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Ultrafast excitation transfer and trapping in a thin polymer film

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Transient absorption anisotropy of a polythiophene polymer in a thin film was studied on a femtosecond time scale. The anisotropy has a non-exponential decay on the sub-picosecond time scale, with a fastest component characterized by an ~40 fs time constant. To simulate the anisotropy decay an incoherent energy migration model has been used. Comparison between the simulated and experimental kinetics enabled us to estimate the nearest-neighbor pair wise hopping time ($\tau_h = 1 \pm 0.1$ ps), the fraction of the interchain aggregates (~10%) and the structural disorder of the polymer. The initial ~30 fs anisotropy decay does not originate from incoherent hopping energy transfer but from some other relaxation among electronic excited states within a spectroscopic unit.

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INTRODUCTION

Light emitting diodes, large area displays, micro cavities and optically pumped lasers are some of the technological devices that can now be manufactured from organic conjugated polymers.[1–4] To take advantage of the full potential of this class of materials it is vital to gain a detailed understanding of the underlying electronic and optical processes. The photophysical dynamics, such as transport of both neutral and charged excitations, in the polymer devices are greatly influenced by the conformational disorder and the packing of the polymer chains. Close packing and high regularity of polyalkylthiophenes have been observed to lead to high mobility of charge carriers,[5] which can be an advantage in, for instance, transistors.[6] For photoluminescence, on the other hand, close packing leads to quenching of the luminescence[7–9] by nonemissive or less emissive states such as charged excitations,[9–11] interchain aggregates,[8,12,13] and excimers.[14]

The packing of regular polymers in thin film has been explored using x-ray diffraction,[15,16] which gives a good understanding of the size of the polymer chains, the distance between them and the organizing of the polymers into micro crystals in the material. The excitation energy and charge migration in thin films of different PPV's has been modeled extensively using incoherent hopping dynamics[17–20] and less abundantly as a correlated quantum mechanical propagation of an electron-hole pair coupled to a classical nuclear bath.[21,22] Others have predicted the polymer chain conformations using single molecule spectroscopy,[23] while we recently have investigated the conformational disorder and excitation energy migration of polymers in solution.[24,25]

Here we seek to predict the conformational disorder of the polymer chains in a thin film of polythiophene polymers by probing the excitation dynamics. We investigate the transient absorption anisotropy decay in a thin film of closely packed and highly irregular polythiophene polymers over a time range of 20 ps with ~10 fs resolution. In general, the dynamics of the transient absorption anisotropy provides information about the motion of transition dipole moments (rotation), here particularly such which are induced by excitation energy migration between differently oriented chromophoric sites on the polymer chain (spectroscopic units). Thus, from the experimentally measured anisotropy dynamics one can receive information about the time scale of the energy transfer process, the length of the excitation migration path and the conformational disorder of the polymer chains in the polymer film. We simulate these processes on computer generated polymer geometries, which are generated by a partially correlated random walk algorithm. The used model describes the energy transport as an incoherent hopping (Förster). By these simulations the pair wise hopping time, the extent of kinks in the polymer chain and the filling factor of the polymer film have been fitted to the measured data for times larger than 100 fs. On the short time scale (<100 fs) an ultrafast component with a time constant around 37 ±5 fs has been found which could not be explained in the framework of the incoherent Förster type hopping.

EXPERIMENTAL

Poly[3-(4-octylphenyl).-(2,2′)-bithiophene] [PTOPT shown in the inset of Fig. 1(a)] was dissolved in chloroform, and spin coated onto a thin glass slide. The synthesis of PTOPT has been described by Andersson *et al.*[26] The time-resolved experiments were performed using a femtosecond transient absorption spectrometer with 20–30 fs light pulses. Light pulses of <150 fs duration at λ = 775 nm were generated by a commercial Clark MXR CPA-2001 laser system based on an ErF/SErF fiber oscillator and a Ti:sapphire regenerative amplifier, pumped by the second harmonic of a Nd:YAG laser operating at 1 kHz. A fraction of ~200 μJ from the 900 μJ output was used to pump a dual noncollinear optical parametric amplifier (NOPA) (Ref. 27) for generation of pump and probe pulses at different wavelengths. The excitation wavelength was 500 nm (close to the PTOPT absorption maximum 0-1 transition) with a spectral width of 17 nm (FWHM) and the probe wavelength was 570 nm (bleaching 0-0 transition) with 32 nm width.

Both pump and probe pulses were compressed to 25 and 21 fs, respectively, by two glass prism compressors. The cross correlation between pump and probe pulses was used

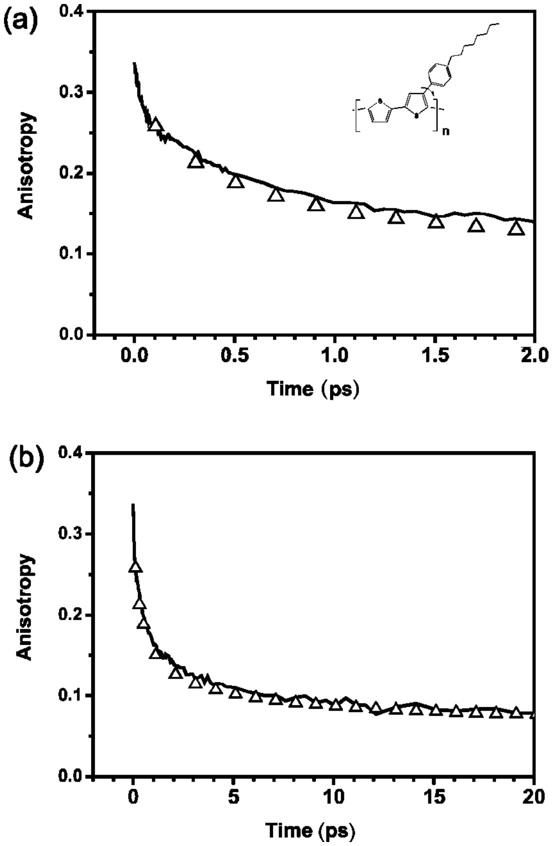

FIG. 1. The experimental (full line) and simulated (triangles) anisotropy of PTOPT in a thin film on a 2 ps (a) and a 20 ps (b) time scale. The structure of PTOPT is shown in (a).

as response function[28] and was measured by sum frequency generation using a 30 μm BBO type I crystal. The duration of the cross correlation was 35 fs (FWHM). The intensity of pump pulses were decreased to $\sim$20 μJ/cm^2 by reflections from beam splitters. The probe pulses were divided into two sets of probe and reference pulses and the intensity of each pulse was decreased to 1% of the pump pulse intensity. No dependence on probe intensity was observed in this intensity region.

Differential absorption and transient anisotropy measurements were performed by setting a 45° angle between the pump and probe pulse polarizations, detecting the probe components parallel $\Delta A_{||}$ and perpendicular $\Delta A_{\perp}$ to the pump polarization simultaneously but independently. Because $\Delta A_{||}$ and $\Delta A_{\perp}$ were measured using components of the same initial pulses, carrying the same fluctuations, the anisotropy $r(t)=(\Delta A_{||}-\Delta A_{\perp})/(\Delta A_{||}+2\Delta A_{\perp})$ was measured with a very high signal to noise ratio.

COMPUTER SIMULATIONS

The simulations consist of two stages, first representations of the polymer film are generated and then the anisotropy decays are calculated for the excitation transfer within and between the polymer chains making up the film. The polymer chains are constructed from bithiophene units [inset of Fig. 1(a)] using a Monte Carlo self-avoiding random walk. In the calculations the excitation is assumed to be delocalized over several bithiophenes, which form a spectroscopic unit. The mean value for the number of bithiophenes per spectroscopic unit was determined to be 3.[29] When building the polymer chain, a vector assigned to each bithiophene defines the direction of the transition dipole moment which is assumed to be along the polymer chain. The length of this vector corresponds to the size of a bithiophene unit. Assuming a harmonic bending potential,[30] the direction vectors of the bithiophene units are selected randomly within a Gaussian distribution. Assuming a bithiophene unit direction vector the next direction vector is calculated by weighting the old vector with three new Cartesian coordinates chosen separately from Gaussian distributions. The width of the Gaussian distribution is the disorder parameter, which determines the range of conformations for the polymers. In our case we have used the same width for all three directions. The side chains of the bithiophenes in PTOPT induce a steric hindrance that prohibits close contact between the polythiophene backbone(s) of the polymer chain(s). In the program this is implemented as a nearest distance constraint, so that two non-neighboring chain links cannot be closer to each other than 4 Å, whether parts of the same polymer chain or different chains. This distance has been estimated from the chemical structure and the crystallographic data of similar but more ordered polymers in a thick film and in powder.[15] The computer realization of the film was generated adding polymer chains, unit by unit, into a small volume with periodic boundary conditions. Ideally the lengths of the polymer chains were $\sim$50 bithiophene units long, in accord with size exclusion chromatography measurements of the polymer.[26] However, we had to allow for shorter chains in order to reach a filling factor resembling the realistic density of a crystalline polythiophene in a thick film (1.05 g/cm^{-3}),[15] while not violating the nearest distance constraint.

The simulation of the energy transfer kinetics was performed assuming a Förster type incoherent hopping mechanism which previously has been used with success to model excitation transfer in polymers.[17–20,24,25] Each bithiophene of a spectroscopic unit interacts with the bithiophenes of every other spectroscopic unit in the polymer film. The lengths of the spectroscopic unit are based on comparison between the luminescence spectrum of the polymer in thin film with spectra of oligothiophenes.[29] The orientation and position of the single bithiophene within a spectroscopic unit is thus needed, even though the excitation is assumed to be delocalized over a spectroscopic unit. This ‘‘line-dipole’’ approximation is a refinement of the raw point-dipole approximation, where a spectroscopic unit is assigned with just one dipole moment and the distance given by the center of mass of the spectroscopic unit. The ‘‘line-dipole’’ approximation can be seen as a first step to use a more realistic interaction law. A more sophisticated approach would be using transition density cubes, which has been employed by Krueger *et al.* for calculating interactions between carotenoid and bacteriochlorophyll.[31] This, however, would require computationally intensive quantum chemical calculations, whereas the correction would not be significant.[32] The theoretical and computational method used here follows that outlined by Pullerits and Freiberg.[33]

The Master equation describing excitation dynamics among the spectroscopic units in polymer film can be represented on a matrix form

$$\dot{P}(t) = \mathbf{R}P(t). \tag{1}$$

$P(t)$ is the vector of the spectroscopic unit population and $\mathbf{R}$ is an $N \times N$ rate matrix, where N is the number of spectroscopic units in one calculation. We point out that there are more than one polymer chain in one polymer calculation, and that we make use of periodic boundary conditions in rate matrix $\mathbf{R}$. Equation (1) can be solved using a Green function formalism[33]

$$P(t) = \mathbf{G}(t)P(0), \tag{2}$$

where $P(0)$ denotes the vector of the initial distribution of excitations and the Green function matrix $\mathbf{G}(t)$ can be expressed via the matrix $\mathbf{R}$'s eigenvectros and eigenvalues, which are found numerically. After averaging over all possible spatial orientations of the sample volume we can express $\Delta A_{||}$ and $\Delta A_{\perp}$ as

$$\Delta A_{||}(t) = \sum_{ij} A_i(\nu_{\text{rec}})(1 + 2\cos^2\alpha_{ij})G_{ij}(t)A_j(\nu_{\text{exc}}), \tag{3}$$

$$\Delta A_{\perp}(t) = \sum_{ij} A_i(\nu_{\text{rec}})(2 - \cos^2\alpha_{ij})G_{ij}(t)A_j(\nu_{\text{exc}}), \tag{4}$$

where α_{ij} is the angle between the transition dipole moments on site i and site j. The parameters used in the rate matrix (Stokes' shift 1000 cm^{-1} and inhomogeneous broadening 600 cm^{-1}) are estimated from steady state spectra and the magic angle (isotropic) transient absorption decay.

The fact that the side chains of PTOPT sit on every other thiophene monomer on the backbone, allows for close face-to-face packing of the monomers/spectroscopic units on different chains with the distance of 4–5 Å mentioned earlier. Pairs of spectroscopic units with such small distances are called interchain aggregates and are in PTOPT found to emit at longer wavelengths with a longer photoluminescence lifetime than the normal non-aggregated sites.[8] In this way the interchain aggregates act as luminescence quenchers. In our simulations inter-chain aggregates are added extrinsically, as "traps" with a longer luminescence lifetime than the normal sites and with a lower absorption and emission yield. The hopping rate from a normal spectroscopic unit to a trap was calculated the same way as the rate between spectroscopic units, whereas the detrapping rate was set to zero. The radiative lifetimes of both normal nonaggregate and interchain aggregate sites are taken from the literature,[8] while the remaining level of the magic angle signal on the >100 ps time scale determines the fraction of interchain aggregates.

The fitting parameters obtained from the simulation are the hopping time (τ_{hp}), which is the Förster transfer time for adjacent spectroscopic units in a straight line and with equal energy, the disorder parameter mentioned above, and the fraction of interchain aggregates. The first two parameters can be determined independently since the disorder parameter mainly affects the remaining degree of anisotropy at long times, while the hopping time (τ_{hp}) rules the overall dynamics of the magic angle and anisotropy decays.

The computer simulated magic angle and anisotropy decays are averaged over hundred different realizations of the polymer geometry for a given disorder parameter. For each realization the hopping transfer is averaged over one thousand different energetic distributions of spectroscopic units.

RESULTS AND DISCUSSION

In Fig. 1(a) the first 2 ps of the experimental anisotropy decay is shown (full line) together with the calculated anisotropy of a computer generated polymer film (triangles). The initial value of the experimental anisotropy 0.33 is considerably lower than the theoretical maximum for a two-level system, which is 0.4. This difference is most likely due to an unresolvably fast component (~ 10 fs) in the anisotropy decay. Within the first 100 fs the anisotropy decays to a value of 0.25 with a corresponding time constant of 37 ± 5 fs.

Transfer processes with time-constants under ~ 50 fs correspond to strong electronic couplings. Consequently these processes are not well described by Förster incoherent hopping theory. This becomes apparent by the inability to reproduce the very fast initial part of the anisotropy decay by the computer simulations, while using realistic parameter values. Therefore we assign the fast component to a process which occurs within a spectroscopic unit. In molecular aggregates it has been predicted that due to the coupling between electronic and nuclear degrees of freedom, changes in the delocalization properties of excited state may occur within a single vibrational period (e.g., 25 fs for a 1200 cm^{-1} mode).[34,35] In addition to the changes in localization/delocalization, also the relaxation between the collective excited states of an aggregate, in the current context a spectroscopic unit, can take place at these timescales.[36,37] Processes such as these will lead to changes in the observed transition dipole moments and corresponding anisotropy decay. It is worth noting that in films of PDOPT, a similar but more crystalline polythiophene, the transient anisotropy takes on the initial value of 0.4 and decays more slowly.[38] In the following we will not further address the initial ~ 40 fs component of the anisotropy decay. We will focus on the kinetics after 100 fs, which can be described as incoherent hopping dynamics.

After cutting off the first 100 fs of the decay we can use rescaled anisotropy kinetics for our simulations. The experimental and calculated anisotropies are shown in Figs. 1(a) and 1(b) for different time scales. The simulated anisotropy reproduces the (rescaled) experimental anisotropy very well, yielding a pair wise hopping time for two adjacent spectroscopic units of 1 ± 0.1 ps. For PDOPT in solution the hopping time we found was approximately two times longer.[24,40] This variation can be explained by the different refractive indices in film and solution.

A typical realization of the polymer geometry as sug-

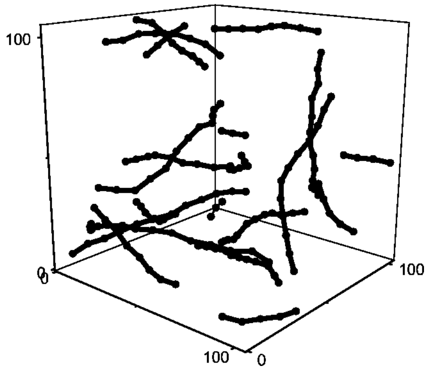

FIG. 2. A possible volume sample of PTOPT in a thin film. Distances given in Å.

gested by the simulations, is shown in Fig. 2. A small volume of 100^3 Å^3 is shown featuring bits of the polymer chains, while the full lengths of the polymers typically lie around 400 Å, acquired in the simulations by applying periodic boundary conditions. The obtained polymer geometries resemble those of PDOPT in solution, however, slightly more curved with a somewhat higher disorder parameter.

The presently predicted structural conformations of PTOPT in film are qualitatively different from those predicted for MEH-PPV's.[25] For MEH-PPV's it has been suggested that defects in the polymerization have the effect of breaking the conjugataion in the polymers,[23] resulting in a "stick" model for MEH-PPV with stiff conjugated segments connected at sharp angles. The polythiophene chains, on the other hand, seem to be smoothly curved. There exist no hints for a break of the conjugation in the polythiophenes; neither by interjectional single bonds between the thiophene monomers nor by deformed thiophene rings. Both would result in sharp kinks as in MEH-PPV. On the contrary, according to quantum chemical calculations[32] a twisting or bending of an intact polythiophene chain will only result in a weakening of the conjugation, i.e., a gradual loss of conjugation along the chain, but no strict geometrical segmentation into spectroscopic units. The difference may have a consequence for how well the hopping model describes the motion of the excitation along the polymer chain for polythiophenes. The hopping model is based on the assumption that the dipole moments are well defined by the polymer geometry. The findings that there may not be a well defined break in conjugation suggest that in reality a model for anisotropy decay in polythiophenes should take into account effects of changes of the dipole moment within a spectroscopic unit.

In Figs. 3(a) and 3(b) are shown the measured (full line) and simulated (dashed line) magic angle transient absorption decay for different time scales. It turned out to be difficult to reproduce the energy dissipation exactly in our simple model. Nevertheless, it is still possible to estimate the fraction of interchain aggregates to approximately one tenth by fitting the remaining level of the magic angle decay at times longer than 100 ps. A decay for a film without long lived weakly luminscent sites would reach a zero base line.

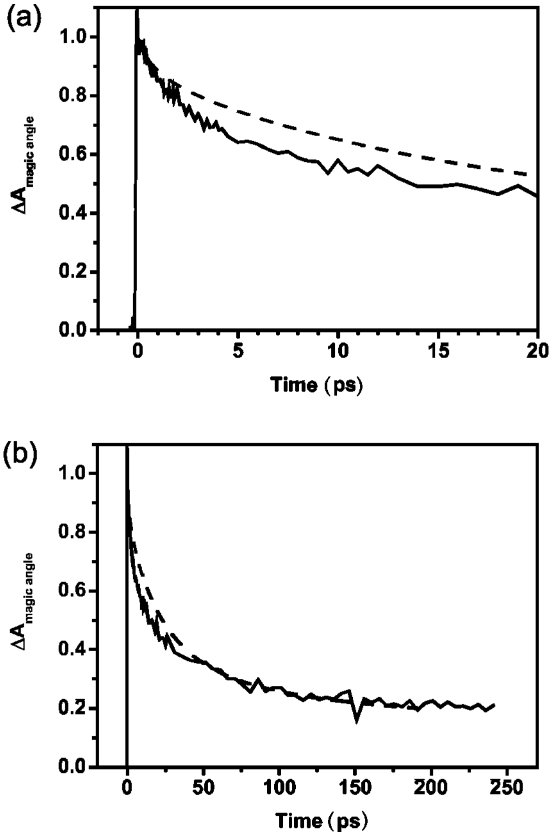

FIG. 3. The normalized experimental (full line) and simulated (dashed) magic angle decay of PTOPT in a thin film on a 20 ps (a) and a 250 ps (b) time scale.

SUMMARY

The experimental transient anisotropy of the thiophene based polymer PTOPT in a thin film has been measured up to 20 ps with a time resolution of 10 fs. The anisotropy decay within the first 100 fs was assigned to ultrafast changes in the delocalization properties of the initially created excitation and/or electronic relaxation within a spectroscopic unit. This ultrafast phase of the dynamics indicates the need for using a quantum stochastic approach[39] to fit the coherent-incoherent fs anisotropies in forthcoming studies of disordered polymers. The slower parts of the anisotropy (>100 fs) were simulated for computer generated polymers resembling the thin film using a kinetic model based on Förster type hopping mechanism for the excitation migration. The anisotropy simulations have revealed the conformational disorder of the polymer chains. Furthermore, the simultaneous simulations of the magic angle decays made it possible to estimate the amount of luminescence quenching interchain aggregates in the film.

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[1] M. R. Andersson, M. Bergren, G. Gustafsson, T. Hjertberg, O. Inganäs, and O. Wennerström, Synth. Met. **71**, 2183 (1995).

[2] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, and A. B. Holmes, Nature (London) **347**, 539 (1990).

[3] G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, Nature (London) **357**, 477 (1992).

[4] O. Inganäs, M. Bergren, M. Andersson, G. Gustafsson, T. Hjertberg, O. Wennereström, P. Dyreklev, and M. Granström, Synth. Met. **71**, 2121 (1995).

[5] R. Österbacka, C. P. An, X. Jiang, and Z. Vardeny, Science (Washington, DC, U.S.) **287**, 839 (2000).

[6] H. Sirringhaus, N. Tessler, and R. H. Friend, Science (Washington, DC, U.S.) **280**, 1741 (1998).

[7] M. Theander, W. Mammo, T. Olinga, M. Svensson, M. R. Andersson, and O. Inganäs, J. Phys. Chem. B **133**, 7771 (1999).

[8] A. Ruseckas, E. Namdas, M. Theander, M. Svensson, A. Yartsev, D. Zigmantas, M. R. Andersson, O. Inganäs, and V. Sundström, J. Photochem. Photobio. A (to be published).

[9] A. Ruseckas, M. Theander, M. R. Andersson, M. Svensson, M. Prato, O. Inganäs, and V. Sundström, Chem. Phys. Lett. **322**, 136 (2000).

[10] G. H. Gelinck, J. M. Warman, and E. G. J. Staring, J. Phys. Chem. **100**, 5485 (1996).

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

[12] J. W. Blatchford, T. L. Gustafson, A. J. Epstein, D. A. VandenBout, J. Kerimo, D. A. Higgins, P. F. Barbara, D.-K. Fu, T. M. Swager, and A. G. MacDiarmid, Phys. Rev. B **54**, R3683 (1996).

[13] U. Lemmer, S. Heun, R. F. Mahrt, U. Scerf, M. Hopmeier, U. Signer, E. O. Göbel, K. Müller, and H. Bässler, Chem. Phys. Lett. **240**, 373 (1995).

[14] S. A. Jenehke and J. A. Osaheni, Science (Washington, DC, U.S.) **265**, 765 (1994).

[15] K. E. Asmundtveit, E. J. Samuelsen, W. Mammo, M. Svensson, M. R. Andersson, L. A. A. Petterson, and O. Inganäs, Macromolecules **33**, 5481 (2000).

[16] C. Y. Yang, F. Hide, M. A. Díaz-García, A. J. Heeger, and Y. Cao, Polymer **39**, 2299 (1998).

[17] K. Brunner, A. Tortschanoff, C. Warmuth, H. Bässler, and H. F. Kauffmann, J. Phys. Chem. B **104**, 3781 (2000).

[18] R. Kersting, B. Mollay, M. Rusch, J. Wenisch, G. Leisning, and H. F. Kauffmann, J. Chem. Phys. **106**, 2850 (1997).

[19] B. Mollay, U. Lemmer, R. Kersting, R. F. Mahrt, H. Kurz, H. F. Kauffmann, and H. Bässler, Phys. Rev. B **50**, 10 769 (1994).

[20] M. Scheidler, U. Lemmer, R. Kersting, S. Karg, W. Riess, B. Cleve, R. F. Mahrt, H. Kurz, H. Bässler, E. Göbel, and P. Thomas, Phys. Rev. B **54**, 5536 (1996).

[21] M. N. Kobrak and E. R. Bittner, J. Chem. Phys. **112**, 5399 (2000).

[22] M. N. Kobrak and E. R. Bittner, J. Chem. Phys. **112**, 7684 (2000).

[23] D. Hu, J. Yu, K. Wong, B. Bagchi, P. J. Rossky, and P. F. Barbara, Nature (London) **405**, 1030 (2000).

[24] M. M.-L. Grage, T. Pullerits, A. Ruseckas, M. Theander, O. Inganäs, and V. Sundström, Chem. Phys. Lett. **339**, 96 (2001).

[25] M. M.-L. Grage, P. Wood, A. Ruseckas, T. Pullerits, W. Mitchell, P. L. Burn, I. D. W. Samuel, and V. Sundström, J. Chem. Phys. (to be published).

[26] M. R. Andersson, T. Olinga, W. Mammo, M. Svensson, M. Theander, and O. Inganäs, J. Mater. Chem. **9**, 1993 (1999).

[27] T. Wilhelm, J. Piel, and E. Riedle, Opt. Lett. **22**, 1494 (1997).

[28] W. Demtröder, *Laser Spectroscopy: Basic Concepts and Instrumentation* (Springer-Verlag, Berlin, 1996).

[29] R. A. J. Janssen, L. Smilowitz, N. Saricifti, and D. Moses, J. Chem. Phys. **101**, 1787 (1994).

[30] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics and Polymer Physics* (World Scientific, Singapore, 1990).

[31] B. P. Krueger, G. D. Scholes, and G. R. Fleming, J. Phys. Chem. **102**, 5378 (1997).

[32] W. J. D. Beenken (private communication).

[33] T. Pullerits and A. Freiberg, Biophys. J. **63**, 879 (1992).

[34] W. J. D. Beenken, M. Dahlbom, P. Kjellberg, and T. Pullerits, J. Chem. Phys. **117**, 5810 (2002).

[35] M. Dahlbom, W. Beenken, V. Sundström, and T. Pullerits, Chem. Phys. Lett. **364**, 556 (2002).

[36] M. Dahlbom, T. Pullerits, S. Mukamel, and V. Sundström, J. Phys. Chem. B **105**, 5515 (2001).

[37] T. Pullerits, J. Chin. Chem. Soc. (Taipei) **47**, 773 (2000).

[38] A. Ruseckas, M. Theander, L. Valkunas, M. R. Andersson, O. Inganäs, and V. Sundström, J. Lumin. **76&77**, 474 (1998).

[39] T. S. Rahman, R. S. Knox, and V. M. Kenkre, Chem. Phys. **44**, 197 (1979).

[40] The simulations in Ref. 24 were for the high-temperature limit, yielding a pair wise hopping time of ~1.3 ps. The pair wise hopping time for PDOPT in solution calculated at room temperature is ~2 ps.