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Structure Property Relationships in Conjugated Organic Systems

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Abstract

A series of π conjugated oligomers were studied by absorption and photoluminescence 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], and more recently, the observation of electro luminescence and stimulated emission from polymeric thin films have rejuvenated interest in this class of materials [2]. 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 of the optical band gap and even the non-linear optical response [3]. However, while the energetics associated with the molecular electronic structures have received considerable attention, little has been paid to the vibrational coupling processes, which compete with radiative relaxation and ultimately limit luminescence efficiencies. Limited studies have been undertaken to examine vibrational relationships in oligomers [4]. This study presents a practical investigation into the effect of the structure on the optical properties of the oligomers examined by means of vibrational spectroscopy. The aim of this paper is to provide insight into the effect increasing conjugation length has on the photophysical properties, particularly electron-vibrational coupling, of acene and phenyl oligomers. Structure property relationships derived are applied to a selection of PPV based polymers (figure 1).

2. Experimental

The acene and phenyl series were purchased commercially and were already purified. For the acenes, benzene to pentacene were measured, whereas for the phenyl series, biphenyl to sexi-phenyl were measured. The polymers poly (2,5-dioctyloxy) 1,4 phenylenevinylene (PPV), poly (2,5-dioctyloxy) 1,4-phenylenevinylene-co-(1,5-dioctyloxy) 2,6-naphthylenevinylene (PNPV), and poly (1,5-dioctyloxy) 2,6-naphthylenevinylene (PNNV)

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were synthesized by condensation of the dialdehyde and diphosphonate ester species in DMF at 80ºC [5].

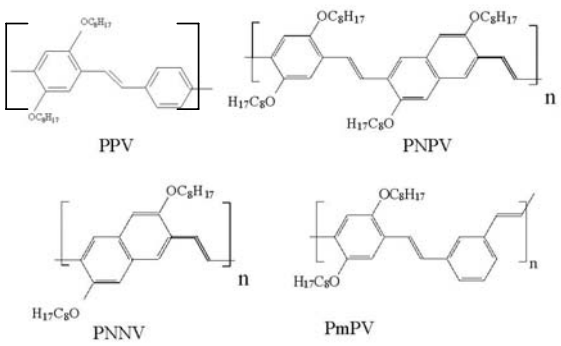

Figure 1. Variations on the PPV structure synthesized for the polymer investigated

Absorption and emission measurements were made in chloroform solution, prepared to a molarity ≈ 10^{-5}. 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. Spectra were corrected in both excitation and emission.

Raman spectroscopy was performed using an Instruments SA Labram 1B confocal Raman imaging microscope system. A Helium-Neon (632.8 nm/11mW) light source was used. The light is imaged to a diffraction limited spot (typically 1μm) via the objective of an Olympus BX40 microscope. All experiments were carried out at room temperature (300K). For the Raman spectroscopy, both the oligomers and polymers were prepared as thin films of thickness ≈ 5mm by compression of the powder.

3. Results and Discussion

For both the phenyl and acene series a linear dependence of the optical absorption (and emission) energies on inverse conjugation length was observed. This is consistent with the documented behaviour of enine oligomers [6], and fits well with the nearly free electron particle in a box model developed for carbocyanine dyes by Kuhn [7]. Notably, as shown in figure 2, the Stokes shift similarly shows a well-defined dependence on the conjugation length, defined in terms of the number of conjugated bonds N. This demonstrates a clear link between the backbone structure and the electron vibrational coupling. The N^4 power law dependence can also be explained by a simple particle in a box model [8]. The electron vibrational coupling can be further probed using Raman spectroscopy. For all oligomers, the Raman spectrum was integrated and the integral was normalised by the molecular weight to yield a value per molecule.

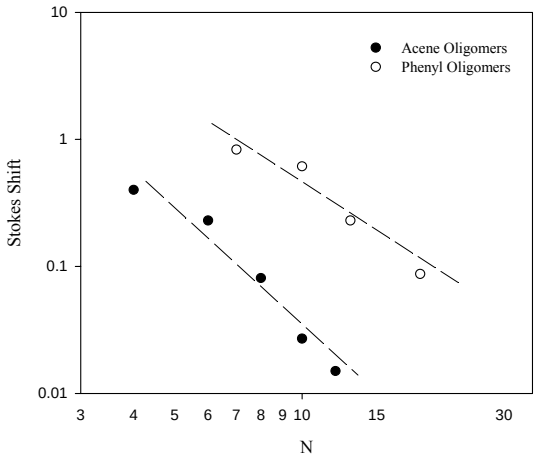

Figure 2. Correlation of Stokes shift and conjugation length for oligomers. Solid lines show a slope of –4.

Figure 2 demonstrates a clear correlation between this vibrational activity and the backbone structure. 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 $N^{2.7}$ [4]. 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 [9]. 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 [10], a parameter which has been shown to vary with an L^4 power dependence [11,12]. In figure 3 the spectrally integrated Raman intensities, in the range 100 cm^{-1}-3500 cm^{-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. This shows that with increasing chain length the vibrational intensity of the molecule increases with an $\sim N^2$ behaviour. For both the acene and phenyl series, a plot of the dominant vinyl stretch in the region of 1550-1650cm^{-1} exhibits a higher order dependence, approaching 4. 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.

It is notable that, in contrast to the behaviour for the Stokes shift, the integrated Raman intensity and the variation with conjugation are almost identical for the two

sets of oligomers. The Raman activity has primary origin in the localised normal modes of vibration, whereas the Stokes shift relies on the distribution of excess energy along the extent of conjugation of the molecule. Thus, the integrated Raman intensity is largely unaffected by the rotational freedom of each of the rings in the phenyl series, whereas this freedom significantly increases the Stokes shift.

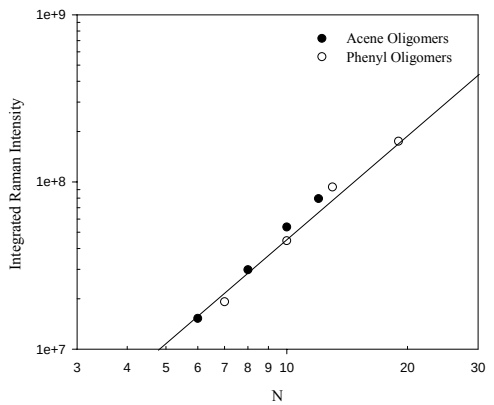

Figure 3. Plot of the normalised, integrated Raman intensity for the oligomers

Both the Stokes shift and normalised Raman activity are well behaved in terms of chain length for the oligomers, and therefore they can be related, as shown in figure 4. As well as the electronic properties, the vibrational properties and therefore electron vibrational coupling are well defined by the backbone structure. The electron vibrational coupling is a determining factor in the nonradiative processes in organic polymers and therefore structural control should lead to optimization of the efficiency of the radiative processes.

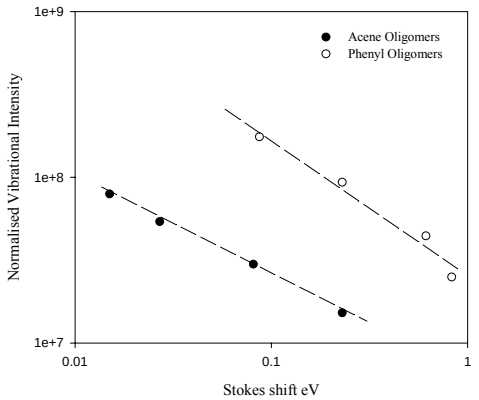

Figure 4. Plot of normalised vibrational intensity versus Stokes shift for the oligomers.

The polymer selection is a systematic variation of solubilised PPV. In PNPV alternating phenyl rings are replaced by the more rigid naphthalene unit, while in PNV the backbone is made up of vinyl coupled naphthylene units. The design principle is to systematically inhibit the electron vibrational coupling along the backbone, minimizing nonradiative relaxation. Through the systematic structural change it is anticipated that structure property relationships for the optimization of radiative efficiencies can be derived.

The change from a para linked phenyl in the PPV to a meta-linked phenyl in the PmPV significantly disrupts the conjugation along the polymer backbone with a concomitant blue shifting of both emission and absorption energies, as shown in figure 5. It can also be clearly seen that as the naphthyl (top) unit is replaced with a phenyl (second bottom) unit that the spectra show a bathochromatic shift. The naphthyl group also introduces a disruption in the conjugation due to its tendency to retain electrons [13]. Therefore the meta linkage provides the largest blue shift closely followed by the PNNV, PNPV and lastly the PPV. So in figure 5 it can be seen that the introduction of the heavier electrophilic napthyl units disrupts and hinders the formation of the conjugation along the back-bone and as such increase the energy of both emission and absorption. It is also noticeable that the meta linkage is far more efficient at breaking up the conjugation along the backbone than the naphthyl units.

In the case of the oligomers, the Stokes shift can be correlated with the integrated Raman activity. The rigid PNV structure has the lowest Raman activity and a similarly small Stokes shift. The more flexible PPV has the largest Raman activity and the largest Stokes shift, while the PNPV is intermediate.

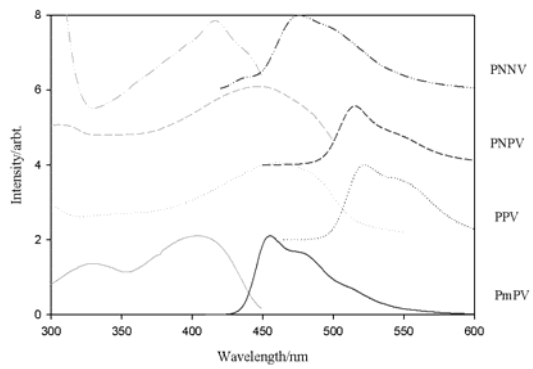

Figure 5. Absorption and emission spectra for the polymers employed (spectra are off set for clarity)

Here it is evident that there is again a power law relationship between the integrated Raman intensity and the Stokes shift, as was seen with the oligomers, suggesting 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. As is the case with the oligomers, the Stokes shift decreases nonlinearly and the Raman intensity increases nonlinearly with the number of available vibrational modes [8,13].

However, in the case of the oligomers, the increase of chain length from phenyl to naphthyl and beyond results in an increasing electronic-vibrational coupling along the extent of the molecule. Within the polymers, the introduction of the naphthyl units reduces the electronic and thus the electron vibrational coupling along the chain. The best coupling is achieved in the fully conjugated PPV system resulting in a strong integrated Raman signal and an efficient distribution of excess excitation energy over the vibrational modes of the backbone, or small Stokes shift. In PmPV, the electronic conjugation is limited by the meta linkage, and thus the π-conjugation contribution to the Raman intensity is limited, and the coupling of the excess excitation energy to the vibrational modes of the backbone is limited beyond a monomer unit. The PNNV and PNPV polymers are intermediate between these extremes.

In figure 6, the integrated relative fluorescence efficiency is plotted as a function of the integrated Raman activity. PNV is arbitrarily set to 1. Although no clearly defined dependence is inferred, there is clearly a trend of increasing relative efficiency with decreasing Raman activity. The fluorescence yield shows an increase in 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. With the exception of the PmPV, the trend is for increasing fluorescence efficiency with decreasing integrated Raman intensity, and by corollary with increasing Stokes shift.

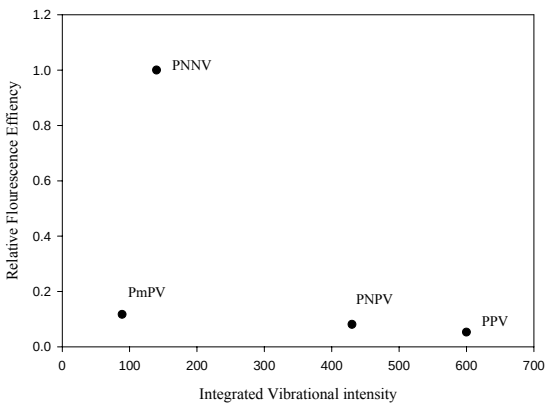

Figure 6. Plot of relative fluorescence yield against vibrational activity for the polymers.

This observation is a clear indication that the Raman activity and the Stokes shift can be used as a guide to the relative efficiency of nonradiative processes in related structures. These parameters are relatively easily ascertained through conventional spectroscopic methods. Design principles, which lead to the minimization of these parameters, should lead to the optimization of radiative efficiencies.

4. Conclusions

The study of the acene and phenylene oligomer series confirms the structural dependence of the electronic properties of π conjugated materials. It furthermore demonstrates that the electron vibrational coupling is similarly well behaved with backbone structure. Both the Stokes shift and the integrated 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 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.

Acknowledgements

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