

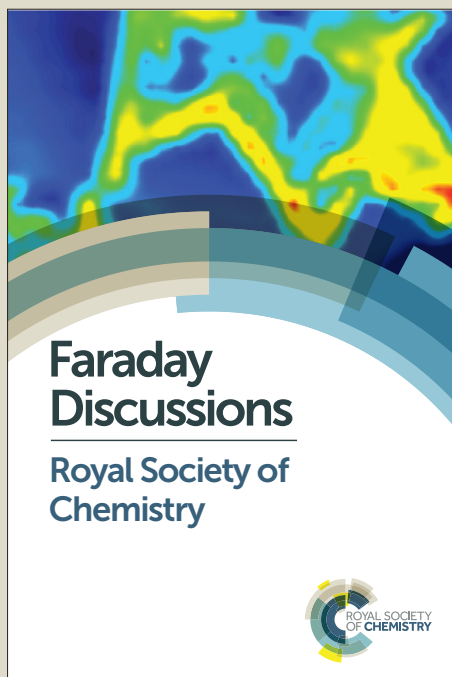
# Faraday Discussions

Accepted Manuscript



This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

**Register now to attend!** Full details of all upcoming meetings: <http://rsc.li/fd-upcoming-meetings>



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## Excited State Dynamics of Organic Semi-Conducting Materials

Kenneth P. Ghiggino,<sup>\*a</sup> Andrew J. Tilley,<sup>a,b</sup> Benjamin Robotham,<sup>a</sup> Jonathan M. White<sup>a,b</sup>

*a) School of Chemistry and b) Bio21 Molecular Science and Biotechnology*

*Institute, University of Melbourne, Parkville, Victoria, Australia, 3010.*

*\*Author for correspondence. Fax: +61 3 93475180; Tel: +61 3 83448939; E-mail:*

*ghiggino@unimelb.edu.au*

•

### Abstract

Time-resolved absorption and emission spectroscopy has been applied to investigate the dynamics of excited state processes in oligomer models for semi-conducting organic materials. Following photo-excitation of a pentamer oligomer that is a model for the conjugated polymer MEH-PPV, an ultrafast component of a few picoseconds is observed for the decay of the initially formed transient species. Variable temperature absorption and emission spectra combined with x-ray crystallography and calculations support the assignment of this rapid relaxation process to an excited state conformational rearrangement from non-planar to more planar molecular configurations. The implications of the results for the overall photophysics of conjugated polymers are considered.

### Introduction

Conjugated polymers are finding widespread application in light-emitting diodes [1-5], photovoltaic cells [6-10] and other organic electronic devices [11-15]. Since the discovery of efficient electroluminescence in conjugated polymers during the 1990s [16], research has focused on improving optoelectronic performance to bring conjugated polymers in line with existing inorganic technologies. Materials based on poly(*p*-phenylenevinylene) (PPV) have received considerable attention owing to their favourable luminescent and semi-conducting properties [17-20]. In recent years, there has been a considerable research effort into understanding the fundamental photophysical and light harvesting properties of this important polymer; in particular, the more useful solubilised analogues such as poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) have been of particular interest [21-25].

In conjugated polymers, a number of competing exciton relaxation pathways are accessible following photoexcitation, often leading to complex photophysical behavior. In MEH-PPV, it is thought that chain defects cause polymer backbone conjugation to be segmented into smaller sub-units, leading to broadened absorption spectra [26,27]. Following photoexcitation, energy transfer from higher energy, shorter segments to lower energy, longer segments has been proposed to lead to emission from a restricted subset of conjugated sequences, resulting in the observed structured solution emission spectrum. However, it is now known that this picture is too simplistic, and that excited states of conjugated polymers are likely governed by complex energy transfer and structural relaxation processes, and that the degree of torsional freedom in individual conjugated segments can influence energy transfer dynamics [28-30]. In addition, quantum coherence has been proposed to contribute to the polymer energy transfer manifold [21,22].

Recently, we reported the synthesis and photophysics of structurally well-defined MEH-PPV oligomers [31]. It was noted in that work that the spectral profiles of the oligomers were quite similar to those of the bulk polymer, suggesting that the observed asymmetry between absorption and fluorescence spectra is due to properties inherent to the individual chromophores that make up the polymer backbone. It was proposed that the ground state likely consists of a population of non-degenerate torsional conformers, each possessing slightly different transition energies, leading to broadened absorption spectra. The possible conformations of a model PPV trimer oligomer are illustrated for example in Figure 1. Molecular mechanics calculations show that the trimer structure is not planar but consists of a family of up to eight twisted conformations that have similar energies (within 0.84 kJ/mol) where the four dihedral angles  $\theta_1$  to  $\theta_4$  deviate from planarity by angles from 10° to 15°. These qualitative predictions receive support from the crystal structure of the trimer (also see Figure 1) which adopts a twisted conformation with dihedral angles  $\theta_1 = -8.7(7)^\circ$ ,  $\theta_2 = 7.4(7)^\circ$ ,  $\theta_3 = -15.0(7)^\circ$ ,  $\theta_4 = -6.9(7)^\circ$  [31]. We also report here that the crystal structure of the bromo PPV dimer ((E)-1-bromo-2-hexyloxy-4-(2'-hexyloxy-5'-methoxystyryl)-5-methoxy benzene, Figure 2) similarly shows a significant deviation from molecular planarity due to non-zero dihedral angles.

In order to explain the reason a structured fluorescence from the oligomers is observed, in contrast to the broad absorption spectra profiles, it is proposed that following photo-excitation rapid conformational relaxation of the twisted conformations to more planar structures occurs. These proposals are consistent with several other theoretical and experimental studies on related systems [32-35].

In the present paper the excited state dynamics of a MEH-PPV oligomer have been investigated using ultrafast transient absorption spectroscopy and other photophysical methods. Earlier work by others on a related PPV trimer using lower resolution time-correlated single photon counting experiments has found evidence for a <50 ps fluorescence decay component following photoexcitation that was attributed to conformational relaxation [34]. Owing to the ultrafast nature of this relaxation process, picosecond transient absorption spectroscopy has been applied here to resolve the time-scale of the initial relaxation processes.

## Experimental

The synthesis of pentamer **1** (Figure 3) is reported elsewhere [31]. UV-Vis absorption spectra were recorded on a Varian Cary 50 Bio spectrophotometer. All solution absorption spectra were recorded against solvent blanks in matched 1.0 cm path length quartz cells. Fluorescence spectra were recorded on a Varian Eclipse fluorescence spectrofluorometer. The optical densities of the solutions were kept below 0.20 at the excitation wavelength to minimize reabsorption effects. Low temperature studies were carried out in an Oxford Instruments Optistat liquid nitrogen cryostat fitted with a temperature controller.

The transient absorption instrumentation has been described elsewhere [36]. In summary it consists of a Ti:sapphire laser (Coherent, Mira) combined with a regenerative amplifier (Coherent, RegA 9050) operating at a 94 kHz pulse repetition rate and with an average output power of ~500 mW at 830 nm. Half of the amplified output was directed to an OPA (Coherent, OPA 9400) and the second harmonic output at 415 nm was used as the pump beam that passes through a light chopper to provide modulation synchronised to one twentieth of the pulse repetition rate (4.7 kHz). The other half of the amplified laser output was focused into a 3 mm sapphire crystal

(Crystalsystems) to provide a continuum probe beam. The relative polarization of the pump and probe beams are set to 54.7 degrees (the magic angle) to remove any distortion effects due to molecular rotation. After passing through the sample contained in a 2mm path length cell the probe beam is delivered to a CMOS detector (Ultrafast Systems) by a 200  $\mu\text{m}$  fiber (Ocean Optics, P200-2-UV-VIS). The time resolution of the system is approximately 200 fs. The kinetics scheme modelling the pentamer transient decay was solved within the MATLAB (Mathworks) software using the ode23s ordinary differential equation solver. Optimisation of the fit was achieved by minimisation of the chi-squared fitting parameter. The goodness of fit was determined by the  $R^2$  regression parameter. The concentration of pentamer **1** was approximately  $1 \times 10^{-6}$  M and  $\sim 10\%$  of the sample was excited by the excitation laser pump pulse as assessed by the ground state depletion. The solutions were stirred continuously throughout the measurement by a magnetic stirrer bar.

## Results and Discussion

### Steady state photophysics

Variable temperature absorption and emission spectra for pentamer **1** are shown in Figures 4 and 5. These spectra were recorded in 2-methyltetrahydrofuran, which provided an optically clear matrix as the solution was cooled.

At room temperature the absorption spectrum of **1** is broad and featureless while, in contrast, the fluorescence spectrum shows vibrational structure. The variable temperature absorption spectra presented in Figure 4 are similar to those for the related tetramer reported elsewhere [31], although the spectra for the pentamer are more red-shifted consistent with the additional backbone  $\pi$ -conjugation. The absorption spectra show a marked increase in vibrational structure as the solution is cooled, coupled with a red-shift in absorption maximum. This behaviour is consistent with absorption by a restricted set of torsional configurations in the low temperature solution environment whereas at higher temperatures additional configurations are accessible. The emission spectrum becomes more structured and increases in intensity as the temperature is lowered but does not show the large red-shift that is observed in

absorption. At low temperature a strong mirror image relationship is apparent between absorption and emission profiles and a reduced Stokes shift compared with the room temperature spectra.

The similarity (in spectral position) between 120 K and room temperature emission spectra suggests that the emitting conformations present at low temperature are similar to those populated at room temperature. This supports a model of conformational relaxation to low energy structures prior to emission in room temperature solutions, and suggests that the large Stokes shift observed in the room temperature spectra arises from planarization of the oligomer backbone following excitation. These findings are also consistent with previous theoretical and experimental studies [37,38], which have found evidence for a large degree of torsional flexibility in the ground state of PPV oligomers.

### **Transient absorption spectroscopy**

To investigate the dynamics of the conformational relaxation process, ultrafast transient absorption spectroscopy was employed. The transient absorption spectrum of pentamer **1** was recorded in dilute chloroform solution at room temperature and is shown in Figure 6.

A clear transient absorption signal can be seen with band maximum centred at 770 nm, while a ground state bleach is evident in the shorter wavelength region (<520nm) where the oligomer absorbs. There is a concomitant recovery of the ground state bleach signal with the decay of the transient, indicating that the transient signal observed corresponds to an  $S_1$ - $S_n$  transition and that the decay reflects the depopulation of the  $S_1$  state. Of particular interest is the initial rapid decay in signal intensity observed within the first 20 ps following the excitation pulse.

The transient decay trace at 770 nm (Figure 7) shows an initial ultrafast component, coupled with a longer-lived decay. The latter component decays on a similar time scale to the fluorescence from the pentamer measured by the time-correlated single photon counting (TCSPC) technique that has a major component lifetime of 800 ps [31]. The time resolution of  $\sim 50$  ps of the TCSPC measurements would not have revealed the shorter decaying components observed in the transient studies reported here.

In order to quantify the ultrafast component from the transient decay, the decay profile was fitted to the simple kinetic model shown in the inset to Figure 7. In this model  $k_1$  is the rate constant for conformational relaxation of the excited population to give the planar species ( $S_1^{\text{planar}}$ ),  $k_2$  is the competing rate of the initially prepared configuration directly to the ground state (including both radiative and non-radiative processes), while  $k_3$  is the total decay rate from the conformationally relaxed planar configurations.

This kinetic model gave an adequate fit to the data ( $R^2$  fitting parameter of 0.996) yielding a value for the conformational relaxation rate ( $k_1$ ) of  $1.47 \times 10^{11} \text{ sec}^{-1}$  (see Figure 7). The fitted values for  $k_2$  and  $k_3$  are  $3.23 \times 10^{10} \text{ sec}^{-1}$  and  $1.10 \times 10^9 \text{ sec}^{-1}$  respectively. Comparison of the fitted  $k_1$  and  $k_2$  rate constants indicates that conformational relaxation is the dominant decay channel for the excited PPV oligomer, with approximately 80% of the initially excited population relaxing to planar states prior to emission. The inverse of  $k_2$  gives the lifetime of the  $S_1^{\text{planar}}$  state (910 ps) that compares well with the fluorescence lifetime recorded from time-correlated single photon counting (800 ps).

In light of the steady state temperature dependent absorption and fluorescence results, it seems reasonable to assign the observed ultrafast decay component to rapid conformational relaxation of the initially excited non-planar configurations of the oligomer to form the more planar relaxed structures from which the majority of fluorescence arises. Further evidence for this conclusion comes from the fluorescence spectrum of the pentamer oligomer when it is dispersed in a solid poly(methyl methacrylate) (PMMA) film at low concentration to avoid aggregation effects. Under these conditions a broad structureless emission spectrum is observed with a maximum at 498 nm compared to the structured emission observed with maximum at 518 nm (cf, Figure 5). This blue shift in the fluorescence maximum and absence of spectral structure in the solid film is consistent with emission originating from the broad set of unrelaxed configurations.

Pentamer **1** can be considered a model for the chromophore subunits of the extended conjugated polymer MEH-PPV. The results of this work indicate that the observed broad absorption but structured emission of MEH-PPV in solution, often attributed to

energy transfer processes from a range of absorbing polymer segments to low energy emitting segments, is more likely the result of rapid conformational relaxation processes within the segments themselves. Nevertheless exciton transfer within a MEH-PPV polymer chain has been demonstrated by a number of bulk and single molecule measurements [e.g. 21, 28, 39]. The short time relaxation behaviour in the pentamer suggests that, in MEH-PPV solutions, conformational relaxation likely competes with intramolecular energy transfer and needs to be considered in any complete theoretical description of the polymer energy transfer dynamics.

### **Conclusion**

Conformational relaxation dynamics of a MEH-PPV oligomer have been investigated using variable temperature steady state measurements and ultrafast TAS. The steady state measurements, combined with x-ray studies and theoretical calculations, provided evidence for a ground state populated by a family of torsional isomers that upon photo-excitation relaxes to more planar arrangements. Transient spectroscopy of the pentamer in room temperature solution showed a clear ultrafast component ( $\sim 7$ ps) in the transient decay that can be attributed to this conformational relaxation process.

### **Electronic Supplementary Information**

Crystallographic information file (CIF) for the bromo PPV dimer (((E)-1-bromo-2-hexyloxy-4-(2'-hexyloxy-5'-methoxystyryl)-5-methoxy benzene). The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre, deposition no. 1023608. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK or via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html)

### **Acknowledgements**

AJT thanks the David Hay Memorial Fund for financial assistance during the preparation of this paper. This research was supported through an Australian Research Council Discovery Project (DP 0986166).



## References

- (1) K. Brunner, A. Dijken, H. Borner, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, *J. Am. Chem. Soc.*, 2004, **126**, 6035.
- (2) M. A. Reddy, G. Mallesham, A. Thomas, K. Srinivas, V. J. Rao, K. Bhanuprakash, L. Giribabu, R. Grover, A. Kumar, M. N. Kamalasanan, R. Srivastava, *Synth. Met.*, 2011, **161**, 869.
- (3) Q. Li, J. Li, H. Ren, Y. Duan, Z. Gao, D. Liu, *Macromol. Rapid Commun.*, 2011, **32**, 736.
- (4) W. Lu, J. Kuwabara, T. Iijima, H. Higashimura, H. Hayashi, T. Kanbara, *Macromolecules*, 2012, **45**, 4128.
- (5) T. W. Yoo, C. Park, T. M. Nguyen, D. U. Kim, L. S. Park, *Mol. Cryst. Liq. Cryst.*, 2011, **551**, 69.
- (6) Y. Zhang, H. L. Yip, O. Acton, S. K. Hau, F. Huang, A. K. Y. Jen, *Chem. Mater.*, 2009, **21**, 2598.
- (7) D. M. Huang, S. A. Mauger, S. Friedrich, S. J. George, D. Dumitriu-LaGrange, S. Yoon, A. J. Moule, *Adv. Funct. Mater.*, 2011, **21**, 1657.
- (8) A. Gupta, S. E. Watkins, A. D. Scully, T. B. Singh, G. J. Wilson, L. J. Rozanski, R. A. Evans, *Synth. Met.*, 2011, **161**, 856.
- (9) H. Zhou, L. Yang, W. You, *Macromolecules*, 2012, **45**, 607.
- (10) H. J. Son, B. Carsten, I. H. Jung, L. Yu, *Energy Environ. Sci.*, 2012, **5**, 8158.
- (11) T. Kojima, D. Kumaki, J-i. Nishida, S. Tokito, Y. Yamashita, *J. Mater. Chem.*, 2011, **21**, 6607.
- (12) T. Lei, Y. Cao, Y. Fan, C-J. Liu, S-C. Yuan, J. Pei, *J. Am. Chem. Soc.*, 2011, **133**, 6099.
- (13) H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J.R. Durrant, P. Shakya Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney, I. McCulloch, *J. Am. Chem. Soc.*, 2011, **133**, 3272.
- (14) A. Facchetti, *Chem. Mater.*, 2011, **23**, 733.
- (15) Z. Li, J. Lu, S-C. Tse, J. Zhou, X. Du, Y. Tao, J. Ding, *J. Mater. Chem.* 21 (2011) 3226.
- (16) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R.N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature*, 1990, **347**, 539.
- (17) D. Braun, A. J. Heeger, *Appl. Phys. Lett.*, 1991, **58**, 1982.
- (18) C. Liednbaum, Y. Croonen, P. van de Weijer, J. Vleggaar, H. Schoo, *Synth. Met.*, 1997, **91**, 109.
- (19) G. Yu, *Synth. Met.*, 1996, **80**, 143.
- (20) S. L. M. van Mensfoort, M. Carvelli, M. Megens, D. Wehenkel, M. Bartyzel, H. Greiner, R. A. J. Janssen, R. Coehoorn, *Nat. Photonics*, 2010, **4**, 329.
- (21) E. Collini, G.D. Scholes, *Science*, 2009, **323**, 369.
- (22) E. Collini, G.D. Scholes, *J. Phys. Chem. A*, 2009, **113**, 4223.
- (23) S. Habuchi, S. Onda, M. Vacha, *Chem. Commun.*, 2009, 4868.
- (24) S. Habuchi, S. Onda, M. Vacha, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1743.
- (25) H. Lin, Y. Tian, K. Zapadka, G. Persson, D. Thomsson, O. Mirzov, P-O. Larsson, J. Widengren, I. G. Scheblykin, *Nano Lett.*, 2009, **9**, 4456.
- (26) B. J. Schwartz, *Annu. Rev. Phys. Chem.*, 2003, **54**, 141.
- (27) S. Saini, B. Bagchi, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7427.
- (28) I. Hwang, G. D. Scholes, *Chem. Mater.*, 2011, **23**, 610.
- (29) Y. Ebihara, M. Vacha, *J. Phys. Chem. B*, 2008, **112**, 12575.

- (30) J-S. Yang, J-L. Yan, C-K. Lin, C-Y. Chen, Z-Y. Xie, C-H. Chen, *Angew. Chem. Int. Ed.*, 2009, **48**, 9936.
- (31) A. J. Tilley, S. M. Danczak, C. Browne, T. Young, T. Tan, K. P. Ghiggino, T. A. Smith, J. White, *J. Org. Chem.*, 2011, **76**, 3372.
- (32) J. Gierschner, H. G. Mack, L. Luer, D. Oelkrug, *J. Chem. Phys.*, 2002, **116**, 8596.
- (33) S. T. Hoffman, H. Bässler, A. Köhler, *J. Phys. Chem. B*, 2010, **114**, 17037.
- (34) R. E. Di Paolo, J. Seixas de Melo, J. Pina, H. D. Burrows, J. Morgado, A. L. Maçanita, *Chem. Phys. Chem.*, 2007, **8**, 2657.
- (35) J. Seixas de Melo, J. Pina, H. D. Burrows, R. E. Di Paolo, A. L. Macanita, *Chem. Phys.*, 2006, **330**, 449.
- (36) S. K. Sugunan, B. Robotham, R. P. Sloan, J. D. Szmytkowski, K. P. Ghiggino, M. F. Paige, R. P. Steer, *J. Phys. Chem. A*, 2011, **115**, 12217.
- (37) F. Sterpone, P. J. Rossky, *J. Phys. Chem. B*, 2008, **112**, 4983.
- (38) J. B. Lagowski, *J. Mol. Struct. THEOCHEM*, 2002, **589-590**, 125.
- (39) E. N. Hooley, A. J. Tilley, J. M. White, K. P. Ghiggino, T. D. M. Bell, *Phys. Chem. Chem. Phys.*, 2014, **16**, 7108.

## Figure Captions

**Figure 1:** Conformations of a PPV trimer where  $\theta_1 - \theta_4$  are the twist dihedral angles (upper figure). X-ray structure of the trimer (for  $R = C_6H_{13}$ ) where  $\theta_1 = -8.7(7)^\circ$ ,  $\theta_2 = 7.4(7)^\circ$ ,  $\theta_3 = -15.0(7)^\circ$ ,  $\theta_4 = -6.9(7)^\circ$ .

**Figure 2:** X-ray structure of a bromo PPV dimer with 30% ellipsoids where  $\theta_3 = 11.9(4)^\circ$ ,  $\theta_4 = -9.4(4)^\circ$  and  $\theta_3 = C14-C9-C8-C7$  and  $\theta_4 = C7-C3-C4-O2$  dihedral angles.

**Figure 3:** Structure of pentamer **1** studied in this work.

**Figure 4:** Absorption spectra of pentamer **1** in 2-methyltetrahydrofuran as a function of temperature.

**Figure 5:** Emission spectra of pentamer **1** in 2-methyltetrahydrofuran as a function of temperature.  $\lambda_{exc} = 470$  nm.

**Figure 6:** Transient absorption spectrum of pentamer **1** recorded in chloroform solution at room temperature. An excitation wavelength of 415 nm was used.

**Figure 7:** Pentamer transient decay recorded at 770 nm. Points: experimental data; solid line: fit to a kinetic model that includes excited state conformational relaxation with  $k_1 = 1.47 \times 10^{11} \text{ s}^{-1}$ ,  $k_2 = 3.23 \times 10^{10} \text{ s}^{-1}$ ,  $k_3 = 1.10 \times 10^9 \text{ s}^{-1}$  (see text). Inset: Kinetic model describing excited state processes in the PPV oligomer defining  $k_1$ ,  $k_2$  and  $k_3$ .

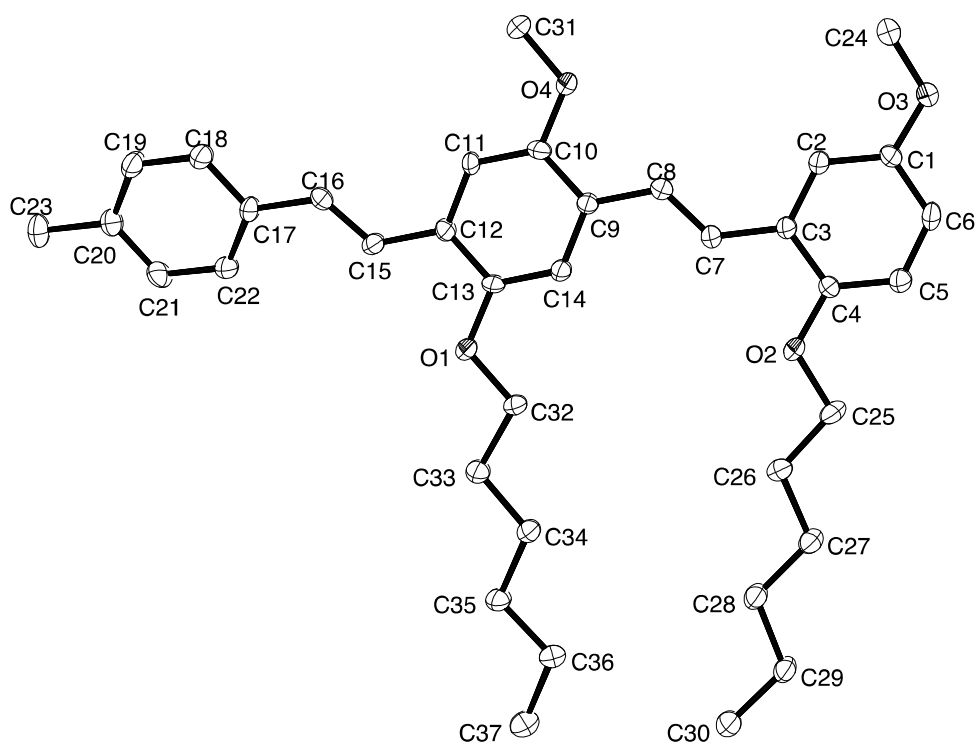
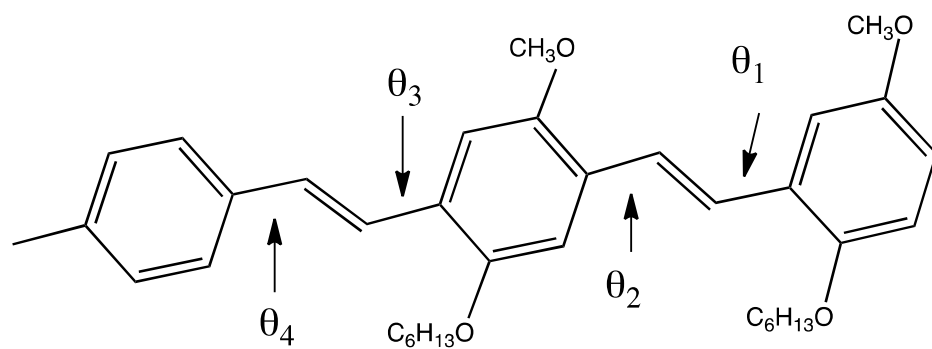


Figure 1

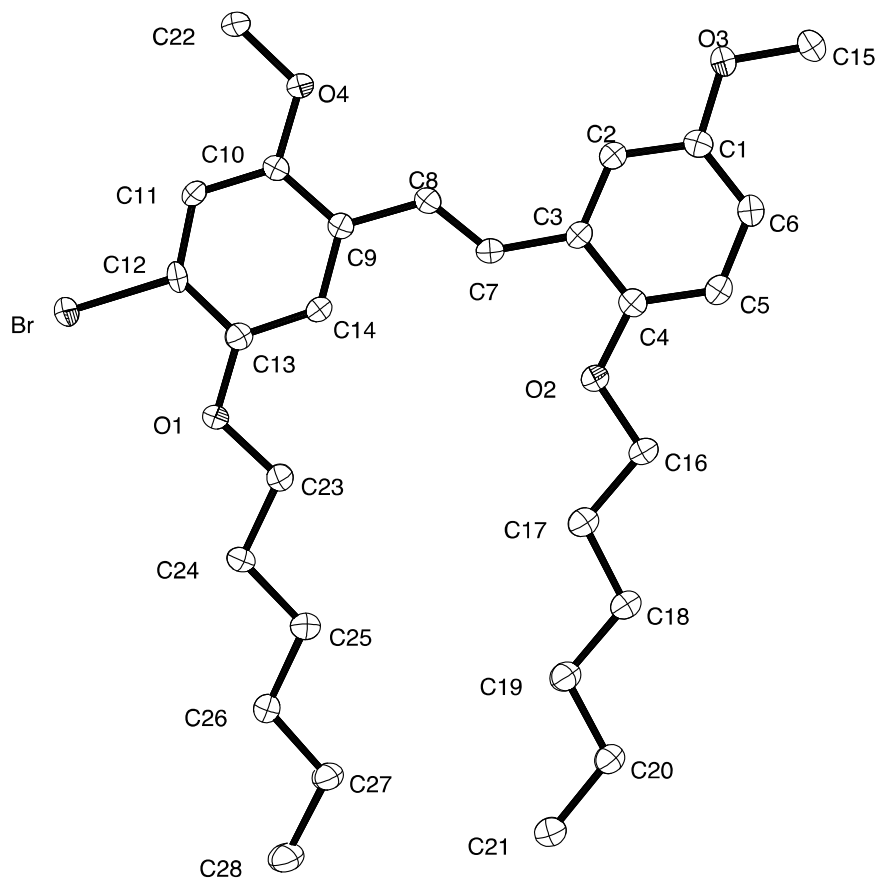


Figure 2

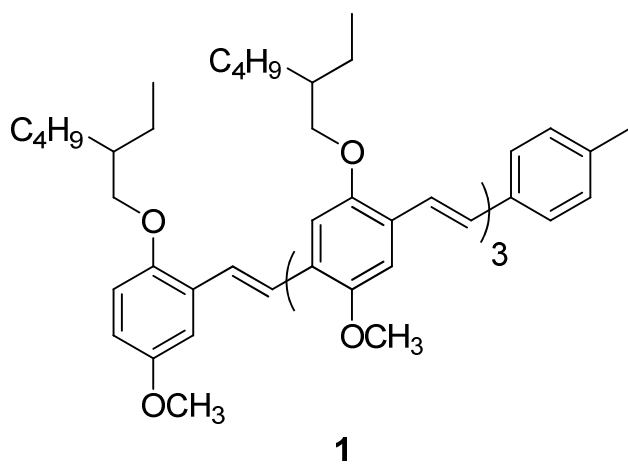


Figure 3

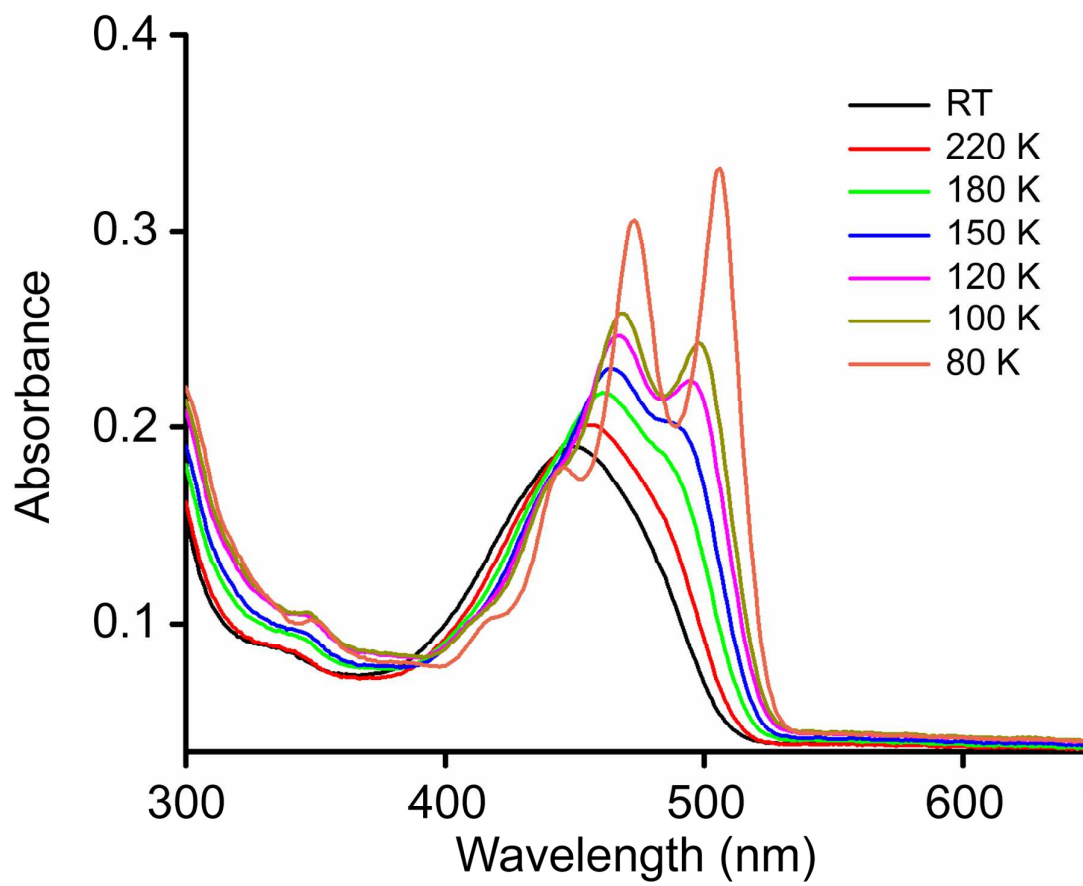


Figure 4

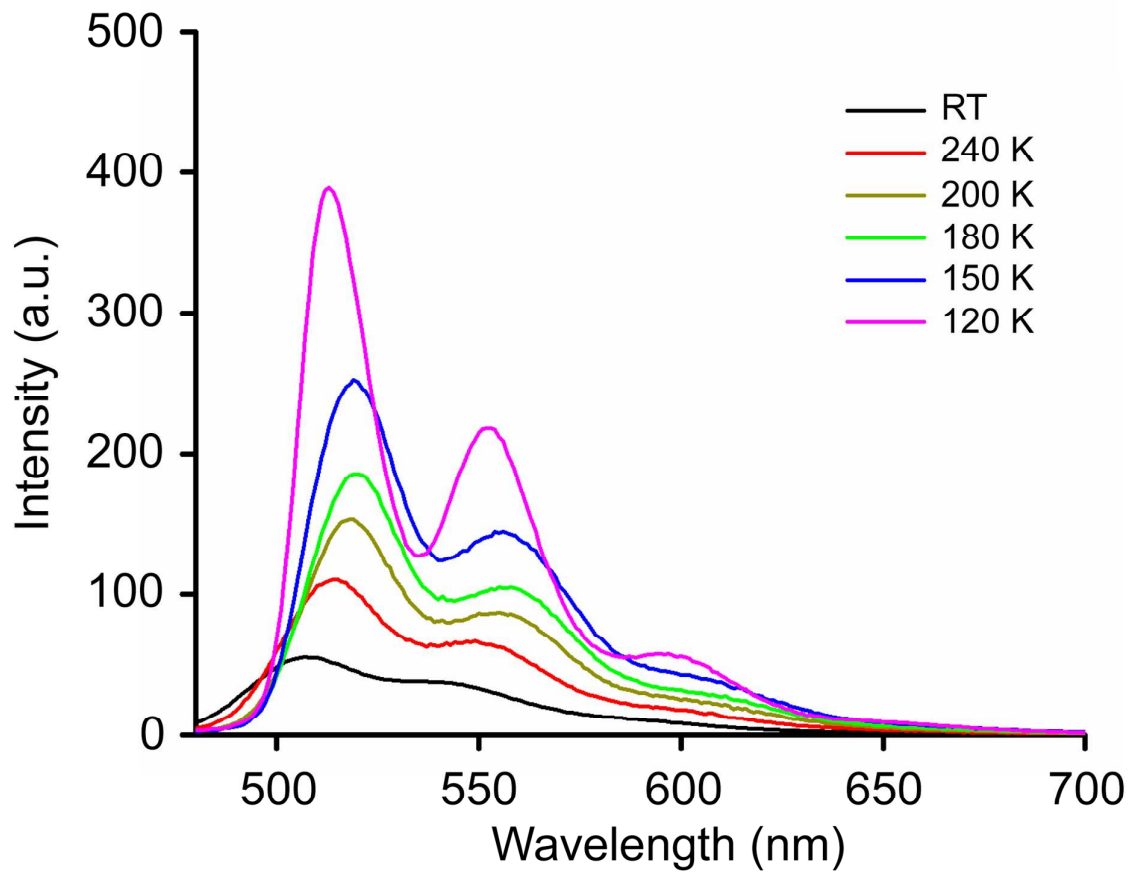


Figure 5



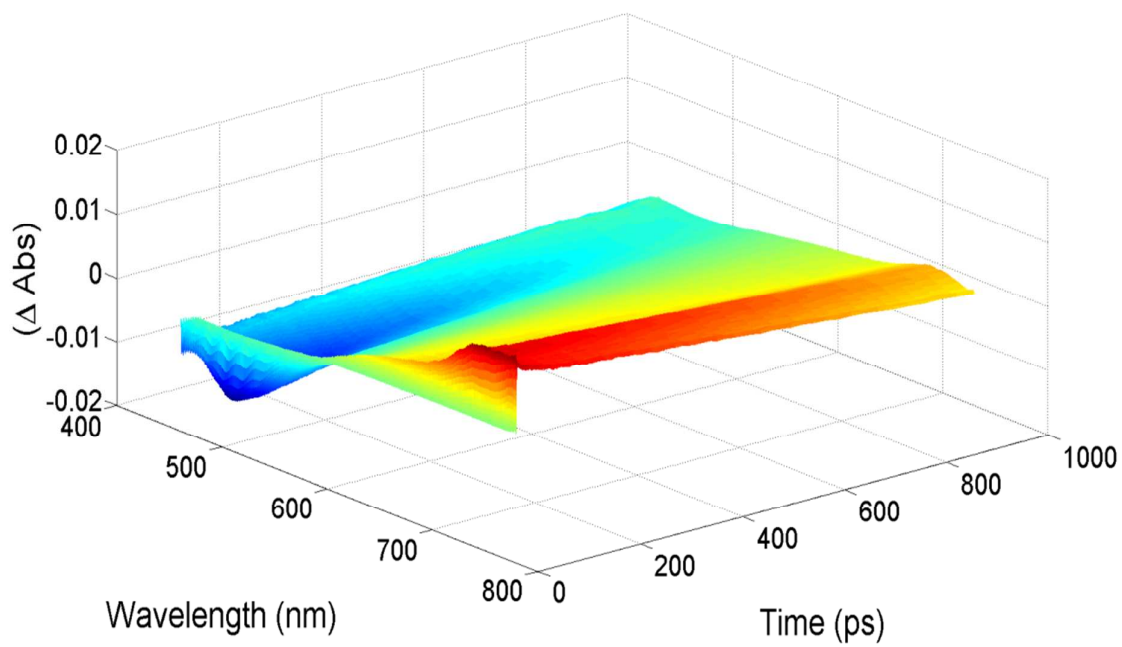


Figure 6

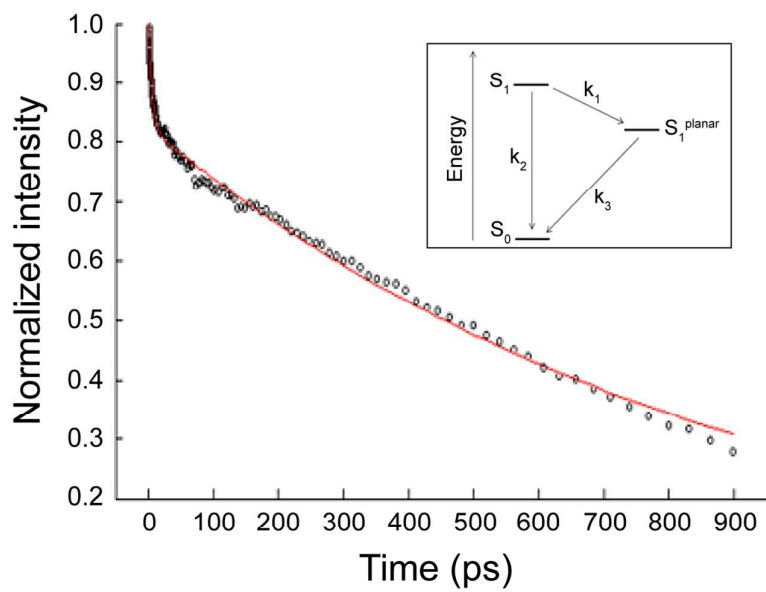


Figure 7

## GRAPHICAL &amp; TEXTUAL ABSTRACT

## Excited state dynamics of organic semi-conducting materials

Kenneth P. Ghiggino\*, Andrew J. Tilley, Benjamin Robotham and Jonathon M. White  
*School of Chemistry, University of Melbourne, Victoria, Australia 3010*

The transient absorption spectrum of a MEH-PPV oligomer following pulsed laser excitation at 415 nm exhibits an ultrafast decay component attributed to an excited state conformational relaxation process.

