sensors. Cyclodextrin-based fluorescent sensors have widely used for sensing neutral molecules.

The cyclodextrins are ideal molecular receptors in building photochemical devices. Cyclodextrins are having no absorption in the ultraviolet and visible part of the spectrum. The three types of cyclodextrins (α, β, γ) have different sizes that can bind guests with some selectively based on size. In addition cyclodextrins are commercially available, water soluble, non-toxic, and chiral.

Modified cyclodextrin with fluorophores have received considerable attention in molecular and ion sensing and in mimicking enzyme-substrate interactions. The possibility of using cyclodextrins for sensing purposes has been exploited by two approaches. One of these approaches is the functionalization of cyclodextrins with fluorescent molecules that include. In these types of supramolecular systems the fluorophore is attached to the cyclodextrin cavity via linker. The cyclodextrin cavity acts as a guest-binding site, the fluorophore acts as a signalling unit. The linker, may be simply a bridge, may involve in a specific-responsive function for the substrate. In such a system, the generation of a signal is based on the competition between the covalently attached included fluorophores and added guest for entering the cavity. The attached chromophore might be partially included in the cavity before adding the guest as shown Figure 3.1. The chromophore will leave the cavity when the guest includes in it. Therefore, a decrease of fluorescence intensity is observed.

![Figure 3.1. A host-guest interaction by cyclodextrin-appended chromophore and the guest G.](image-url)
The change in the fluorescence intensity of the fluorophore upon inclusion of the guest in the cavity is the most common sensing strategy in these supramolecular systems. The example shown in Figure 3.1 represents a cyclodextrin labelled with the dansyl group. The labelled cyclodextrin was titrated with 1-adamantanol, which resulted in a decrease in fluorescence intensity and a red shift in the emission spectra. In the absence of 1-adamantanol the dansyl group binds in the cyclodextrin cavity, resulting in a blue shifted and enhanced emission. Addition of 1-adamantanol displaces the dansyl group, resulting in greater exposure to the aqueous phase and a red shift in the emission spectra. Many supramolecular systems for sensing organic guest based on guest-binding mechanism have been reported in literature. In one of these systems recently reported the cyclodextrin-appended anthracene (ANCD) was used to detect the pyromellitic dimer (PMDI) derivative in solution, Figure 3.2. PMDI was the focus of many reports due its electron accepting properties. An important characteristic of these materials is their ability to undergo redox reactions in electrolyte solutions. It has been shown that polyimide derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) can undergo two reversible redox reactions in electrolyte solutions involving the pyromellitic diimide moiety. The PMDI has a more negative reduction potential \( E_{1/2} = -1.2 \text{ V vs Fc}^{+/0} \) compared to other commonly used acceptors like naphthalenediimide \( E_{1/2} = -0.95 \text{ V vs Fc}^{+/0} \). The inclusion of PMDI in the \( \beta \)-cyclodextrin cavity has been detected by quenching of the anthracene emission through photoinduced electron transfer from the latter to the PMDI. A similar system was reported for sensing of anions. In this system \( \gamma \)-cyclodextrin was attached to a pyrene through a spacer, Figure 3.3. This system was used as a probe for bicarbonate. The CD-PY system shows a pyrene emission between 370-400 nm and excimer like fluorescence centred at 475 nm. When NaHCO\(_3\) was added, a new fluorescent band appeared around 390-460 nm. Different anions have been investigated; none of them has shown a new band except the bicarbonate. This result was attributed to the ability of HCO\(_3^{-}\) to bind to the triamine linker and changes the conformation of the pyrene rings.
This change in the conformation decreases the overlap between the two \( \pi \) surfaces, resulting in the blue shift of the excimer fluorescence as shown in Figure 3.3(bottom). The pH-dependence fluorescence properties of amino-cyclodextrin derivatives that have one \(^8\), two \(^9\), three \(^{10}\) amines sites have been reported. In the \( \gamma \)-cyclodextrin-(amine)\(_3\)-pyrene system, the protonation of these amine sites linked to the fluorophores may enhance the fluorescence of the pyrene moiety and \textit{vice versa}. These results have
been explained on the basis of chelation-enhanced fluorescence \(^{11}\) or photo-induced electron-transfer mechanism. \(^{12}\)

**Figure 3.3.** A bicarbonate sensor comprised of \(\gamma\)-cyclodexrin-appended pyrene (top), the excimer formation after the addition of NaHCO\(_3\) (bottom), and fluorescence spectra of pyrene-modified cyclodextrin alone (blue) and after addition of NaHCO\(_3\) (Red).\(^{7}\)
Another approach in using cyclodextrins for molecular sensing involves cyclodextrin functionalised with photoactive metal centres:

In these types of supramolecular assemblies the properties of the metal complexes have been combined with the characteristics of the cyclodextrins to obtain a new system that have applications in sensing, directional energy and electron transfer. The cyclodextrin cavity acts as a binding site for the analyte. The photoactive metal centre acts as a signalling unit that response to the included guest in the cyclodextrin cavity. In designing these systems three factors should be taken into consideration:

(i) The distance between the metal centre and the included guest. A nanoscale distance is necessary to control long-range energy and electron transfer (ii) the association constant of the included guest/analyte in the cavity. (iii) The photophysical properties of the metal such as long-lived luminescence lifetimes for electronic communication. Following photoexcitation the lifetime of the excited state must be sufficient to accommodate transfer of an electron to the electron acceptor, which is covalently/non-covalently linked to a donor. transition metal polypyridyl complexes containing, for example, Ru(bpy)$_3$, or Re(bpy)(CO)$_3$, display a long list of properties that satisfy most of the kinetic, thermodynamic, spectroscopic and excited state requirements needed for a photosensitiser and therefore have been widely used.\textsuperscript{13,14} The presence of a transition metal in the molecule introduces exceptional new types of excited states and reactivity patterns which give rise to unique photochemistry and photophysics.\textsuperscript{15} Lanthanides can be used in molecular sensing. Eu(III) and Tb(III) were found to be ideal luminescent probes due to their long lifetimes and visible emission, Eu(III) emits red and Tb(III) emits green light. Cyclodextrin modified with lanthanides such as Eu(III) and Tb(III) have been used to detect aromatic hydrocarbons such as benzene, toluene, or biphenylene.\textsuperscript{16} Before the addition the guest there was no luminescent signal from the lanthanide. After the addition of the aromatic guest a strong luminescence signal of lanthanide was observed. This result was explained to be as a result of the inclusion of aromatic guest in the cavity, which sensitised the lanthanides. In this example “switch-on” behaviour of the luminescence signal was reported.
Persubstituted β-cyclodextrin with bipyridyl and urea was shown to bind Eu (III) and Tb (III) ions. Luminescent trimer has been reported whereby; cyclodextrin was functionalised with three Eu (III) terpyridyl complexes as shown in Figure 3.4.

**Figure 3.4.** Luminescent cyclodextrin trimer.

Transition metals also have been appended to cyclodextrin for sensing purposes. Rhenium and ruthenium photoactive metal centres were covalently linked to the primary side of cyclodextrin. For example, rhenium tricarbonyl was coordinated to a bipyridine β-cyclodextrin, the Re (I) metal centre was found to be sensitive to the presence of aromatic amines in the cavity. Quenching of the Re(I) luminescence intensity was observed upon inclusion of aromatic guest. Many examples of ruthenium terpyridyl complex attached to cyclodextrins have reported. These systems have been utilized for detecting aromatic guests such as benzoquinones and anthraquinones in solutions, Figure 3.5. Quenching of the ruthenium luminescent signal upon inclusion of the guest in the cavity was observed.
The quenching was attributed to the intramolecular electron transfer form the Ru(II) to the aromatic guest. One of the drawbacks of Ru(tpy)$_2$ though is that this unit is relatively weakly luminescent and short lived. A ruthenium tris-bipyridine with six attached β-cyclodextrin was reported by Nelissen et al. $^{21}$ This system (Figure 3.6) has been selectively used to detect steroids based on switch-on behaviour of luminescent signal. $^{22}$

Figure 3.6. “switch-on” steroids sensor based on β-cyclodextrin attached to Ru(II) complex.$^{21}$
The switch-on behaviour was based on the competitive binding of the steroids and bipyridinium moiety to the cyclodextrin cavity. When the bipyridinium ion is added to the Ru-(CD)$_6$, Figure 3.6, the ruthenium emission is quenched via Intramolecular electron transfer. Replacing the bipyridinium moiety by steroids shuts the intramolecular electron transfer.

3.2.2 The acid-base properties of transition metal complexes: pH probes.

In aqueous solution the water molecules act as a proton donor or a proton acceptor in the presence of acid or base undergoing excited state deprotonation or protonation, respectively. The acid-base properties of an excited molecule are different from those in the ground state due to the redistribution of the electronic density upon excitation. In the case where acids and bases are stronger in the excited state than the ground state, photoinduced proton transfer may occur upon excitation. Therefore, the acidic properties of a proton donor group can be enhanced so that the pK$^*$ of this group in the excited state is much lower than the pK in the ground state. The same for basis where the pK$^*$ is much higher than pK. These processes are represented in scheme 3.1:

**Scheme 3.1.** The processes associated with the excitation of Acid in aqueous solution.
Where $\tau_0$, $\tau_0'$ are the excited state lifetimes of the acidic (AH*) and basic (A*-*) forms, respectively, and $k_1$ and $k_{-1}$ are the rate constants for deprotonation and reprotonation, respectively. $k_r$ and $k_{r'}$ are the radiative rate constants, respectively. The excited-state equilibrium constant is $K^* = k_1 / k_{-1}$. The change of the fluorescence intensity with time of the acidic form AH* and the basic form A*- following $\delta$-pulse excitation can be written according to Scheme 3.1:

$$\frac{d[AH^*]}{dt} = -(k_1 + 1/\tau_0)[AH^*] + k_{-1}[A^{-*}][H_3O^+]$$

Equation 3.1

$$\frac{d[A^{-*}]}{dt} = k_1[AH^*] - (k_{-1}[H_3O^*]+1/\tau_0')[A^{-*}]$$

Equation 3.2

The steady state intensities can be written after integrations

$$I_{AH^*} = C\phi \frac{1+k_{-1}\tau_0'[H_3O^*]}{1+k_1\tau_0+k_{-1}\tau_0'[H_3O^*]}$$

Equation 3.3

$$I_{A^{-*}} = C\phi' \frac{k_1\tau_0}{1+k_1\tau_0+k_{-1}+k_{-1}\tau_0'[H_3O^*]}$$

Equation 3.4

$C$ is a multiplication factor that must be introduced to take into consideration the experimental conditions.

Under specific conditions where the back reaction is too slow during the excited-state lifetime, the kinetic scheme can be simplified and leads to the following equations:

$$I_{AH^*} = C\phi_0 \frac{1}{1+k_1\tau_0}$$

Equation 3.5

$$I_{A^{-*}} = C\phi'_0 \frac{k_1\tau_0}{1+k_1\tau_0}$$

Equation 3.6

Prediction of pK* by means of Förster cycle:

Förster cycle is shown in scheme 3.2 which can be used to predict theoretically the pK* in conjunction with spectroscopic measurements:

According to this cycle:

$$N_a h\nu_{AH} + \Delta H^{o*} \Leftrightarrow N_a h\nu_A + \Delta H^o$$

Equation 3.7
Scheme 3.2. Förster cycle

\[
\begin{align*}
\text{AH}^* & \quad \text{Δ}H^0 \quad \text{A}^* \\
\quad \updownarrows \quad \text{hv}_{\text{AH}}(0-0) \quad \text{hv}_{\text{A}^-}(0-0) \quad \text{A}^- \\
\text{AH} & \quad \text{Δ}H^0
\end{align*}
\]

Where \( \text{Δ}H^0 \) and \( \text{Δ}H^0^* \) are the standard molar ionization enthalpies of \( \text{AH} \) and \( \text{AH}^* \), respectively, \( \text{hv}_{\text{AH}} \) and \( \text{hv}_{\text{A}^-} \) are the energy differences, corresponding to the 0-0 transition, between the excited state and the ground state of \( \text{AH} \) and \( \text{A}^- \), respectively, and \( N_a \) is Avogadro’s number. This equation can be rewritten as:

\[
\text{Δ}H^0^* - \text{Δ}H^0 = N_a(\text{hv}_{\text{AH}} - \text{hv}_{\text{A}^-})
\]

Assuming \( \text{Δ}S^0 = \text{Δ}H^0 \), and \( \text{Δ}H^0^* = \text{Δ}S^0^* \), then

\[
\text{Δ}H^0^* - \text{Δ}H^0 = \text{Δ}G^0^* - \text{Δ}G^0
\]

The standard free energy of \( \text{AH} \) and \( \text{AH}^* \) can be given as:

\[
\begin{align*}
\text{Δ}G^0^* &= -RT \ln K = 2.3 RT \ pK \quad \text{Equation 3.8} \\
\text{Δ}G^0 &= -RT \ln K^* = 2.3 RT \ pK^* \quad \text{Equation 3.9}
\end{align*}
\]

Where \( R \) is the gas constant and \( T \) is the absolute temperature. By subtracting equations 3.7 and 3.8 and converting the frequencies into wavenumbers the equation can be written as:

\[
pK^* - pK = 2.1 \times 10^{-3} \left( \bar{\nu}_{\text{A}^-} - \bar{\nu}_{\text{AH}} \right) \quad \text{Equation 3.10}
\]
\( \bar{\nu}_{A^-}, \bar{\nu}_{AH} \) corresponding to the 0-0 transitions of the AH and A\(^-\) and they are usually estimated by means of the average of the wavenumbers corresponding to the maxima of absorption and emission:

\[
\nu_{0-0} = \frac{\nu_{\text{abs}}^{\text{max}} + \nu_{\text{em}}^{\text{max}}}{2}
\]

Equation 3.11

The kinetic cycle and emission data can be used to calculate pK\(^*\). The inflection point, pH\(_i\) obtained from the emission titration curve can be corrected for the difference in the lifetimes of the protonated (\(\tau_{HA}\)) and the deprotonated (\(\tau_{A^-}\)) species according to the following equation: \(^{24}\)

\[
pK_{a}^* = pH_i + \log\frac{\tau_{\text{acid}}}{\tau_{\text{base}}}
\]

Equation 3.12

The acid–base properties of transition metal complexes containing ionizable ligands such as carboxy polypyridyls, triazols, imidazoles and CN\(^-\) can provide important information about the nature and the location of the excited state. A small change in the acidity from the ground state to the excited states often implies that ligand-containing acid-base functional groups are not involved in the excited state. The pK\(_a\) of the excited can be evaluated from the pH- dependence of the emission spectrum according to Equation 3.12. The acid-base properties of transition metal complexes containing ionizable ligands have been used towards designing pH probes. [Ru(LL)\(_2\)(MebpyCOOH)]\(^{+2}\) complexes, where LL represents bpy, phen, Mebpy, Me\(_4\)bpy, (MeO)\(_2\)bpy, (EtO)\(_2\)BPy, Cl\(_2\)bpy, and NO\(_2\)phen have demonstrated dependence of absorption and fluorescence on the pH. \(^{25}\) All complexes have shown similar spectral changes toward pH. [Ru(tpy-py)\(_2\)][PF\(_6\)]\(_2\) and osmium counterpart have been investigated to be used as pH probes. \(^{26}\) Figure 3.7 shows the proton acceptor positions in those complexes.
Both of them have shown pH dependence of the absorption and emission spectroscopy. The lifetimes also are affected by adding H⁺ ions. These changes have been explained on the basis that protonation of the pyridine units lowers the energy of their π⁺ orbitals which in turns increases their electron-accepting properties.
A long-lifetime pH probe has been reported, based on \( \text{Ru}([\text{bpy}]_2(\text{deabpy}))(\text{PF}_6)_2 \), Figure 3.8, which showed a pH dependent excited-state lifetime. Decreasing lifetimes have been observed with increasing the pH of the solution. This occurs as a result of protonation of deabpy ligand which becomes a better electron acceptor, lowering the energy of the MLCT, and thereby decreasing the lifetimes.

In this chapter, we report on the pH sensitivity of the luminescence of \([\text{Ru}(\text{bpy})_2(\text{phen-CD})]^2+\), Scheme 3.3, and on the ability of the structure to support photoinduced electron transfer between an included guest and the ruthenium center and discuss the possibility of modulating this communication through protonation/ deprotonation of the amine bridge. The Aphen-CD is \(6^\text{A}-(5\text{-amino-1, 10-phenanthroline})-6^\text{A}\text{-deoxy-}\beta\text{-cyclodextrin}\) and bpy is 2,2'-bipyridine.

**Scheme 3.3.** The structure of \([(\text{bpy})_2(\text{Aphen-}\beta\text{-CD})]^2+, \text{CDRu.}\)
3.3 Experimental:

3.3.1 Synthesis of 6'-deoxy-6'-p-toluenesulphonyl- β-cyclodextrin, (β-CD-OTs): 28

To a solution of β-CD (57.07 g, 44 mmol) in NaOH (1500 cm³, 0.4 mol dm⁻³), P-toluenesulphonyl chloride (54.62, 286.5 mmol) was added with vigorous stirring at 0 °C. The resulting solution was stirred for a further 3 hours at the same temperature and then filtered by gravity to remove the excess of p-toluenesulphonyl chloride. The filtrate was neutralized with HCl (1 mol dm⁻³) and a white precipitate formed, which was collected by gravity filtration. The crude product was recrystallized from hot water and dried in vacuo. 1H NMR (400 MHz, DMSO) δ H OTs, 7.740 ppm (d, 2H), H Otsg, 7.426 ppm (m, 2 H), OH Glu 2+3 4.6 - 4.154, 5.891 - 5.722 ppm (m, 14 H), OH Glu-6 4.600 - 4.154 ppm (m, 7 H's), H Glu-1 4.901 - 4.794 ppm (m, 7 H's).

3.3.2 Synthesis of 5-Amino-1, 10-phenanthroline: Aphen

This compound was prepared by reduction of 5-nitro-1, 10-phenanthroline using H₂S (g) in aqueous medium. H₂S was generated by heating a solution of 4.2 g of sulfur and 16 g of sodium sulfide Na₂S in water for 30 min. 5 cm³ of this solution was added to 1.0 g of 5-nitro-1, 10-phenanthroline solution. The mixture was heated with vigorous stirring for 1 hr. The solution was filtered and kept overnight. The yellow powder then was collected and dried in vacuo. The solid was recrystallized from water. Yield 65 %. ¹H-NMR (400 MHz, DMSO) 6.2 (s, 2H), 6.85(s, 1H), 7.5 (m, 1H), 7.75 (m, 1H), 8.15 (d, 1H), 8.65 (d, 2H), 9.05 (d, 1H).
3.3.3 Synthesis of the ligand 6^A-(5-amino-1, 10-phenanthroline)-6^A-deoxy-β-cyclodextrin, (CD-aphen):

CDOTs (1.2 g, 1.0mmol), NaI (0.02 g, 7 mmol), (5-amino11, 10-phenanthroline (0.3 g, 1.5 mmol) were dissolved in 30 ml NMP. The solution was stirred at 80°C for 24 Hrs under inert gas. NMP was removed under vacuum. Acetone was added to precipitate the product. This was purified using column chromatography on Sephadex G-25 with water as an eluent. The purity was confirmed by ^1H-NMR.

3.3.4 Synthesis of Ruthenium (II)(Bisbipyridine)(6^A-(5-amino-1, 10-phenanthroline)-6^A-deoxy- β-Cyclodextrin (CDRu):

β-CD-Aphen (0.65g, 0.49 mmol), Ru(bpy)_2Cl_2 (0.24 g, 0.44mmol) were refluxed in 2:1 (v/v) ethanol:water for 24 hrs. Ethanol was removed by vacuum evaporation. Concentrated aqueous NH_4PF_6 was added to precipitate the product, which was purified using size-exclusion chromatography on Sephadex G-75, with water as eluent. {M/z=878.8 of [M-2PF_6]^2}, 1637 of –[M-PF_6]^+1}, structure was confirmed using 1D and 2D ^1H-NMR which conformed to previously reported values.  

3.4 Results and Discussion:

3.4. 1 Synthesis:

The synthetic approach to the complex (CD-Ru) is shown in scheme 3.4. The β-cyclodextrin aminophenanthroline ligand is synthesized by reacting the appropriate aminophenanthroline with tosyl cyclodextrin derivatives. Monotosylate β-cyclodextrin has been synthesized as reported.

CDRu was synthesized by treating the ligand β-CD- aphen with one equivalent of cis-Ru(bpy)_2Cl_2. The complex was purified using size-exclusion chromatography Sephadex G-75 and water as an eluent.
Scheme 3.4. Synthesis of CD-Ru complex.

3.4.2 Characterization

3.4.2.1 NMR Spectroscopy:

The purity and structural confirmation for complex and ligands were obtained by $^1$H-NMR, mass spectroscopy. $^1$H NMR spectra were recorded in DMSO $[D_6]$. $^1$H NMR data for the ligand Aphen-$\beta$-CD is shown in Figure 3.9. The aromatic region (6 to 10 ppm) exhibits resonances associated with the aminophenanthroline moiety. The resonances associated with $\beta$-CD were observed at high field between 3 and 5 ppm. The relative integration of signal intensities in the aromatic region with the anomeric protons (H$_{\text{Glu-1}}$ protons) is 1:1 signal ratio confirming monosubstitution of the cyclodextrin by the phenethroline unit. The proton numbering for the cyclodextrin and ruthenium complex are shown in scheme 3.5. The chemical shifts of cyclodextrin protons in DMSO-$d_6$ are as reported previously. The assignment of the spectra of CD-Aphen and CDRu is non-trivial owing to the asymmetry of the compounds. In each case there are seven chemically non-equivalent sugar rings, each of which, in principle, gives rise to a distinct set of signals for the sugar ring protons. While assignment and solution conformation(s) of $\beta$-cyclodextrin, and other symmetrically substituted cyclodextrins has been reported, there is only limited NMR data available regarding spectral parameters that may be used to characterize monosubstituted $\beta$-cyclodextrin. In principle each sugar contains a distinct spin system, then starting from the anomeric H$_{\text{1}}$ proton, which resonates downfield, typically at ca. 5 ppm, one should be able to assign sequentially the protons.
in a given sugar from a COSY spectrum. However, due to the severe spectral overlap in the region 3-4 ppm in the present system identification is still difficult with COSY. Therefore, other 2D NMR techniques required such as HOHAHA, NOE, and NOEESY. The H-1" (the anomic protons) in β-cyclodextrin is expected to appear at 4.86 ppm and H-2" (non-anomeric) around 3.2 ppm.

![NMR spectrum](image)

**Figure 3.9.** The 400MHz 1D ¹H NMR results for β-CD-Phen in DMSO [d₆]. See text for assignments of anomeric, primary and secondary protons of β-cyclodextrin.

The secondary hydroxyls of the cyclodextrin (OH₂, OH₃) appear between 5.6-5.8 ppm, which agrees with the reported values. The broad peak between 4.5 and 4.7 corresponds to the primary hydroxyls (OH₆).
Scheme 3.5. Proton numbering of cyclodextrin glucose unit and the ligands in the ruthenium complex.

The $^1$H NMR spectrum of CDRu is shown in Figure 3.10. The aromatic region of the spectrum showed the expected chemical shifts pattern for a hetroleptic complex with general formula $[\text{Ru(bpy)}_2\text{L}]^{2+}$ where L is the ligand that differs from bipyridine. The spectrum is the sum of the resonances belonging to the cyclodextrin phenanthroline ligand and those unsubstituted bipyridine ligands.

The complexation of the CD-aphen was confirmed by upfield shift of H-6,6' of the bipyridine and H-1, H-9 of the aphen. In the aromatic region the resonances of the substituted aminophenathroline are observed as a multiplet at 8.8 ppm (H2, H9), 7.4 ppm (H3), 7.6 ppm (H8), 7.8 ppm (H7), 8.4 ppm (H4), 7.0 ppm (H6). And those of the bipyridine ligands are observed as a doublet at 9.0 ppm (H3), a doublet at 8.20 ppm (H4), a doublet at 8.20 ppm (H6), and a doublet of doublet at 7.60 ppm (H5). Similar
results have been observed for a reported ruthenium complex attached to cyclodextrin\textsuperscript{34}. All NMR data and their assignments were collected in Table 3.1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.10.png}
\caption{The 400 MHz $^1$H NMR of CD-Ru in DMSO [d$_6$].}
\end{figure}

The resonances associated with $\beta$-CD were observed at low frequency between 3 and 5 ppm. The integration of signal intensities of the aromatic region with the anomeric protons ($H_{\alpha\beta-1}$ protons) gives 26:7 signal ratio confirming the monosubstitution of the cyclodextrin by the [Ru(bpy)$_2$phen-NH]- unit. $^1$H NMR results confirmed the formation of CDRu complex.
Table 3.1. $^1$H NMR data of CD-OTs, CD-aphen, and CDRu. Values are in ppm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>β-CD</th>
<th>aphen</th>
<th>bpy</th>
</tr>
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<tbody>
<tr>
<td>β-CD-aphen</td>
<td>H$_{Glc-1}$</td>
<td>(d, d)</td>
<td>(d, d)</td>
</tr>
<tr>
<td></td>
<td>OH$_{Glc-2+3}$</td>
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<td>(1H)</td>
</tr>
<tr>
<td></td>
<td>OH$_{Glc-6}$</td>
<td>(1H)</td>
<td>(IH)</td>
</tr>
<tr>
<td></td>
<td>H$_{aphen-2,9}$</td>
<td>(1H)</td>
<td>(IH)</td>
</tr>
<tr>
<td></td>
<td>H$_{aphen-3}$</td>
<td>(1H)</td>
<td>(IH)</td>
</tr>
<tr>
<td></td>
<td>H$_{aphen-4}$</td>
<td>(s)</td>
<td>(IH)</td>
</tr>
<tr>
<td></td>
<td>H$_{aphen-7}$</td>
<td>(d, d)</td>
<td>(1H)</td>
</tr>
<tr>
<td></td>
<td>H$_{aphen-8}$</td>
<td>(m)</td>
<td>(4)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>H$_{bpy-4}$</td>
<td>m</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>H$_{bpy-5}$</td>
<td>m</td>
<td>m</td>
</tr>
<tr>
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<td>5.847-5.699</td>
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</tr>
</tbody>
</table>

Table continued...
3.4.2.2 Electronic and photophysical properties $[\text{Ru(bpy)}_2(\text{phen-CD})]^2^+ $:

The UV/Vis spectra for the complex show a maxima around 455 nm assigned as a $[\text{Ru}(t_2g)^6 \rightarrow \text{Ru}^{2+}(t_2g)^5\pi^1(\text{bpy})]$, Figure 3.11. The complex shows an absorption that conforms with that for $[\text{Ru(bpy)}_3]^{2+}$. This was previously confirmed by resonance raman spectroscopy and transient absorption spectroscopy.\(^{35}\) The bands at 185 nm and 285 nm are assigned to LC ($\pi - \pi^*$) transitions.\(^{36}\) Another MLCT band at 240 nm is assigned to d-$\pi^*$ transitions. The shoulders at 322 nm and 344 nm might be MC transitions. The complex exhibits an intense luminescence centred at 618 nm, with a lifetime of 850 ns in deoxygenated DMF, which is reduced to 168 ns in aerated media.

Figure 3.11. pH-dependent UV-Vis spectrum of $(5 \times 10^{-4} \text{ M})\text{CD-Ru}$ in Britton Robinson buffer, pH range from 7-12.7.
The absorption spectrum of CD-Ru at different pH values is shown in Figure 3.11. Only relatively slight changes were observed in the absorption spectra.

### 3.4.3 pH Dependence of the photophysics of [Ru(bpy)₂(phen-CD)]²⁺:

As both the amine linker and the cyclodextrin moieties possess ionizable sites, it was of interest to see if deprotonation /protonation of these sites had an impact on the photophysics of metallo-cyclodextrin. Ultimately, the objective in these studies was to determine if protonation/deprotonation of the amine linker could be used as a means of modulating the communication between an included species and the luminophore. The pKₐ for the secondary hydroxyl groups of unsubstituted β-CD were previously reported to be 12 and 13.2. The pKₐ value for the primary amine in the precursor complex [Ru(bpy)₂(NH₂phen)](PF₆)₂ was found to be 7.5 from fluorescence titration. Figure 3.12a shows emission spectra of [Ru(bpy)₂(phen-CD)]²⁺. Increasing the pH of the medium results in significant changes to the emission intensity of [Ru(bpy)₂(phen-CD)], without a change in the emission maximum. Correspondingly, increasing the pH decreased the luminescence lifetime of the complex, for example, in deaerated solution, the lifetime of [Ru(bpy)₂(phen-CD)]²⁺ decreased by half, from approximately 1μs to 500 ns in deaerated aqueous buffer as shown in Figure 3.12b.

The quenching of luminescence intensity and the decrease in the lifetimes upon increasing pH can be attributed to the photoinduced electron transfer from the deprotonated amine group to the [Ru(III)(bpy)₂aphen]⁺² moiety. This one of the mechanisms that has been proposed for the quenching of the [Ru(bpy)₃]⁺² by covalently linked amino groups. Figure 3.13 shows the plot of changes of emission intensity with pH. A single inflection point was observed over this pH range and a pKₐ of approximately 11.5 was determined from the derivative of the plot. Comparison with pKₐ of other secondary amines suggests that the amine is the most likely site of deprotonation at this pH. Deprotonation of the CD hydroxyls are anticipated to occur at higher pH and would not be anticipated to elicit such a strong impact on the photophysics of the remote Ru centre.
Figure 3.12. (a) pH fluorescence titration of $[\text{Ru(bpy)}_2(\text{phen-CD})]^{2+}$, $2.4 \times 10^{-5}$ mol dm$^{-3}$, excited at 455 nm in Britton Robinson buffer, pH range from 7-13.2, (b) luminescent decay of $[\text{Ru(bpy)}_2(\text{phen-CD})]^{2+}$, $2.4 \times 10^{-5}$ mol dm$^{-3}$ at neutral, pH 9 and pH 12.
It has been reported that the pKₐ value for unsubstituted β-CD was determined to be 12.2, and in another report obtained using NMR titration, pKₐ₁ and pKₐ₂ values for deprotonation of first and second hydroxyl groups of unsubstituted β-CD were calculated as approximately 13.5, where these authors found it difficult to calculate the pKₐ₃ and pKₐ₄. The pKₐ value for the deprotonation of –NH₂⁺ group was found to be 7.5, using fluorescence titration of [Ru(bpy)₂(deabpy)].(PF₆)₂. Fluorescent studies on amino-β-CD derivatives have shown the effect of protonation and deprotonation of amine site on the fluorescence intensity of the fluorophores. Increasing the pH would deprotonate the –NH₂⁺ leading to decrease in luminescence intensity.

![Figure 3.13](image)

**Figure 3.13.** Plot of fluorescence intensity and change in fluorescence intensity at 618 nm as a function of pH.
It is proposed that the pH-dependent fluorescence of CD-Ru is controlled by the protolytic equilibrium of amine protons (Scheme 3.6 A, B).

**Scheme 3.6.** Protolytic equilibria of amine and hydroxyl protons

A-

B-
The effect of these equilibria on the emission intensity and lifetimes can be explained as follows:

E. Norkus et al. assumed that in basic media both primary and secondary hydroxyls of β-CD are deprotonated at pH>12.43. The oxyanion formed at 6-position may form H-bonding of $\text{O}--\text{H}--\text{N}$ (Scheme 3.6). In acidic medium the fluorescent intensity and emission lifetimes would have different effect on the photophysical properties of the CDRu complex as protonation would lead to enhancement of fluorescence intensity for the fluorophore via a chelation-enhanced mechanism as shown in Scheme 3.7. The results indicate that the CD-Ru complex may find a use as a pH sensor.

**Scheme 3.7.** Proposed Photo-induced electron transfer in CD-Ru complex.
3.4.4 Electrochemical Data:

To study the effect of protonation and deprotonation of the amino group on the oxidation potential of the Ru metal centre cyclic voltammetry in basic and acidic medium have been carried out. The electrochemistry of metal complexes have been discussed in detail in Section 1.7.

Cyclic voltammogram for CDRu in dry DMF is shown in Figure 3.14A. The anodic peak is one reversible oxidation at 1.41 V vs. Ag/Ag$^+$ and three cathodic peaks are quasi-reversible ligand based reduction peaks. The electrochemical data are collected in Table 3.2.

**Table 3.2.** Electrochemical data for CD-Ru in DMF, the complex was deprotonated using saturated solution of NaOH, and protonated using conc. H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$/V Anodic</th>
<th>$E_{1/2}$/V Cathodic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CDRu]$^{+3}$ protonated</td>
<td>1.23</td>
<td>-0.619, -1.03 (irr.), -1.44 (irr.)</td>
</tr>
<tr>
<td>Dry DMF [CDRu]$^{+2}$</td>
<td>1.41</td>
<td>-1.10, -1.20, -1.45</td>
</tr>
<tr>
<td>Deprotonated [CDRu]$^+$</td>
<td>1.20</td>
<td>-1.419, -0.750 (irr)</td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$_2^+$</td>
<td>1.35</td>
<td>-0.976, -1.152, -1.462</td>
</tr>
</tbody>
</table>

Figure 3.14B. Exhibits CVs of CDRu in DMF and after addition of H$_2$SO$_4$ and NaOH. In all CVs the metal-based and ligand reductions oxidation are obvious all media accompanied with a lack of reversibility for the oxidation process in acidic (Figure 3.14a) and basic media (Figure 3.14b), and poorly defined reduction processes and increased intensity. This may be attributed to the protonation/deprotonation of aminophenanthroline ligand. Even though the oxidation potential is less affected by the protonation/deprotonation of the amino group. The metal based oxidation is 49 mV.
lower than that of [Ru(bpy)$_3$]$^{2+}$ which has an oxidation potential of 1.35 V versus Ag/Ag$^+$. The σ-donor ability of the deprotonated aminophenanthroline (Aphen) is much stronger than that of bpy. This explains the decrease of the oxidation potential of CDRu.

Figure 3.14. (A) Cyclic voltammograms of 1×10$^{-3}$ M CDRu in argon purged DMF, 0.1M TBABF$_4$ using glassy carbon as working electrode, platinum wire as a counter electrode, and Ag/Ag$^+$ as a reference electrode, the scan rate is 500 mv s$^{-1}$e.$^2$, (B) cyclic voltammograms of CDRu in dry DMF after addition conc. H$_2$SO$_4$, (a) and after an addition of saturated solution of NaOH (b).
after addition NaOH. The stronger σ-donor of aminophenanthroline upon deprotonation increase the electron density at the metal centre and it becomes easier to oxidise. In related complexes, protonation of ionisable ligand causes a shift in the oxidation to higher potential. In our case different behaviour was observed where the protonation of CDRu results in decrease of the oxidation potential. This behaviour might be attributed to the presence of cyclodextrin. The lack of reversibility observed for the oxidation process upon protonation or deprotonation of the ligand is possibly best explained by overlap between the metal oxidation and the aminophenanthroline based redox process. The CV of CD-Aphen shows a reversible oxidation potential 0.80 V and irreversible oxidation around −0.80 V versus Ag/Ag⁺. The reduction waves of CDRu by comparison with [Ru(bpy)₃]²⁺ and other polypyridyl complexes are assigned to bpy and aphen based reductions. The reduction processes are not well resolved and become irreversible by protonation and deprotonation. These results have reported before and attributed to surface adsorption. In addition, most of the results obtained on related complexes couldn’t obtain satisfactory reduction potentials in acidic solutions.

3.4.5 Luminescence Quenching of [Ru(bpy)₂(phen-CD)]²⁺ by anthraquinone guests:

The ability of cyclodextrins to form inclusion complexes with polyaromatic guests is well known and discussed in detail in Section 1.1.3.⁴⁶ We investigated the inclusion of Anthraquinone (AQ) and Anthraquinone-carboxylic acid (AQC), Figure 3.15, with [Ru(bpy)₂(phen-CD)]²⁺ as both are known to include in β-CD and both are oxidants with appropriate thermodynamic properties to encourage photoinduced electron transfer from an excited Ru(II) polypyridyl centre.⁴⁶⁻⁴⁷ As [Ru(bpy)₂(phen-CD)]²⁺ exhibits a relatively long-lived excited state, we anticipated particularly efficient quenching by these systems.
3.4.5.1 Quenching studies in a neutral aqueous solution of CDRu:

Quenching studies were performed on CDRu complex in neutral and basic solution of \([\text{Ru(bpy)}_2(\text{phen-CD})]^2+\) using AQ and AQC. The values of emission intensities were corrected for dilution factor.

Figure 3.16 shows the effect of addition of anthraquinone (AQC) on the emission intensity of \([\text{Ru(bpy)}_2(\text{phen-CD})]^2+\) at pH 7. An efficient quenching of the ruthenium-excited state was reflected in substantial decreases in the luminescence intensity with increasing quencher concentration.

Figure 3.15. Redox active guests under investigation; anthraquinone and anthraquinone carboxylic acid.
Figure 3.16. Emission spectra of CD-Ru (2.0×10^{-5} M) in a quenching experiment upon addition 0 M -5.71×10^{-4} M of AQc in neutral aqueous solution.

The quenching can be attributed either to static or dynamic quenching which have been discussed in detail in section 1.5. In the present system the static quenching results from the inclusion of AQcMs in the cyclodextrin cavity, which allows the guest to reside in a close proximity to communicate with the Ru centre. This type of quenching is called an associative quenching.
Therefore, to confirm that associative quenching was occurring, we studied the impact of increasing anthraquinone concentration on the luminescent lifetime of [Ru(bpy)$_2$(phen-CD)]$^{2+}$. Figure 3.17 shows the luminescent decay of [Ru(bpy)$_2$(phen-CD)]$^{2+}$ in aerated aqueous media and on the addition of 5.71×10$^{-4}$ M AQC. In the absence of quencher, the lifetime conformed to a single exponential decay with $\tau_0$ of 168 ns. Addition of quencher, either AQ or AQC, results in a biexponential decay, the first component, $\tau_1$, is essentially unchanged from that of [Ru(bpy)$_2$(phen-CD)]$^{2+}$. The second component is short lived...
with a lifetime of 5 ns for AQ and 4 ns for AQC (Table 3.3). The former we attribute to unassociated complex and the short lifetime component to the complex containing included anthraquinone. These lifetimes do not change, within experimental error, on increasing a quencher concentration although their relative percentage contribution to the overall decay does change.

**Table 3.3.** Fluorescence lifetimes and electron-transfer rate constants of self-assembling systems consisting of CD-Ru and quinones in neutral and basic solutions.

<table>
<thead>
<tr>
<th>Quinone</th>
<th>$\tau_1$ (neutral) ns</th>
<th>$\tau_2$ (neutral) ns</th>
<th>$\tau_1$ (basic) ns</th>
<th>$\tau_2$ (basic) ns</th>
<th>$K_{ass}$ (M$^{-1}$)</th>
<th>$k_{et}$ (s$^{-1}$) (neutral)</th>
<th>$k_{et}$ (s$^{-1}$) (basic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>without</td>
<td>168 ± 9</td>
<td>56 ± 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AQC</td>
<td>161 ± 10</td>
<td>5.0 ± 0.5</td>
<td>52 ± 5</td>
<td>3.62 ± 0.5</td>
<td>14,657 ± 2200</td>
<td>1.93 x 10$^8$</td>
<td>2.5 x 10$^8$</td>
</tr>
<tr>
<td>AQ</td>
<td>158 ± 7</td>
<td>4.0 ± 0.4</td>
<td>54 ± 5</td>
<td>4.20 ± 0.4</td>
<td>4920 ± 560</td>
<td>2.4 x 10$^8$</td>
<td>2.2 x 10$^8$</td>
</tr>
</tbody>
</table>

This is consistent with associative or static quenching, a modified Stern-Volmer equation may be used to plot $I_0/I$ vs [Q] the slope of this plot, where the slope, $K_{SV}$ in equation 3.13, becomes $K$ which corresponds to the association constant between host and guest. The data were collected and represented as a Stern-Volmer plot in Figure 3.18 using the following Equation:

$$\frac{I_0}{I} or \frac{\tau_0}{\tau} or \frac{\phi_0}{\phi} = 1 + K_{sv}[Q]$$

Equation 3.13
Where $I_0$ and $I$ are the luminescence intensities of $[\text{Ru(bpy)}_2(\text{phen-CD})]^2+$ in the absence and presence of quencher, respectively, $\tau_0$, $\tau$ and $\phi_0$, $\phi$ are the respective excited state lifetimes and luminescence quantum yields in the absence and presence of quencher, $[Q]$ is the concentration of the quenching species and $K_{SV}$ is the Stern-Volmer constant which is the product of the quenching rate constant ($k_q$) and $\tau$. See Equations 1.17-1.21 for more details.

**Figure 3.18.** Stern-Volmer plot $I_0/I$ and $\tau_0/\tau$ vs quencher concentration $[Q]$. $2.00 \times 10^{-5}$ M of CDRu in DMF solution with addition of 0 M - 5.71$ \times 10^{-4}$ M AQC.
For static luminescence quenching, the slopes of $I_0/I$, $\phi_0/\phi$ or $\tau_0/\tau$ plots versus quencher concentration $[Q]$ are expected to be the same and equal to $k_q \tau_0$.

Similar behaviour was observed when AQ was added to the CD-Ru. The luminescence intensity decreased upon addition of AQ, Figure 3.19, with negligible changes to luminescent lifetimes, Figure 3.20.

**Figure 3.19.** Emission spectra of CD-Ru ($2.0 \times 10^{-5}$M) in a quenching experiment upon addition of 0 M - $5.71 \times 10^{-4}$ M AQ in neutral aqueous solution.
**Figure 3.20.** Time-resolved emission decay of \((2.0 \times 10^{-5} \text{M})\) CDRu in DMF in the absence and presence of \(0 \text{ M} - 5.71 \times 10^{-4} \text{ M}\) AQ in neutral aqueous solution.

The Stern-Volmer plots for luminescence intensity and lifetimes of AQ experiments are shown in Figure 3.21. According to the lifetimes results the quenching can be considered as purely static, which is similar to that observed for AQC-CDRu complex.
The stability constant for inclusion complexes formed between CD-Ru and the quinones in neutral aqueous solution was evaluated from the slopes of $I_0/I$ vs $[Q]$ and found to be $14,657 \pm 2200 \text{M}^{-1}$ for AQC and $4920 \pm 560 \text{M}^{-1}$ for AQ. $K_s$ is much lower in the case of AQ than in the case of AQC. The appearance of a short lived component of the luminescence decay and the decreased intensity of the inclusion complexes is attributed to photoinduced electron transfer on the basis of thermodynamic considerations, whereby the driving force for the electron transfer was evaluated using the Equation 3.14.

Figure 3.21. Stern-Volmer plots $I_0/I$ and $\tau_0/\tau$ vs quencher concentration $2.00 \times 10^{-5}$ M of CDRu in DMF solution with addition of $0 \text{ M} - 5.71 \times 10^{-4} \text{ M} \cdot \text{AQ}$. 
\[
\Delta G^0 = [E_{(D.+/D)} - E_{(A/A.-)}] - E_{0.0}
\]

Equation 3.14

Where \( E_{(D.+/D)} \) and \( E_{(A/A.-)} \) are the oxidation and reduction potentials of donor and acceptor sites respectively. \( E_{0.0} \) is the zero-zero spectroscopic energy. The reduction potential of AQ is -0.58 V and AQC is -0.74V. The ground state oxidation potential of Ru (II/III) is 1.10 V vs Ag/AgCl. Providing exergonic driving forces of -0.42 eV and -0.26 eV respectively for excited state electron transfer. Energy transfer from ruthenium to the anthraquinone is precluded, as it would be strongly endoergonic. The driving force of electron transfer for AQ is higher in than that AQC. Therefore, based on these values the strongest quenching would be expected to follow the more favourable driving force. The rates of photoinduced process can be assessed from Equation 3.15.

\[
k_{et} = 1/\tau_2 - 1/\tau_1
\]

Equation 3.15

Where \( \tau_2 \), the lifetime of the inclusion complex, taken to be the short component of the decay, and \( \tau_1 \), the lifetime of \([Ru(bpy)_2(phen-CD)]^{2+}\). The photoinduced electron transfer and quenching of the excited states were discussed in detail in Sections 1.8 and 1.5, respectively. Anthraquinone inclusion at the CD is anticipated to induce negligible structural perturbation at the ruthenium centre. On this basis it is reasonable to assume electron transfer alone is responsible for the reduced lifetimes and that the non-radiative decay pathways available the ruthenium centre remain unchanged for the inclusion complex. The electron transfer process responsible for Ru quenching process is shown in Figure 3.22. From Equation (3.15) then, the rate of electron transfer was estimated to be \( 2.4 \times 10^8 \text{ s}^{-1} \) for the AQ inclusion complex and \( 1.9 \times 10^8 \text{ s}^{-1} \) for AQC. As described, \( \Delta G \) for electron transfer was estimated to be approximately 50% lower for AQC compared with AQ. The electron transfer rate is correspondingly, greater for the AQ complex, but the discrepancy between the two values is not as large as expected on thermodynamic grounds. However, as described, \( K_{assoc} \) for AQC and \([Ru(bpy)_2(phen-CD)]^{2+}\) is considerably larger than for AQ, which is likely to be due to cooperative hydrophobic-hydrophobic and H-bonding interactions for AQC. It is tempting to speculate that the enhanced electron transfer rates observed for AQC is attributed to
the H-bonding interaction, as such bonding is widely recognized to promote electron transfer.

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Figure 3.22. Photo-induced electron transfer from Ru centre to anthraquinone.

3.4.5.2 Quenching of CDRu by anthraquinone guests in basic solution:

The effect of both AQC and AQ on the luminescence intensity of CDRu in basic solution was investigated. The luminescence from the metal complex is quenched upon addition of AQC to basic solution of CDRu as shown in Figure 3.23. Figure 3.24 shows the luminescent decay of [Ru(bpy)$_2$(phen-CD)]$^{2+}$ in aerated aqueous media and on the addition of 2050 μl of AQC in basic solution. The lifetime results are 1/3 to that observed in neutral solution. In the absence of quencher, the lifetime conformed to a single exponential decay with $\tau_0$ of 56 ns. Addition of quencher, either AQ or AQC, results in a biexponential decay, the first component, $\tau_1$, is essentially unchanged from that of [Ru(bpy)$_2$(phen-CD)]$^{2+}$. The second component is short lived with a lifetime of 4.20 ns for AQ and 3.62 ns for AQC (Table 3.3). The former we attribute to unassociated complex and the short lifetime component to the complex
containing included anthraquinone. These lifetimes do not change, within experimental error, on increasing a quencher concentration although their relative contribution to the overall decay does change. Stern-Volmer plot of the luminescence intensity shows pronounced positive deviations from linearity without reaching a plateau at high quinone concentrations Figure 3.25.

Figure 3.23. Emission spectra of aqueous solution of CDRu (2.0×10^-5 M) in a quenching experiment upon addition of 0 M - 5.71×10^-4 M AQC at pH 12.2.
Figure 3.24. Time-resolved emission decay of \((2.0 \times 5^5)\) deprotonated CDRu in DMF in the absence and presence of 0 M - \(5.71 \times 10^{-4}\) M AQC at pH 12.2.
This situation can be explained on the basis that a static quenching occurs. The same behaviour was observed in the interaction between the AQ and CDRu in basic solution. Figure 3.26 shows the effect of increasing concentrations of AQ on the emission intensity of CDRu. Quenching of the emission intensity with no change on lifetimes was observed, Figure 3.27. The Stern-Volmer plots for AQ similar to that observed for AQC Figure 3.28. The association between host-guest inclusion might be inhibited upon deprotonation of β-Cyclodextrin leading to lower association but the quenching is still purely static as shown in Figure 3.28.
Figure 3.26. Emission spectra of deprotonated CD-Ru (2.0×10^5 M) in a quenching experiment upon addition of 0 M - 5.71×10^{-4} M AQ.
The state of protonation of the amine bridge has surprisingly little effect on the rate of $k_{et}$ for the $\text{[Ru(bpy)}_2\text{(phen-CD)]}^{2+}\text{-AQ}$ complex where the difference in rate for neutral and basic media is negligible. The electron transfer rate is measurably greater for the AQC complex in basic media, increasing from $1.9 \times 10^8$ s$^{-1}$ at pH 7 to $2.5 \times 10^8$ s$^{-1}$ at pH 12. However this is attributed to deprotonation of the carboxyl on AQC, which reduces the thermodynamic driving force for electron transfer and may also enhance H-bridging between the carboxylate and the hydroxyls of the CD, which should remain protonated at this pH.

**Figure 3.27.** Time-resolved emission decay of $(2.0 \times 10^{-5}\text{M})$ deprotonated CDRu in DMF in the absence and presence of $0$ M - $5.71 \times 10^{-4}$ M AQ.
Figure 3.28. Stern-Volmer plots $I_0/I$ and $\tau_0/\tau$ vs quencher concentration $2.00\times10^{-6}$ M of deprotonated CDRu in DMF solution with addition of 0 M - $5.71\times10^{-4}$ M AQ.
3.5. Conclusions:

We have conducted detailed photophysical studies on the luminescent host [Ru(bpy)$_2$(phen-CD)]$^{2+}$. The complex exhibits a strong pH dependent luminescence, which is attributed to protonation/deprotonation of the secondary amine bridge linking the CD and ruthenium polypyridyl centre. From emission studies, the pK$_a$ for the amine was determined to be 11.5. [Ru(bpy)$_2$(phen-CD)]$^{2+}$ forms host guest complexes with AQ and AQC, with association constants of 4,920 ± 560 M$^{-1}$ and 14,657 ± 2,200 M$^{-1}$. The anthraquinone guest appears to participate in efficient photoinduced electron transfer from the excited ruthenium polypyridyl centre. The possibility that protonation/deprotonation at the amine linker can be used to modulate electronic communication between the CD and luminophore was explored. However, the rate of photoinduced electron transfer appeared to be relatively insensitive to the state of protonation of the bridge.
3.6 References


Chapter 4

Intramolecular Photoinduced Electron Transfer in Ruthenium Polypyridyl Functionalised β-Cyclodextrin Capped with a Hydroxo-Bridged Cu(II) Dimer.
4.1 Introduction:

4.1.1 Cu(II)-cyclodextrin complexes mimics of biological copper:

Cu(II) is an essential trace element that is widely distributed in animal and plant tissues. Besides Fe$^{3+}$, and Zn$^{2+}$, it ranks third in abundance in human among the essential heavy metal.\(^1\) It also acts as a cofactor for a number of metalloenzymes such as catalase, peroxides and cytochromeoxidaze to facilitate enzyme function.\(^2\)

The construction of Cu(II) -complexes with cyclodextrin derivatives as a receptors have been the focus of several reports.\(^3\) Among other applications, these complexes have been studied as chiral recognition receptors\(^4\) and superoxide dimutase mimics.\(^16\)

Correlations of the chiral recognition properties and scavenger activity with the geometrical features of the complexes and the role of the CD residue have been made.\(^5\)

Imidazole bridged dicopper(II) have attracted much attention as models for metalloenzymes, which contain the structural units.\(^6\) Copper-zinc superoxide dismutase (SOD) contains in the active site an imidazolate bridged mixed metal centre with one copper (II) and one zinc (II) ion.\(^7\) The Cu(II) ion is coordinated, in an approximately square planar structure, to four histidine imidazoles (His -44,-46, -61, and -118). Zn (II) is coordinated, in approximately tetrahedral arrangement, with three histidine imidazoles (His-61, -69, -78, and Asp-81). Histidine binds to the Cu (II) and the Zn (II) through a side chain (a histidine imidazolate bridged). Cu-ZnSOD model exhibits biocatalytic activity towards the dismutation of superoxide anion according to the following equation.\(^8\)

\[
\begin{align*}
O_2^- + [\text{Cu}^{II}] & \rightarrow O_2 + \text{Cu}^{I} \\
O_2^- + \text{Cu}^{I} + 2H^+ & \rightarrow H_2O_2 + \text{Cu}^{II}
\end{align*}
\]

Evidence implicating $O_2^-$ as a mediator of diseases such as neuronal apoptosis, cancer, and acquired immunodeficiency syndrome, continues to accrue.\(^9\)

All reported mimics of Cu, Zn-SOD focused on the peculiarity of the imidazole bridge, and almost no mimics of the biological functions of Arg\(^{141}\) have been reported. Many
studies on mutants of the enzyme have revealed that several charged residues in Cu, Zn-SOD, such as Arg141 next to the copper (II) ion, promote electrostatic steering of the superoxide substrate to and from copper ion in the active site (Arg$^{141}$, bovine erythrocyte SOD numbering corresponds to Arg143 for plants and human Cu, Zn-SOD).$^{10}$ Several studies have shown that mutation of Arg$^{141}$ to less positive residues causes a decrease of SOD activity.$^{11}$ Another showed that the rate of dismutation could be improved by increasing the charge density on the electrostatic patch.$^{12}$

![Figure 4.1.](image)

Mao et al. have reported two complexes that mimic the active site of SOD in addition to the function Arg$^{141}$ residue that are shown in Figure 4.1.$^{13}$

In these mimics a supramolecular model system is designed through inclusion of an imidazolate-bridged dinuclear complex with β-cyclodextrin (β-CD) or mono-6-deoxy-6-guanidinocycloheptaamylose (GCD) to mimic both the imidazolate-bridged active site and the Arg-143. They observed the guanidyl-modified β-CD cation located in the effective range around the Cu (II) ion is crucial for attracting the superoxide anion to and from the active copper ion and may play role of Arg141 in the Cu, Zn-SOD.

In addition to Cu-Zn, copper sulfur chemistry has attracted biochemists because of the copper-thiolate and copper-thioether bonds encountered in a wide variety of proteins$^{14}$ and particularly in redox-active proteins with electron-transfer functions. They include mononuclear type 1 blue copper proteins and dinuclear Cu$_A$ centers from cytochrom c oxidase (CcO)$^{15}$ or nitrous oxide reductase (N$_2$OR).$^{16}$ The latter involves a dicopper
unit with delocalized mixed-valent core in its resting state. The copper atoms are bridged by two S (Cys), leading to an essentially planar Cu₂S₂ structure. Two N (His) and two additional ligands (one S (Met) and one O carbonyl of a glutamate inCcO or of a tryptophan in N₅OR in axial positions complete the coordination sphere. The purple color of the Cuₐ center is the result of predominant S(Cys)-Cu charge-transfer transitions at ~480 and ~530 nm and a broad class III Mixed-valent charge-transfer band around ~830 nm.¹⁷

\[
\text{Figure 4.2.} \quad \beta\text{-cyclodextrin-based ligand dimer, and its copper(II) complexes as a metalloenzyme mimic (A) and the mechanism of the function of this system (B).}^{18}
\]
Particulate methane oxidaze monooxygenase (PMMO) is a complex membrane protein (αβγ) that contains approximately 15 copper ions, sequestered into catalytic trinuclear clusters (C clusters) and electron-transfer copper ions known as E clusters. They proposed that C clusters mediate alkane hydroxylation and dioxygen reduction chemistry, while the E clusters provide a buffer of reducing equivalents to rapidly reduce the C cluster ions during turnover.

Another Cu(II)-CD complex, shown in Figure 4.2, was reported to mimic the function metalloesterase for the hydrolysis of p-nitrophenyl acetate (p-NPA), adamantate (p-NPAD) and amino acids. The proposed mechanism of the function of this system, Figure 4.2, is as catalyst (C), which binds substrate (S) to form catalyst-substrate complex mainly through hydrophobic interaction. The hydroxide ion bound to the Cu (II) center, Cu(II)-OH, attacks carbonyl carbon of substrate to form transition intermediate. Hydrolyzed products such as p-nitrophenolate are produced by breakdown of the intermediate, and liberate from binding sites.

### 4.1.3 Fluorescent Copper Chemosensors:

Sensors are generally consists of a signaling unit, a spacer, and a recognition unit. Chemosensors can be defined as molecules that can selectively recognize and signal the presence of a specific analyte. The design of chemosensors is a key achievement of supramolecular chemistry. One of the most important signaling methods is fluorescence spectroscopy, because it offers several advantages such as high sensitivity and low cost instrumentation. In fluorescence chemosensors the presence of the substrates is transduced as a significant change in the emitting properties of the luminophore. Fluorescent chemosensors are designed using different approaches, which are shown in Figure 4.3. Their names are based on the construction of the sensors. In the first approach, called intrinsic chemosensors, the binding unit is part of the π-system.
The second type is called the conjugate chemosensors in which the binding subunit is electronically insulated from the fluorescent subunit by an inert spacer.\textsuperscript{25}

The most developed approach in chemosensors is the template-assisted self-assembly chemosensing strategy. These chemosensors are based on the self-assembly or self-organizination the fluorescence dye and the receptor on a proper template forming on organized assembly.

**Figure 4.3.** The difference between the design and function of intrinsic and conjugate chemosensors.\textsuperscript{24}
Different types of templates have been used to guide the self-organization of the chemosensors spanning from micelle aggregates to monolayers, to glass surfaces, and more recently, to nanoparticles. A multicomponent approach is commonly employed whereby a binding unit is covalently connected to a luminophore in a single molecule. In designing supramolecular systems for metal cations, the binding unit (receptor) is chosen so it coordinates the target metal.
and without electronically influences the structure of the connected fluorophore. The signaling unit is covalently linked to the binding site or receptor. In these systems coordination of the metal ion to the binding site induces significant changes in the emitting properties of the luminophore. Cyclodextrin has been used in the design of supramolecular systems for metal ion detection. Ruthenium polypyridyl complexes were linked to numerous other units to produce more sophisticated photomolecular devices for signaling metal ions in solution. Examples of these systems are shown in Figure 4.4. In these systems, perturbations of the luminescence intensity were monitored in the presence of metal ions in solution. Quenching of luminescence intensity was observed in the presence of metal ions. System A in Figure 4.4 consists of bis(2-picolyl)amine (bpa) amino acid ligand covalently linked to \([\text{Ru(bipy)}_3]^{2+}\). This ligand shows high affinity towards coordination of Cu(II). Furthermore, the pH-titration of A showed the quenching of luminescence intensity over the entire pH range, from 2 to 12, in the presence of Cu(II) in solution. It was found the quenching process is independent on the pH. Electrochemistry results for A showed that the Cu\(^{II/1}\) redox process is a reversible process which can be used for redox switching of ruthenium based emission. Reduction of Cu(II) by hydrazine results in a restoration of the ruthenium based emission, and reoxidation of Cu\(^{+1}\) by H\(_2\)O\(_2\) leads to quenching. Therefore, this system was proposed to act as redox switch (on-off) of the luminescence intensity of luminophore. The mechanism of quenching was attributed to energy transfer rather than electron transfer.

System B, Figure 4.4 also behaves as an-on-off sensor for both Cu(II) and Ni(II) by energy transfer mechanism. A reduction of the luminescence intensity, less than 5 % of its maximum, was observed upon coordination of the metal ion to the ligand. On the basis of the coordination affinity of the ligand 1,9-Diamino-5-(2, 29-bipyridin-5-ylmethyl)-3,7-diazenonane-4,6-dione, this system was capable of sensing Cu(II) and Ni(II) among series of divalent first-row transition metal cations. At pH 7 the ligand was found to be selective towards Cu(II). The ligand C Figure 4.4 was found to be sensitive to the presence of Cu(II) and Ni(II) in solution. Quenching of the ruthenium fluorescence was observed upon coordination of Cu(II) and Ni(II) ions to the cyclam moiety. Another supramolecular system where the copper coordinates in 1:1 ration with ligand and
results in a very weak fluorescent complex. This was attributed to a partial inclusion of dansyl group in the CD cavity. Addition of bidentate molecules with poorly coordinating groups, such as D- or L-mandelic acid and D- or L-lactic acid leads to the enhancement fluorescence intensity. The increase in the fluorescence intensity was ascribed to the displacement of the dansyl from copper ion.

4.1.3 Cyclodextrins as first sphere ligands.

Cyclodextrins may play the role of second-sphere ligands by modification of the primary or the secondary hydroxyls with hydrophylic ligands such as amines. Metal ions cannot form real inclusion complexes with CDs. However, they are able to bind to CDs whereby metal ions coordinate to hydroxyl groups of the CD molecule. Binuclear metal complexes of Mn(III), Cr(III), Ni(II), Fe(III), Co(II) and Cu(II) have been reported by our group. In these metallocyclodextrin complexes hydroxy-bridged structures are proposed which feature first sphere coordination. Our group has also exploited this approach in constructing a supramolecular system in which Ru metal complex covalently linked via its second coordination sphere to the primary side of β-CD and Mn(III) coordinated to the secondary side of β-CD via its first coordination sphere. This system was an attempt to mimic the electron transfer process in PSII. The system which shown in Figure 4.5 designed by functionalization of cyclodextrin with aminophenanthroline ligand and then coordination of CD-aphen to Ru centre. Then Mn(III) was coordinated to the secondary side following the method of Nair and Dismukes. Binuclear Hydroxy-bridged structures were proposed in which metal ion is coordinated to O-2 and O-3 of two adjacent pyranose rings of the β-CD. An efficient electron transfer was observed from Mn(III) to the excited *Ru.
We followed these approaches to report in this chapter the synthesis of a donor-acceptor system incorporating a ruthenium polypyridyl functionalized β-cyclodextrin moiety with an hydroxo-bridged Cu(II) dimer and also provide evidence for photoinduced electron transfer between the copper centre and the ruthenium. We illustrate the effects of solution phase binding of Cu$^{2+}$ and Zn $^{2+}$ on the luminescence intensity of the ruthenium appended CD and on the photophysics of the isolated supramolecular complex. This work has implications, both for bioinorganic model complexes and may providing means of binding copper with concomitant transduction of its binding through fluorescence signal for use in metal ion sensing.

**Figure 4.5.** Dimanganese-hydroxy-bridged b-CD bound to ruthenium complex.
4.2 EXPERIMENTAL

4.2.1 Synthesis:

$6^A$-deoxy-$6^A$-P-toluenesulphonyl-$\beta$-cyclodextrin, cis-Ru(bpy)$_2$Cl$_2$, $6^A$-(5-amino-1, 10-phenanthroline)-$6^A$-deoxy-$\beta$-cyclodextrin, and Cu$_2$CD were synthesized and purified according to published procedures. $^{33,34}$

4.2.2 Ruthenium(II)(bisbipyridine)($6^A$-(5-amino-1, 10-phenanthroline)-$6^A$-deoxy-$\beta$-Cyclodextrin: CDRu was synthesized as described previously, and purified using size-exclusion chromatography on Sephadex G-75, with water as eluent. \{M/z = 878.8, [M-2PF$_6$]$^+$, 1637, [M-PF$_6$]$^+$, structure was confirmed from 2D $^1$H NMR which conformed with to previously reported values.

4.2.2 Synthesis of dicopper –dihydroxo-Ruthenium (II)(bispyrididine) ($6^A$-deoxy- 5-amino-1, 10-phenanthroline)-$6^A$-deoxy-$\beta$-cyclodextrin: Cu$_2$CDRu:

(0.10g, 0.05 mmol) CDRu was dissolved in 0.5M NaOH, (0.03g, 0.1 mmol) Cu (CH$_3$CHOO)$_2$ (cupric acetate) was added, the mixture was stirred for 2 hrs under N$_2$. Ethanol was added to precipitate the product. The dark red product was recrystallized from 0.2M NaOH.$^{35}$ \{M/z=2022, [Cu$_2$CDRu][PF$_6$]}. 
4.3 RESULTS AND DISCUSSION:

4.3.1 Synthesis:

Scheme 4.1. Synthetic route to Cu$_2$CDRu

The synthetic steps leading to production of Cu$_2$CDRu are shown in Scheme 4.1. The synthesis of the phenanthroline substituted β-CD and ruthenium polypyridyl complex, CDRu, was reported previously and the mass spectral, $^1$H NMR and elemental analysis conformed to those reported.$^{36}$ The ability of β-CD to coordinate Cu(II) is well established. Under alkaline conditions combination of cupric acetate and β-CD yields a 2:1 hydroxy-bridged Cu(II) dimer coordinated to the deprotonated hydroxyls on the secondary face of β-CD.$^{30}$ This complex is quite stable in alkaline solution.$^{37,38,30}$ An analogous procedure to that reported for β-CD was followed here, except that CDRu complex was employed instead of β-CD, this was treated with cupric acetate in 0.5 M NaOH. The resulting paramagnetic complex was studied using mass spectrometry, magnetochemistry, vibrational spectroscopy which all confirmed that the Cu had coordinated in 2:1 ratio. The coordination mode to the CD is expected to be the same as that described for free β-CD and this is consistent with our vibrational spectral and magnetic results. The complex was stable in the solid state, in the absence of air, for months and in aqueous alkaline media for at least a week. It was stable for several hours in DMF; however, the copper centre was very labile in neutral aqueous media.
4.3.2 Magnetic Susceptibility Electron Spin Resonance studies:

The effective magnetic moment for Cu$_2$CDRu was found to be 1.075 $\mu_B$ per Cu at 294 K which is lower than the anticipated value of 1.79 $\mu_B$ for the spin only value of the $d^9$ electronic configuration of Cu (II), calculated on the basis that no magnetic interactions are occurring between the metal ions. These results indicate a weak antiferromagnetic exchange interaction between the two high spin Cu (II) metal ions acting through the hydroxyl bridged system. These values are in good agreement with those reported for the unfunctionalised Cu$_2$(II,II) CD complex.

*Figure 4.6.* EPR spectra of Cu$_2$CDRu measured on a neat powdered sample at 298 K. The spectrum of the neat powder at 294 K is shown in Figure 4.6. The spectrum of the neat powder, at 294 K, exhibits four very broad lines between 2500-3500 G. A four line rhombic spectrum that is typical of distorted square pyramidal copper (II) ion (I =3/2)
The lines broadening probably due to Cu (OH)$_2$Cu unit superimposed on which were the four parallel Cu-hyperfine lines ($g = 2.24$ and $A = G$) and a $g_{\perp}$ line at 2.05. These data are consistent with the reported values of hydroxy-bridged Cu (II) dimmers.$^{39}$

4.3.3 Vibrational Spectroscopy

The FTIR spectra of the CDRu complexes before and after coordination to Cu were compared.$^{40}$ The FTIR results are shown in Figures 16, 17, 18 and 19 in the appendices. The region between 1200 and 1000 cm$^{-1}$ are dominated by exocyclic OH modes, which are strongly enhanced and shifted to higher frequency on coordination of the Cu site. These changes conformed to those reported previously for Cu$_2$CD and are attributed to perturbations of CH$_2$ and OH bending modes induced by coordination of metal to the secondary side of CD. There is also significant broadening to the OH stretch band with the appearance of a shoulder at approximately 3200 cm$^{-1}$ which is not apparent in CDRu. This is attributed to coordination of the metal to the CD secondary hydroxyls, which disrupts the H-bonding structure present in the uncomplexed CD.

4.3.4 Electronic Spectroscopy.

Figure 4.7 shows the UV-vis spectra of CDRu under neutral aqueous conditions and pH 12 respectively. In the latter case this corresponds to the pH at which the copper is coordinated. The spectra exhibit maxima around 455 nm attributed to Ru ($d\pi$) to L ($\pi^*$) MLCT transitions and ligand centred (LC) features below 300 nm.
Figure 4.7. Electronic absorption spectroscopy of Cu₂CDRu (heavy line), CDRu at pH 7 (dotted line), and CDRu at pH 12 (light line) in DMF.

The spectra are essentially identical, indicating any new transitions on coordination of the copper do not arise from deprotonation of the CD. The absorbance spectrum of Cu₂CDRu is shown in Figure 4.7. Coordination of the dinuclear copper centre to the CDRu complex results in a slight red shift of the MLCT and the appearance of a feature centred around 620 nm, this feature is weak and very broad extending to approximately 700 nm and is attributed to the Cu(II) d-d transition, interestingly, this transition is shifted somewhat to the blue by comparison with the Cu₂CD complex. In addition, there are changes in the UV spectral region, spectral fitting suggest that a new feature is centred around 320 nm, a similar feature appears in the spectrum of the Cu₂CD complex and is also associated with the copper coordination, possibly attributed to a Cu→OH charge transfer transition. There is no evidence for any new optical transitions arising from interaction between the Ru and Cu centres in the trinuclear complex, as the electronic spectrum of Cu₂CDRu appears to be largely a composite of
the two separate complexes.

To gain insight into the origin of the optical transitions and the impact of copper coordination, resonance Raman spectroscopy was conducted for CDRu and Cu$_2$CDRu, Figure 4.8. In resonance Raman spectroscopy, the exciting laser line is resonant with an optical transition and this yields enhancements in vibrational modes associated with the chromophores of up to 7 orders of magnitude. This provides a relatively unambiguous means of characterizing optical transitions. The results are shown in Figure 4.8, for optical excitation at 488, and 514.5 nm. The Raman spectra exciting at 514 nm are relatively similar for Cu$_2$CDRu and CDRu. The spectra contain the signature bipyridyl modes and Ru-N stretch (371 cm$^{-1}$) typical of resonance with a Ru (d$\pi$) to L ($\pi^*$) MLCT, where L is phen or bpy and confirms the identity of the lowest energy optical transition. Exciting at 488nm, however there are significant differences between the complexes in which the copper is present and absent.
Figure 4.8. Resonance Raman spectroscopy of (a) CDRu and (b) Cu$_2$CDRu excited at 488nm (top) and (a) CDRu and (b) Cu$_2$CDRu 514.5 nm (bottom).

Both Cu$_2$CDRu and CDRu share common features attributed to ligand and Ru- modes,
but in addition, the Cu$_2$CDRu complex contains additional modes, most notably an intense feature at 565 cm$^{-1}$. This feature is attributed to a Cu-O stretch mode, which is enhanced from resonance with the underlying copper based electronic transition. This provides useful evidence for the presence of the copper dimer. Similarly this feature is present when exciting at 458 nm in addition to a new feature at 1095 cm$^{-1}$, which is likely to originate from the CD backbone. Interestingly, when exciting at 488 or 458 nm, the resonance Raman spectrum is dominated by vibration not associated with the Ru(d$\pi$) to $\pi^*$ transition, MLCT and this is likely to arise from post-resonance with the new feature at 320 nm in which it seems Cu participates. Resonance Raman spectroscopy of the low energy d-d optical transition at 620 nm was probed with 633 excitation, unfortunately luminescence interference at this wavelength prevented the collection of meaningful data.

4.3.5 Electrochemistry

Cyclic voltammetric data for CDRu, Cu$_2$CD and Cu$_2$CDRu in dry DMF is provided in Table 4.1. The electrochemistry of CDRu was reported previously, a reversible ruthenium based oxidation is observed at 0.95 V, which conforms well to the reported value. In the cathodic region, three reversible one electron reductions are observed corresponding to reduction of the bpy and phen moieties.
Table 4.1. Electrochemical data for Cu₂CD, Cu₂CDRu and CDRu in dry DMF E₁/₂ values determined by cyclic voltammetry. Potentials (V) vs. Ag/AgCl. The processes are reversible except when indicated (irr).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ru(II)/Ru(III)</th>
<th>(bpy/bpy⁻)</th>
<th>M(II)/M(III)</th>
<th>M(II)/M(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDRu</td>
<td>0.95</td>
<td>-1.21, -1.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₂CDRu</td>
<td>1.03</td>
<td>-1.33, -1.57</td>
<td>0.703 irr.</td>
<td>-0.90,</td>
</tr>
<tr>
<td>Cu₂CD</td>
<td></td>
<td></td>
<td>0.592 irr.</td>
<td>-1.229</td>
</tr>
</tbody>
</table>

The cyclic voltammogram for Cu₂CDRu in dry DMF using a platinum working microelectrode is shown in Figure 4.9 (a). Cu₂CDRu voltammetry displays a reversible oxidative process at 1.03 V vs Ag/AgCl, attributed to the Ru(II)/Ru(III) couple and ligand based reductions at -1.33 and -1.57 V vs Ag/AgCl. In addition, new irreversible waves at 0.78 V and -0.774 V vs Ag/AgCl, not observed in the parent complex, CDRu, Figure 4.9 (b,c). For comparison, Figure 4.9 (d) shows the CV for Cu₂CD in dry DMF, which exhibits an irreversible anodic wave at 0.59 V vs Ag/AgCl and a cathodic, quasi-reversible wave at E₁/₂ = -1.23 V (ΔEp= 0.23 V).
Figure 4.9. Cyclic voltammograms in dry DMF, versus 0.01 Ag/AgCl of (a) Cu$_2$CDRu, on a platinum microelectrode (50 μm dia.) as a working electrode, at ν=500 mv (b, c) CDRu on a platinum microelectrode at ν=500 mv (d) Cu$_2$CD on a glassy carbon as a working electrode and dry DMF at ν= 500 mv. 0.1 M tetrabutylammoniumperchlorate as a supporting electrolyte was used in all experiments.
The electrochemistry of this species has not, to our knowledge been reported previously. The latter process is assigned to the Cu(II)/Cu(I) redox couple and former to the Cu(III)/Cu(II) couple. These data are consistent with reported values for hydroxy-bridged Cu (II) dimers and are similar to those obtained for Cu (II, II) complexes with ligands other than cyclodextrin. The irreversibility of the oxidation response probably indicates that the oxidized copper undergoes bond cleavage within the timescale of the electrochemical experiment.

The changes to the electrochemistry of the copper centres on coordination to CDRu by comparison with Cu\textsubscript{2}CD were surprisingly large. The ruthenium oxidation shifts anodically by approximately 80 mV on coordination of the copper centers, which may be attributable to the influence of electrostatics. However, the new oxidation process for Cu\textsubscript{2}CDRu at 0.703 V attributed to Cu(III)/Cu(II) is shifted by 111 mV by comparison with Cu\textsubscript{2}CD. The identity of the new reduction process in Cu\textsubscript{2}CDRu is not entirely clear, but if attributed to the copper centre, it has shifted by over 300 mV. Overall, this suggests that derivatisation of the CD with the ruthenium centre exerts a surprisingly significant influence over the copper centre.

### 4.3.6 Photophysical properties:

As reported previously, CDRu exhibits an intense luminescence attributed to the $^3$MLCT state with $\lambda_{\text{max}}$ of 618nm, Figure 4.10, a quantum yield of 0.013 and a lifetime of 900 ns. The luminescence lifetimes and emission quantum yields values are significantly reduced upon coordination of copper to the secondary rim of CDRu in both aerated and deaerated media, Table 4.2. The quantum yield is reduced by over 50% compared with the free CDRu in DMF and the lifetime is reduced from 900 ns to 336 ns in deaerated DMF.
Table 4.2. Spectroscopic and photophysical data of CDRu, Cu₂CDRu and [Ru(bpy)₃]⁺² as a reference in spectroscopic grade DMF.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Abs. λ&lt;sub&gt;Max&lt;/sub&gt; (nm)</th>
<th>λ&lt;sub&gt;Max&lt;/sub&gt;(nm)</th>
<th>t&lt;sub&gt;deaerated&lt;/sub&gt; (ns)</th>
<th>t&lt;sub&gt;aerated&lt;/sub&gt; (ns)</th>
<th>Φ&lt;sub&gt;aerated&lt;/sub&gt;</th>
<th>ε [M⁻¹ cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDRu</td>
<td>450</td>
<td>618</td>
<td>900</td>
<td>249</td>
<td>0.013</td>
<td>7500</td>
</tr>
<tr>
<td>Cu₂CDRu</td>
<td>455</td>
<td>618</td>
<td>336</td>
<td>159</td>
<td>0.006</td>
<td>6750</td>
</tr>
<tr>
<td>[Ru(bpy)₃]⁺²</td>
<td>450</td>
<td>605</td>
<td>935</td>
<td>247</td>
<td>0.028</td>
<td>12500</td>
</tr>
</tbody>
</table>

The association of copper with the CD was investigated using steady state and time resolved luminescence, whereby increasing aliquots of Cu(II) acetate were combined with aqueous solution of CDRu (2 x 10⁻⁶ M) at pH 12. Figure 4.11 (b) and (c) shows a comparison of the effects of addition of Cu(II) and Zn(II) on a solution of CDRu at high pH. Zn²⁺ is expected to bind to the CD centre in an analogous way to Cu, however, with its d¹⁰ electronic configuration it is unlikely to be involved in either energy or electron transfer with the ruthenium centre.⁵⁰,⁵¹ As anticipated, on the basis of the isolated Cu₂CDRu complex, binding of Cu to
Figure 4.10. Luminescence spectroscopy; excited at 450 nm and emission decays; excited at 355 nm of (a) CDRu and (b) Cu₂CDRu in DMF; emission decays were monitored at 618 nm.

CD results in a decrease to the luminescence intensity by up to approximately 50%, whereas Zn²⁺ had negligible impact on luminescence intensity as shown in Figure 4.11a. Correspondingly, for Zn²⁺, within experimental error, no change to
Figure 4.11. The change of luminescence intensity of CDRu with increasing concentration of metal ions, Cu$^{2+}$ and Zn$^{2+}$, (a), emission spectra of CDRu, 2.1 x 10$^{-6}$ mol dm$^{-3}$, at pH 12 on addition of increasing aliquots (up to 1000 μl) of aqueous (b) 0.01 M [Cu(CH$_3$COO)$_2$].H$_2$O and (c) 0.01 M [Zn(CH$_3$COO)$_2$].2H$_2$O.
the luminescent lifetime of CDRu was observed, Figure 4.11C. In addition, for Cu\(^{2+}\) the luminescence quenching was confirmed to be static. Addition of this metal ion to a solution of CDRu caused a biexponential luminescent decay, whose components matched the lifetime of CDRu and Cu\(_2\)CDRu. Increasing concentrations of copper did not change the lifetimes, but merely changed the ratio of the short and long components in the luminescent decay.

4.3.7 Nature of the Excited State Process.

The reduction in lifetime and luminescent quantum yield in the CDRu observed on coordination of the copper dimer suggests that a photoinduced process is occurring in Cu\(_2\)CDRu. Introduction of new non-radiative pathways as a consequence of structural changes on formation of the metallocyclodextrin can be excluded on the basis that no photophysical changes were observed on binding of Zn\(^{2+}\). In a related study Balzani et al.\(^{51}\) reported on a Cu(I)–Catenate moiety covalently linked to \([\text{Ru(tpy)}_2]\)\(^{2+}\). The oxidation potential of Ru (III)/ (II) occurred at +1.2 V and that of Cu II/I at +0.58 V vs SCE at a Pt working electrode. They observed quenching of ruthenium based emission at 77 K and 298 K. They suggested energy transfer from Ru(II)* to Cu(I) at 77 K with a rate constant of 3×10\(^8\) s\(^{-1}\) and a thermodynamically allowed photoinduced electron-transfer from Cu(I) to Ru(II) at 298 K with a rate constant of 1×10\(^{10}\) s\(^{-1}\). Energy transfer is a possibility in the present case as the d-d transition at 620 nm for Cu\(_2\)CDRu overlaps effectively with the ruthenium emission. However, as the 620 nm absorbance is forbidden, it is very weak, (\(\varepsilon = 33 \text{ M cm}^{-1}\)) and unlikely, on the basis of Laporte and spin selection rules to facilitate efficient energy transfer. On the other hand, photoinduced electron transfer is thermodynamically feasible wherein \(\Delta G\) for a process in which the copper centre is reduced by excited state ruthenium, calculated from electrochemical and photophysical data is estimated to be exoergic at -0.16 eV. Reduction of the copper by photoexcited ruthenium is anticipated to be very modestly exoergic at approximately -0.05 eV. The driving force for an excited-state electron-transfer can be evaluated from the
approximation which was discussed in detail in Section 1.8:

$$\Delta G^0 \equiv [E(B/B^+) - E(A/A^-)] - \Delta E^\infty$$  \hspace{1cm} \text{Equation 4.1}$$

where $E(B/B^+)$, $E(A/A^-)$ are the energies (eV) of one-electron reduction processes and $E^\infty$ is the spectroscopic energy, taken as the energy of the maximum of the emission spectrum at 77 K. $\Delta E_{\text{CDRu}}^\infty = 2.069$ eV, $\Delta E_{\text{Cu2CDRu}}^\infty = 2.085$ eV. See Equations 1.29 and 1.30 for more details.

To confirm that electron transfer is the origin of the luminescence quenching in Cu$_2$CDRu transient absorption studies were conducted on this complex and on CDRu for comparison.

![Figure 4.12](image)

**Figure 4.12.** Transient absorption of Cu$_2$CDRu (b) in deoxygenated water at pH 12, 100, 200, 300, 440, 600, and 700 ns after the excitation at 355 nm. Inset, shows growth of the absorbance at 510 nm.
Firstly, following 355 nm excitation of a deoxygenated solution of CDRu, the depletion of the MLCT band is observed at 450 nm and negative amplitude signal (-ΔA) in the region 600 - 700 nm arises from stimulated emission from the triplet MLCT state. Unsurprisingly, the kinetics for both grow in of the depletion and emission are the same and match the luminescent lifetime.

Figure 4.12 shows the transient absorption spectra of Cu$_2$CDRu. On excitation at 355 nm depletion of the MLCT occurs around 450 nm, however, in addition, a new absorption feature around 510 nm grows in. The luminescence, seen as depletion centered around 610 nm is lost at a rate that matches the luminescence decay rate of Cu$_2$CDRu. However, the MLCT depletion remains relatively unchanged during the decay of the luminescence, while the 510 feature grows in.

Over the time scale of the experiment, the MLCT is not recovered and the 510 feature remains. This confirms that the ruthenium is photooxidised through a photoinduced electron transfer and conforms well to the process predicted on thermodynamic grounds. The identity of the 510 nm absorbance is unclear but may be due to Cu(I). The kinetics for grow in of this band are complex and appear be second order, inset. This may be due to chemical reaction following reduction of the copper centre. The rate constant for the photoinduced electron transfer was calculated according to Equation 4.2.

\[ k_{et} = \frac{1}{\tau_{\text{complex}}} - \frac{1}{\tau_{\text{model}}} \]  

Equation 4.2

Where $\tau_{\text{complex}}$ represents the luminescent lifetime of Cu$_2$CDRu, and $\tau_{\text{model}}$ represents lifetime of the model complex, CDRu in absence of any photoinduced process. For Cu$_2$CDRu $k_{et}$ was found to be 1.86 x 10$^8$ s$^{-1}$ which is consistent with rates measure for Mn(III) centre. See Equations 1.34, 1.35, and 1.36 and Section 1.8 for more details.

The rate of electron transfer was measured over range of concentrations of Cu$_2$CDRu and laser powers, since a bimolecular reaction would be expected to be dependent on both these factors. However $k_{et}$ was found, within experimental error, to be independent of these parameters confirming that the electron transfer is an intramolecular process.
Table 4. 3. Concentration dependence of rate of electron transfer ($K_{et}$) in Cu$_2$-CD-Ru, lifetimes measured in DMF, excited at 355 nm and detected at 620 nm.

<table>
<thead>
<tr>
<th>[complex] $M$</th>
<th>$T$ (ns)</th>
<th>$1/\tau$ ($10^6$ s$^{-1}$)</th>
<th>$K_{et}$($10^6$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5E-4</td>
<td>336 ± 20</td>
<td>2.9</td>
<td>1.8</td>
</tr>
<tr>
<td>1.2E-4</td>
<td>330 ± 23</td>
<td>3.0</td>
<td>1.9</td>
</tr>
<tr>
<td>8.75E-5</td>
<td>361 ± 18</td>
<td>2.7</td>
<td>1.6</td>
</tr>
<tr>
<td>7.5E-5</td>
<td>328 ± 29</td>
<td>3.0</td>
<td>1.9</td>
</tr>
<tr>
<td>6.0E-5</td>
<td>308 ± 26</td>
<td>3.0</td>
<td>2.1</td>
</tr>
<tr>
<td>5.4E-5</td>
<td>308 ± 19</td>
<td>3.0</td>
<td>2.1</td>
</tr>
<tr>
<td>4.6E-5</td>
<td>308 ± 22</td>
<td>3.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>
4.4. Conclusions

A new supramolecular donor acceptor system incorporating a ruthenium polypyridyl functionalized β-cyclodextrin moiety with an hydroxo bridged Cu(II) dimer is described. IR and magnetochemistry confirm that the structure of hydroxo bridged Cu(II) dimer is conserved from the parent Cu₂CD complex. Efficient photoinduced electron transfer from the copper centre to the pendant ruthenium polypyridyl centre is evident, with a rate constant of $1.86 \times 10^8$ s$^{-1}$. The electron transfer process from transient absorption spectroscopy is attributed to a photooxidation of the excited ruthenium center by the copper dimer and this mechanism is consistent with thermodynamic predictions. The luminescence intensity of the ruthenium appended CD is correspondingly statically quenched on exposure to aqueous Cu (CH$_3$COOH)$_2$. This work suggests that luminescently labeled CDs may have value in metal sensing provided the luminophore is sufficiently long lived. The synthetic versatility of the ruthenium polypyridyl unit may mean that in the future the redox properties of this centre can be modified to tune selectivity for different metal ion.
4.5 References


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Chapter 5

Novel Photoactive C$_{60}$ bridged Tetrameric Osmium and Ruthenium $\gamma$
Cyclodextrin Supermolecules: Assembly and Spectroscopy
5.1 Introduction:

5.1.1 Fullerene Physical properties

The fullerenes and their monofunctionalized derivatives have been the focus of much research recently in the design of devices such as molecular switches, receptors, photoconductors and photoactive dyads.\textsuperscript{1,2,3} Fullerenes are large carbon cage molecules, Figure 5.1, considered to be the three-dimensional analogues of benzene. The most abundant form of fullerene is Buckminster fullerene (C\textsubscript{60}) with 60 carbon atoms arranged in a spherical structure. The shape of the molecule is known as truncated icosahedron,\textsuperscript{4} which contains 12 pentagons and 20 hexagons.\textsuperscript{5}

![Figure 5.1. The structure of C\textsubscript{60}, C\textsubscript{70}.\textsuperscript{6}](image)

An important property of the C\textsubscript{60} molecule is its high symmetry. Fullerenes contain two types of bond lengths, C\textsubscript{5}-C\textsubscript{5} single bonds in the pentagons 1.45 ± 0.015 Å and C\textsubscript{5}-C\textsubscript{6} double bond in the hexagons 1.4 ± 0.015 Å.\textsuperscript{7} Each carbon atom forms bond to three adjacent atoms with sp\textsuperscript{2} hybridisation. The C\textsubscript{60} molecule is about 7 Å in diameter. On exposure to strong UV-light, the buckyballs polymerize.\textsuperscript{8} Other than C\textsubscript{60}, fullerenes can contain from 30 to 980 carbon atom forming different structures, with different properties and field of applications. As hexagons are added or removed from the basic soccer ball structure, the molecule begins to lose its roundness. C\textsubscript{70}, which has 25 hexagons is shaped more like or a rugby ball. Giant fullerenes take on a pentagonal shape. The loss of roundness leads to loss of stability, C\textsubscript{60}
Fullerenes are insoluble in polar or H-bonding solvents and sparingly soluble in alkanes. Good solvents for fullerenes are carbon disulfide, O-dichlorobenzene, toluene, and xylene.  

5.1.2 Spectroscopic and photophysical properties of Fullerenes:

The electronic structure of \( C_{60} \) has been studied density functional calculations for the solid, the experimental photoemission and reverse-phase emission spectra. \(^{11}\) The most important electronic states for \( C_{60} \) are the highest occupied molecular orbital (HOMO), which five fold degenerate \( h_u \) symmetry, and the lowest unoccupied molecular orbital (LUMO) which is three-fold degenerate with \( t_{1u} \) symmetry which is shown in Figure 5.2. The calculated energy difference between HOMO and LUMO is 1.87 eV.

\[ \begin{align*}
\text{Figure 5.2. Structure of [60]fullerene and illustration of the } \pi-\pi \text{ orbital energy levels in } C_{60}. & ^{12} \\
\end{align*} \]

\( C_{60} \) and \( C_{70} \) point groups are \( I_h \), \( D_{5h} \), respectively, are highly symmetric molecules. \( C_{60} \) has an extremely reactive exterior and nearly inert interior. The absorption spectroscopy of the fullerene in toluene is shown in Figure 5.3. The characteristics of the absorption spectrum of \( C_{60} \) are a strong absorption in the UV – with maxima at 259 nm and 328 and 407 nm these peaks corresponding to \( a_{1g} \rightarrow 6t_{1u} \), \( a_{1g} \rightarrow 3t_{1u} \) and \( a_{1g} \rightarrow 1t_{1u} \) transitions. In contrast the
visible region is characterised by only relatively weak transitions between 420 – 650 nm that corresponds to [60] fullerene orbitally forbidden singlet-singlet transitions.\textsuperscript{13}

![Graph showing UV-Vis absorption of [60] Fullerene in Toluene at room temperature.]

**Figure 5.3.** UV-Vis of [60] Fullerene in Toluene at room temperature.

### 5. 1. 2. 1 Photophysics of C\textsubscript{60}

Upon excitation with UV-Vis radiation the ground state of C\textsubscript{60} is excited to its first singlet state \(^1\text{C}_{60}\), which rapidly decays in near-quantitative yield (\(\Phi \approx 0.96\)), to the triplet excited state with a lifetime of 1.3 ns, the lifetime of \(^3\text{C}_{60}\) is 135 \(\mu\)s, due to an efficient intersystem crossing (ISC)\textsuperscript{14} \(^3\text{C}_{60}\) is the longest-lived as well as the lowest-lying excited state (1.56 eV) of C\textsubscript{60}, so that deactivation pathways, which are competing with the non-radiative transition to the ground state, generally emanate from \(^3\text{C}_{60}\) as the excited state. \(^3\text{C}_{60}\) can be deactivated through energy transfer or through photoinduced electron transfer from an electron donor (D) species, yielding the radical anion C\textsubscript{60}\textsuperscript{−} and the radical cation D\textsuperscript{+}.\textsuperscript{15} C\textsubscript{60} has exceptionally small reorganisation energy (between -0.7 and -0.3 eV depending on the solvent). When the reorganization energy (\(\lambda\)) of the electron transfer is small, the Marcus Inverted region (\(\lambda < \Delta G^0_{et}\)) where the rate constant of electron transfer decreases with increasing driving force (\(\Delta G^0_{et}\))
ΔG^0_{et} is reached at smaller -ΔG^0_{et}. The maximum value of the rate constant for electron transfer is obtained when -ΔG^0_{et} equals λ. Experimentally, this means that all [60]fullerene-containing donor–acceptor dyads possess, upon photoexcitation, a long-lived charge separated (CS) state because of the acceleration and deceleration of the charge separation and recombination rates, respectively.

The photophysical properties of C_{60} have been extensively studied. The fluorescence quantum yield of C_{60} at room temperature is considered to be very weak due to efficient intersystem crossing from the singlet excited state to the triplet state and also to the forbidden electronic transitions between the excited singlet states and ground state. Figure 5.4 shows the fluorescence spectra of C_{60} in solutions at room temperature. The well resolved spectrum has been obtained using DMSO. This result was attributed to strong interaction between DMSO and C_{60}.

![Fluorescence spectra](image.png)

**Figure 5.4.** The fluorescence spectra of C_{60} in (a) toluene, (b) CS_{2} and (c) DMSO.

Typical transient absorption spectra of fullerene are shown in Figure 5.5. In elucidating the photoinduced electron transfer processes of C_{60}, the absorption spectra of transient intermediates, such as triplet excited state ^3C_{60}^- and the anion C_{60}^- have been reported.
The singlet excited state gives rise to a characteristic singlet-singlet absorption around 920 nm whose lowest vibronic state has energy of 1.99 eV. The triplet-triplet absorption spectrum reveals a maximum in the visible region (750 nm) these features are useful probes for uni- and bimolecular transfer reactions.  

Figure 5.5. Transient absorption of C_{60} in benzonitril obtained by laser flash photolysis after Δ 800 ns, ○ 20 μs ■ 50 μs excited at 532 nm.

5.1.3 Electrochemistry of Fullerenes:

After the elucidation of the structure of C_{60}, theoretical predictions indicated that the lowest unoccupied molecular orbital (LUMO) of C_{60} was energetically low lying and triply degenerate, Figure 5.2, and thus capable of accepting at least 6 electrons upon reduction. In addition C_{60}, along with the family of higher fullerenes, is fully conjugated though, with no possible electron delocalization because of distinct and different single and double bond lengths. Consequently, electroanalytical techniques such as cyclic voltammetry (CV), and
differential pulse voltammetry (DPV) have been extensively used to investigate the electron rich fullerenes and their derivatives in solution. The systematic electrochemical proof of the triple degeneracy of the LUMO, Figure 5.2, of $C_{60}$ came in several steps with the detection of $C_{60}^{2-}$, $C_{60}^{3-}$, $C_{60}^{4-}$, and $C_{60}^{5-}$. The hexaanion species, $C_{60}^{6-}$, eluded detection until 1992, mainly due to limitations in the potential "window" available with the solvents used. In 1992, Echegoyen et al. managed to generate and detect stable $C_{60}^{n-}$ ($n = 1-6$) using CV and DPV. The voltammetric experiments were carried out under vacuum, using the mixed solvent system acetonitrile-toluene (1:5), and at low temperature (-10 °C). The potentials measured ($E_{1/2}$) were -0.98, -1.37, -1.87, -2.35, -2.85, and -3.26 V vs Fc/Fc$^+$ as shown in Figure 5.6. The separation between any two successive reductions under these conditions was relatively constant at ca. 450 ± 50 mV. They emphasized that the penta- and hexaanions are stable and exhibit reversible behavior on the voltammetric time scale. However, when produced by controlled potential coulometry, only the anions $C_{60}^{-1}$ up to $C_{60}^{-4}$ are stable. The electrochemical characterization of $C_{70}$ followed a simultaneous, similar historical path. Its LUMO was predicted to be only doubly degenerate, but the calculated energy difference between the LUMO and the LUMO$^{+1}$ was small enough that six 1-electron reductions were anticipated for $C_{70}$. Kadish and co-workers detected up to four electron reductions using the same mixed solvent system described above, Echegoyen et al. was able to generate and detect $C_{70}^{n-}$ ($n = 1-6$).
It was also predicted theoretically that oxidation of \( \text{C}_{60} \) would be difficult. The gas-phase ionization potential of \( \text{C}_{60} \) was measured to be ca. 7.6 eV.\(^3\)

The first chemically reversible and electrochemically quasireversible oxidation of \( \text{C}_{60} \) and \( \text{C}_{70} \) was reported by Echegoyen et al. in 1993, after several other reports described the process as irreversible.\(^3\)

Voltammetric studies showed that the first 1-electron oxidation of \( \text{C}_{60} \) in 1,1,2,2-tetrachloroethane (TCE) indeed occurs at a very positive potential, +1.26 V vs Fc/Fc\(^+\), confirming the theoretical prediction. For \( \text{C}_{70} \), the same process occurs at a potential 60 mV more negative than that of \( \text{C}_{60} \), at +1.20 V.\(^3\)

The difference between the first oxidation and the first reduction of \( \text{C}_{60} \) (at room temperature), a measure of the HOMO-LUMO gap in solution, is then calculated to be 2.32 V. For \( \text{C}_{70} \), this gap is somewhat smaller at 2.22 V.
These results showed the rich redox chemistry of $C_{60}$ and $C_{70}$, with eight and nine accessible oxidation states, respectively.

5.1.4 Supramolecular Fullerene Chemistry:

The chemistry of fullerene as part of supramolecular array has been covered in a number of reviews and articles. In these reviews they illustrated how molecular complexation of pristine fullerene developed from solid state enclathration by π-rich compounds to inclusion complexation by designed macrocyclic receptors in the liquid phase. In addition to the non-covalent supramolecular assemblies, covalently linked days and trays of fullerene-chromophores have been developed in an attempt to mimic natural photosynthesis and the creation of photomolecular devices. Specific examples are mentioned vide infra.

5.1.4.1 Fullerenes chromophores systems:

A large number of donor-functionalised [60] fullerenes incorporated in well-defined two-dimensional and three-dimensional networks have been synthesised in the last two decades. Functionalization of pristine $C_{60}$ with chromophores, such as metalloporphyrins or transition metal complexes, have developed important objectives. The primary aim is to promote the visible absorption characteristics of the resulting dyads, and to increase the light efficiency of the fullerene core. Specifically, suitable photosensitizers extend the absorption of the fullerene which upon excitation leads to energetically high-lying excited states. This allows the fullerenes, bearing a photoactive and electroactive moiety, to operate exclusively as either electron or energy acceptor moieties. A good example, in which shows an efficient charge separation, has been detected, consists of [Ru(bpy)$_3$]$^{2+}$ separated from $C_{60}$ using an androstane bridge.
Figure 5.7. Examples of reported Ru-C₆₀ dyads ¹³⁸ᵇ, ²³⁸ᵃ, and ³³⁸ₑ.

In this system the charge separated state [Ru(bpy)₃]⁺³⁻C₆₀⁻ has been successfully generated with intramolecular electron transfer rate of 0.69 x 10⁹ s⁻¹ and lifetime of 304 ns in dichloromethane-toluene 1:1 v/v. Figure 5.7 shows some other examples of C₆₀-Ru dyads recently reported.

In dyad 1, Figure 5.7 a strong quenching of the ruthenium luminescence intensity was observed accompanied with the reduction of the emission lifetime. Inferring a highly efficient electronic coupling between the donor and the acceptor component in the dyad. Furthermore, transient absorption experiments carried out on this system confirmed the formation of the ³C₆₀, a broad transient with a maximum at 700 nm, suggesting a rapid transfer of the energy of ruthenium triplet state to C₆₀.³⁸ᵇ In dyad 2 the triplet excited of ruthenium-porphyrin, ³(π−π*)RuP, was deactivated by the attached C₆₀.³⁸ᵃ The transient absorption confirmed that energy transfer from the photexcited RuP ot C₆₀ rather than charge separation takes place.
In Figure 5.7 quenching of the luminescent intensity of the ruthenium appended to C\textsubscript{60} was observed. The quenching was attributed to intramolecular electron transfer from \textsuperscript{3}Ru to C\textsubscript{60}. This result was discerned from the lack of quenching of the ruthenium emission intensity at low temperature.\textsuperscript{38e}

Fullerene-porphyrin-ferrocene triads, tetrads, and pentands have been prepared to mimic ET in natural synthesis photosynthesis.\textsuperscript{39} Ferrocene –Zinc – porphyrin- C\textsubscript{60} triads is one of the most efficient artificial systems.\textsuperscript{40} In this system a charge-separation state has been detected with a lifetime up to 16 \textmu s. In another system a ferrocene-zinc-porphyrin trimer- fullerene pentad \textsuperscript{41} exhibited a lifetime of 0.53 s for the charge-separated state. Fullerene–porphyrin– Cu (phen)\textsubscript{2}–ferrocene aggregates have recently been prepared . The Cu(phen)\textsubscript{2} in this heteroleptic tetrads was used to mediate electron transfer between the components.\textsuperscript{42} The electron transfer pathway in this system was proposed as follows upon photoexcitation of the porphyrins unit, PET will generate the following CS state C\textsubscript{60}\textsuperscript{-1}. Por\textsuperscript{+}.Cu(phen)\textsubscript{2}\textsuperscript{+}.Fc\textsuperscript{-}. Then following another CS, this leads to C\textsubscript{60}\textsuperscript{-1}. Por.Cu(phen)\textsubscript{2}\textsuperscript{+2}.Fc and the final state will be C\textsubscript{60}\textsuperscript{-1}. Por.Cu(phen)\textsubscript{2}\textsuperscript{+}.Fc\textsuperscript{+}. It was proposed that this system should operate as A-D-D-D.

5.1.4 Inclusion complex of C\textsubscript{60} by \gamma-cyclodextrin:

Pristine C\textsubscript{60} in not water soluble, but its solubility is very important for its practical application in biological or medical fields.\textsuperscript{43} Many approaches have been reported to increase the water solubility of C\textsubscript{60}. These approaches involve functionalization of C\textsubscript{60} with hydrophilic groups or addends\textsuperscript{44}, or inclusion of [60]fullerene in suitable water-soluble host species such as micelles \textsuperscript{45}, \gamma-cyclodextrin \textsuperscript{46}, calixarenes \textsuperscript{47} or by incorporating [60]fullerene in polymeric structures \textsuperscript{48}.

The formation of non-covalently bonded supramolecular inclusion complexes with cyclodextrins (CDs) has been shown to be an effective method to solubilize fullerenes in aqueous solution.
Several methods have been reported for the preparation of water-soluble α-, β-, γ-CD/Fullerene complexes. Because of the dimensional difference, a complete inclusion is not possible, but the secondary hydroxyls of the γ-cyclodextrin rims can be connected by H-bonds and possibly mediated by water molecule. A ditopic host is formed in this way, figure 5.8, which makes the supramolecular complex more stable. Gao et al. have recently prepared α-CD/C₆₀ inclusion complex using monoanionic C₆₀, which was generated by a chemical reduction using 1-methylnaphtalene radical anion. The preliminary results of UV-Vis., MS and \textsuperscript{13}C NMR indicate that anionic C₆₀ can form an inclusion supramolecular complex with α-cyclodextrin, while the neutral C₆₀ cannot under the same conditions. The inclusion complex of γ-CD and C₆₀ in aqueous solution displays many interesting properties such as DNA cleavage, dinitrogen fixation as well as C=C, C=O, N-N\textsuperscript{+} bonds reduction under mild conditions, and to protect C₆₀ from ozonation. The ability of cyclodextrin to encapsulate C₆₀ has been exploited to form supramolecular dyads and polyads where C₆₀ can act as a bridge for mediating electron and energy transfer. Our group have recently reported a novel supramolecular donor and acceptor species in which fullerene is capped by...
two sensitizers functionalized β-cyclodextrin units Figure 5.9.\textsuperscript{57} In this system vibrational spectroscopy was used to confirm the partial inclusion of C\textsubscript{60} in the cyclodextrin cavity.

\textbf{Figure 5. 9.} The assembly of Ru-C\textsubscript{60}-Ru triad.\textsuperscript{57}

Furthermore, Reductions of the ruthenium emission intensity and lifetime were observed. Both energy and electron transfer were proposed to be responsible for the quenching. The rate of intramolecular transfer between Ru-C\textsubscript{60} was estimated to be $1\times10^7$ s\textsuperscript{-1} suggesting electron transfer is most likely process to occur.

Liu et al. have recently reported a novel self-assembly supramolecular system consisting of luminescent CD-Tb polyads and photosensitizing C\textsubscript{60} units through the end-to end-inclusion complex, shown in Figure 5. 10.\textsuperscript{58}
They demonstrate that a pyridine → Tb → C₆₀ intermolecular energy transfer process is operative when a solution of this assembly is exposed to UV light.

5.1.5 Fullerenes in Self-assembled monolayers:
Surface modification with C₆₀ and its covalent derivatives is currently of substantial interest, owing to the possibility of transferring the unique [60] fullerene properties to bulk materials by surface coating. Monolayers, containing redox active centers at a fixed distance from a surface, instead of freely diffusing, form an important class of new hybrid materials offering potential technological applications ranging from bioactive materials to advanced nanostructured devices for electronic applications. This approach, in particular, has gained a lot of attention from electrochemist. C₆₀ films can be used in designing photoelectric conversion devices, superconductivity, nonlinear optics, ion-selective electrode, single-molecule devices, and organic memory devices. The self-assembled monolayer is by far the most effective method to organize a two-dimensional highly ordered fullerene-containing assembly on various substrates. However, detailed discussion of this topic is beyond the scope of this thesis.
5.1.6 Covalently and non-covalently linked multicomponent supramolecular assemblies:

Covalently linked dyads and triads consisting of donor and acceptor chromophores have been constructed to control long-range energy and electron transfer and to mimic the primary events in PSII. Construction of these dyads has been the subject of many reviews. Many of these dyads and triads have employed osmium and ruthenium as a donor and acceptor respectively. Figure 5.11 shows an example of dyads reported.

![Diagram of covalently linked heteronuclear dyad](image)

**Figure 5.11.** Covalently linked heteronuclear dyad.
For complexes of the same ligands the MLCT level lies at higher energy in the Ru(II) than in the Os(II) complexes\textsuperscript{65}. Therefore in Ru(II)-BL-Os(II) complex an intercomponent energy transfer process from Ru-based to the Os-based can take place. The free energy change ($\Delta G^0$) for the energy transfer reaction can be expressed by the differences between the zero-zero spectroscopic energy of the donor and acceptor excited states\textsuperscript{66}, That can be estimated from the luminescence band maxima of Ru and Os reference complexes taken at 77 K. An evaluation of the rate constant of the energy transfer process can be obtained from the following equations:

\[
K_{en} = \frac{1}{\tau(\text{l}0/\text{l} - 1)} \quad \text{Equation 5. 1}
\]

\[
K_{en} = \frac{1}{\tau} - \frac{1}{\tau} \quad \text{Equation 5. 2}
\]

Where $I_0$ and $\tau_o$ are the luminescence intensity and lifetimes, respectively of the species that can be quenched, the Ru (II)-based component, the $I$ and $\tau$ are the residual luminescence intensity and lifetimes after quenching. Evidence of energy transfer as the sole quenching can be obtained by the sensitization experiments or by risetime measurements\textsuperscript{67}.

Many examples have been reported where energy transfer in Ru\textsuperscript{II}-BL-Os\textsuperscript{II} was observed. In the systems [(tpy)Ru(tpy-En-tpy)Os(tpy)]\textsuperscript{4+} \textsuperscript{68, 69}, and [(bpy)$_2$Ru(pb-En-pb)Os(bpy)$_2$]\textsuperscript{4+}, [(bpy)$_2$Ru(mb-En-mb)Os(bpy)$_2$]\textsuperscript{4+}, [(bpy)$_2$Ru(ob-En-ob)Os(bpy)$_2$]\textsuperscript{4+}, triplet energy transfer from the ruthenium(II) unit to the osmium(II) complex was occurred on a picosecond time scale with a rate constant $k_{en}$ around $10^{10}$ s$^{-1}$. An electron exchange mechanism was suggested as a mechanism to account for the energy transfer in these systems.

In a mixed metal compounds such as Ru\textsuperscript{II}-BL-Os\textsuperscript{III}, The Ru-based luminescence is quenched by an electron transfer mechanism, leading to Ru\textsuperscript{III}-BL-Os\textsuperscript{II}. The transient Ru\textsuperscript{III}-BL-Os\textsuperscript{II} then decays to its intervalence ground state isomer Ru\textsuperscript{II}-BL-Os\textsuperscript{III} by back electron transfer process.\textsuperscript{70}

Multi-step reactions are usually required to link metallic building blocks together by means of covalent bonds; such multistep processes result in poor yields and synthetic complexity.\textsuperscript{71} Non-covalently assembled systems, on the other hand were fond to be efficient. They allow
the control of the photoinduced processes by a simple choice of the photoactive components.\textsuperscript{71}

\textbf{Figure 5.12.} Aqueous Assembly of Anth-Ru(αβ)-Os-ada.\textsuperscript{77}

Hydrogen bonding,\textsuperscript{72} \(\pi\)-stacking\textsuperscript{73} and metal-ligand coordination\textsuperscript{74} are the non-covalent interactions often exploited for the design of supramolecular assemblies. These interactions, however, are not very effective for designing water-soluble supramolecular systems. As a result of their water solubility, guest-encapsulation properties and ability to mimic natural enzymatic systems, cyclodextrins are increasingly used in the design of supramolecular electron- and energy-transfer systems.

Components linked by hydrophobic interactions were found to be the most efficient interactions. The best example is the inclusion properties of cyclodextrin that can be
exploited in designing supramolecular self-assembly in which the cyclodextrin cavity can harbour non-polar molecules.\textsuperscript{75}

Many examples have been reported where the donor and the acceptor are bound to cyclodextrin via covalent and non-covalent interactions.\textsuperscript{76} Recently, Pikramenou et al have reported a triad based on cyclodextrins Figure 5.12. This self-assembled junction consists of one \( \beta \), and two \( \alpha \) cyclodextrin attached to ruthenium centres. Guest molecules Anthracene and Os-Ada were designed with tails tailored for recognition of \( \alpha \) and \( \beta \)-cyclodextrins, respectively. In this system unidirectional two-step photoinduced energy transfer process has been obtained.\textsuperscript{77}

5.2 Experimental

5.2.1 Synthesis and characterization:

5.2.1.1 Synthesis of Di-6\( ^{A} \), \( ^{6X} \)-Deoxy-p-toluenesulphonyl-\( \gamma \)-cyclodextrin, \( \gamma \)-CD-(OTs)\(_2\):

To a solution of \( \gamma \)-CD (57.07 g, 44 mmol) in NaOH (1500 cm\(^{-3}\), 0.4 mol dm\(^{-3}\)), p-toluenesulphonyl chloride (54.62, 286.5 mmol) was added with vigorous stirring at 0\(^{\circ}\)C. The resulting solution was stirred for a further 3 hours at the same temperature and then filtered by gravity to remove the excess of p-toluenesulphonyl chloride. The filtrate was neutralized with HCl (1 mol dm\(^{-3}\)) and a white precipitate formed, which was collected by gravity filtration. The crude product was recrystalized from hot water and dried in vacuo. \( C_{62}H_{62}O_{44}S_{2}H_{2}O \) MW = 1622 g/mol. Mol. Ion. Peak at m/z= 1627.4 [M+ + H]. 1H NMR (400 MHz, DMSO) . \( \delta \)

\( H_{\text{Os}} \), 7.740 ppm (d, 4H), H\( _{\text{Ot}} \), 7.426 ppm (m, d, 4 H). \( \text{OH}_{\text{Gl-2}\text{+3}} \) 4.6 - 4.154 , 5.891 -5.722 ppm (m, 16 H), \( \text{OH}_{\text{Gl-6}} \) 4.600 -4.154 ppm (m, 8H’s), \( \text{H}_{\text{Gl-1}} \) 4.901- 4.794 ppm (m, 8 H’s).

5.2.1.2 Synthesis of di-6\( ^{A} \), \( ^{6X} \)-deoxy -6-(5-amino-1,10-phenanthroline-\( \gamma \)-cyclodextrin, \( \gamma \)-CD-(Aphen):\( \gamma \)-CD-(OTs)\(_2\) ( 1.0 g,0.45 mmol), Nal (0.178 g, 1.18 mmol) and 5-amino-1,10-phenanthroline (0.193 g , 4.5 mmol) were reacted in DMF (50 cm\(^3\)) in an inert atmosphere at 90\(^{\circ}\)C for 24 hrs . The reaction mixture was cooled and poured into acetone.
The products precipitated from the solution. The precipitates were collected by filtration and washed with methanol to remove unreacted aminophenanthroline. The solid was recrystallized from warm water. The final product was purified using Biobeads S-X-3. C_{79}H_{111}Cl_2N_6O_{45}S Calculated 43.40 % C, 5.11%H, and 3.84 % N. Found 43.01 % C, 4.98 % H, and 3.7% N . m/z = 1672 ([M^+ + H]). ^1H-NMR (400 MHz, DMSO) 4.5 ( m, 6H), 4.8 (m, 8H), 5.8 (m, 16H), 6.2 (s, 2H), 6.85(s, 2H), 7.5 (m, 2H), 7.75 (m, 2H), 8.15 (d, 2H), 8.65 (d, 4H), 9.05 (d, 2H).

5.2.1.3 Synthesis of Di-6^A, 6^X-Deoxy-(Ruthenium-(6^A, 6^X-(5-amino-1,10-phenanthroline)-6^A, 6^X-γ-cyclodextrin: [Ru2-γ-CD]^4+

(0.124, 0.05 mmol) γ-CD-(Aphen)_2 was dissolved in ethanol: water (2:1) and heated gently in an inert atmosphere. Ru(bpy)_2Cl_2(0.0634, 0.1 mmol ) in ethanol: water (2:1) was then added dropwise to reaction mixture over a period of 15 mins. The resulting solution was refluxed at 80 °C for 36 hrs. The reaction mixture was concentrated, almost to dryness, by rotary evaporation. The reaction was then cooled and poured into acetone to precipitate the product. The precipitate was collected by filtration. The product washed repeatedly to remove unreacted Ru(bpy)_2Cl_2. The final product was dried in vacuo and purified using gel permeation chromatography on BioBeads S-X-3. C_{112}H_{137}Cl_{13}F_{24}N_{14}O_{38}P_{4}Ru_2. Calculated %: C 38.10%; H 3.91%; N 5.55%. Found 37.47% C, 3.88% H, 5.35% N. C_{112}H_{127}O_{36}N_{14}Ru_2Cl_3 ; m/z= 2651 ; [M-Cl]^+ , C_{90}H_{111}O_{38}N_{10}Ru; m/z= 1054.1; [M-Ru(bpy)_2-2Cl]^+2 , C_{78}H_{103}O_{36}N_{7}Ru; m/z= 1890; [M-Ru(bpy)aphen-2Cl]^+2 .

^1H-NMR (400 MHz, DMSO) 4.5 (m, 6H), 4.8 (m, 8H), 5.8 (m, 16H), 6.2 (s, 2H), 6.85(s, 2H), 7.5 (m, 2H), 7.75 (m, 2H), 8.15 (d, 2H), 8.65 (d, 4H), 9.05 (d, 2H).

5.2.1.4 Synthesis of Di-6^A, 6^X-Deoxy-(Osmium-(6^A, 6^X amino-1,10- phenanthroline)-6^A, 6^X-γ-cyclodextrin dimer:: [Os2-γ-CD]^4+

This complex was prepared and purified using the same procedure mentioned above for ruthenium dimer using (0.124, 0.05 mmol) γ-CD-(Aphen)_2 and (0.0751 g, 0.10 mmol ) Os(bpy)_2Cl_2; C_{112}H_{127}Cl_{24}F_{24}N_{14}O_{38}Os_{2}P_{4}. Calculated %: C 32.902; H 3.131; N 4.796. Found %: C 31.51; H 2.92; N 4.77. C_{112}H_{127}O_{36}N_{14}Os_{2}Cl_{3}6H_2O ;m/z= 2994 ; [M-Cl]^+ , C_{90}H_{111}O_{38}N_{10}Os; m/z=1240 ; [M-Os(bpy)_2- 2Cl]^+2 , C_{78}H_{103}O_{38}N_{7}Os ; 1960 ; [M-Os(bpy)_2aphen- 2Cl]^+2 . ^1H-NMR (400 MHz, DMSO) 4.5 (m, 6H), 4.8 (m, 8H), 5.8 (m, 16H),
7.0 (s, 2H), 7.1 (s, 2H), 7.4 (m, 2H), 7.7 (m, 2H), 7.8 (m, 8H), 8.1-8.4 (m, 24H), 9.1 (m, 8H).

5.2.1.5 Synthesis of [Ru$_2$-C$_{60}$-Os$_2$]+8 Tetramer:

The mixture of Ru$_2$-γ-CD (0.0772 g, 0.025 mmol), Os$_2$-γ-CD (0.0817 g, 0.025 mmol) and C$_{60}$ were mixed in DMF/Toluene (50-80% v/v) DMF. The resulting solution was refluxed at 90 °C for 3 days. The inclusion of C$_{60}$ into γ-CD cavity was monitored by UV-Vis. spectroscopy. The organic solvents were removed by rotary evaporation. Toluene was added and the suspension was filtered then washed with 100 ml of Toluene to remove any un-included C$_{60}$. The resulting dark brown solids were washed with ethanol to remove excess γ-CD then washed with diethyl ether and dried in vacuo. The product was purified using gel permeation chromatography Bio-Beads S-X-3. C$_{284}$ H$_{278}$ F$_{48}$ I$_{6}$ N$_{34}$ O$_{76}$ Os$_2$ P$_8$ Ru$_4$. Calculated %: C 43.240; H 3.557; N 6.037, Found %: C 41.34, H 3.280, N 6.06.

5.2.1.6 Synthesis of [Os$_2$-C$_{60}$-Os$_2$]+8 and [Ru$_2$-C$_{60}$-Ru$_2$]+8 tetramer:

The same procedures were followed to prepare these tetramers as outlined above for [Ru$_2$-C$_{60}$-Os$_2$]+8. The elemental analysis of [Ru$_2$-C$_{60}$-Ru$_2$][PF$_6$]$_8$: C$_{284}$ H$_{262}$ Cl$_2$ F$_{48}$ N$_{30}$ O$_{76}$ P$_8$ Ru$_4$. Calculated %: C 46.80; H 4.42; N 6.049; found %: C 46.88; H 3.48; N 5.83. The elemental analysis of [Os$_2$-C$_{60}$-Os$_2$][PF$_6$]$_8$: C$_{284}$ H$_{278}$ F$_{48}$ I$_{7}$ N$_{28}$ O$_{88}$ Os$_4$ P$_8$. Calculated %: C 41.093; H 3.370; N 4.72; found %: C 39.87; H 3.23; N 4.96.

5.3. Results and discussions

5.3.1 Synthesis and characterization of the dimers and tetramers:

The γ-cyclodextrin diphenanthroline ligand was synthesized by the reacting the appropriate aminophenanthroline with tosyl cyclodextrin derivatives. Ditosylate γ-cyclodextrin was synthesized as reported. The synthesis steps for the ligand are shown in scheme 5.1.
Scheme 5.1. Synthesis of Ru and Os – γ-cyclodextrin dimmers.

5.3.2 Characterisation

5.3.2.1 NMR Spectroscopy

[Ru₂-γ-CD]⁺⁴ and [Ru₂-γ-CD]⁺⁴ were synthesized by treating the ligand (aphen)₂-γ-CD with two equivalents of cis-Ru(bpy)₂Cl₂. The C₆₀ tetramers were prepared following the same procedure that used for (γ-CD)₂C₆₀.⁸⁰

¹H NMR, elemental analysis and MS/ESI were used to confirm the purity for the ligand, dimers. Tetramers were characterized using elemental analysis.

¹H NMR data for the ligand (aphen)₂-γ-CD is shown in Figure 5.13. The aromatic region (6 to 10 ppm) exhibits resonances associated with the aminophenanthroline ligand. Resonances associated with γ-CD were observed at low frequency between 3 and 5 ppm.
The integration of signal intensities of the aromatic region with the anomeric protons (H\textsubscript{Glu-1} protons) see Scheme 1 was approximately 2:1 signal ratio confirming the cyclodextrin was bifunctionalized by the ligand unit. The proton numbering for the cyclodextrin and ruthenium complex are shown in Scheme 5.2. The chemical shifts of cyclodextrin protons in DMSO-\textit{d}\textsubscript{6} are as previously reported.\textsuperscript{82} The H-1 (the anomeric protons) in \(\gamma\)-cyclodextrins are expected to appear at 4.86 ppm and H-2 (non-anomeric) around 3.2 ppm. The secondary hydroxyls of the cyclodextrin (OH\textsubscript{2}, OH\textsubscript{3}) appear between 5.6- 5.8 ppm, which agrees with the reported values. The broad peak between 4.5 and 4.7 corresponds to the primary hydroxyls (OH\textsubscript{6}).
It's noteworthy that the doublets at 7.15 and 7.48 ppm represent the chemical shifts of included p-toluenesulfonate in the cyclodextrin cavity. This result was confirmed by comparing the chemical shifts of the toluene moiety in p-toluenesulfonyl chloride and Di-6\(^{\text{A}}\), 6\(^{\text{X}}\)-Deoxy-p-toluenesulphonyl-\(\gamma\)-cyclodextrin.

The 2D COSY \(^1\text{H}\) NMR of the cyclodextrin-bis-aminophenanthroline ligand is shown in Figure 5.14. The vicinal H-C-C-H couplings are obvious for aminophenanthroline protons and the cyclodextrin protons. There are cross peaks apparent in both the aromatic and anomeric moieties. There is coupling of H\(_{6a,b}\) with H\(_1\), H\(_5\) with OH\(_6\) and H\(_5\) with H\(_1\). These results are in line with a classical \(^4\text{C}_1\) chair conformation of the pyronase ring. In the aromatic region the cross peaks correspond to coupling between H\(_8\) and H\(_7\), which resonate at 7.6 ppm. Another cross peak resonate at 8.2 ppm corresponds to coupling between protons H\(_2\) and H\(_3\) of the cyclodextrin-phenthroline moiety confirming the substitution of aminophenanthroline with the cyclodextrin moiety. The \(^1\text{H}\) NMR spectra of the [Ru\(_2\)-\(\gamma\)-CD]\(^{4+}\) and [Os\(_2\)-\(\gamma\)-CD]\(^{4+}\) are shown in Figures 5.15 and 5.16, respectively. In both
complexes, a significant upfield shift of the aromatic resonances was observed upon coordination of metal ligand. The aromatic region of the spectrum showed the expected chemical shift pattern for a heteroleptic complex with general formula [Ru(bpy)$_2$L]$^{2+}$ where L is the ligand that differs from bipyridine. The spectrum is the sum of the resonances belonging to the cyclodextrin phenanthroline ligand and bipyridine ligands. In the aromatic region the resonances of the aminophenanthroline are observed as a multiplet at 8.8 ppm (H2, H9), 7.4 ppm (H3), 7.6 ppm (H8), 7.8 ppm (H7), 8.4 ppm (H4), 7.0 ppm (H6). And those of the bipyridine ligands are observed as a doublet at 9.0 ppm (H3), a doublet at 8.20 ppm (H4), a doublet at 8.20 ppm (H6), and a doublet of doublet at 7.60 ppm (H5). Similar results have been observed for a reported ruthenium complex attached to cyclodextrins.83

Figure 5.14. The 400 2D $^1$H NMR of (Aphen)$_2$-$\gamma$-CD in DMSO.
Figure 5.15. The 400 $^1$H NMR of [Ru$_2$-$\gamma$-CD]$^{4+}$ in DMSO.

On the basis of the integration of both the aromatic and the anomeric region, the number of protons we expected for each [Ru(bpy)$_2$aphen]$^{2+}$ are 46 protons to 8 anomeric protons ($H$$_Glu-1$) of cyclodextrin. In both the spectra of [Ru$_2$-$\gamma$-CD]$^{4+}$ and [Os$_2$-$\gamma$-CD]$^{4+}$ the integration corresponds well with the expected values.
Figure 5.16. The 400 $^1$H NMR of [Os$_2$-γ-CD]$^{+4}$ in DMSO.

The electrospray mass spectrum (ES/MS) and elemental analysis were used to confirm the purity and the molecular weight of the dimers and tetramers. The proposed structure for [Ru$_2$-C$_{60}$-Os$_2$] tetramer is shown in Figure 5.17.
Figure 5.17. Proposed structures of heteronuclear C₆₀ tetramer of Osmium and Ruthenium dimers.

5.3.2.2 Mass Spectroscopy:

The ES/MS results of the chloride salts of [Ru₂-γ-CD]Cl₄ and [Os-γ-CD]Cl₄ in water/methanol mixture are shown in Tables 5.1 and 5.2 and in the appendix.
Table 5.1. Assignments of characteristic ES/MS of [Os$_2$-$\gamma$-CD] Cl$_4$.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Assigned Formula</th>
<th>Fragmentation</th>
</tr>
</thead>
<tbody>
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<td>2762</td>
<td>C$<em>{112}$H$</em>{127}$O$<em>{38}$N$</em>{14}$Os$_2$Cl$_3$</td>
<td>[M-Cl]$^+$</td>
</tr>
<tr>
<td>2480</td>
<td>C$<em>{90}$H$</em>{111}$O$<em>{38}$N$</em>{10}$Os</td>
<td>[M-Os(bpy)$_2$-4Cl]$^{+2}$</td>
</tr>
<tr>
<td>1960</td>
<td>C$<em>{78}$H$</em>{103}$O$_{38}$N$_7$Os</td>
<td>[M-Os(bpy)$_2$aphen-4Cl]$^{+2}$</td>
</tr>
</tbody>
</table>

Table 5.2. Assignments of characteristic ES/MS of [Ru$_2$-$\gamma$-CD] Cl$_4$.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Assigned Formula</th>
<th>Fragmentation</th>
</tr>
</thead>
<tbody>
<tr>
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<td>[M-Cl]$^+$</td>
</tr>
<tr>
<td>2108.4</td>
<td>C$<em>{90}$H$</em>{111}$O$<em>{38}$N$</em>{10}$Ru</td>
<td>[M-Ru(bpy)$_2$-4Cl]$^{+2}$</td>
</tr>
<tr>
<td>1890</td>
<td>C$<em>{78}$H$</em>{103}$O$_{38}$N$_7$Ru</td>
<td>[M-Ru(bpy)aphen-4Cl]$^{+2}$</td>
</tr>
</tbody>
</table>

5.4 Electronic absorption:

The absorption spectrum of [Ru$_2$-C$_{60}$-Os$_2$]$^{+8}$, [Os$_2$-C$_{60}$-Os$_2$]$^{+8}$, [Ru$_2$-C$_{60}$-Ru$_2$]$^{+8}$ are displayed in Figure 5.18 where the spectra of the homonuclear Os and Ru C$_{60}$ tetramers are also shown for comparison purposes.

The spectrum of the homonuclear dimer is shown in Figure 5.18 (A). It’s well known that the bands in the visible region are due to metal ligand charge transfer MLCT transitions for both Osmium and ruthenium complexes in the d$^6$ state. In the spectra of the Os-based chromophoric units, even the formally forbidden triplet-triplet transitions (550 – 750 nm regions) displays a considerable intensity because of the heavy atom effect.
Figure 5.18. UV-Vis. of Tetramers ([Ru$_2$-C$_{60}$-Os$_2$]$^{+8}$(orange), [Os$_2$-C$_{60}$-Os$_2$]$^{+8}$ (green), [Ru$_2$-C$_{60}$-Ru$_2$]$^{+8}$ (blue), and C$_{60}$ (+light blue) in 1.5 $\times 10^{-4}$M DMF, the inset; [Ru$_2$-$\gamma$-CD]$^{+4}$ (blue), and [Os$_2$-$\gamma$-CD]$^{+4}$ (black) in water.
In Figure 5.18 (b) the spectra of heteronuclear tetramers along with C$_{60}$ are shown. The electronic spectroscopy of the complexes are tabulated in Table 5.4 exhibits the characteristic features of [60] fullerene absorbance i.e. (1) narrow peaks at 259 nm, 328 nm, and 407 nm, corresponding to the allowed $a_{1g} \rightarrow 6t_{1u}$, $a_{1g} \rightarrow 3t_{1u}$ and $a_{1g} \rightarrow 1t_{1u}$ transitions. The extinction coefficients of the dimers and tetramers are increased compared to that of [Ru(bpy)$_3$]$^{2+}$ as shown in Table 5.3. The extinction coefficient of C$_{60}$ at 420 nm was found to be 256 dm$^3$ mol$^{-1}$ cm$^{-1}$.

C$_{60}$ inclusion causes significant alteration to the electronic spectroscopy of both dimers. A weak broad continuum from 430 to 640 nm corresponding to C$_{60}$ orbitally forbidden singlet-singlet transition appears. This is particularly evident in the spectra of [Ru$_2$-C$_{60}$-Os$_2$]$^{8+}$, [Os$_2$-C$_{60}$-Os$_2$]$^{8+}$, where the spectra of the metal centers and the C$_{60}$ are better resolved and the transition due to the guest can been seen to extend out to approximately 750 nm. The electronic absorption of the tetramers display absorptions assigned to the ruthenium-bpy $\pi-\pi^*$ MLCT and fullerenes moieties. Except for one broad, long-wavelength fullerene centered band, which is masked by the metal-to-ligand charge transfer (MLCT) absorption of both osmium and ruthenium. There is no evidence of any new transitions attributable to direct ground state interaction between the metal center and included fullerene. The absorption spectra of the mixed metal complex are the superposition of the spectra of both homonuclear species. These results indicate that metal-based units in the dinuclear complexes are independent of each other. Therefore this indicates very weak intercomponent interaction between the active centers.

5.5 Raman Spectroscopy:

The Resonance Raman spectroscopy of the dimers and tetramers excited at 458, 488, 514 nm are shown in Figures 5.19, 5.20 and 5.21 respectively. Spectra of the dimers and tetramers exciting at 455 and 488 nm show at typical features associated with Ru(dπ)→(bpy)(\pi*) MLCT transitions. Signature bipyridyl transitions are apparent at 1602, 1551, 1484, 1313, 1261, 1160, 1013, and 665 cm$^{-1}$ with a weak Ru-N at mode visible at 370 cm$^{-1}$, see Figure 5.21. The bipyridyl C-C modes between 1400 and 1600 cm$^{-1}$ are broad and exhibit shoulders, most notably at 1532 cm$^{-1}$ which is attributed to the CD-aminophenanthroline unit.
At 488 nm, excitation which is resonant with the C\textsubscript{60} absorbance, extending from approximately 400 – 700 nm, Figure 5.19, the spectra reflect the participation of this transition with the appearance of the pentagonal pinch mode observed at

![Figure 5.19](image-url)

**Figure 5.19.** Resonance Raman Spectroscopy of Ru-dimer [Ru\textsubscript{2}-\gamma-CD]\textsuperscript{4+} (a), Os-dimer [Os\textsubscript{2}-\gamma-CD]\textsuperscript{4+} (b), \gamma-CD (c), C\textsubscript{60} (d) Tetramer [Ru\textsubscript{2}-C\textsubscript{60}-Os\textsubscript{2}]\textsuperscript{8+} (e) excited at 458 nm.
1463 cm$^{-1}$ reflects C$_{60}$ absorbance resonance and is a typical marker for C$_{60}$. This band can also be observed in the spectra of tetramers excited at 458 and 514.5 cm$^{-1}$ which marked with red asterisk. For Ru and Os- dimers excited at 468 nm the MLCT transitions of these metals are also resonant.

Figure 5.20. Resonance Raman Spectroscopy of [Ru$_2$-γ-CD]$^{4+}$ (a), [Os$_2$-γ-CD]$^{4+}$ (b), Tetramer[Ru$_2$-C$_{60}$-Os$_2$]$^{8+}$ (c) excited at 514 nm.
Figure 5.21. Resonance Raman Spectroscopy of Ru-dimer $[\text{Ru}_2\gamma\text{-CD}]^{+4}$ (d), Os-dimer $[\text{Os}_2\gamma\text{-CD}]^{+4}$ (c), C$_{60}$ (b) Tetramer $[\text{Ru}_2\text{C}_{60}\text{-Os}_2]^{+8}$ (a) excited at 488 nm.
5.5 Electrochemistry:

The electrochemistry of the osmium dimer displays two well resolved reversible oxidations and two reductions waves Figure 5.22. The first oxidation peak is observed at 1.18 V and the second is observed at 0.66 V vs Ag/Ag⁺. The first reduction observed at -0.23 V and the second was observed at -1.13 V. The oxidations are assigned to Os(II)/Os(III) processes, which is confirmed by spectroelectrochemistry vide infra. From the comparison of the redox potentials of [Os₂-γ-CD]⁺⁴ with those of the ligand γ-CD-(Aphen)₂ both oxidations are assigned to Os(II)/Os(III) processes, which is confirmed by spectroelectrochemistry vide infra. the first reduction may be assigned to the reduction of aminophenanthroline ligand, and the second reduction at -1.13 V is assigned to the reduction of bpy moiety.

Figure 5.22. Cyclic voltammogram of [Os₂-γ-CD]⁺⁴ in nitrogen purged acetonitrile-0.1 M TEABF₄ at platinum as a working electrode and scan rate of 0.1 V s⁻¹.

The electrochemistry of [Ru₂-γ-CD]⁺⁴ is shown in Figure 5.22. In the anodic region the oxidation wave is assigned to the two poorly one electron Ru²⁺/Ru³⁺ couple. The overlapping
nature of these two oxidations indicates that there is no significant coupling between the two ruthenium centres. The cathodic processes are reminiscent of those for [Os₂-γ-CD]⁺⁴, two reductions are observed at –0.23 and –1.13 V, the later irreversible with a cathodic shift observed for both reductions as shown in Figure 5.23.

![Cyclic voltammogram of [Ru₂-γ-CD]⁺⁴](image)

**Figure 5.23.** Cyclic voltammogram of [Ru₂-γ-CD]⁺⁴ in nitrogen purged acetonitrile-0.1 M TEABF₄ at platinum as a working electrode and scan rate of 0.10 V s⁻¹.

The cyclic voltammetry of [Ru₂-C₆₀-Os₂]⁺⁸ is shown in Figure 5.24 dissolved in DMF. In the anodic region of the CV, two metal-based oxidations are located at 0.67 V and another one located at 0.36 V were observed.
Based on comparison with the CVs of the both Ru and Os dimers, the band at 0.67 V may be assigned to Ru based oxidation and the band at 0.40 V can be assigned to Os-based oxidation. Both Ru and Os-based oxidations are negatively shifted by comparison with that of ruthenium and osmium dimers. This is attributed to the interaction between metal centres and electron rich C₆₀ moiety. These results agree with the previously reported CV’s of Ru-C₆₀ dyads. In dyad 1 Figure 5.7 the Ru-based oxidation was observed at 0.69 V which is negatively shifted by 0.25 V relative to [Ru(bpy)₃]⁺² in CH₂Cl₂.
5.6 Spectroelectrochemistry (SEC):

Spectroelectrochemistry is used to probe the electrochemistry and elucidate the changes to the electronic absorption spectroscopy of the complexes that accompany oxidation states changes.

![Graph showing absorbance vs. wavelength for Os[2-γ-CD]+4 on a potential range between 0.4–0.8V](image)

**Figure 5.25.** Oxidative spectroelectrochemistry of [Os2-γ-CD]+4 on a potential range between (0.4–0.8V).

In this experiment the complex is oxidized or reduced by bulk electrolysis and the changes in the electronic absorption spectra are monitored. To assign the origin of the electrochemical oxidations of the osmium dimer CV, we carried out oxidative spectroelectrochemistry of [Os2-γ-CD]+4 (Figure 5.25 and 5.26), applying a potential between 0.4–0.6V on i.e. beyond the
oxidation peak observed at 0.4V in the CV of the osmium dimer Figure 5.22. The spectrum was initially recorded with no potential applied and then 2 min intervals after the application of + 0.4 V. The Os(dπ→bpy(π*)) CT transition at 476 nm is lost with the loss of MC Os (d–d) transition band at 369 nm. The ligand-based bands are greatly affected by the oxidation of Os centre.

The transition at 322 nm can be assigned as a bpy (π→π*) transition and undergoes a slight red shift due to the stabilization of that (bpy) π* orbital upon metal oxidation. One sharp isosbestic point was observed at 348 nm with the expected appearance of a very weak band around 720 nm. This new transition is likely to be a (π)→Os (d π) ligand-metal charge transfer of the OsIII. On the basis of these results the first oxidative process has may be assign to the OsII/III species.

Figure 5.26 shows the second oxidative spectroelectrochemistry of [Os2-γ-CD]+2. The same experiment was carried on the complex applying (0.8-1.1) V i.e. beyond the electrochemical process at 1.1V in Figure 5.22. The spectrum is similar to that obtained upon the application of 0.4 to 0.8 V. An isosbestic point around 344 nm with a slight red shift of the transition at 322 nm characterizes the spectrum. There was no evidence of LMCT band was observed. On the basis of the spectrum obtained between 0.8-1.1 V this peak may be assigned to another OsII-OsIII process.

When the oxidised species reached equilibrium, the voltage was changed and held at 0.0 V in order to reduce the Os(III). The band at 293 nm was seen to return to 95 % of the intensity of absorbance spectrum before electrolysis. The same can be said of the MLCT and a concomitant disappearance of the LMCT occurs.
Figure 5.26. Oxidative spectroelectrochemistry of [Os$_2$-γ-CD]$^{4+}$ on a potential range between(0.8 – 1.00V).
5.7 Photophysical properties:

To investigate the extent of electronic interaction between the MLCT excited states of Ru and Os and the fullerene ground state, time-resolved emission measurements were carried out with the [Os₂-C₆₀-Os₂]⁺₈, [Ru₂- C₆₀ –Ru₂]⁸⁺, and [Ru₂-C₆₀-Os₂]⁺₈ and their studies compared to those compounds without C₆₀.

The photophysical data are summarized in Table 5.3 and the lifetime decays are shown in Figure 5.28. Emission decays measured from Time Correlated Single Photon Counting (TCSPC) \( \tau_{em} \) presented in were extracted from exponential fits to these data.

Steady state luminescence spectra of [Ru₂-γ-CD]⁺⁴, [Ru₂-C₆₀ –Ru₂]⁸⁺, and [Ru₂-C₆₀-Os₂]⁺₈ are shown in Figure 5.27. All spectra have been obtained with dilute solutions (optical density < 0.1) and were absorbance matched at the excitation wavelength. The ruthenium MLCT excited state of [Ru₂-γ-CD]⁺⁴ is strongly luminescent (\( \Phi_{em} = 0.021 \)) and also long-lived with \( \tau = 755 \) ns in deaerated aqueous solution. The quantum yield and the lifetime are typical, albeit higher, compared with other ruthenium polypyridyl complexes. Relative to [Ru₂-γ-CD]⁺⁴, the ruthenium MLCT emission of C₆₀ tetramer of this dimer is significantly quenched.

Upon excitation at 420 nm the \( \Phi_{em} \) values (which has been corrected for C₆₀ contribution to absorbance) reduced from 0.021 to 0.014. As the inclusion complex is a tetramer and contains four metal centres, extinction coefficients for the complexes increase accordingly and the probability of excitation occurring is twice that for the [Ru₂-γ-CD]⁺⁴. We would therefore, in the absence of any additional quenching process, expect a concomitant increase of the quantum yield of the inclusion complexes.

However, considerably reduced \( \Phi_{em} \) is observed even accounting for the C₆₀ contribution to absorbance. The lifetime which now conformed to a biexponential decay, Figure 5.28, exhibited two lifetimes with \( \tau_1 = 567 \) ns and \( \tau_2 = 96 \) ns. The % contribution to the emission
Figure 5.27. Luminescence spectra of Tetramers ([Ru₂-γ-CD]⁺⁴ (a), [Ru₂-C₆₀-Ru₂]⁺⁸ (b), [Ru₂-C₆₀-Os₂]⁺⁸ (c), [Os₂-γ-CD]⁺⁴ (d), [Os₂-C₆₀-Os₂]⁺⁸ (e), 1.5 × 10⁻⁵ M in DMF excited at 460 nm.

The intensity from the long and short component for [Ru₂-C₆₀-Ru₂]⁺⁸ was 63 % τ = 567 ns and 27 % τ = 96 ns. The relatively large contribution from the long component does not represent the % concentration of the free complex. The greater Φ_em of this species makes it's contribution artificially high. The % contribution from the short component which has inherently weaker emission is relatively high indicating that a very high % of the emitting molecules are quenched by C₆₀ and have short emission lifetimes. Nevertheless, the three complexes show λ_max emission at 608 nm.
Luminescence spectra of $[\text{Os}_2\gamma\text{-CD}]^{4+}$ and $[\text{Os}_2\text{C}_6\text{O}_2\text{Os}_2]^{8+}$ are also shown in Figure 5.27. The $\lambda_{\text{max}}$ of osmium emission is centred at 711 nm with $\tau = 329$ ns and $\Phi = 0.0019$. The luminescence quantum yield ($\Phi_{\text{em}}$) was similarly reduced to 0.00091 after the inclusion of $\text{C}_6\text{O}_2$. Lifetime of $[\text{Os}_2\text{C}_6\text{O}_2\text{Os}_2]^{8+}$ is fitted to a biexponential decay, Figure 5.28, exhibited two lifetimes $\tau_1 = 272$ ns and $\tau_2 = 25$ ns. The % contribution from the short component, which has inherently weaker emission, is 5 % indicating that a very low % of the emitting molecules are quenched by $\text{C}_6\text{O}_2$. In the case of heteronuclear tetramer we tried to monitor the luminescence of the ruthenium centre by exciting the $[\text{Ru}_2\text{C}_6\text{O}_2\text{Os}_2]^{8+}$ and $[\text{Ru}_2\gamma\text{-CD}]^{4+}$ at 420 nm, although it is impossible to completely avoid a simultaneous direct excitation of the osmium excited state as the absorption spectrum of the osmium component strongly overlaps with the ruthenium-based component.

![Figure 5.28. Lifetime decays of Tetramers $([\text{Ru}_2\gamma\text{-CD}]^{4+}$ (a), $[\text{Ru}_2\text{C}_6\text{O}_2\text{Ru}_2]^{8+}$ (b) $[\text{Ru}_2\text{C}_6\text{O}_2\text{Os}_2]^{8+}$ (c), $[\text{Os}_2\gamma\text{-CD}]^{4+}$ (d) $[\text{Os}_2\text{C}_6\text{O}_2\text{Os}_2]^{8+}$ (e) and. The spectra of tetramers were recorded in $1.5 \times 10^{-5}\text{M DMF}$, and that of dimers were recorded in $\text{H}_2\text{O}$.](image)

The mixed nuclear tetramer $[\text{Ru}_2\text{C}_6\text{O}_2\text{Os}_2]^{8+}$ exhibits two emission bands, corresponding to the Ru(II) and Os(II) metal centres. The luminescence intensities of both Ru and Os in $[\text{Ru}_2$-
were quenched. The relative emission intensity of \([\text{Ru}_2-C_60-\text{Ru}_2]^{8+}\) is of 3.3, when we compare those values with that of Ru and Os in \([\text{Ru}_2-C_60-\text{Os}_2]^{8+}\), these values were reduced to 2.59 and 1.45 respectively. This is reflected in the reduction of quantum yield \(\Phi_{\text{em}}\) (which has been corrected for \(C_{60}\) contribution to absorbance) of the ruthenium based emission from 0.014 in \([\text{Ru}_2-C_60-\text{Ru}_2]^{8+}\) to 0.0013 in \([\text{Ru}_2-C_60-\text{Os}_2]^{8+}\).

**Table 5.3.** Photophysical properties of homonuclear dimers and tetramers in water(\(^\ast\)) and in DMF (\(^\Delta\)).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Abs. (\lambda_{\text{Max}}) (nm)</th>
<th>Emission (\lambda_{\text{Max}}) (nm)</th>
<th>(\tau_{\text{deaerated}}) (ns)</th>
<th>(\Phi_{\text{aerated}})</th>
<th>(\varepsilon[M^{-1} \text{cm}^{-1}]) ((\lambda_{\text{Max}}))</th>
<th>% contribution to decay</th>
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<td>(\gamma)-CD-Ru(_2^*)</td>
<td>455</td>
<td>608</td>
<td>755</td>
<td>0.021</td>
<td>24850 (455 nm)</td>
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<tr>
<td>(\gamma)-CD-Os(_2^*)</td>
<td>430, 474, 590, 670</td>
<td>711</td>
<td>329</td>
<td>0.0019</td>
<td>16000 (474 nm)</td>
<td></td>
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<tr>
<td>[Ru(bpy)(_3)]^{2+}</td>
<td>450</td>
<td>612</td>
<td>935</td>
<td>0.028</td>
<td>12500 (455 nm)</td>
<td></td>
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<tr>
<td>[Os(bpy)(_2)Aphen](^{2+})</td>
<td>430, 474, 590, 670</td>
<td>714</td>
<td>55</td>
<td>0.0074</td>
<td>984 (474 nm)</td>
<td></td>
</tr>
<tr>
<td>Ru(<em>2-C</em>{60})-Os(_2)(^\Delta)</td>
<td>450, 529, 655</td>
<td>616, 703</td>
<td>77, 6.6</td>
<td>0.0013</td>
<td>31805 (450 nm)</td>
<td>68.8 %, 31.2 %</td>
</tr>
<tr>
<td>Ru(<em>2-C</em>{60})-Ru(_2)(^\Delta)</td>
<td>450, 375</td>
<td>608</td>
<td>567, 94</td>
<td>0.014</td>
<td>63882 (450 nm)</td>
<td>63 %, 27 %</td>
</tr>
<tr>
<td>Os(<em>2-C</em>{60})-Os(_2)(^\Delta)</td>
<td>370, 424, 480, 590, 660</td>
<td>717, 650</td>
<td>272, 25</td>
<td>0.00091</td>
<td>39509 (480 nm)</td>
<td>95 %, 5 %</td>
</tr>
</tbody>
</table>

On the basis of these values a strongly quenched emission from the ruthenium-based moiety is observed. However, only slight quenching of the osmium-based moiety is observed. Although, the fact that both Ru and Os emit suggests their intermetal energy transfer, common in Ru-Os dimers, does not occur here as the Förster overlap is not changed by
CD/C₆₀ formation. Energy transfer by Dexter mechanism must be blocked by C₆₀ and CD bridge, this may be related to large distance between Ru and Os which Dexter is sensitive to and also potentially poor electronic coordination of γ-CD, as Dexter is double electron transfer. Or the Ru is quenched by C₆₀, reducing the lifetime. Therefore, Ru→Os energy transfer cannot occur.

The photoinduced communication between the two metal centres, Ru(II) and Os(II), on or across the cyclodextrins cavity appears to be energy transfer from ruthenium to osmium arising from the low-lying ³MLCT state of Osmium. The energy transfer level diagram of the heteronuclear tetramer [Ru₂-C₆₀-Os₂]⁺⁺ is depicted in Figure 5.29. Excluding the possibility of intermolecular energy-transfer (high dilution technique) and the independence of rate of ET on the laser power, an intramolecular (intercomponent) energy or electron transfer process can be used to explain the results. To distinguish between energy and electron transfer transient absorption experiments were carried out.

5.8 Transient absorption spectroscopy:

To obtain a better understanding of the mechanism of quenching of the ruthenium excited state in these complexes transient absorption spectroscopy on all compounds was carried out. This technique allows us to assign the product of electron or/and energy transfer process within the complexes by the characterisation of the absorption spectra of the excited state and its products. All transient absorption experiments were carried out in oxygen free solutions exciting with 20 ns pulse at 355 nm.

Figure 5.29 presents the time dependent spectral changes (ΔA) observed on 355 nm photolysis (20 ns pulse) of a deoxygenated solution of [Ru₂-γ-CD]⁺⁺. The spectra are characterized by the pulse-induced depletion of the 450-nm Ru(II) MLCT band and a second negative amplitude signal (-ΔA) at 600 – 700nm maximum at 620 nm. This negative signal represents the stimulated emission of the excited ruthenium.
Figure 5.29. Transient absorption spectra for a 50 μM degassed solution of [Ru$_2$-$\gamma$-CD]$^{4+}$, recorded 20 ns after 355 nm laser pulse; 100 accumulations; step size = 20 ns and gate width = 40 ns.

The transient absorption spectra of [Ru$_2$-C$_{60}$-Ru$_2$]$^{8+}$ are presented in Figures 5.30 and 5.31. The first portion, in the range of 420 – 650 nm is shown in Figure 5.30. The figure shows features similar to those observed in [Ru$_2$-$\gamma$-CD]$^{4+}$ transient absorption. The depletion of Ru(II) at 450 nm and luminescence of the excited ruthenium at 620 nm.
**Figure 5.30.** Spectral region A (420-650 nm), transient absorption spectra of a 50 μM degassed solution of \([\text{Ru}_2\text{-C}_6\text{O} - \text{Ru}_2]^{8+}\). Recorded 20 ns after 355 nm laser pulse; step size = 20 nm and gate width = 40 ns.

In Figure 5.31 the spectra of \([\text{Ru}_2\text{-C}_6\text{O} - \text{Ru}_2]^{8+}\) in the region between 620 to 850 nm are presented. The spectra show a grow in the region between 700 nm up to 850 nm. The positive \(\Delta A\) at \(\lambda \geq 700\) nm may attribute to the triplet-triplet absorption of C\(_{60}\). As shown in previously reported transient absorption data of Ru-C\(_{60}\) dyads. This species results from a rapid intramolecular energy transfer from \(^3\text{Ru}^*\) to C\(_{60}\).
Figure 5.31. Spectral region B (620 – 850 nm) of transient absorption spectra of a 50 μM degassed solution of [Ru₂- C₆₀ –Ru₂]²⁺ recorded 20 ns after 355 nm laser pulse; step size = 20 nm and gate width = 40 ns; 10 accumulations.

On the basis of the above results we assume intramolecular energy transfer rather than charge separation, has taken place from Ru to C₆₀ in [Ru₂- C₆₀ –Ru₂]²⁺. Fullerene singlet-singlet absorption evolves at 880 nm in toluene, which on longer time-scale leads to population of triplet manifold through efficient intersystem crossing, as shown by growth of the characteristic, triplet-triplet absorption maximum at 700 nm.
Figure 5.32. The transient absorption spectrum of a 50 μM degassed solution of [Os₂-γ-CD]⁴⁺. Recorded 20 ns after 355 nm laser pulse; step size = 20 ns and gate width = 40 ns; 10 accumulations.

The transient absorption of [Os₂-C₆₀-Os₂]⁸⁺ is shown in Figure 5.33 and 5.34. The first spectral region, Figure 5.33, shows the depletion due to the Os(II) MLCT in the region between 420 and 480 nm with depletion observed in the region between 500 and 650 nm as observed for [Os₂-γ-CD]⁴⁺. Figure 5.34 shows spectral region between 630 and 850 nm. No evidence of triplet-triplet absorbance of C₆₀ was observed.
Figure 5.33. Spectral region A (420 – 650 nm) of the transient absorption of a 50 μM degassed solution of [Os₂-C₆₀-Os₂]⁸⁺ recorded 20 ns after 355 nm laser pulse.

The transient absorption spectra observed for [Ru₂-C₆₀-Ru₂]⁸⁺ are similar to those observed for the Ru-C₆₀ dyads shown in Figure 5.7. In dyad 1 the transient of the triplet-triplet C₆₀ absorption was observed as a broad band with maximum at 700 nm. They attribute the quenching of the ruthenium emission to the intramolecular energy transfer from the triplet-excited state of ruthenium to C₆₀. In dyad 2 they were able to detect the transients of both energy and electron transfer products from the ruthenium-excited states to C₆₀.
Similar results were recently reported in Ru- C₆₀ and Re- C₆₀. In these hybrids ruthenium or rhenium complex and C₆₀ are covalently linked via crown ether. A quenching of ruthenium and rhenium excited states were observed in both dyads. Transient absorption of these dyads has shown the MLCT excited state is deactivated via energy transfer by detecting the transient of triplet-triplet C₆₀ at 720 nm. The transient absorption of [Ru₂-C₆₀-Os₂]⁸⁺ is shown.

Figure 5.34. Spectral region B (620 – 850 nm) of transient absorption of a 50 μM degassed solution of [Os₂-C₆₀-Os₂]⁸⁺. Recorded 20 ns after 355 nm laser pulse; step size= 20 ns; gate width= 40 ns.
in Figures 5.35 and 5.36. The first spectral region of the transient absorption spectrum of [Ru₂-C₆₀-Os₂]⁺⁺⁺ is shown in the range between 418-650 nm is shown in Figure 5.35. The excitation wavelength of 355 nm was chosen to excite as much as possible into the ¹MLCT of the ruthenium. Although, it is impossible to avoid a simultaneous direct excitation of the excited state of the osmium since the absorption spectrum of the osmium component strongly overlaps with the ruthenium-based component. The first portion (418-470 nm) is characterised by the depletion between 418 – 470 nm, absorption in the region between 470-560 nm. A negative amplitude signal was observed in the region between 500 and 700 nm. These features are similar to that as for [Ru₂-y-CD]⁺⁺⁺. The absorption may be assigned to the formation of [Ru³⁺(bpy)₂(bpy)·⁻]⁺⁺⁺ species.

Figure 5.35. Spectral region A of transient absorption spectrum of a 50 μM degassed solution of [Ru₂-C₆₀-Os₂]⁺⁺⁺, recorded 20 ns after 355 nm laser pulse.
Assuming the presence of mixed valence species Ru(II)- $C_{60}$-Os(III). The non-emissive Os (III) - based unit quenches the emissive the Ru(II)-based unit. The quenching process leads to the formation of Ru(III)- $C_{60}$- Os(II) whose transient can be observed between 468 nm to 568 nm. The formation of the intervalence-transfer product was proposed to occur by a direct way or first via an energy- transfer step. P. Belser et al. reported similar transient on covalently linked ruthenium and osmium dyads.

In the second spectral region of the transient spectra of $[Ru_2-C_{60}-Os_2]^{8+}$ Figure 5.36 is characterized by absorption grows around 700 nm, characteristic of the absorbance of the fullerene triplet excited states.

Figure 5.36. Second spectral region B (620 – 850 nm) of the transient absorption spectrum of a 50 μM degassed solution of $[Ru_2-C_{60}-Os_2]^{8+}$ recorded 20 ns after 355 nm laser pulse.
Two depletions, the first one between 623 nm and 673 nm and a second depletion between 773 nm and 823 nm separate the two absorbances. These depletions can be assigned to the spin-allowed and spin-forbidden Os(II)-bpy MLCT absorption transitions. The spectral features of [Ru₂-C₆₀-Os₂]³⁺ are similar to that observed for [Os₂-C₆₀-Os₂]³⁺, Figure 5.34. The transient spectra of both complexes [Os₂-C₆₀-Os₂]³⁺ and [Ru₂-C₆₀-Os₂]³⁺ are dominated by the Os-based characteristics with the expected difference between the intensity ratio of C₆₀ based absorption and osmium MLCT bleaching. The intensity of the C₆₀ absorption is reduced compared to the osmium MLCT bleaching, in agreement with the reduction in the population of the C₆₀ triplet.

Figure 5.37. Kinetic profiles for the formation of the transient monitored at 780 nm in [Ru₂-C₆₀-Ru₂]³⁺ (o), [Os₂-C₆₀-Os₂]³⁺ (+), and [Ru₂-C₆₀-Os₂]³⁺ (Δ).
Moreover, the disappearance of the ruthenium depletion is another spectral feature of [Ru₂-C₆₀-Os₂]^{8+}. The population of the triplet-triplet excited state of C₆₀ is accompanied by the bleaching around 650 nm, which confirms the formation of the ΣMLCT Osmium Figure 5.36. The kinetic profiles for the formation of the C₆₀ triplet were monitored at 780 nm. The data are shown in Figure 5.37 and corresponds to the data obtained by time-resolved emission data. There was no evidence on the time scale explained here for photoinduced electron transfer from Ru to C₆₀.

5.9 Photoinduced intramolecular transfer:

On the basis on the results obtained energy transfer from Ru centre to C₆₀ appears to occur for [Ru₂-C₆₀-Os₂]^{8+}, and [Ru₂-C₆₀-Ru₂]^{8+}, whereas no quenching in [Os₂-C₆₀-Os₂]^{8+} complexes. As expected for an energy transfer process, the decay of the Ru-based excited state is accompanied by the rise of the C₆₀-based triplet excited state. The rate constant of the energy-transfer process can be calculated from the following equation:

$$K_{en} = 1 / \tau - 1 / \tau_0$$  \hspace{1cm} \text{Equation 5.3}

Where \( \tau \) and \( \tau_0 \) are the luminescence lifetimes of the Ru-based component in the [Ru₂-C₆₀-Os₂]^{8+}, and [Ru₂-γ-CD]^{4+} model compounds respectively.

From the lifetime values shown in Table 3, the intramolecular energy transfer rate constant from Ru to C₆₀ (\( K_{en} \)) was estimated to be \( 1.1 \times 10^7 \) s\(^{-1}\) for [Ru₂-C₆₀-Ru₂]^{8+} and \( 9.3 \times 10^6 \) s\(^{-1}\) for [Ru₂-C₆₀-Os₂]^{8+}.

In comparison with reported values, \( K_{en} \) of [Ru₂-C₆₀-Os₂]^{8+} is lower than the reported values for the systems shown in Figure 5.11. In Ru-C₆₀ dyad shown Figure 5.7 (3), the rate of intramolecular energy transfer was found to be \( 2.5 \times 10^8 \) s\(^{-1}\).

In those systems the energy-transfer processes have been interpreted as occurring via Förster type mechanism or both Förster and Dexter-type mechanisms.
Förster mechanism is long-range mechanism, and it’s based on coulombic interactions, and the Dexter-type mechanism is a short-range mechanism that requires orbital overlap between the donor and acceptor.

Although the energy transfer from Ru to Os is exoergic with $\Delta G = -0.37$ eV, calculated from the triplet state energies of the ruthenium ($^3\text{MLCT} = 2.10$ Ev) and osmium component ($^3\text{MLCT} = 1.73$ eV), it doesn't occur in our complexes. The schematic energy-level diagram of the $\text{[Ru}_2\text{-C}_{60}\text{-Os}_2]^8$ is shown Figure 5.38. The triplet state energy of C$_{60}$ is determined as 1.50 Ev. Therefore, the energy transfer from Ru to C$_{60}$ is also exergonic with $\Delta G = -0.60$ eV, which was confirmed to occur in our complexes by transient absorption spectroscopy.

![Figure 5.38. The energy level diagram of $\text{[Ru}_2\text{-C}_{60}\text{-Os}_2]^8$.](image)

The triplet-excited state of C$_{60}$ is lower in energy than the lowest excited states of both ruthenium and osmium. An indication that the triplet state is lower is demonstrated by the quenching of the excited state lifetimes of both ruthenium and osmium in $\text{[Ru}_2\text{-C}_{60}\text{-Ru}_2]^8$, and $\text{[Os}_2\text{-C}_{60}\text{-Os}_2]^8$.
5.10 Conclusions

We have synthesised and characterised two novel dimeric Ru$_2$-γ-CD and Os$_2$-γ-CD complexes and their C$_{60}$ inclusion tetrameric complexes, [Os$_2$-C$_{60}$-Os$_2$]$^{8+}$, [Ru$_2$-C$_{60}$-Ru$_2$]$^{8+}$ and [Ru$_2$-C$_{60}$-Os$_2$]$^{8+}$. Inclusion of C$_{60}$ in the γ-CD cavity was confirmed by elemental analysis, Raman and UV-Vis spectroscopy and cyclic voltammetry. Significant reduction in the lifetime and quantum yields of emission of the metal centres were noted in the presence of C$_{60}$ despite the fact that per molecule the number of emitting centres has doubled. This emission quenching has been attributed to an electron transfer process which, based on thermodynamic considerations, is thought to be from the excited metal to the included C$_{60}$. The rate of electron transfer was estimated to be $k_{et}$ [Ru$_2$-C$_{60}$-Ru$_2$]$^{8+}$ = $1.1 \times 10^7$ s$^{-1}$ and $k_{et}$ [Ru$_2$-C$_{60}$-Os$_2$]$^{8+}$ = $1.3 \times 10^8$ s$^{-1}$. No significant evidence was observed for energy transfer in [Os$_2$-C$_{60}$-Os$_2$]$^{8+}$.
5.11 References


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Chapter 6

Heterometallic Ruthenium - Iridium Supramolecular Assemblies
6.1 Introduction:

The photophysics of heavy complexes and their use as photoactive components in the construction of systems for photonic applications have been studied.\textsuperscript{1} In particular, Ru(II), Pt(II), Os(II), Ir(III) complexes with suitable ligands are emissive at room temperature and possess interesting photophysical and redox properties. Luminescent ruthenium complexes with bipyridine ligands, have received great attention so far and spectroscopic studies have shown that their luminescence arises from the lowest triplet Metal to ligand Charge Transfer state $^3$MLCT that, due to its phosphorescence character, is long living. Compared to Ru and Os, Iridium complexes have longer exited-state lifetimes and higher luminescence efficiencies due to the efficient intersystem crossing between singlet and triplet excited states arising from the strong spin-orbit coupling of Iridium metal ion. The remarkable photophysical properties of Iridium complexes make them promising materials for photonic applications, such as sensitizers for singlet oxygen, photocatalysts for CO$_2$ reduction, and light emitting devices.\textsuperscript{2} However, research on Iridium complexes has been limited due to the difficulty of their synthesis. Recently Thompson and co-workers synthesized a variety of Ir complexes containing different ligands that include 2-phenylpyridine, diketones and diamines, including 2,2'-bipyridine.\textsuperscript{3, 4} Photophysical studies on these Iridium complexes show that they exhibit high luminescence efficiencies arising from the Ir$\rightarrow$ Ligand MLCT and intraligand $^3\pi\text{-}^3\pi^*$ transitions.\textsuperscript{5} Polypyridine compounds are often characterized by long lived excited states due to a mixing of metal-to-ligand charge transfer (MLCT) and ligand centered LC states. Replacing one or two of the diimine ligands with structurally similar ortho-metalating chelates such as 2-phenylpyridine, leads to higher metal centered (MC) excited state due to the ligand field of the C$^\text{N}$ versus N$^\text{N}$ coordinating ligands. Furthermore their strong $\sigma$-donation causes a decrease of the energy of the MLCT state increasing the energy gap between energy of the MLCT and LC states. This results in a better absorption of visible light, a lower energy emission and shorter excited state lifetimes.\textsuperscript{7} Biscyclometalated Iridium (III) complexes such as [Ir(ppy)$_2$(bpy)]$^+$ have excited state properties quite similar to those [Ru(bpy)$_3$]$^{2+}$ and have been receiving increased attention over the past decade. They too have studied as sensitizers of energy and electron
Whittle and Williams have recently reported a new family of cationic Ir(III) complexes that contain two cyclometallating tetradentate ligands Figure 6.1. Dimetallic complexes of these mononuclear complexes have also been prepared. The absorption spectra of all the complexes in acetonitrile solution at room temperature show very intense bands in the region between 220 nm and 330 nm. These bands were assigned to spin allowed $^1\pi - \pi^*$ transition of the ligands. A relatively sharp and well-defined band centered at 285 nm, which was attributed to the introduction of the pendant aryl unit. A series of bands in the region 330 – 450 nm were attributed to spin allowed spin-allowed CT transitions. A weak band around 480 nm attributed to the absorption of the lowest energy triplet-state facilitated by the high spin-orbit coupling constant of the iridium centre. The new complexes are luminescent in solution at room temperature $\lambda$≈630 nm, displaying a single
structureless emission band in each case typical of phosphorescence from excited states of primarily CT character. The emissive state was regarded as having mixed $^3d$ (Ir)/π(N^C^N) → π* (N^N^C) character ($^3$MLCT/LLCT). The luminescence lifetimes, $\tau$, were found to be in the range 100-200 ns. The dinuclear complexes (Figure 6.1) are similarly luminescent in solution, displayed emission profiles, lifetimes, and quantum yields that are very similar to those of the parent complex. The differences between the dinuclear and mononuclear counterparts are the emission of the former was displaced to lower energy and the emission decay becomes biexponential. The shorter component of the lifetime was around 3 μs which is similar to that of the monometallic complexes and the longer component around 70 μs is much longer than anticipated for an excited state of metal centre. They attributed the longer component to be originated from $^3\pi - \pi^*$ excited state associated with the bridging ligand.

For the iridium (III) complexes of tpy derivatives studied up to now, the luminescent state has been found to be dominantly ligand centered, $^3$LC. This contrast to what happens for closely investigated polypyridine complexes of transition metals such as ruthenium (II), Osmium(II) and Rhenium(I) which are currently being employed as photosensitisers and emitting states of which are triplet metal-to-ligand states ($^3$MLCT) in nature. Iridium (III) complexes of polypyridine ligands are increasingly being employed in relevant applications. For iridium (III) terpyridine (2,2':6',2''-terpyridine, tpy) complexes some interesting perspectives concern their use as biological labeling reagents as well as the building up of dyads and triads as models for photoenergy conversion schemes. [Ir(tpy)$_2$]$^{3+}$ and derivatives like those of the [Ir(tppy)$_2$]$^{3+}$ family (tppy= 4'-tolyl-tpy) exhibit a favorable optical properties which include intense luminescence quantum yield of 10$^{-2}$ and lifetimes in microseconds time range. Furthermore, the luminescent levels for these complexes come at ca. 2.5 eV so that they have potential to act as efficient photosensitizers. The possibility of developing linear arrays by attaching suitable groups at the 4'-position of tpy groups coordinated at the Ir(III) ion is very appealing. Studies on derivatives of [Ir(tpy)$_2$]$^{3+}$ have shown that the introduction of simple, conjugating aryl substituents (e.g. tolyl) onto the 4' position of the terpyridine leads to the stabilization of the LC state and a lengthening of the excited state lifetime, an effect which is more pronounced for a biphenyl substituent.
[Ir(ppy)$_2$]$^{3+}$ is an appealing candidate to compete with Ru and Os counterparts in designing covalently linked triads to mimic the charge separation of photosynthesis. One such triad consists of zinc or free base tetra-aryl porphyrin as a donor and a photoactive centre, an [Ir(ppy)$_2$]$^{3+}$ as a primary acceptor, and a tetra-aryl porphyrin as a secondary acceptor is shown in Figure 6.2.

Figure 6.2. Triads using Iridium (III) as a harvesting metal.

A novel system has been reported where the electroluminescent iridium (III) and ruthenium (II) polypyridyl complexes were combined with 2-ureido-4[1H]ureidopyridinone moieties within one molecule (3) Figure 6.3. In these compounds the combination of transition-metal complexes with quadruple hydrogen-bonding motifs has been exploited to design a supramolecular architecture that may find applications in labeling biological substrates and for electronic devices (5 and 7 ) Figure 6.3. $^{13}$
Figure 6.3. Supramolecular Hydrogen-bonded bipyridine ligand (3), iridium (III) and Ruthenium (II) polypyridyle complexes (5 and 7), the corresponding model complexes (5’ and 7’) and the homonuclear dimers of both mononuclear complexes.\textsuperscript{13}

The iridium(III) complexes 5 and 5’ reveals a strong absorption at about 260 nm, which was be attributed to the ligand-centred $\pi - \pi^*$ transitions on bpy and bpy-, while broad
absorption bands at 370 nm were due to typical spin-allowed $^1$MLCT transitions [$d\pi$(Ir) – $\pi^*$]. Excitation at 370 nm leads to a broad emission band. A change of the emission color was observed from yellow (solid, $\lambda_{\text{max}} \approx 545$ nm) to orange (solution, $\lambda_{\text{max}} \approx 575$ nm). Complexes 7 and 7' have shown absorption and emission spectroscopy characteristic of [Ru(bpy)$_3$]$^{2+}$, with absorption band between 445 and 465 nm originated from $^1$MLCT was detected and emission band centered at 618 nm in solution phase and 628 nm in solid phase. They observed that the hydrogen bonding does not disturb the optical properties of the metal complexes, demonstrating their potential for light emitting devices as well as for sensing applications.

$[\text{Ir}(\text{tpy})_2]^3^+$ and $[\text{Ru}(\beta$-CD-mbpy)$_3]^2^+$ has been used in designing a self-assembled system via non-covalent interaction in water, Figure 6.4. $[\text{Ir}(\text{tpy})_2]^3^+$, in which tpy is substituted at 4' position with a biphenyl or adamantyl group, acts as a donor and Ru complex is an acceptor. The inclusion ability of biphenyl and adamantyl groups in the cyclodextrin cavity has been exploited to bring the two metal centres to close proximity. Therefore, better metal-metal communication was achieved. The photoinduced communication between ruthenium and iridium through non-covalent bonds is attributed to an energy transfer from iridium to ruthenium. The rate of energy transfer was estimated to be $3.3 \times 10^8$ s$^{-1}$ in the case of adamantyl and $2.9 \times 10^7$ s$^{-1}$ in the case of biphenyl.
Figure 6.4. Assembled Ir$^{III}$ metal complex with [Ru($\beta$-CD-mbpy)$_3$]$^{2+}$.

The lifetime measurements showed the presence of two components; a short component corresponding to the complexed iridium system and a long component corresponding to the free complexes. Therefore, a vectorial energy transfer was easily achieved by selecting suitable photoactive components non-covalently linked by cyclodextrin.

We report here on a self-assembled trimer formed between [Ru $^{II}$ (bpy)$_2$ aphen]$^{+3}$ and [Ir(tpy-py)$_2$]$^{+3}$ by $\beta$-cyclodextrin. We have exploited the photophysical properties and
inclusion ability of pyrene to design heterometallic supramolecular system Scheme 6.1. Pyrene has been chosen in this system due to its interesting photophysical properties. Pyrene has a long singlet lifetime; it readily forms excimers; and it acts as an energy acceptor via nonradiative energy transfer from several dyes. In addition the vibronic band structure of its emission is sensitive to the environment. We are interested in investigating the photoinduced process that may occur between the two metals units via non-covalent interaction.

Scheme 6.1. The self-assembled [Ir-(RuCD)$_2$] in water.

6.2 Results and discussions:

6.2.1 Self-Assembly

The synthesis of a similar complex Ir(tpy)(tpy-py)$^+$ was reported elsewhere. In this complex a pyrene pendant was incorporated with one of the terpyridine ligands. In our laboratory we have prepared a symmetric complex in which both terpyridine ligands are incorporated with pyrene pendants Scheme 6.2. This complex was provided by R. Marthi.

6.3 Synthesis of [Ir(tpy-pyrene)$_2$(PF$_6$)$_3$

A mixture of IrCl$_3$.3H$_2$O (85mg, 0.24mmol) and 4’-(pyrene-1-yl)-2,2’:6’2’’-terpyridine (130 mg, 0.30 mol) in ethylene glycol (10mL) was heated under vigorous reflux for 15 min (oil
bath temperature 215°C). After allowing cooling to room temperature, the red solution was diluted with water (30mL). Addition of a saturated aqueous solution of potassium hexafluoro phosphate (10mL) tends to a red precipitate, which was separated by filtration and washed with toluene.\(^{18}\) \(\text{H}^1\text{NMR} (400\text{MHz}, \text{CD}_3\text{CN}) \delta 7.26(\text{m,2H}), 7.67(\text{m,6H}), 7.80(\text{t,2H}), 8.22(\text{d,2H}), 8.31(\text{d,2H}), 8.45(\text{d,2H}), 8.88(\text{d,2H})\).

**Scheme 6.2.** Synthetic scheme of [Ir(tpy-pyrene)\(_2\)](PF\(_6\))\(_3\).

Our assembly was prepared in solution by mixing 2 mmol of CDRu to 1 mmol of [Ir(tpy-pyrene)\(_2\)](PF\(_6\))\(_3\) in water and stirring for 24 hrs.

### 6.4 Electronic and photophysical properties [Ir-(RuCD)\(_2\)] assembly:

The absorption spectra of [Ir-(tpy-py)\(_2\)]\(^{+3}\) and [CDRu] are shown in Figure 6.5. Both spectra were measured in water. The absorption spectrum of [CDRu] shows absorption band centred at 455 nm which is attributed to the MLCT of \((\text{Ru} \delta \pi \rightarrow \text{bpy} \pi^*)\).

The absorption spectrum of [Ir-(tpy-py)\(_2\)]\(^{+3}\) shows a band at 435 nm which was attributed to the intraligand charge transfer ILCT, in which the pendant pyrene group behaves as the donor, and metal bound terpyridyl moiety as electron acceptor. The appearance of such bands in the complexes can be related to the increased acceptor properties of the terpyridyl \(\pi^*\) orbitals upon coordination to the metal ion. The spectrum of [Ir-(RuCD)\(_2\)] is the sum of the spectra of both [Ir-(tpy-py)\(_2\)]\(^{+3}\) and [CDRu]. This indicates that the metal-metal communication in the ground state is negligible.\(^{19}\)
Figure 6.5. UV-Vis absorption spectra of [Ir-(RuCD)$_2$] (a), CDRu (b), [Ir-(tpy-py)$_2$]$^{3+}$ (c) and in water.

Emission spectroscopy of [Ir-(tpy-py)$_2$]$^{3+}$ is shown in Figure 6.6. After exciting the complex at 435 nm the spectrum shows two maxima one intense feature at 430 nm and another weaker feature at 785 nm. The intense visible band may attributed to ($^3\pi_{py}$-$\pi^*_{py}$) of the pyrene unit and band at 785 nm we attribute to $^3$ILCT ($\pi_{py}$-$\pi^*_{py}$) . The fluorescence spectra of the self-assembled [Ir-(CDRu)$_2$]$^{3+}$ in DMF is also shown in Figure 6.6. A significant reduction of fluorescence intensity of both the $^3$LC ($\pi_{py}$-$\pi^*_{py}$) and $^3$ILCT ($\pi_{py}$-$\pi^*_{py}$) of [Ir-(tpy-py)$_2$]$^{3+}$ was observed. The band at 620 nm is a typical $^3$MLCT polypyridine Ru complex emission. The luminescence decays will be discussed in detail in section 6.8.

The behaviour of the pyrene-substituted iridium compounds contrasts with the results of several recent investigation into pyrene appended [Ru(bpy)$_3$]$^{2+}$ or [Ru(phen)$_3$]$^{2+}$
In such cases the pyrene unit acts as a “store” of the excited state energy, with a triplet-triplet thermal equilibrium being established between the emissive \(^3\text{MLCT}\) excited state of the ruthenium centre, and the \(^3\pi - \pi^*\) state of the pyrene unit. This leads to large augmentations of the observed luminescence lifetime compared to the unsubstituted complexes, for example, up to 148 \(\mu\)s for tris-pyrenyl substituted [Ru(phen)\(_3\)]\(^{2+}\) derivative. That the iridium complex does not profit from a similar effect is apparently due to the more highly oxidizing nature of the IrN\(_6\)\(^{3+}\) core compared to RuN\(_6\)\(^{3+}\), allowing the former to participate in the ILCT.

![Figure 6.6. Luminescence emission spectra of 0.5 \(\times\) 10\(^{-5}\) M [Ir-(tpy-py)\(_2\)]\(^{3+}\), and [Ir-(CDRu)\(_2\)] in DMF; Excited (\(\lambda_{\text{exe}}\)) at 420 nm.](image)

To obtain a better understanding of the mechanism of quenching of iridium \(^3\text{ILCT}\) and \(^3\text{LC}\) excited states time-resolved emission were carried to monitor the emission
intensity and decays upon addition increasing aliquots of CDRu to [Ir-(tpy-py)$_2$]$^{+3}$. The titration results are shown in section 6.7.

6.5 Resonance Raman Spectroscopy:

This technique was employed to assign the origin of the new optical transition apparent in the electronic absorption spectra.

![Resonance Raman Spectroscopy of [Ir-Ru$_2$] in DMF (a), [Ir-(tpy-py)$_2$]$^{+3}$ (b) and [CDRu] (c) excited at 488 nm in DMF.](image)

**Figure 6.7.** Resonance Raman Spectroscopy of [Ir-Ru$_2$] in DMF (a), [Ir-(tpy-py)$_2$]$^{+3}$ (b) and [CDRu] (c) excited at 488 nm in DMF.

The excitation wavelength resonant with the absorbance under investigation leads to resonance enhancement by up to 7 orders of magnitude, which helps in identifying the new transitions. Figure 6.7 shows resonance raman spectra of CDRu, [Ir-(tpy-py)$_2$]$^{+3}$ and [Ir-(CDRu)$_2$] in DMF with the new optical transition observed at 485 nm in the electronic absorption spectroscopy of the inclusion complex [Ir-(tpy-py)$_2$]$^{+3}$. The spectrum of [CDRu] exhibits the typical signature of seven vibrations associated with the bipyridyl ligands as well as a Ru-N mode at 370 cm$^{-1}$, consistent with resonance of the Ru ($d\pi$-$\pi^*$) metal to ligand charge transfer. The spectrum of [Ir-(tpy-py)$_2$]$^{+3}$ exhibits terpy bands at 1618, 1600, 1515, 1483, 1389, 1373, 1352, 1302, 1237, 1051 cm$^{-1}$. The peaks at 865
and 656 cm$^{-1}$ are assigned to the solvent. Figure 6a shows that the inclusion complex $[\text{Ir-(tpy-py)}_2]^{3+}$ exhibits the same features of both complexes with a new enhanced feature apparent at 1029 cm$^{-1}$ which is not present in the spectra of the separate complexes. This new peak can be assigned to the included pyrene in the beta-cyclodextrin cavity. The bipyridyl features are shifted in comparison to that observed for that of CDRu.

6.6 Electrochemistry:

Figure 6.8a shows the cyclic voltammetry of $[\text{Ir-(tpy-py)}_2]^{3+}$. The CV displays one pyrene oxidation at 1.37 V and another metal-based reduction at -0.88 V vs Ag/AgCl. These values are previously reported for pyrene substituted terpyridine. Figure 6.8b shows the CV of $[\text{Ir-(CDRu)}_2]$, two new peaks, one 1.1 V and another one at -1.25 V vs Ag/Ag+, are apparent. These two new peaks are assigned to Ru-based oxidation and bipyridine reduction processes respectively by comparison with CDRu complex. The electrochemistry of tpy-py ligand has been reported before which displays a one-electron reduction process at -1.66 V in solution in DMF at room temperature. This value was found to be less negative than the reduction potentials of both terpyridine and pyrene (which have very similar values to one another), indicating that the pyrene-substituted terpyridine is much more readily reduced than either of two constituent components. The reduction was found to be one-electron process, they concluded that the pyrene and the terpyridine units don’t act independently, but rather that the electron enters a molecular orbital which centered over the whole molecule i.e., the LUMO in tpy-py has a considerably extended $\pi$-system compared to the two components.

The complex shows a single, quasi-reversible, oxidation process at +1.36 in acetonitrile. This is in contrast to bis-terpridyl iridium complexes such as $[\text{Ir(tpy)}_2]^{3+}$, which show no oxidation process within the solvent window, supporting the notion that it is the pyrene unit which is the site of oxidation, and hence the origin of the ICT process.
Figure 6.8. Electrochemistry of $[\text{Ir-}(\text{tpy-py})_2]^{3+}$ (a) and $[\text{Ir-}(\text{CDRu})_2]$ (b) in Nitrogen-purged acetonitrile with 0.1 M TBABF4 on a platinum electrode vs. Ag/Ag+.
6.7 Titration of $[\text{Ir-}(t\text{py-}p\text{y})_2]^{3+}$ with $\text{CDRu}$:

6.7.1 Electronic Spectroscopy:

The addition of $\text{CDRu}$ to $[\text{Ir-}(t\text{py-}p\text{y})_2]^{3+}$ was followed using UV-Vis spectroscopy Figure 6.9. In the difference absorption spectra, Figure 6.10, a new absorption band, not observed in $\text{CDRu}$ or iridium ions alone, developed at 485 nm, which indicates some kind of electronic communication between Iridium and Ru in the novel system $[\text{Ir}-(\text{CDRu})_2]$.

![Figure 6.9](image)

**Figure 6.9.** The change in UV-Vis absorption spectra of $1.4 \times 10^{-5} \text{M} \ [\text{Ir-}(t\text{py-}p\text{y})_2]^{3+}$ with increasing aliquots of $1.4 \times 10^{-3} \text{M} \text{[CDRu]}$ in water.
The spectra were generated by subtracting the spectra of the separate solutions from the experimental spectrum of the mixture. The process was carried out as a function of increasing concentration of CDRu.

Figure 6.10. Difference absorption spectra of titration of $1.4 \times 10^{-5}$M [Ir-(tpy-py)$_2$]$^{3+}$ with increasing aliquots of $(1.4 \times 10^{-3}$ M) [CDRu] in water.
6.7.2 Luminescence Spectroscopy:

To explore the nature of communication between [Ir-(tpy-py)$_2$]$^{3+}$ and CDRu flourimetric titration was carried out. The addition of increasing concentrations of CDRu to [Ir-(tpy-py)$_2$]$^{3+}$ resulted in significant quenching of the excited state of this complex as shown in Figure 6.11. The luminescence intensity of the two maxima was significantly decreased with increasing CDRu concentrations. The concentration of [Ir-(tpy-py)$_2$]$^{3+}$ is kept constant in all experiments to avoid self quenching and the effects of aggregation on the emission intensity of iridium-pyrene conjugates. The pyrene emission has been corrected for CDRu contribution to absorbance. The trimer was excited at 435 nm to assure the excitation of most of the iridium although it is impossible to completely avoid a simultaneous direct excitation of the ruthenium excited state as the absorption spectrum of the iridium component strongly overlaps with the ruthenium-based component.

No distortion to pyrene emission spectrum as its quenched which confirms the non-radiative energy transfer, change in lifetimes *vide infra* also confirms this.

The lifetimes of [Ir-(tpy-py)$_2$]$^{3+}$ obtained by time-correlated single photoncounting (TCSPC) with increasing CDRu concentrations are shown in Figure 6.12. for [Ir-(tpy-py)$_2$]$^{3+}$ a biexponential decay was observed with lifetimes of $\sim 170 \pm 10$ ns and $83 \pm 5$ $\mu$s. In the presence of increasing aliquots of CDRu triexponential decay was observed with lifetimes of $\tau_1 = 365 \pm 20$ ns, $\tau_2 = 147 \pm 16$ ns, and $\tau_3 = 53 \pm 7$ ns. Flash photolysis experiments were followed to confirm these results *vide infra*. 
Figure 6.11. Fluorescence intensity titration of $[\text{Ir-(tpy-py)}_2]^{*3}$ (1.4 x 10^{-5}M) with increasing aliquots of [CDRu] (1.4x10^{-3} M) in water excited at 435 nm.
6.8 Concentration quenching of [Ir-(tpy-py)$_2$]$^{3+}$:

Before going any further in discussing the mechanism of quenching we investigated the effect of increasing of [Ir-(tpy-py)$_2$]$^{3+}$ on its emission intensity to take this effect into consideration. Figure 6.13 shows the effect of increasing concentration of [Ir-(tpy-py)$_2$]$^{3+}$ on its luminescence behaviour in water. The two emission bands were quenched upon increasing the concentration of the complex. These results can be explained on the basis of pyrene–pyrene aggregation.$^{22}$ The high quantum yield of fluorescence of pyrene

Figure 6.12. Time-resolved emission decays of [Ir-(tpy-py)$_2$]$^{3+}$ (1.4X10$^{-5}$ M) with increasing aliquots [0 μl → 550 μl] of (1.4X10$^{-3}$) CDRu, excited at 435 nm in deoxygenated with water; monitored at 400 nm.
tends to drop in going from non-polar to polar solvents. This decrease was attributed to a large extent to aggregation, which causes interaction between $n$-systems in the ground state and excited states.\textsuperscript{23}

When an electronically excited pyrene encounters a second pyrene in the ground state, an excimer forms. The pyrene excimers formation can be either static or dynamic.\textsuperscript{24} The growth of emission intensity of the excimer under normal conditions indicates the formation of dynamic, but not for the static.

\textbf{Figure 6.13.} The changes of luminescence spectra of [Ir-(tpy-py)$_2$]$^{3+}$ with increasing concentration in water excited at 435 nm. The asterisk assigns the raman line of water.
The titration of pyrene with CDRu was carried out to investigate pyrene/CDRu interaction. This was conducted at concentration at which little excimer formation is expected and generally easier to add Ru to Ir due to concentration effect on excimer formation.

![Graph showing changes in luminescence spectra of pyrene upon increasing concentration of CDRu in water.](image)

**Figure 6.14.** The changes in luminescence spectra of pyrene $0.4 \times 10^{-5}$M upon increasing concentration of CDRu in water ($1 \times 10^{-5}$ M).

The results of titration are shown in Figure 6.14. Reported studies on the pyrene/β-CD interaction have used the ratio of intensities of the first to the third vibronic bands of the pyrene fluorescence to follow the degree of complexation. This ratio is a diagnostic tool
of the environment around pyrene and is more reliable parameter than the overall fluorescence intensity.\textsuperscript{25} We monitored the emission of the pyrene at 465 nm with increasing CDRu concentrations. Quenching of the pyrene-based emission was observed. These results can be explained on the basis that energy transfer occurs from the $^3$LC ($\pi_{py}-\pi_{py}^*$) to the $^3$MLCT of Ru upon inclusion of pyrene in the cyclodextrin cavity.

To obtain better understanding about what type of complex formed between CDRu and pyrene, Stren-Volmer plot was used. Stern-Volmer plot of the luminescence intensity shows pronounced positive deviations from linearity without reaching a plateau at high CDRu concentrations as shown in Figure 6.15.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{stern-volmer.png}
\caption{Stern-Volmer plots $I_0/I$ vs quencher concentration $0.4 \times 10^{-5}$ M of pyrene in DMF solution with addition of 2050 $\mu l$ of $1.0 \times 10^{-3}$ M of CDRu in aliquots.}
\end{figure}
This situation can be explained on the basis that both static and dynamic quenching occurs. The association constant couldn’t be calculated from the data obtained here due to the non-linearity of Stern-Volmer plot.

6.9 Lifetimes measurements:

We carried out the lifetime measurements using flash photolysis in addition to the single photon counting technique. Figure 6.16 shows the lifetime decays of \([\text{Ir-}-(\text{tpy-py})_2]^{3+}\) after addition of CDRu measured by flash photolysis experiments. The results of the decay fitting are collected in Table 6.1.

To monitor the luminescence of the iridium guest, an excess of the ruthenium complex was used to ensure most cyclodextrin cups were filled. Monitoring the iridium luminescence lifetime at 785 nm, after 355 nm excitation, showed the presence of short and long-lived components. The magnitude of each is shown in Table 6.1 and depends on the concentration of the pyrene. The short component exhibited a lifetime of 35 ns and the long components, 1.2 μs and 788 ns, were observed. The amplitude of the short-lived species increases with increasing the CDRu concentration. The amplitude of the long-lived component doesn’t change while the other components show a bit of change within experimental error. Although the relative percentage contribution of each component to the decay doesn’t change.

To assign each component of the decay complex we attempted using the CCD detector with laser flash photolysis to monitor the decays at each individual component wavelength, as the CCD allows for complete spectral acquisition with a 300 nm window. We monitored the emission of ruthenium center at 600 nm and iridium center at 800 nm. We detected a 708 ns decay from the ruthenium decay and 1.41 μs from the iridium decay. The reported values of the lifetimes of pyrene-CD inclusion complex in water are about 130 ns.²⁶
Figure 6.16. Emission spectra and decays of [Ir-(CDRu)$_2$] in nitrogen-purged water excited at 355nm using Nd: YAG laser excitation source and CCD detector see experimental section.

In that report the decay data with β-CD was found to be double exponential decay. One of the lifetimes was always very near the 130 ns of the pure pyrene, while the other was substantially longer (~300 ns). They explained this on the basis that the lifetime $\tau$ of 1:1 (Py: CD) complex is similar to the free pyrene, around 130 ns, and the long lived 300 ns component arises from the 1:2 species of Pyrene:(γ-CD)$_2$. The lifetimes values we
obtained are close to these values; two lifetimes of pyrene were obtained, Table 6.1, \( \tau_1 = 106 \text{ ns} \) and \( \tau_2 = 387 \text{ ns} \). On the basis of the reported

Table 6.1. Emission lifetimes of \([\text{Ir-(CDRu)}_2]\) in deaerated water excited at 355 nm and detected at 400 nm, 600 nm, and 800 nm respectively.

<table>
<thead>
<tr>
<th>[CDRu]</th>
<th>Py decay Detected at ( \lambda = 400 \text{ nm} )</th>
<th>Ru decay Detected at ( \lambda = 600 \text{ nm} )</th>
<th>Ir decay Detected at ( \lambda = 800 \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_1 ) (ns) % ( \tau_2 ) (ns) %</td>
<td>( \tau_1 ) (ns) % ( \tau_2 ) (ns) %</td>
<td>( \tau_1 ) (ns) % ( \tau_2 ) (ns) %</td>
</tr>
<tr>
<td>0 M</td>
<td>35.4 35 171 65</td>
<td>160 75 1150 25</td>
<td></td>
</tr>
<tr>
<td>2 \times 10^{-5} M</td>
<td>53.9 44 203 56</td>
<td>153 19.6 766 80.4</td>
<td>121 2.5 774 97.5</td>
</tr>
<tr>
<td>4 \times 10^{-5} M</td>
<td>106 81 387 19</td>
<td>127 15 708 85</td>
<td>593 85 1.41 14.5</td>
</tr>
</tbody>
</table>

results \( \tau_1 \) corresponds to Py:CD complex and \( \tau_2 \) corresponds to free pyrene. In our case we don’t expect to have 1:2 species, the 1:1 is the only complex expected, Scheme 6.1. Comparing the lifetimes of the inclusion complex \([\text{Ir-(CDRu)}_2]\) with the reported results we may be able to assign the 127 ns to the \(^3\text{ILCT}\) of the CD:PY species and 1.41 \( \mu \text{s} \) to \(^3\text{MLCT}\) of \( \text{Ru} \) the luminescence lifetime.

Figure 6.17. Ru –Pyrene dyad.\(^{16}\)
The interesting result is the extension of the luminescence lifetime of Ru from around 0.200 μs to 1.41 μs. Similar result was previously reported Ford and Rodgers who observed reversible triplet energy state between a [Ru(bpy)]^2+ subunit and pyrene linked to the metal complex via along hydrocarbon chain, Figure 6.17. In bichromophoric dyads where the spacer is not rigid, clearly segmental diffusion within the molecule can bring the D-A pair into molecular arrangements in which electron-exchange interactions can occur.

In most of reported dyads T-T energy transfer was efficient. As expected from thermodynamic considerations, and demonstrated in the case of intermolecular T-T processes in fluids, reversible T-T energy transfer becomes possible when the energy levels of the D and A triplet states are close (within a few kcal mol^-1) if the intrinsic τ_1 lifetimes are sufficient to sustain the excited-state population.

In this assembly the two triplet states are localized on both terminals of the dyads. The equilibrium between the two triplet states, the metal and the pyrene, results in an extension of the luminescence of the lifetime of the metal complex from the ca. 1 μs to 11.2 μs in degassed solution at room temperature. On the basis of the above results we attribute to the quenching of the luminescence in the [Ir-(CDRu)] to the energy between the two triplet states of pyrene appended typyridine and the ruthenium center.

To obtain structural information about our supramolecular assembly, we can use the extent of energy transfer between the donor and the acceptor to calculate the distance between the pyrene and the Ru centre using equation 6.1:

\[ R_0 = 9.78 \times 10^3 [κ^2 η^{-4} Q_D J(λ)]^{1/6} \]  

Equation 6.1

Where Q_D is the donor quantum yield in the absence of the acceptor which is around 0.65 M^-1 cm^-1; η is the refractive index of the medium which is assumed to be 1.4 for dyads in aqueous solution; J(λ) is the overlap integral expresses the degree of spectral overlap between the donor emission and the acceptor; κ^2 is a factor that describing the relative orientation in space of the transition dipoles of the donor and acceptor and is usually assumed to be equal to 2/3, which is appropriate for dynamic random averaging of the donor and acceptor; the wavelength is expressed in cm.
Figure 6.18. The integral overlap between the emission spectrum of $[[\text{Ir-}(\text{tpy-py})_2]^{+3}$ (donor) and the absorption spectrum of CDRu (acceptor).

On the basis of the overlap between the pyrene emission and the absorption of CDRu and after the emission spectrum was normalized to unity the $J(\lambda)$ was estimated to be $6.23 \times 10^{-14} \text{M}^{-1} \text{cm}^3$. The value of $R_o$ was estimated to be $\sim 43 \text{ Å}$.

In Fluorescence resonance in energy transfer (FRET) the donor molecules emit at a shorter wavelengths, which overlap with the absorption spectrum of the acceptor. The overlap of the pyrene based emission in $[[\text{Ir-}(\text{tpy-py})_2]^{+3}$ with CDRu emission is shown Figure 6.18. The distance at which RET is 50% efficient, called the Förster distance, is
typically in the range of 20-60 Å. On the basis of our calculation we propose that the donor and the acceptor in our system are within the Förster distance. Therefore, the energy transfer is reliable. To obtain better information about the extent of energy transfer one should calculate the transfer efficiency. The efficiency of energy transfer (E) is the fraction of photons absorbed by the donor that are transferred to the acceptor. The transfer energy is typically measured using fluorescence intensity of the donor, in the absence ($\Phi_D$) and in the presence ($\Phi_{DA}$) of the acceptor according to Equation 6.2:

$$E = 1 - \frac{\Phi_{DA}}{\Phi_D}$$  \hspace{1cm} \text{Equation 6.2}$$

And can also be calculated from the lifetimes according to Equation 6.3:

$$E = 1 - \frac{\tau_{DA}}{\tau_D}$$  \hspace{1cm} \text{Equation 6.3}$$

On the basis of the lifetimes obtained we calculated the transfer efficiency to be 0.67 which indicates an efficient energy transfer from pyrene to Ru centre.
Conclusions

In this chapter we have examined photoinduced transfer process between Ru and Ir metal centers in water mediated by non-covalent interactions through a cyclodextrin cavity. On the basis of the inclusion ability of β-CD and the redox properties of pyrene we have studied Ru-Ir interaction in trimer [Ir-(RuCD)$_2$] in aqueous solution. The ruthenium "wheel" cyclodextrin system in [Ir-(RuCD)$_2$] would allow vectorial control of energy transfer between the two metal centers in aqueous solutions. Formation of the Ru-Py-Ir trimer through cyclodextrins induces significant changes in the photophysical behavior of both pyrene and appended Ruthenium. We couldn’t detect a significant change in the photophysical of Iridium metal centre. This means that communication between the two metal centers is very weak. This behavior may be attributed to the presence of pyrene moiety which blocks the interaction between the two metal centers. In [Ir-(RuCD)$_2$] pyrene acts as a store for the energy instead of mediating the transfer process. Future work on these complexes will include further studies on the nature of the electron transfer process. This will include, for example, more detailed transient absorption spectroscopy to discern the direction of transfer either Ir→Ru or Py→Ru or both.
4.5 References:


17 Mrs Reena Marthi – PhD transfer report, school of chemical sciences, Dublin City University.


Conclusion and future perspectives

Cyclodextrins are attractive molecular receptors for building supramolecular assemblies. They are versatile molecules; they are natural, water-soluble cyclic oligosaccharides with rigid, bucket shaped hydrophobic cavities for inclusion of small molecules and they can be selectively functionalized on both rims. We have exploited the properties of cyclodextrins with the photophysical properties of ruthenium, osmium and iridium complexes to design photoactive active cyclodextrins. In this thesis the first complex we have made comprised of [Ru(bpy)$_2$aphen]$^{2+}$ covalently linked to the primary rim of β-cyclodextrin. The detailed synthesis and characterization of the complex was shown in chapter three. Purity of the complexes was confirmed by elemental analysis, mass-spec and HPLC. The complexes were characterized using IR, Raman and Resonance Raman spectroscopy, $^1$H-NMR and COSY spectroscopy, magnetic moments, electronic spectroscopy, and electrochemistry.

We have conducted detailed photophysical studies on the luminescent host [Ru(bpy)$_2$(phen-CD)]$^{2+}$. The complex exhibits a strong pH dependent luminescence, which is attributed to protonation/deprotonation of the secondary amine bridge linking the CD and ruthenium polypyridyl centre. From emission studies, the $pK_a$ for the amine was determined to be 11.5. [Ru(bpy)$_2$(phen-CD)]$^{2+}$ forms host guest complexes with AQ and AQC, with association constants of 4,920 ± 560 M$^{-1}$ and 14,657 ± 2,200 M$^{-1}$, respectively. The anthraquinone guest appears to participate in efficient photoinduced electron transfer from the excited ruthenium polypyridyl centre. The rate of electron transfer was estimated to be $2.4 \times 10^8$ s$^{-1}$ for the AQ inclusion complex and $1.9 \times 10^8$ s$^{-1}$ for AQC. In the absence of quencher, the lifetime conformed to a single exponential decay with $\tau_0$ of 56 ns. Addition of quencher, either AQ or AQC, results in a biexponential decay, the first component, $\tau_1$, is essentially unchanged from that of [Ru(bpy)$_2$(phen-CD)]$^{2+}$. The second component is short lived with a lifetime of 4.20 ns for AQ and 3.62 ns for AQC.

In chapter four a novel supramolecular donor acceptor system incorporating a ruthenium polypyridyl functionalized β-cyclodextrin moiety with an hydroxo-bridged Cu(II) dimer is described. IR and magnetochemistry confirm that the structure of hydroxo-bridged Cu(II) dimer is conserved from the parent Cu$_2$CD complex. Efficient photoinduced electron transfer from the copper centre to the pendant ruthenium polypyridyl centre is
evident, with a rate constant of $1.86 \times 10^6 \text{ s}^{-1}$. The electron transfer process from transient absorption spectroscopy is attributed to a photooxidation of the excited ruthenium center by the copper dimer and this mechanism is consistent with thermodynamic predictions. The luminescence intensity of the ruthenium appended CD is correspondingly statically quenched on exposure to aqueous Cu (CH$_3$COOH)$_2$. This works suggests that luminescently labeled CDs may have value in metal sensing provided the luminophore is sufficiently long lived. The synthetic versatility of the ruthenium polypyridyl unit may mean that in the future the redox properties of this centre can be modified to tune selectivity for different metal ion.

In chapter five we have synthesized and characterized two novel dimeric [Ru$_2$-$\gamma$-CD ] $^{4+}$ and [Os$_2$-$\gamma$-CD ] $^{4+}$ complexes. These complexes were non-covalently linked to form [Os$_2$-C$_{60}$-Os$_2$]$^{8+}$, [Ru$_2$-C$_{60}$-Ru$_2$]$^{8+}$ and [Ru$_2$-C$_{60}$-Os$_2$]$^{8+}$ tetramers. Inclusion of C$_{60}$ in the $\gamma$-CD cavity was confirmed by elemental analysis, ES-MS, Raman and UV-Vis spectroscopy and cyclic voltammetry. Significant reduction in the lifetime and quantum yields of emission of the metal centers were noted in the presence of C$_{60}$ despite the fact that per molecule the number of emitting centres has doubled. This emission quenching has been attributed to an electron transfer process which, based on thermodynamic considerations, is thought to be from the excited metal to the included C$_{60}$. The rate of electron transfer was estimated to be $k_{et}$ [Ru$_2$-C$_{60}$-Ru$_2$]$^{8+}$ $= 1.1 \times 10^7 \text{ s}^{-1}$ and $k_{et}$ [Ru$_2$-C$_{60}$-Os$_2$]$^{8+}$ $= 1.3 \times 10^8 \text{ s}^{-1}$. No significant evidence was observed for energy transfer in [Os$_2$-C$_{60}$-Os$_2$]$^{8+}$. A work on these complexes is being carried out to form self assembled monolayers surface active derivatized cyclodextrin on a gold surface. [Os$_2$-$\gamma$-CD ] $^{4+}$, C$_{60}$, and surface active cyclodextrin are being used to form these monolayers.

In chapter six we have examined photoinduced transfer process between Ru and Ir metal centers in water mediated by non-covalent interactions through a cyclodextrin cavity. On the basis of the inclusion ability of $\beta$-CD and the redox properties of pyrene we have studied Ru-Ir interaction in trimer [Ir-(RuCD)$_2$] in aqueous solution. The ruthenium "wheel" cyclodextrin system in [Ir-(RuCD)$_2$] would allow vectorial control of energy transfer between the two metal centers in aqueous solutions. Formation of the Ru-Py-Ir trimer through cyclodextrins induces significant changes in the photophysical behavior of both pyrene and appended Ruthenium. We couldn't detect a significant change in the photophysical of Iridium metal centre. This means that communication between the two metal centers is very weak. This behavior may be attributed to the
presence of pyrene moiety which blocks the interaction between the two metal centers. In [Ir-(RuCD)₂] pyrene acts as a store for the energy instead of mediating the transfer process. Future work on these complexes will include further studies on the nature of the electron transfer process. This will include, for example, more detailed transient absorption spectroscopy to discern the direction of transfer either Ir→ Ru or Py→Ru or both.
Appendix 1

NMR, MS and FTIR Spectra

Figure 1. $^1H$ NMR spectra of 5-amino-1,10-phenanthroline (400 MHz, DMSO $d_6$).
Figure 2. $^1$H NMR spectra of Cis-Ru(bpy)$_2$Cl$_2$ (400 MHz, DMSO d$_6$).
Figure 3. $^1$H NMR spectra of $\gamma$-CD-(OTs)$_2$ (400 MHz, DMSO $d_6$).
Figure 4. $^1$H NMR spectra of β-CD-OTs (400 MHz, DMSO $d_6$).
Figure 5. ESI -MS of CDRu. The 1637.3 corresponds to m/z of [CDRu-PF₆]⁺⁻¹.
Figure 6. ESI-MS of γ-CD-(Aphen)₂.
Figure 7. ESI-MS of $\gamma$-CD-(OTs)$_2$. 
**Figure 8.** ESI-MS of CDRu. The peak at 878.8 corresponds to m/z of [M-2PF₆]⁺².
Figure 9. ESI-MS of Cu₂CDRu the peak at 2022 corresponds to [Cu₂CDRu+PF₆].
Figure 10. ESI-MS for $[\text{Ru}_2\gamma-\text{CD}]\text{Cl}_4$; the peak at 2735 corresponds to m/z of the $[\text{M-Cl}]^+$.
Figure 11. ESI-MS for [Ru2-γ-CD]Cl4; the peak at 878.3 corresponds to m/z of the [M-Ru(bpy)aphen-4Cl]2+. 
Figure 12. ESI-MS for $[\text{Ru}_2\gamma\text{-CD}]\text{Cl}_4$; the peak at 1054.2 corresponds to m/z of $[M-\text{Ru(bpy)}_2-4\text{Cl}]^{+2}$. 
Figure 13. ESI-MS for \([\text{Os}_2\gamma-\text{CD}]\text{Cl}_4\); the peak at 2994 corresponds to m/z of the \([\text{M-Cl}]^+\).
Figure 14. ESI-MS for \([\text{Os}_2\gamma-\text{CD}]\text{Cl}_4\); the peak at 1240 corresponds to m/z of \([M-\text{Os(bpy)}_2-4\text{Cl}]^{2-}\).
Figure 15. ESI-MS for $[\text{Os}_2\gamma-\text{CD}]\text{Cl}_4$; the peak at 989.2 corresponds to m/z of $[\text{M-Os(bpy)}_2\text{aphen-4Cl}]^{+2}$. 
Figure 16. IR spectra of CDRu in KBr disks.
Figure 17. IR spectra of Cu$_2$CDRu in KBr disks.
Figure 18. IR spectra of Cu$_2$Ru in KBr disks.
Figure 19. Difference ir spectra of CDRu - Cu₂CDRu.
Appendix 2

Publications