26 October 2001

Chemical Physics Letters 347 (2001) 318–324

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Exciton migration to chain aggregates in conjugated polymers: influence of side-chain substitution

L.M. Herz [a,*], C. Silva [a], R.T. Phillips [a], S. Setayesh [b], K. Müllen [b]

[a] *Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK*

[b] *Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany*

Received 9 August 2001; in final form 6 September 2001

Abstract

We have performed time-resolved photoluminescence (PL) measurements to study the transfer of excitons from non-interacting polymer chains to chain aggregates for thin films of polyindenofluorene with different attached side chains. The transfer time is shown to be fast (≈35 ps) and side-chain independent indicating that the substitution of different side chains does not affect the local concentration of aggregate sites within aggregate-containing domains, but rather the extent to which such domains are formed. We find the aggregate emission efficiency to be relatively high ($\gtrsim$ 20%) while still lower than the efficiency of emission from non-interacting chains. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Luminescent conjugated polymers have attracted much interest in the past decade due to their use as active materials in cheap and efficient light-emitting diodes [1]. However, one issue still causing concern is the formation of chain aggregates in polymer films, which usually gives rise to additional, red-shifted bands in the luminescence spectra [2–8]. The existence of aggregates is generally considered to be detrimental to the luminescence efficiency since interchain interactions lead to a splitting of the excitonic states with the lowest state being only weakly coupled to the ground state [9]. This problem has been addressed by the substitution of bulky side chains to the polymer backbone to prevent the ordered chain packing that facilitates interchain interactions [10,11]. One example is a recently synthesized polyindenofluorene derivative [12] whose film morphology and emission spectra were shown to depend strongly on the type of side chain attached to the backbone.

In this Letter, we examine the origin of the changes in the emission spectra and luminescence efficiencies for these polyindenofluorene materials with the type of side chains used. Such changes may be due to a variation in the strength of the interchain interactions, resulting in a change in the aggregate emission efficiency with the type of side chains attached. They may also be caused by a side-chain dependent probability of aggregate formation in the polymer films. Both of these possibilities will be addressed in the following.

2. Experimental

The synthesis of poly-6,6′,12,12′-tetraalkyl-2,8-indenofluorene with either octyl (PIFTO) or

---

[*] Corresponding author.
E-mail address: lmh33@cam.ac.uk (L.M. Herz).

PII: S0009-2614(01)01080-6

2-ethylhexyl (PIFTEH) side chains is described in [12]. Thin films of PIFTO and PIFTEH were produced by spin-casting from *p*-xylene solutions onto Spectrosil substrates. The films were prepared and stored in an inert atmosphere and kept under vacuum ($\leqslant 10^{-5}$ mbar) during the measurements to prevent oxidation.

Time-resolved photoluminescence (PL) experiments were performed on PIFTEH and PIFTO films using the femto-second up-conversion technique [13,14]. The sample was excited with the frequency doubled output from a mode-locked Ti:Sapphire laser supplying 200-fs pulses at an energy of 3.1 eV at a repetition rate of 76 MHz. The average power on the sample was 220 μW on a spot of ≈110-μm diameter. PL originating from the sample was up-converted in a β-barium-borate crystal using the fundamental laser beam at 1.55 eV as a gate. Sum-frequency photons were dispersed in a monochromator, and detected via photon counting. The overall temporal resolution of the system was about 400 fs. To measure time-integrated PL, the PL was diverted to a double-grating spectrometer (Spectramate 1680) and detected with a Si photodiode using a lock-in technique. Both time-resolved and time-integrated spectra were corrected for spectral response. All experiments were conducted at room temperature.

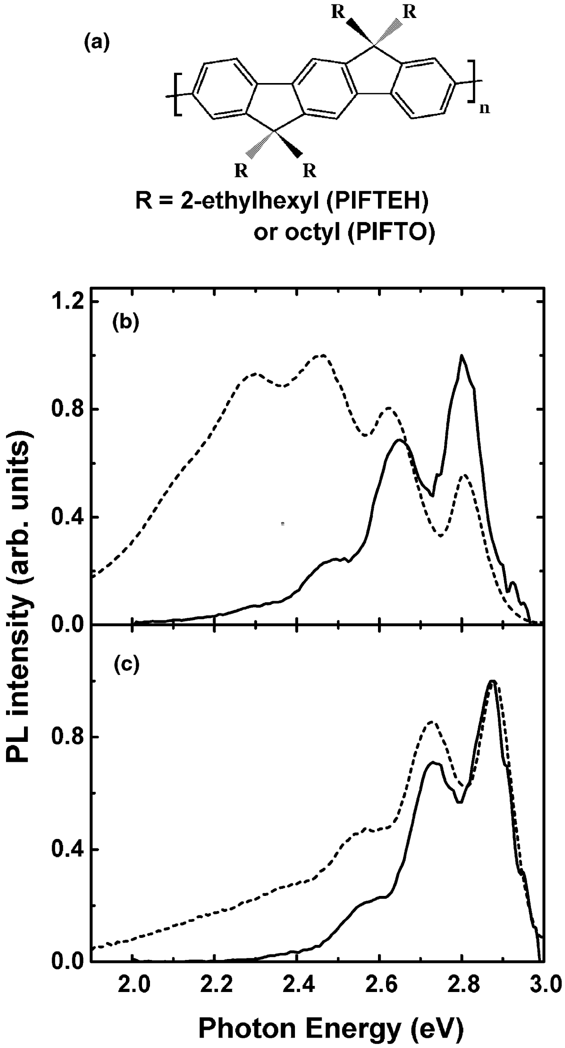

Fig. 1. (a) Chemical structure of PIFTO and PIFTEH. (b and c): Time-integrated PL spectra (dashed line) and time-resolved spectra at 10 ps after excitation (solid line) for PIFTO (b) and PIFTEH (c).

3. Results and discussion

Fig. 1 shows the time-integrated PL spectra for thin films of PIFTO and PIFTEH together with their time-resolved PL spectra at early times after excitation. The time-integrated spectra show pronounced differences in shape: While the PIFTEH spectrum is dominated by the 0–0 emission band centred at 2.88 eV and its vibronic progressions, the PIFTO spectrum features a prominent broad emission centered at ≈2.4 eV underlying the vibronic replica of the 0–0 transition at 2.82 eV. In contrast, the time-resolved PL spectra at 10 ps after excitation are of very similar shape, the only significant difference being the energy shift between the PIFTEH and the PIFTO transitions caused by the enhanced torsion angle of the indenofluorene repeat units due to the sterically more demanding ethylhexyl side chains in PIFTEH [12]. The comparison between time-integrated and time-resolved PL spectra at early times suggests that the emission from PIFTEH and PIFTO films originates from two different species: excitons located on 'isolated' or non-interacting chains (in the following referred to as 'bulk' excitons) whose separation from nearby chains is large enough for the excitonic wave function to be confined to a single chain, and, most likely, excitons recombining in aggregate regions of the film, where polymer chains are close enough (typically a few Angstroms) for the wave function to be delocalized over more than one chain [19]. This assumption is supported by the observed temporal evolution of the luminescence spectra from PIFTO films, displayed in Fig. 2. At early times after excitation, the recombination of bulk excitons gives rise to a typical vibronic structure in the blue spectral region, which decays on a timescale of ≈35 ps. On a corresponding timescale a rise in the PL intensity at the low energy end of the spectrum (2.0–2.4 eV) can be found. At long (>600 ps) delay times, a broad long-lived emission band centered at 2.4 eV remains. Similar luminescence dynamics have been found for thin films of ladder-type poly-(*para*)-phenylene (LPPP) [2] and poly-dioctylfluorene (PFO) [13] where they were ascribed to the efficient transfer of excitons located on non-interacting chains to long-lived aggregate states. The decay dynamics of the luminescence from polyindenofluorene films together with the strong dependence of the time-integrated PL spectra on the type of the attached side-chains therefore suggest that the broad underlying emission we observe from polyindenofluorene films is also caused by excitations recombining from chain aggregates. Comparing the time-integrated PL spectra of PIFTEH and PIFTO it becomes clear that emission from aggregate states plays a much stronger role in PIFTO than in PIFTEH films. In the following we will investigate the mechanisms responsible for this effect.

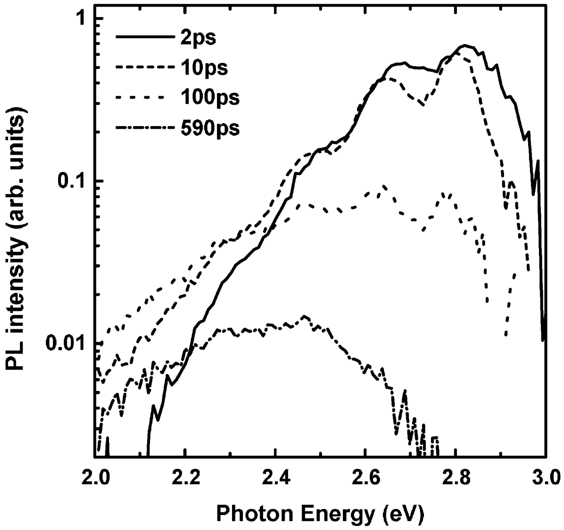

Fig. 2. Time-resolved PL spectra for a PIFTO film at various times after excitation.

In order to allow a comparison between the two materials we must first separate the relative contributions to the total luminescence from bulk states and aggregate states. This can be achieved by scaling the time-resolved PL spectrum at early times after excitation (when it is dominated by recombination of bulk excitons) to coincide at the 0–0 transition with the time-integrated PL spectrum. Since the high-energy end of the spectrum is dominated by the emission from bulk states (see Fig. 2) the subtraction between the time-integrated PL and the time-resolved PL spectrum at early times will yield the aggregate spectrum. Spectral integration of both the aggregate photon emission spectrum and the time-resolved (bulk) emission spectrum then permits the determination of the fraction of the total number of photons emitted from either bulk states or aggregate states, in the following referred to as x and a, respectively. Using this procedure, we obtain values of $x_{\mathrm{TEH}} = 0.55$ and $a_{\mathrm{TEH}} = 0.45$ for PIFTEH and $x_{\mathrm{TO}} = 0.2$ and $a_{\mathrm{TO}} = 0.8$ for PIFTO, with an error of 10%. This corresponds to a ratio between aggregate to bulk state emission, a/x, which is larger for PIFTO that for PIFTEH films by a factor of 5 thereby causing the observed strong variation in the time-integrated emission spectra for the two materials.

With the knowledge of the values for x and a an estimate can be made for the luminescence efficiencies of the aggregate and bulk state emission, η_a and η_x, from

$$\frac{x}{\eta_x} + \frac{a}{\eta_a} = (1 - q)\frac{1}{\eta}, \tag{1}$$

where η is the PL efficiency of the film and q is the fraction of the excitations initially generated as charged photocarriers which do not contribute to the PL. At the low excitation fluences employed for our measurements (≈30 nJ/cm^2 per pulse) the probability of charge generation in these materials is low so that $q = 0$ can be assumed [15]. Comparing the luminescence efficiencies measured for PIFTEH ($\eta_{\mathrm{TEH}} = 0.36$) and PIFTO ($\eta_{\mathrm{To}} = 0.24$) films [16] it seems also reasonable to assume that a larger contribution of aggregate luminescence (as in PIFTO) leads to a reduction in the luminescence efficiency of the film, and therefore $\eta_a < \eta_x$. Table 1 lists the estimates of the ranges for η_a and η_x in PIFTEH and PIFTO films we obtained using these assumptions, as well as the values for x, a and η listed above.

There are two points to be made about the ranges obtained for the aggregate efficiency η_a in PIFTO and PIFTEH. The first is that the values for η_a must be rather similar in PIFTO and PIFTEH. This leads us to conclude that the differences between PIFTO and PIFTEH regarding the contribution of aggregate emission to the total PL cannot simply be caused by the aggregates in the two materials having a different luminescence efficiency, since this would essentially require the aggregate efficiency in PIFTO to be approximately five times higher that in PIFTEH. The differences between PIFTO and PIFTEH must therefore lie in a variation of the total amount of aggregation present in these materials. The second point is that the aggregate emission efficiency is rather high in these samples even if still lower than the emission efficiency of bulk excitons. Similar results have been presented by Samuel et al. for cyano-polyphenylenevinylene (CN-PPV) whose aggregate-dominated film emission efficiency was found to be relatively high (0.35) but still lower than that of CN-PPV in solution (0.52). If we take an aggregate emission lifetime of $\tau = 550$ ps measured in the low energy end of the PIFTO spectrum (2.1 eV) and assume $\eta_a \approx 0.22$ for PIFTO we obtain a radiative lifetime of $\approx$2.5 ns for PIFTO aggregates [1]. Assuming a radiative lifetime of $\approx$1 ns for bulk excitons [17] this result suggests that the emissive aggregate transition in these materials has a dipole transition strength lower by a factor of $\approx$2–3 than that of the excitonic transition. In general, interaction between two polymer chains leads to a splitting of the exciton state into two non-degenerate states. For a geometry in which the chains are exactly superimposed on each other, the energetically lower state may be expected to be dipole-forbidden due to like parity and therefore act as a trap [9]. However, recent calculations have shown that the large electron–phonon coupling in π-conjugated polymers alters the parity of the aggregate excited state resulting in a non-zero dipole moment for the transition to the ground state [18,19]. Moreover, the strength of the dipole transition from the lowest excited state depends strongly on many configurational factors, such as the interchain separation, the relative chain orientation, the chain (or exciton delocalization) length and the slip fraction or shift between two parallel chains [19,20], some of which can be strongly influenced by the film's casting conditions [8,21]. We conclude that the configurational conditions for aggregates in the polyindenofluorene films we prepare are such that while the efficiency of the aggregate emission is reduced compared to that of bulk excitons, it is still sufficiently high to render these polymers useful as active materials in light-emitting diodes.

Table 1
Ranges estimated for the luminescence efficiencies of aggregates, η_a, and bulk excitons, η_x, in PIFTO and PIFTEH films

	η_x	η_a
PIFTO	0.24–1	0.20–0.24
PIFTEH	0.36–1	0.20–0.36

Note that if the fraction q of initially created charged photocarriers is not zero, this will only result in an increase of both the upper limit to η_a and the lower limit to η_x.

Further information about how the presence of aggregation affects the emission from the polyindenofluorene films can be gained from their time-resolved emission dynamics displayed in Fig. 3. Part A of this figure shows the PL transients for PIFTO both in the spectral region of aggregate emission (2.110 eV) and at the peak of the 0–1 vibronic transition of bulk excitons (2.648 eV). The latter features a fast initial decay with 1/e-time of $\approx$35 ps, followed by a weaker long-lived tail. The initial fast decay of the bulk excitonic

---

[1] Note, however, that we are unable to rule out the possibility of additional longer-lived decay mechanisms due to the experimental limit on the maximum delay for which we can observe the emission.

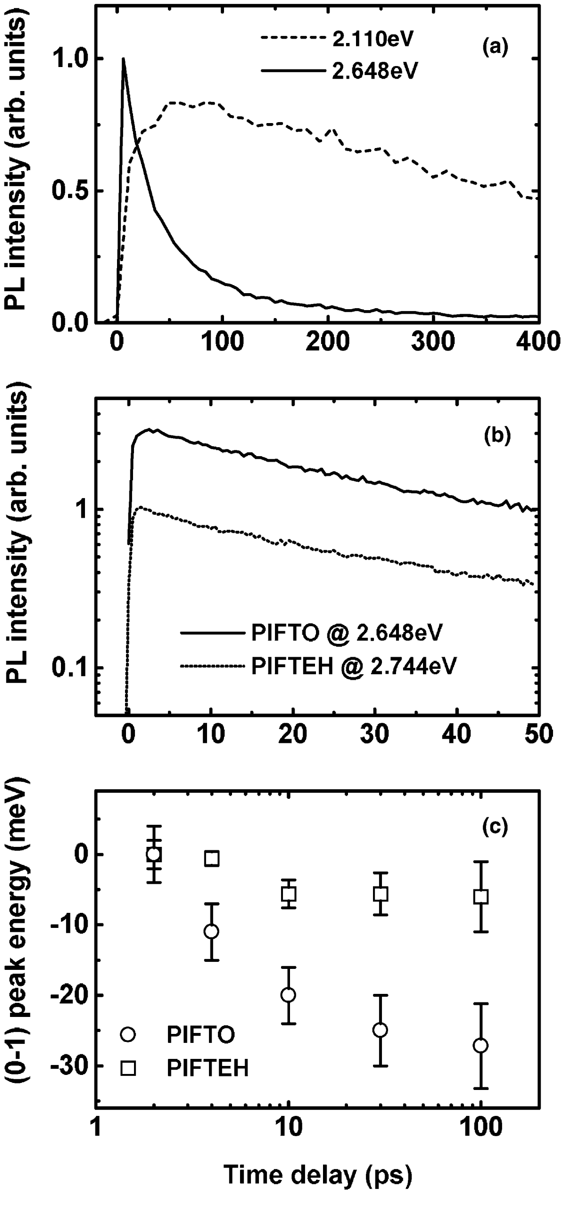

Fig. 3. (a) PL decay for PIFTO in the spectral region of aggregates (2.110 eV) and at the 0–1 vibronic transition of bulk excitons (2.648 eV). (b) PL decay at the 0–1 vibronic transition of bulk excitons for PIFTO and PIFTEH films. (c) Peak position of the 0–1 transition versus time after excitation for PIFTO and PIFTEH films.

emission cannot be due to capture of excitons into non-radiative traps, since the value ranges for η_x given in Table 1 imply a life-time of a few 100 ps for the bulk excitons, if a typical radiative lifetime $\tau_R = 1$ ns is assumed [17]. It must therefore be due to fast transfer of bulk excitons to the energetically lower lying aggregate sites, as supported by the corresponding rise of the emission in the spectral region of the aggregate states.

In Fig. 3b the fast decay of the bulk excitonic emission from PIFTO is compared with that from PIFTEH. Surprisingly, the shapes of the decay curves are almost identical, indicating that the transfer of excitons from bulk (non-interacting) polymer chains to chain aggregates occurs at the same rate in the two materials. Similar behaviour is also observed for the energy relaxation in both polymers, as shown in Fig. 3. The mean energy of the bulk excitonic 0–1 transition peak decreases fast at early times with equilibrium reached between 20 and 40 ps after excitation, which is the time taken for bulk excitons to transfer to aggregate sites. This observation supports the notion of the transfer to aggregate sites being best described as a hopping process of excitons within a Gaussian energy distribution of bulk exciton states with an extended low energy tail due to aggregate states [2,22–24]. Within 30–40 ps the system has energetically relaxed and a large fraction of the bulk excitons has transferred to aggregate sites. We find that this underlying migration of excitons through the Gaussian density of states causes only a slight variation of about 10% and 20% in the luminescence decay times measured for PIFTEH and PIFTO films within a spectral window of 120 meV centred on the (0–1) emission peak. The decay times of 35 ps measured for both samples at the peak of the (0–1) transition therefore reflect the lifetime of bulk excitons with sufficient accuracy.

The identical initial decay of the bulk excitonic emission in PIFTEH and PIFTO seems to imply that the concentration of aggregate traps is very similar for both samples, apparently in contradiction with our previous deduction that PIFTO must contain more aggregates than PIFTEH in order to account for the differences in the shapes of the PL spectra. Indeed, if the aggregate concentration were higher in PIFTO than in PIFTEH a faster decay should be observed due to the increased probability of the bulk exciton to encounter an aggregate site during its hopping migration through neighboring sites. Moreover, the exciton mobility, which is directly connected with the hopping rate, cannot be much different for the two samples as their absorption spectra are very similar [16] indicating a comparable width of the density of states and therefore a similar exciton mobility [22]. However, this apparent contradiction can be resolved considering the results by Blatchford et al. for thin films of poly(*p*-pyridyl vinylene) (PPyV) which indicate that aggregate formation occurs largely within aligned domains of the polymer film [3]. The scenario for PIFTEH and PIFTO films is then best described by domains in which chains are likely to aggregate, embedded in a surrounding of non-interacting chains. Our observation of identical transfer rates from bulk excitonic states to aggregate states in PIFTEH and PIFTO films then implies that the *local* concentration of aggregate states within domains where aggregation is likely to occur is very similar for the two materials. However, the amount or area coverage of these domains must vary between the two films. This assumption is supported by a comparison of the time-integrated aggregate emission spectra (obtained as outlined above) with the time-resolved film emission spectra at 590 ps after excitation, when transfer of bulk excitons to aggregate sites has long been completed (Fig. 4). For PIFTO, the PL spectrum at 590 ps delay resembles closely the aggregate emission spectrum indicating that most of the bulk excitons are created within domains where fast transfer to aggregate sites is likely to occur. In contrast, the PIFTEH PL spectrum at 590 ps after excitation still displays the vibronic features of the bulk exciton emission superimposed on the broad luminescence originating from aggregate states. At long delay times the excitations in PIFTEH therefore consist of two different species, both having lifetimes of a few 100 ps: excitons trapped in aggregate states and bulk excitons created sufficiently far away from aggregate-containing domains to evade trapping into aggregate states during their natural lifetime.

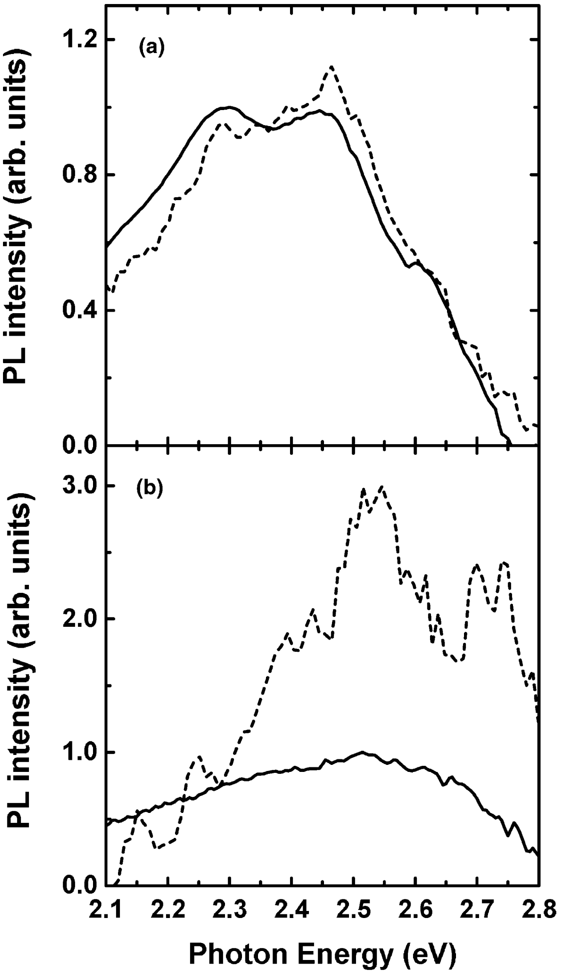

Fig. 4. Time-integrated aggregate emission spectra (solid line) together with the time-resolved PL spectra at 590 ps (dashed line) for PIFTO (a) and PIFTEH (b) films.

4. Conclusion

In summary, we have shown that the spectral differences between the emission from films of polyindenofluorene with different side chains have to be explained in terms of a variation in the extent to which aggregate-containing domains are formed rather than by a variation in the aggregate emission efficiencies between the films. The transfer rate of bulk excitons to aggregate states was determined to be almost identical for the two materials indicating that the local concentration of aggregates within these domains is very similar. PIFTO films must therefore contain a larger total volume of such domains than PIFTEH films, in order to account for the stronger emission from chain aggregates in PIFTO. Our findings are supported by AFM images of PIFTEH and PIFTO film surfaces showing a much more pronounced surface texture for PIFTO than PIFTEH, in accordance with the formation of larger aggregate domains in PIFTO films [16].

Acknowledgements

We gratefully acknowledge financial support by the European Commission (TMR programme 'Ultrafast Quantum Optoelectronics').

References

[1] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks,, C. Taliani, D.D.C. Bradley, D.A.D. Santos, J.L. Brèdas, M. Lögdlund, W.R. Salaneck, Nature 397 (1999) 121.

[2] R.F. Mahrt, T. Pauck, U. Lemmer, U. Siegner, M. Hopmeier, R. Hennig, H. Bässler, E.O. Göbel, P.H. Bolivar, G. Wegmann, H. Kurz, U. Scherf, K. Müllen, Phys. Rev. B 54 (1996) 1759.

[3] J.W. Blatchford, T.L. Gustafson, A.J. Epstein, D.A.V. Bout, J. Kerimo, D.A. Higgins, P.F. Barbara, D.K. Fu, T.M. Swager, A.G. MacDiarmid, Phys. Rev. B 54 (6) (1996) R3683.

[4] I.D.W. Samuel, G. Rumbles, C.J. Collison, Phys. Rev. B 52 (16) (1995) R11573.

[5] M. Yan, L.J. Rothberg, E.W. Kwock, T.M. Miller, Phys. Rev. Lett. 75 (10) (1995) 1992.

[6] U. Lemmer, S. Heun, R.F. Mahrt, U. Scherf, M. Hopmeier, U. Siegner, E.O. Göbel, K. Müllen, H. Bässler, Chem. Phys. Lett. 240 (1995) 373.

[7] G. Kranzelbinder, H.J. Byrne, S. Hallstein, S. Roth, G. Leising, U. Scherf, Phys. Rev. B 56 (1997) 1632.

[8] T.Q. Nguyen, I.B. Martini, J. Liu, B.J. Schwartz, J. Phys. Chem. B 104 (2000) 237.

[9] M. Kasha, Rad. Res. 20 (1963) 55.

[10] R. Jakubiak, Z. Bao, L. Rothberg, Synth. Met. 114 (2000) 61.

[11] S. Setayesh, A.C. Grimsdale, T. Weil, V. Enkelmann, K. Müllen, F. Meghdadi, E.J.W. List, G. Leising, J. Am. Chem. Soc. 123 (2001) 946.

[12] S. Setayesh, D. Marsitzky, K. Müllen, Macromolecules 33 (2000) 2016.

[13] L.M. Herz, R.T. Phillips, Phys. Rev. B 61 (2000) 13691.

[14] L.M. Herz, C. Silva, R.H. Friend, R.T. Phillips, S. Setayesh, B. Becker, D. Marsitzki, K. Müllen, Phys. Rev. B 64 (2001) 1652XX.

[15] C. Silva, A.S. Dhoot, D.M. Russel, M.A. Stevens, A.C. Arias, J.D. MacKenzie, N.C. Greenham, S. Setayesh, K. Müllen, R.H. Friend, Phys. Rev. B 64 (2001) 125211.

[16] C. Silva, D.M. Russell, M.A. Stevens, J.D. Mackenzie, S. Setayesh, K. Müllen, R.H. Friend, Chem. Phys. Lett. 319 (2000) 494.

[17] N.C. Greenham, I.D.W. Samuel, G.R. Hayes, R.T. Phillips, Y.A.R.R. Kessener, S.C. Moratti, A.B. Holmes, R.H. Friend, Chem. Phys. Lett. 241 (1995) 89.

[18] E.M. Conwell, Phys. Rev. B 57 (22) (1998) 14200.

[19] J. Cornil, D.A. dos Santos, X. Crispin, R. Silbey, J.L. Brèdas, J. Am. Chem. Soc. 120 (1998) 1289.

[20] S. Siddiqui, F.C. Spano, Chem. Phys. Lett. 308 (1999) 99.

[21] R. Deans, J. Kim, M.R. Machacek, T.M. Swager, J. Am. Chem. Soc. 122 (2000) 8565.

[22] H. Bässler, in: H. Fritzsche, M. Pollak (Eds.), Hopping and Related Phenomena, World Scientific, Singapore, 1990.

[23] B. Movaghar, M. Grünewald, B. Ries, H. Bässler, D. Würtz, Phys. Rev. B 33 (1986) 5545.

[24] R. Kersting, U. Lemmer, R.F. Mahrt, K. Leo, H. Kurz, H. Bässler, E.O. Göbel, Phys. Rev. Lett. 70 (24) (1993) 3820.