



## Correlation of vibrational intensity with fluorescence lifetimes in $\pi$ conjugated polymers

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### ABSTRACT

A series of novel  $\pi$  conjugated polymers, originating from the archetypical Polyphenylene vinylene, in which the phenyl units are successively replaced by the larger naphthyl and anthryl acene units, were previously found to have a well-defined relationship between their relative fluorescence yields and their vibrational characteristics, as determined by Raman spectroscopy. In this study the Strickler–Berg equation is used to probe the influence of continual substitution of higher order acene units into the conjugated backbone in terms of the variation of the radiative and non-radiative rates. The deconvolution of the radiative and non-radiative rates enables the correlation of the reduction of the Raman intensity and concomitant increase in the fluorescence yield with the reduction of the non-radiative rate. This confirms that the reduction of the non-radiative rate is the dominant process introduced by the vibrational confinement originating from systematic substitution of higher order acene units into the polymer backbone.

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### 1. Introduction

There has been an upsurge in the interest in conjugated polymers over the past two decades due to their unique optical and electronic properties [1–5]. Ease of fabrication, low cost, fast response time, wide viewing angle and light weight are just a few of the many properties that make conjugated polymers of great importance with a view to the advancement of opto-electronic devices [6–9]. Possibly the biggest advantage of conjugated polymer is the inherent ability to tune the optical and electronic properties by the subtle manipulation of the polymer backbone structure [10]. However, although much attention has been paid to control of the electronic absorption, little is known about structural control of the fluorescence efficiency or yield. This can be affected to potentially control either the radiative (electronic) or non-radiative (electron-vibrational) properties of the system.

It is well documented that the variation of the electronic properties of simple short chain molecules (oligomers) can be accurately described in terms of inverse conjugation length [11–13]. This well-defined relationship has been extended to the vibrational characteristic of these short chain organic molecules [14]. Systematic studies of oligomeric series have thus contributed

greatly to the understanding of both the electronic and vibrational processes in more complex polymer systems. Although they may break down in the infinite-chain-length limit of polymeric systems, well-defined relationships shown to exist for simple conjugated molecules can be used as a guide to establish similar empirical relationships for more complex  $\pi$  conjugated systems [15,16].

In the series of novel PPV derivatives, shown in Fig. 1, it has been demonstrated that both the electronic and vibrational activities of these complex systems can be controlled and optimized by systematic variation of the polymer conjugated backbone [17,18].

The vibrational intensity and fluorescence yield are seen to be well behaved with respect to systematic structural variation (Fig. 2), suggesting that limiting the vibrational activity of the polymer systems has the effect of reducing the non-radiative pathways. The goal of optimisation of the fluorescence yield, by minimisation the vibrational activity of the system, though a process of decoupling the vibrational frequencies has thus been shown to have merit. Regardless of the nature (electronic or vibronic) of the decoupling of the electronic and vibrational states, the end result is highly significant. Limitation of the vibrational activity of the systems becomes a viable route towards optimisation of the fluorescence yield. Thus structural modification can be used for optimisation of radiative processes and fluorescence yield, and structure–property relationships to guide synthetic strategies can be elucidated.

The aim of this communication is to report the progress in elucidating the decay processes of the polymers through investigation of their dynamics and associated lifetimes. The Strickler–

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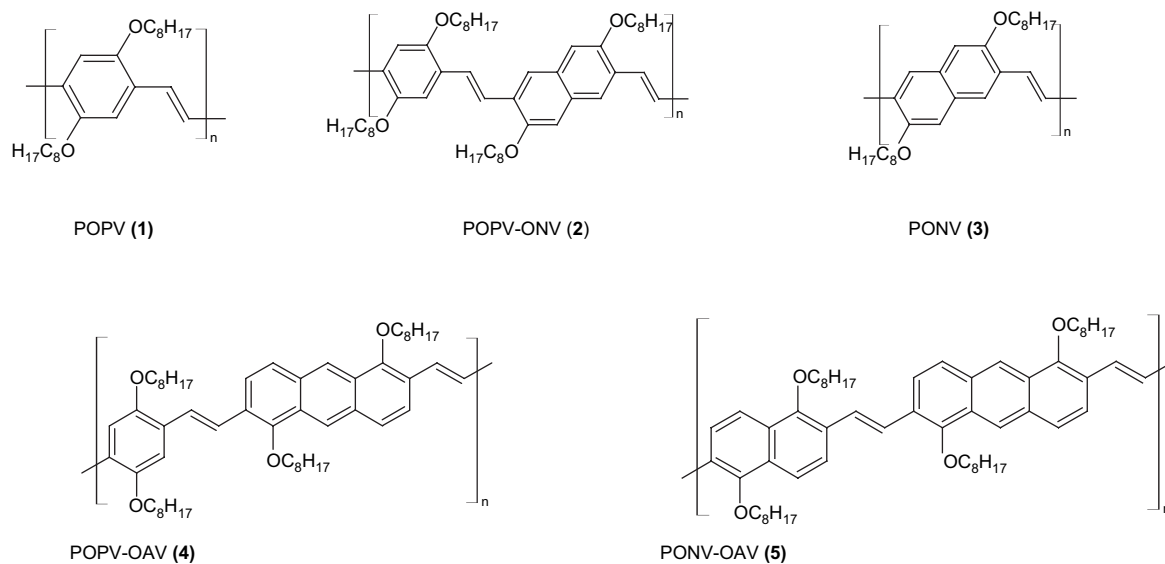


Fig. 1. Polymer structures 1–5.

Berg equation [19] will be used in conjunction with the electronic spectroscopy data to calculate the radiative and non-radiative rates for the progressive polymer systems.

$$1/\tau_0 = 2.880 \times 10^{-9} n^2 \langle \nu_f^{-3} \rangle A_v^{-1} \frac{g_l}{g_u} \int \epsilon d \ln \nu \quad (1)$$

where  $n$  is the refractive index of the medium,  $\nu_f^{-3}$  is the integral over the fluorescence spectrum,  $g_l$  and  $g_u$  are the degeneracies of the lower and upper states, respectively, and  $\epsilon$  is the extinction coefficient.

The calculated non-radiative rates will be compared to the vibrational activity as measured by Raman spectroscopy in order to establish that this parameter can indeed be successfully used as a guide to the non-radiative decay rate in polymeric systems. The use of time correlated single photon counting (TCSPC) will be used to validate the calculated rates, and their structural dependencies. Thus the study will confirm that Raman spectroscopy can be used to probe structural variances in non-radiative rates, that these variances can be correlated with structural variances of fluorescence efficiencies, and that the strategy of reducing the electron-vibrational coupling to optimise fluorescence efficiencies is valid.

## 2. Experimental

The polymer systems (Fig. 1) investigated were Poly(2,5-bis(*n*-octyloxy)-phenylvinylene), POPV (1), Poly(2,5-bis(*n*-octyloxy)-1,4-phenylene vinylene-1,5-bis(*n*-octyloxy)-2,6-naphthylene vinylene), POPV-ONV (2), Poly(2,6-bis(*n*-octyloxy)-1,5-naphthylenevinylene), PONV (3), Poly(2,5-bis(*n*-octyloxy)-1,4-phenylene vinylene-*co*-1,5-bis(*n*-octyloxy)-2,6-anthracene vinylene), POPV-OAV (4), and Poly(2,5-bis(*n*-octyloxy)-1,5-naphthylenevinylene-*co*-1,5-bis(*n*-octyloxy)-2,6-anthracene vinylene), PONV-OAV (5). Synthesis of the polymers 1–5, has been described elsewhere [20,21]. The polymers were prepared in chloroform solution of  $\approx 10^{-6}$  M for all fluorescence and absorption measurements.

Concentration dependent studies were undertaken to ensure that the samples were unaffected by aggregation [22]. 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. These measurements were used to calculate relative fluorescence yields. All yields were calculated relative to MEH-PPV with a reported fluorescence yield value of 0.32 in solution [23].

Fluorescence lifetimes were measured using a computer controlled time correlated single photon counting spectrometer FL900 from Edinburgh Instruments. A nanosecond nF900 flash-lamp excitation source using deuterium gas at a pressure of  $\sim 0.40$  bar provided the fluorescence excitation pulses at 300 nm. A Peltier cooled Hamamatsu R955 side-window photomultiplier tube (PMT) was used in an orthogonal geometry. All decay curves were corrected using a deconvolution with the instrument response function obtained using a scattering solution. The profile of the instrument response pulse had a FWHM of  $\sim 1$  ns which was the detection limit of the system. All samples were run using a variation in concentrations from  $10^{-4}$  M to  $10^{-9}$  M at 300 K and in all cases the lifetime was found to be concentration independent within 0.1 ns.

## 3. Results

In an effort to extend the empirical relationships shown to exist for the vibrational characteristics of the polymers' systems [18] it was decided to investigate the variation of the radiative and non-radiative rates, as the larger acene units were inserted in to the backbone, using the Strickler–Berg equation. It has been shown

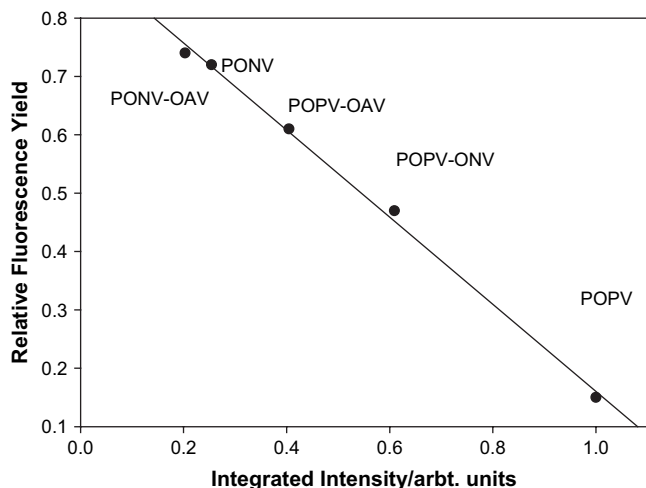


Fig. 2. Variation of the fluorescence yield with relative integrated Raman intensity; solid line is a linear fit.

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