2005-01-01

Vibrational Coupling in Conjugated π Systems with a view to Optimization of Fluorescence Yield through Phonon Confinement

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Recommended Citation

Vibrational coupling in conjugated π systems with a view to optimization of fluorescence yield through phonon confinement

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ABSTRACT

A series of π conjugated systems were studied by absorption, photoluminescence and vibrational spectroscopy. As is common for these systems, a linear relationship between the positioning of the absorption and photoluminescence maxima plotted against inverse conjugation length is observed. The relationships are in good agreement with the simple particle in a box method, one of the earliest descriptions of the properties of one-dimensional organic molecules. In addition to the electronic transition energies, it was observed that the Stokes shift also exhibited a well-defined relationship with increasing conjugation length, implying a correlation between the electron-vibrational coupling and chain length. This correlation is further examined using Raman spectroscopy, whereby the integrated Raman scattering is seen to behave superlinearly with chain length. There is a clear indication that the vibrational activity and thus nonradiative decay processes are controllable through molecular structure. The correlations between the Stokes energies and the vibrational structure are also observed in a selection of PPV based polymers and a clear trend of increasing luminescence efficiency with decreasing vibrational activity and Stokes shift is observable. The implications of such structure property relationships in terms of materials design are discussed.

1. INTRODUCTION

Conjugated monomeric and polymeric materials have attracted significant attention over the past decades due to their potential applications in a range of technological areas. Organic dyes are well established in laser applications [1], organic molecules and polymers have long been vaunted as candidates for non-linear optical devices [2,3], and in the past decade, the observation of electro luminescence and stimulated emission from polymeric thin films has rejuvenated interest in this class of materials [4,5].

Low cost and ready processability of these materials are often cited advantages, but potentially the greatest bonus is that the optical and electronic properties can be chemically tuned over a broad range. In addition to the practical advantages, this tunability enables structure property relationships to be derived to aid material optimisation, as well as a fundamental understanding of the underlying physical processes in these materials.

To this end, systematic studies of oligomeric series have contributed greatly. Although they may break down in the infinite chain length limit of polymeric systems, simple models may be applied to such molecular series to demonstrate the effect of the π delocalisation on the optical band gap [6] and even the non-linear optical response [7]. However, while the energetics associated with the molecular electronic structures has received considerable attention, little has been paid to the vibrational coupling processes, which compete with radiative relaxation and ultimately limit luminescence efficiencies. Extended conjugated systems are well known for the correlation between electron and vibrational degrees of freedom [8] and this indicates that the vibrational relationships can be defined in terms of structural variations. Several studies have been undertaken to examine vibrational-structural relationships in oligomers, from both a theoretical and experimental view point [9, 10]. This study presents an investigation into the effect of oligomeric structure on easily measurable spectroscopic parameters examined through means of optical and vibrational spectroscopy, which will help to establish empirical relationships from which insight into design characteristics can be achieved. The study is aimed at developing a further understanding of the non-radiative decay processes in these materials, and their structural dependence.
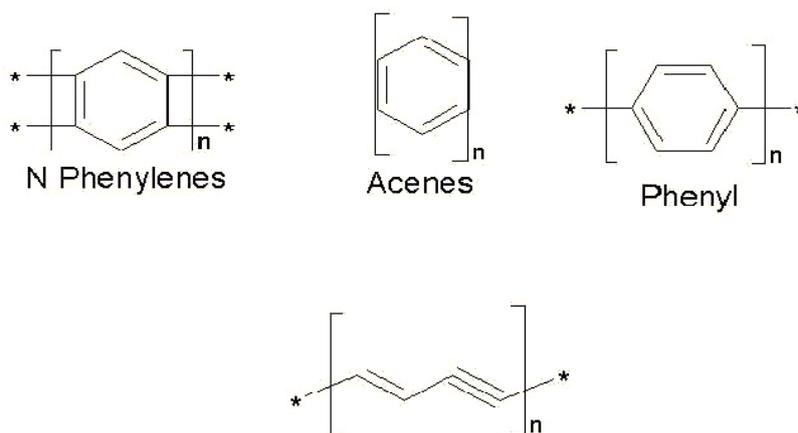
Figure 1. N-phenylenes, acene, phenyl and enyne oligomer structures.

The acene and phenyl oligomers, shown in figure 1, are used to provide insight into the effect of increasing conjugation length on the photophysical properties, particularly electron-vibrational coupling, of organic materials. Results are compared to those of other related oligomeric series where available from literature, particularly the N-phenylenes [11] and enyne oligomers [2] shown in figure 1. Optical absorption and photoluminescence spectroscopies are used to elucidate the electronic behaviour and Raman spectroscopy coupled with Stokes shift are used as a probe of the vibrational coupling.

2. EXPERIMENTAL

The acene and phenyl series were purchased commercially. The oligomers were prepared in a chloroform solution of molarity $\approx 10^{-5}$ for the absorption and luminescence spectroscopies. Self-absorption and aggregation effects were minimised with the use of low concentrations [12]. These solutions were sonicated for 15 min to aid solubilisation. The absorption spectroscopy was carried out using a Perkin Elmer Lambda 900 UV/VIS/NIR absorption spectrometer. The luminescence measurements were performed using a Perkin Elmer LS55 luminescence spectrometer. The other oligomeric data shown was taken from literature and is used in a mainly comparative nature.

Raman spectroscopy was performed using an Instruments SA Labram 1B confocal Raman imaging microscope system. A Helium-Neon (632.8nm/11mW) light source was used. The light is imaged to a diffraction-limited spot via the objective of an Olympus BX40 microscope. All experiments were carried out at room temperature (300K). For the Raman spectroscopy, the same oligomers were used but prepared as thin films of thickness ≈ 0.5mm by compression of the powder. A number of studies have shown that there is negligible difference between solution and solid state Raman spectra in similar systems, as they are dominated by the intramolecular vibrations of the polarisable π – conjugated backbone and intermolecular modes are low energy and at most weakly coupled to the electronic system [13-15]. A $\times 10$ objective was used, to maximise the focal depth and so sample the bulk of the film. The focal depth of the system was calculated to be 0.183mm, over 100 times greater than that achieved with a $\times 100$ objective. This and the large spot size ($\sim 10 \mu$m) helped to eliminate the effects of any slight variation in sample density. The conditions were identical for all samples, and spectral intensities were reproducible within 1%. The measurement does not enable the calculation of absolute Raman cross-sections but the reproducibility allows a semi-quantitative comparative study.

3. RESULTS

In figure 2a, the absorbance spectra of the phenyl series are shown for example. It is evident that with increased conjugation there is a considerable bathochromic shift, as predicted by Kuhn *et al* [16] Biphenyl has of an absorption

shoulder at 270nm, however by the time the series reaches a six-ringed structure (sexiphenyl) the longest wavelength absorption peak has shifted to 380nm. By addition of four phenyl monomer units the band–gap has reduced by 110nm (1.32eV). The vibronic substructure also becomes increasingly evident as the chain length is increased. The presence of vibronic sub-structure in the absorption spectra suggests a planar rigid molecular and there is a marked increase in the prominence of the vibronic structure as the oligomers go from the relatively flexible phenyl to the more rigid planar acene series [17].
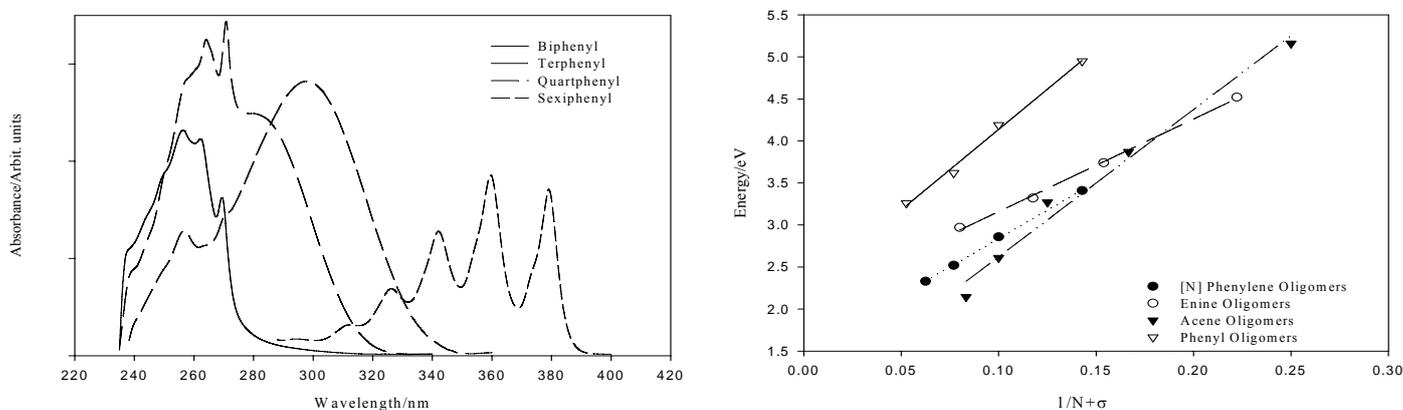

Figure 2a/2b. Position of maximum absorbance against $1/(N+\sigma)$ and Progression of Phenyl oligomers from 2 to 6 repeat units.

In the free electron model first described by Kuhn for carbocyanine dyes [18] and adapted by Rustagi and Ducuing [3], the dependence of the optical band gap on the conjugation length is given by

$$\Delta E = V_o + \left(\frac{h^2}{4mL_o^2} - \frac{V_o}{4}\right)\frac{1}{N+\sigma} \qquad \textbf{Equation 1.}$$

where h is Planck's constant and m is the electron mass, V_0 in the infinite chain length band-gap, m is the mass of the electron, L_0 is the average length of one conjugation and 2N is the number of electrons in the one dimensional box of length 2L, σ accounting for end-group terminations. This model predicts a systematic decrease in the band separation with increasing conjugation and has been shown to fit well with the observed behaviour of the length dependence of the absorption gap for enyne oligomers [2].

Figure 2b shows a plot of the energies of the first absorption maxima of the various oligomeric series plotted against inverse conjugation length. Along with the acene and phenyl series mentioned earlier, enyne [2], and [N] phenylene [11] oligomers are also presented. For all series, σ is taken to be zero, as they are terminated by a C-H unit, except the enyne series for which σ is taken to be 0.5, as they are terminated by a CH_3 group [2]. For the aromatic oligomers, N is taken to be the total number of double bonds in the molecule e.g. for Naphthalene N = 6, for bi-phenyl N = 7.

In all the oligomer series, the variation in both the absorption and emission band gap with increasing conjugation fits well to a simple nearly free electron model. Such well-defined behaviour is well established and is the basis for our understanding of linear conjugated systems [2, 19 -22]. It is clear however, that both the short chain limit and the rate of decrease with increasing chain limit differ significantly with monomeric structure and the degree of coupling between the monomeric units. The differences in the long chain limit of the phenyl versus the acenes series mirrors the differences in bandgaps of cis versus trans polyacetylene, [7] and zig-zag versus armchair single wall carbon nanotubes [23]. In extrapolation to the infinite chain limit questions have been raised as to the role of electron vibrational coupling. Polarons, bipolarons, self-trapped excitons have all been reported in polymeric systems and the debate continues over the chain length at which excited states are no longer distributed over the molecule continues [24,25]. That the oligomer series are well behaved according to this simple model indicates that excited states are distributed over the extent of the

oligomer and are thus molecular in nature. As well as introducing controversy over the nature of the excited species in these systems [26, 27], electron-vibrational coupling plays a dominant role in determining nonradiative processes. To optimise radiative relaxation in these systems, design principles to control the nonradiative relaxation of excited species are desirable.

A previous paper [ref] shows an intrinsic link between the Stokes shift and the molecular structure of the oligomer and furthermore this correlation was extended to encompass the vibrational activity of the molecule as measured by Raman spectroscopy. The variation of vibrational activity has been studied by many with differing degrees of systematicity in the method. Regardless of the structural make-up of the oligomers employed a power law relationship was always observed with the Raman intensity as a function increasing conjugation length. This shows that although the electronic properties of simple oligomeric series are well known to vary in a well-defined manner with conjugation, the vibrational activity and the Stokes shift can also be seen to be well-defined in terms of molecular/conjugation length. In figure 3a the spectrally integrated Raman intensities, in the range $100cm^{-1}$-$3500cm^{-1}$, are plotted as a function of the chain length N. All integrated Raman intensities were normalised for molecular weight so as to give a true reflection of the variation of the intensity with increasing molecular length. The graph yields an approximate power law relationship of order 2 for both the phenyl and acene systems. For the acene and phenyl series, a plot of the dominant vinyl stretch in the region of 1550-$1650cm^{-1}$ against N exhibits higher order dependence, approaching 4, as shown in figure 3(b). Theoretical studies, based on nodal analysis combined with ab initio calculations, predict an N^4 dependence of the Raman intensity for the C=C stretch of polyene systems [10]. A novel approach to the spectroscopic determination of non-linear optical properties of conjugated materials has demonstrated that Raman cross-sections can be utilised to determine the third order hyperpolarisability of centrosymmetric conjugated molecules [13] a parameter which has been shown to vary with an L^4 power dependence [38]. In previous studies, the dependence of the intensity of specific peaks of the Raman spectra of polyene oligomers has been seen to show a length dependence of the order $N^{2.7}$ [7]. This shows that the conjugated C=C stretch is the most strongly dependent on the conjugation length, and integrating over the entire Raman spectrum reduces the observed power law dependence. In either representation, the spectroscopic data is well behaved in terms of the structural variation indicating that the electron – vibrational coupling may be characterised through routine spectroscopic investigations.
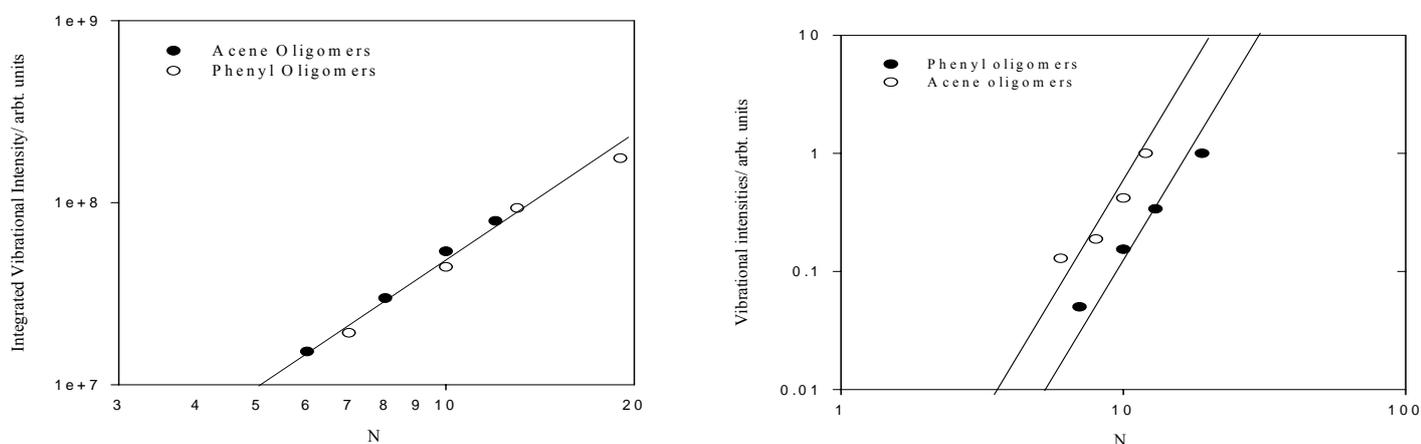

Figure 3a/3b. Integrated Raman intensity plotted against N. Figure (a) integrated from 100-$3200cm^{-1}$; figure (b) the relative intensities of the C=C vibrational modes along the backbone. The solid lines show slopes of 2(a) and 4(b).

Both the electronic and vibrational spectroscopic properties of the structurally well defined, commercially available oligomeric series are well defined indicating that simple structure property relationships can be derived for both radiative and nonradiative processes in these systems. In advance of extending the study to the structurally and morphologically more complex polymeric ststems, it is informative to consider more complex model structures.
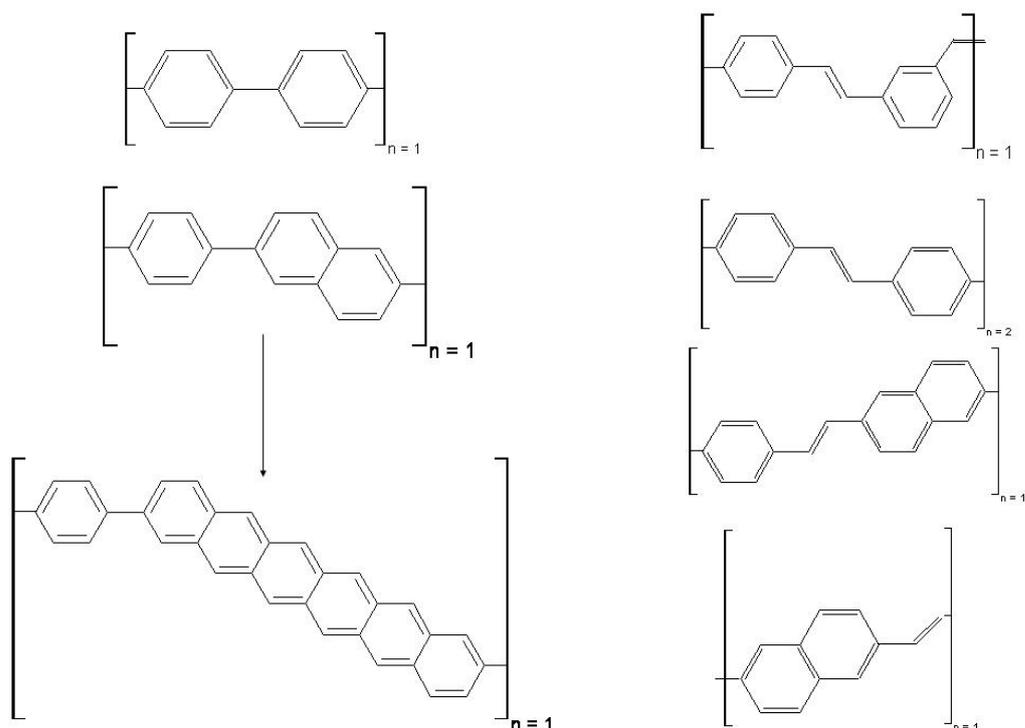
Figure 4 Structures of model oligomers (1MO→5MO), left, and synthesised polymers, right. The [ ] n=1 is not really right.

In figure 4a (what is a and b)the model oligomers are shown, these structures where chosen specifically to investigate the ability of bulkier substituents to restrict vibrational coupling, in short chain molecules, by essentially preventing coherent electron-phonon interaction along the π conjugated back-bone. The molecular structures, above, represent an intermediary between the novel polymers synthesised, figure 4b, and the simple well-defined oligomers shown earlier and can be used as a guide to the effect larger molecular substitutions have on the overall vibrational progression of the series. Having already developed a clear understanding of the well-defined progression of the vibrational coupling in the acene and phenyl series, the empirical relationships uncovered can then be applied to the modelled oligomers to see if this relationship holds true for oligomers where the progression is not from one monomer to two but the addition of a bulkier side group.

Problems in the synthesis of the entire molecular series shown above necessitated the use of a modelling package (HyperChem) as the most acceptable solution was to gain vibrational information. The disadvantages of not being able to physically study the oligomers are that the Raman spectrum was not available and thus the vibrational data obtained from the simulation program are restricted to IR active modes, which are not as sensitive to the changes along the back-bone as was seen using Raman spectroscopy. It has been documented that the Raman intensity shows a superlinear increase with increasing conjugation length, but the IR signal tends to show a much less dramatic change as the conjugation length is varied. However the overall trends observed in the IRir and Raman should be the same as both are measures of vibrational coupling albeit by differing means.

A semi-empirical quantum mechanical method approach was used to calculate the vibrational spectrum of the oligomers, which form the base of this study. The PM3 method, which incorporates a reparameterisation of the AM1

method, was chosen as it contains a larger database from which to approximate the required parameters and as such is deemed to be more accurate for organic molecules. The molecules were geometrically optimised using a Polak-Ribiere conjugate gradient. Configuration interaction (C.I.) of singly excited states was use to calculate the electronic transitions. The vibrational spectrum was calculated from the molecule in a non-excited state. Table 1 lists the wavenumbers of the dominant vibrational modes, ring breathing and the ring stretch respectively, in the spectrum with the accompanying vibrational intensities. In calculating the total intensity the IR spectra where integrated from $20cm^{-1}$ to $3500cm^{-1}$.

Name	Ring stretch λ/cm^{-1} (intensity/km/mol)	Ring breathing λ/cm^{-1} (intensity/km/mol)	Total intensity intensity/km/mol
Biphenyl	1558.03 *(13.97)*	758.61 *(60.99)*	**187.8**
Terphenyl	1561.53 *(27.74)*	771.96 *(71.24)*	275.84
Quaterphenyl	1563.14 *(44.12)*	777.08 *(75.81)*	365.41
Pentaphenyl	1564.2 *(62.18)*	778.49 *(76.49)*	456.41
Sexiphenyl	1564.75 *(81.32)*	778.74, *(76.87)* 850.87 *(84.79)*	548.24
Bezene	1547.41 *(4.00)*	711.51 *(43.35)*	98.36
Napthalene	1411.51 *(5.52)*	798 *(48.09)*	143.87
Anthracene	1400.88 *(7.51)*	757.49 *(38.35)*	189.45
Tetracene	1400.43 *(9.82)*	767.41 *(41.15)*	237.66
Pentacene	1401.92 *(13.10)*	761.61 *(38.59)*	288.75
Sexacene	1403.23 *(16.36)*	761.38 *(39.48)*	342.71
1MO	1507.53 *(6.36)*	783.31 *(48.2)*	233.10
2MO	1496.36 *(10.5)*	765.79 *(35.31)*	280.40
3MO	1484.81 *(7.97)*	777.35 *(38.1)*	330.10
4MO	1485.19 *(8.79)*	776.74 *(30.86)*	383.78
5MO	1401.20 *(9.486)*	775.75 *(33.66)*	436.17
6MO	1405.32 *(14.10)*	776.18 *(32.55)*	498.00

Table 1. Infra-red intensities for model oligomers and the acene and phenyl series.

With the information from the above table, a graph of both the dominant ring stretching mode and the total vibrational intensity of the system were plotted as a function N, with N being outlined earlier for figure 2. The IR data for the modelled molecules can be seen in figure 5. The total integrated IR intensity plotted as a function of N can be seen in figure 5b. It is apparent that as the conjugation length of the molecule is increased the IR intensity increases. However it

is a linear increase as the graph demonstrates careful – this is a log log graph. This dependence is significantly less that the power dependence observed in the aforementioned Raman study due to the fact that the IR mode's dependence with increasing conjugation length will be dominated by the ability of the ……………………………………………………………………………..ir dependence description Depends on dipole rather than polarisability

A more refined look at the modes at which the bonded carbons could couple to each other, i.e. the ring stretching modes, reveals a more complicated and less uniform behaviour being demonstrated between the various series examined (Figure 5a). The acene and phenyl series show behaviour which again is similar to that observed in Raman spectroscopy. Both show a power dependence of 1 and 2 for the acene and phenyl respectively. The phenyl is closer to the power relationship observed in the earlier Raman? vibrational work and match well with theoretical predictions [ref] but both the model and acene series show a variation for the expected intensity enhancements. As this plot is solely reliant on the ability of the coupling modes to contribute constructively to produce a peak intensity which is representative of the molecules as a whole it doesn't take into account softening of the vibrational spectrum which is a significantly observable factor in the acene series [29] and other acene derivatives. This spectral softening will broaden the vibrational band thus essentially smearing the intensity over a broader range of wavelengths, this phenomenon is present in the phenyl but not to such a degree. This accounts for the some of the variation for the power dependence seen in the phenyl but it would be extremely tenuous to suggests this is the only factor that contributes to the obvious structure-vibrational variation that are apparent the two series present that contain acene moieties.

The examination of the peak intensity for the ring stretching shows the effective coupling across the carbon-carbon single bond on both the phenyl and model oligomers and the effective coupling along the molecule as a whole when considering the fused ring nature of the acenes. As such it should be a better indication of the ability of the said molecule to communicate across the π conjugated backbone and hence allow empirical relationships to be drawn concerning the ability of the varying moieties to effectively vibrational couple to each other. The results show that as the number of monomer units is increased there is a well-defined relationship between the vibrational intensity of the ring stretching peak and the back-bone structure for both the acene and phenyl oligomers, which show a linear and power of 2 dependence respectively. However the model oligomers, which include phenyl moieties linked to an acene chain of increasing length, show on first inspection a further reduced vibrational intensity with an almost linear relationship, similar to the acenes. On closer inspection however, it can be seen that although there is an overall linear trend, the variation of the individual bands tend to be of amore complicated nature.When going from biphenyl to the MO1 (one phenyl replaced by naphthalene) there is a significant drop in the vibrational intensity, the addition of a further fused ring then shows an increase in the peak vibrational intensity. Compare Phenyl/acene oligomer with corresponding acene – MO1 is also less that naphthalene. After initial zigzag they increase according to the acene power dependence indicating that there is little e-phonon coupling with the Phenyl?
This behaviour can be explain due to change of the constructive/ destructive interference of the coupling vibrational modes as the molecule changes from two to three fused rings. With the further addition of more rings the alternated trend of large decrease then a small increase in intensity is continued but eventually reaches a plateau, leaving the overall trend of that of a decrease in the degree of coupling as the larger bulkier substitutions are added to disrupt the back-bone continuation.
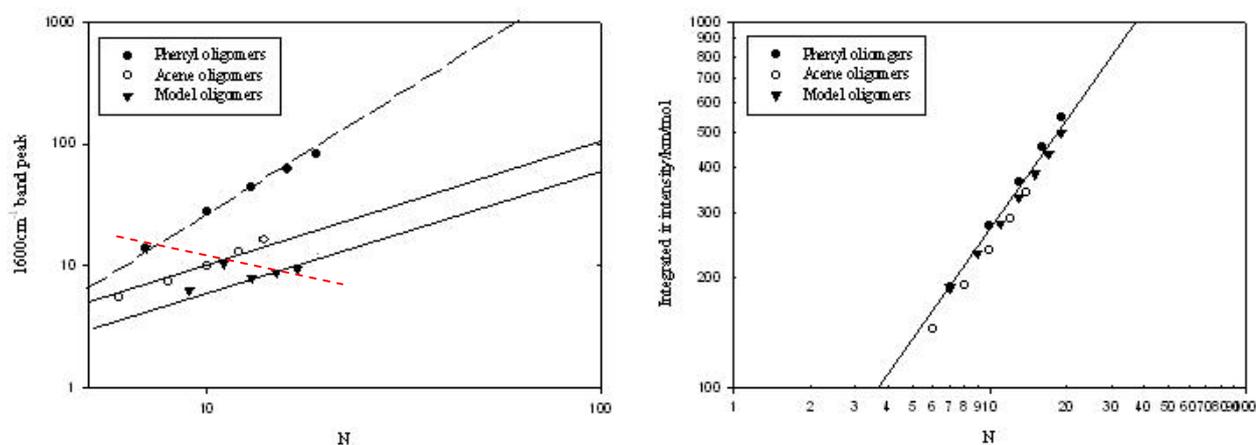Any reference for the zigzag?

Figure 5a/5b. Integrated IR intensity plotted against N. Figure (a) the relative intensities of the C=C vibrational modes along the backbone; figure (b) integrated from 100-3500cm^{-1}. The solid lines show slopes of 1 and the dotted line shows a slope of 2.

Can you draw the zig zag, but not in colour

Having modelled the intermediary oligomers and plotted them to establish if the empirical relationships elucidated during the Raman study were borne out in the theoretical IR spectral data. The well-defined relationship for the acene and phenyl oligomers between the structure and the vibrational properties hold true for the IR albeit with a reduction to a linear dependence for the total vibrational intensity and also a reduction to linear for the acene series when considering the ring stretching mode of vibration. When considering the model oligomers it is evident that as the molecular heavier and less electron donating substituent replaces the phenyl moiety that there is an overall reduction in the vibrational intensity of the co-operation in the ring stretching mode of vibration. This trend allows the conclusion that as the backbone is systematically disrupted it is possible to minimise the vibrational activity and hence in doing so reduce or tailor the non-radiative decay.

With these relationships established for both the phenyl and acene in both IR and Raman spectroscopy and the confirmation of the decrease in IR vibrational activity in the modelled oligomers the next stage was to synthesise novel polymer systems which incorporated the knowledge gained for the exploration of the well-defined oligomer systems. The polymers were synthesised by P. Lynch *et al*[ref] and can be seen in figure ??. The polymers were investigated using both florescence and uv/visible spectroscopy which again showed a well-defined progression in electronic structure as well as Stokes shift [ref]. The results shown below are of the Raman spectroscopic characterisation which will be discussed in terms of their structure property relationships to attempt to reconcile them with the already examined oligomers structures. The aim is to attempt to limit the non-radiative decay which finds an avenue to relinquish energy through electron-phonon coupling. As such the addition of molecular heavier substituents should allow the limitation of the co-operation coupling along the back-bone. This was shown to have a significant effect on the ring stretching intensity in the model oligomers and as the polymers also incorporate a vinylene bond it is of interest to see if the effect of limiting the vibrational coupling can be extended past the ring stretching modes and incorporated into an overall trend in the molecular structure which will act to optimise the yield.
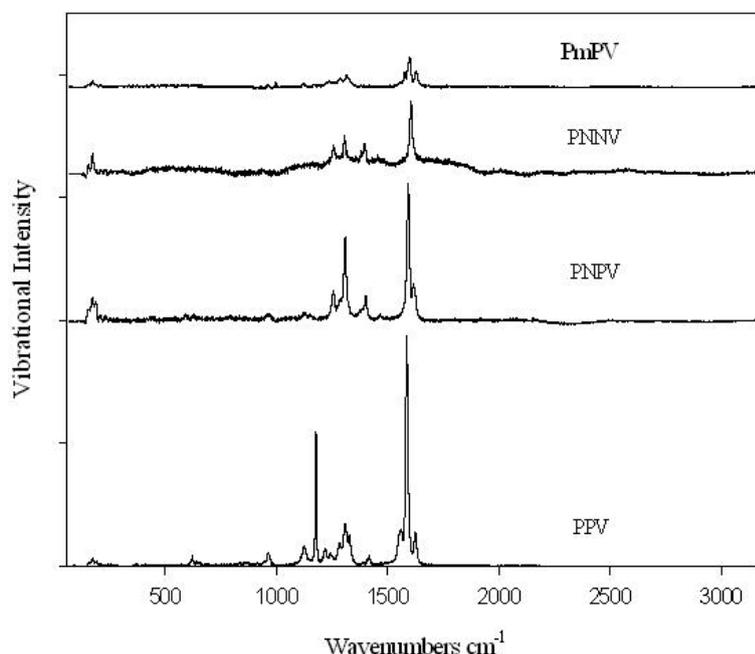
Figure 6. Polymer Raman spectra (offset for clarity)

Figure 6 is a graph of the Raman spectra of all the polymers studied. The 1600cm-1super vibrational modes which corresponds to the ring and also a C=C stretching along the conjugated backbone is increasing evident as the series goes from the PmPV, PNNV, PNPV and finally to the original material PPV Use same labels as paddy. The other characteristic peak observed occurs at 1100cm-1 to 1300cm-1. It can be clearly seen that as the conjugation is disrupted along the back-bone the Raman intensities peaks appear to decrease dramatically (you need to summarise the results of the UV/vis) .

LINK

In figure 7a the variation of the vibrational sum against Stokes shift is plotted. Here it is evident that there is again a power law relationship as was seen with the oligomers. In the previous study it was shown that well defined oligomers show an approximate power relationship (-0.5) between Stokes shift and vibrational activity. The polymers used here also show a well defined relationship which suggests that for a given polymeric series which has systematic changes in back-bone structure there is a well definable and systematic change in the electron-vibrational coupling mechanisms. The general trend here is the same as that observed for the oligomers. However the Stokes shift does not decease with the number of calculated modes available as in the case of the oligomers. This is due to the limitations on the available modes placed upon the system due to the poor electronic communication across the vinyl bond. The plot of the experimental modes shows a decrease in Stokes shift as the number of modes is increased which correlates well with the behaviour observed for the oligomers. This result also reinforces the assumption that the disruption on the conjugated backbone does indeed limit the modal access of the molecule. Since the Stokes shift in this case is determined by the electronic coupling, as is the Raman intensity, the overall result and trend mirror that of the oligomers (figure 7.8??). The power law dependence for the polymers was calculated to be –2 as opposed to the -0.5 relationship observed for the oligomers.
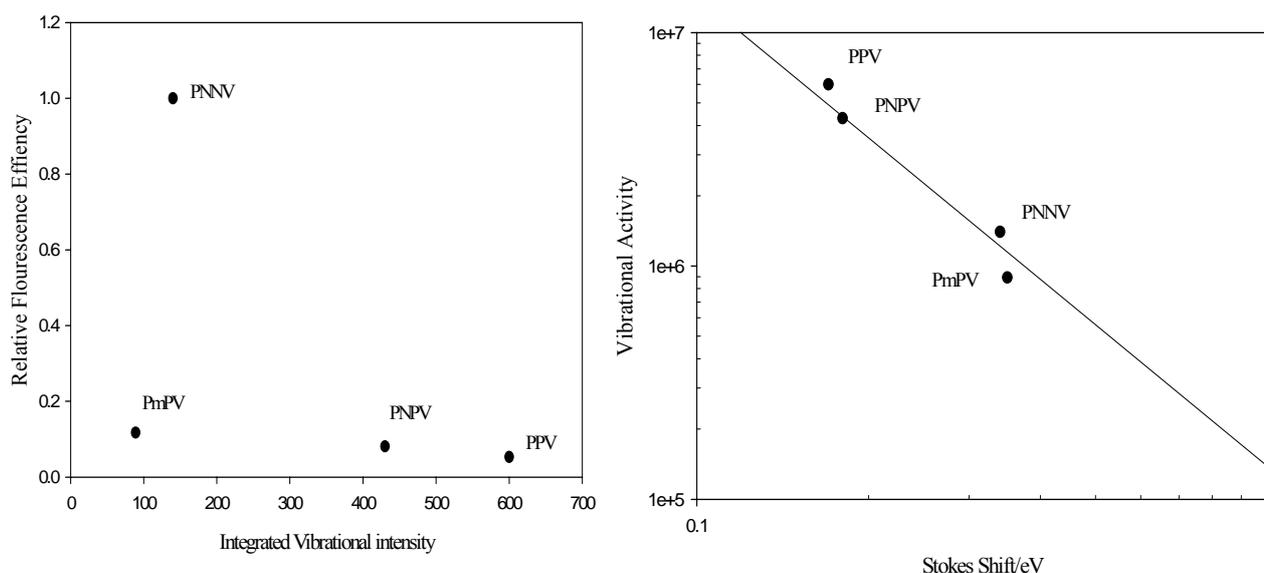
Figure 7. Figure captions – switch figures around

Figure 7b shows the variation of the fluorescence yield with vibrational intensity again a clear relationship can be seen which fits well with the predicts of the model oligomers suggested earlier. The electron-phonon coupling along the backbone is reduced due to the introduction of the napthyl units along the backbone. The napthyl units do not contribute as much as the phenyl to a strong conjugation along the length of the backbone thus effectively limiting the amount of vibrational coupling along the entirety of the backbone structure. The fluorescence yield shows a clear trend of increasing efficiency as the napthyl units are added. The PmPV is shown to have a higher yield than its sister PPV due to the meta linkage not being fully conjugated but still has a significantly low yield in comparison to the PNPV and PNNV, this is due to the fact that its conjugation is disrupted. It is still essentially the same as the PPV apart from the one meta linkage and as such an increase in fluorescence is expected but not in the same league as with the napthyl substituted polymers.

Elaborate

4. CONCLUSION

The study of the acene and phenyl oligomer series confirms the structural dependence of the electronic properties of π conjugated materials. It furthermore demonstrates that the electron vibrational coupling are similarly well behaved with backbone structure. Both the Stokes shift and the integrate Raman intensity are shown to be well-correlated measures of the electron vibrational coupling in the oligomer series and in the selection of polymers employed. Furthermore, it is demonstrated that these parameters can be employed as indicators of the efficiency of the nonradiative processes and can be readily employed as the foundation for structure property relationships for the optimization of radiative processes. The model oligomer series demonstrate that…. between acene units and phenyl units is weak and the introduction of such units into the backbone disruptselectron phonon coupling. This is cinfirmed in the polymeric series. The study should, of course be extended by expanding the polymer series, and synthesis of the anthracene, anthracene-phenyl, and anthracene – naphthalene equivalents are currently underway. Furthermore, the structural dependence of other competing processes such as intersystem crossing remains to be elucidated. This study does however show that control over the vibrational as well as the electronic properties is warranted and further highlights the importance of systematic studies based on well-defined materials such as oligomers.

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