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Exciton dynamics in supramolecular assemblies of *p*-phenylenevinylene oligomers

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Abstract

We have investigated the dynamics of photoexcitations in chiral assemblies of *p*-phenylenevinylene oligomers functionalized with hydrogen-bonding motifs. In the regime of low excitation densities, the luminescence transients are influenced by the migration of excitons to defect sites, indicative of fast diffusivity of excitons along the molecular assemblies. In addition, at high excitation densities, bimolecular exciton annihilation is shown to result in the fast depopulation of the stacks' excitonic energy levels.

Keywords: Oligo(phenylenevinylene)s; Photoluminescence; Time-resolved optical spectroscopy; Self-assembly

1. Introduction

Conjugated polymers [1] and organic molecules [2] have been the subject of intense research over the past decade, stimulated by their successful implementation as active materials in optoelectronic devices. While conjugated polymers feature good processability and therefore low cost of manufacture, conjugated molecules benifit from a well-defined chemical structure which allows the formation of ordered structures with high charge-carrier mobilities. Recent work has sought to combine the advantages of high intermolecular order and ease of processing by design of molecular systems which self-organize into supramolecular structures [3–5]. One novel approach employs a combination of hydrogen-bonding and solvophobic effects to assemble organic molecules reversibly into helical polymeric structures [6,7]. Here we report on our investigations into the dynamics of photoexcitations in helical stacks of MOPV4, a π-conjugated oligo(*p*-phenylenevinylene) derivative with chiral side-chains and hydrogen-bonding ureidotriazine units (Fig. 1) .

2. Experimental

The synthesis and characterization of MOPV4 had been outlined elsewhere [7]. MOPV4 was dissolved in dodecane and the solution held in a cuvette within a temperature-controlled mount. In order to study the dynamics of photoexcitations at low (1.7×10^{-5} excitons per MOPV4 molecule) and at high (≈0.0061–0.082 excitons per MOPV4 molecule) excitation densities, we have conducted both time-resolved photoluminescence (PL) and pump–probe experiments, respectively.

All time-resolved PL measurements were taken for solution concentrations of $2.5 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$ using the femtosecond up-conversion technique. A detailed description of the set-up has been published elsewhere [8,9]. Briefly, MOPV4 was excited with the frequency-doubled output from a mode-locked Ti:Sapphire laser supplying 200 fs pulses at a photon energy of 3.06 eV. Photoluminescence emerging at right angle to the exciting beam was collected with a pair of off-axis paraboloids and up-converted in a β-barium borate (BBO) crystal using the fundamental laser beam as a gate. Since only the vertically polarized component of the emitted PL could be upconverted, the excitation polarization was rotated with help of a $\lambda/2$-plate and a Glan–Thompson polarizing prism to permit measurement of the PL polarized either parallel or perpendicular to the polarization of the exciting light. The overall temporal resolution of the system was approximately 350 fs. To take

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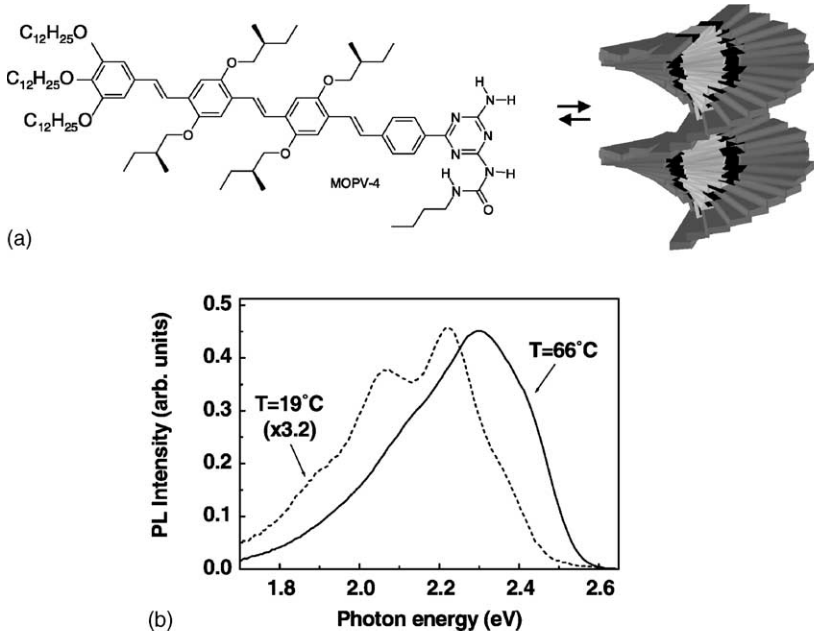

Fig. 1. (a) Chemical structure of MOPV4 together with a schematic representation of the chiral stacks formed from dimerized MOPV4 in dodecane solution. (b) Time-integrated photoluminescence spectra of MOPV4 in dodecane for two solution temperatures.

time-integrated PL spectra the vertical polarization component was selected with a Glan–Thompson polarizing prism and dispersed in a double-grating spectrometer (Spectromate 1680). The PL was detected with a Si-photodiode using a lock-in technique, and corrected for spectral response taking a black-body emitter as a reference.

For time-resolved pump–probe measurements, 100 fs pulses at a 1 kHz repetition rate were derived from a home-built amplified Ti:Sapphire laser system. The pump beam at 3.06 eV was created from second-harmonics generation in a 0.5 mm thick BBO crystal and focussed to a 125 μm waist diameter in the centre of a 1 mm path of solution of MOPV4 (at a concentration of $4.1 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$). The weaker probe beam consisted of a white-light continuum created by part of the amplifier output in a 2 mm thick sapphire plate, and was focussed to a 50 μm waist in the same solution region. Both pump and probe beams were linearly polarized in the horizontal plane. Measurements of the fractional change in probe transmission due to the pump pulse ($\Delta T/T$) were made by detecting a spectrally narrow part of the probe light transmitted through the solution, and that of a reference beam using a pair of Si photodiodes and a lock-in technique. Pump fluences used ranged from 20 to 700 $\mu\mathrm{J\,cm^{-2}}$ corresponding to excitation densities of ≈0.0061–0.082 excitons per MOPV4 molecule.

3. Results and discussion

The associative properties of MOPV4 have been discussed in detail by Schenning et al. [7]. It was shown that in dodecane, MOPV4 molecules dimerize via quadrupole hydrogen bonding between ureidotriazine units and subsequently form chiral stacks as a consequence of solvophobic effects and π–π interactions (see Fig. 1a for illustration). The stacking of MOPV4 dimers was found to be reversible: as the solvent temperature was raised past a “transition temperature” T_c, the assemblies increasingly began to dissociate, until at a temperature $T \gg T_c$ only monomeric and dimeric species remained. The transition temperature was demonstrated to increase with increasing concentration of MOPV4; for a concentration of $2.5 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$ T_c was found to be approximately 65 °C [10].

Fig. 1b displays the time-integrated PL spectra of MOPV4 in dodecane at 19 and 66 °C for a co-linear polarization of the exciting and the detected light. As the solvent temperature is lowered the photoluminescence intensity is strongly reduced, while the average energy of the emitted photons decreases. This red-shift of the photoluminescence is a direct consequence of the π-stacking of *p*-phenylenevinylene oligomers: the delocalization of excitons across more than one molecule leads to a splitting of the excitonic levels [11] with recombination occuring predominantly from the energetically lowest state into which the exciton quickly relaxes.

In Fig. 2, the decay of the time-resolved photoluminescence at 2.226 eV is shown for the same polarization conditions as outlined above. At high temperatures (66 °C) MOPV4 exists largely in its monomeric or dimeric form and the luminescence decay within the first few hundred picoseconds is mono-exponential with a time constant of 1.013 ns. However, as the solution temperature is reduced, the PL decay assumes a strongly non-exponential form with a fast (≈20 ps) initial followed by a long-lived decay over a few hundred picoseconds. At the low excitation densities

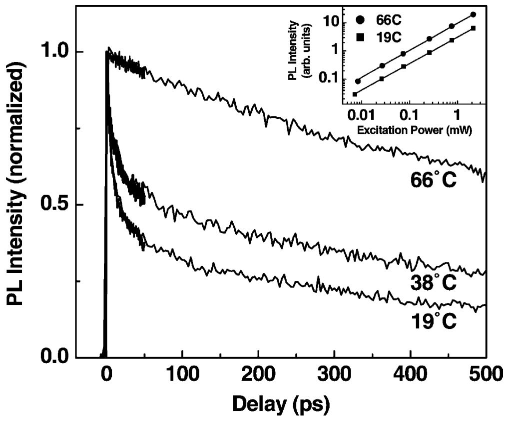

Fig. 2. Photoluminescence decay dynamics of MOPV4 in dodecane at 2.226 eV for various solution temperatures. The inset shows the time-integrated PL intensity at 2.214 eV as a function of excitation power, together with fits assuming a power law. (An excitation intensity of 1 mW here corresponds to a creation of 4.85×10^{-5} excitons per MOPV4 molecule per pulse.)

employed in the time-resolved PL experiments, it is highly unlikely that these dynamics are affected by non-linear phenomena, such as bi-molecular exciton annihilation. This is underlined by the excitation-power dependance of the time-integrated PL intensity, measured at a photon energy of 2.214 eV (Fig. 2, inset). The dependence of the PL intensity I_{PL} on the excitation power I_{ex} can be approximated by a power law, $I_{\mathrm{PL}} = aI_{\mathrm{ex}}^{n}$ with $a = 3.11$ for a solution temperature of $T = 19\,^{\circ}\mathrm{C}$, $a = 9.68$ for $T = 66\,^{\circ}\mathrm{C}$ and $n = 0.94 \pm 0.02$ ($T = 19\,^{\circ}\mathrm{C}$), $n = 0.96 \pm 0.02$ ($T = 66\,^{\circ}\mathrm{C}$) the latter two values being identical within the experimental error. As we have outlined in a previous study, the PL decay dynamics in the regime of low excitation density are instead strongly influenced by the migration of excitons along the stacking direction of the MOPV4 assemblies [12]. Two main mechanisms are responsible for the observed fast initial decay. Firstly, the existence of non-radiative traps within some of the MOPV4 molecules will lead to an efficient quenching of the PL as excitons migrate along the MOPV4 assemblies. Such traps may for instance be introduced as a result of carbonyl substitution on the vinyl group under the exposure of the compound to oxygen. This mechanism has previously been shown to create strong quenching sites in thin films of poly(phenylenevinylene) [13,14]. Secondly, a detailed study of the PL polarization anisotropy as a function of time after excitation revealed a fast depolarization of the emitted photoluminescence following excitation with linearly polarized light [12]. This is a direct consequence of the helical nature of the stacks: if the exciting light is propagating along the stacking axis, MOPV4 molecules whose dipole moments are oriented parallel to the polarization of the light are more likely to be excited, resulting in a periodically varying excitation density along the stacks. This anisotropic distribution of excitations will in turn cause the initially emitted luminescence to be partly polarized. However, as the excitations diffuse along the stacks, their dipole moments will turn about the stacking axis resulting in the depolarization of the photoluminescence.

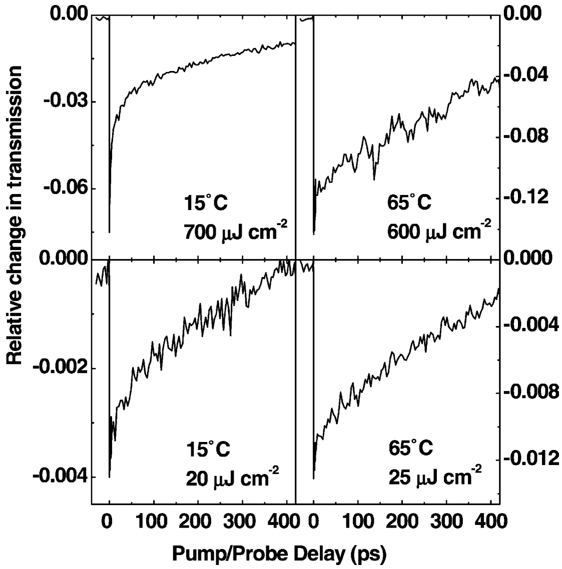

Fig. 3. Fractional change in probe transmission due to the presence of the pump pulse, measured at a probe photon energy of 1.459 eV for different pump fluences and temperatures of the MOPV4 solution. (At a pump fluence of 20 μJ an excitation density of 0.0061 excitons is created per MOPV4 molecule per excitation pulse.)

Fig. 3 shows differential transmission transients at a probe energy of 1.459 eV, measured for MOPV4 solutions both at high (top) and at low (bottom) excitation densities, for a temperature at which MOPV4 assemblies are formed (15 °C, left) and for a temperature at which MOPV4 stacks have largely dissociated (65 °C, right). We assign these negative differential transmission signals to the photoinduced absorption from excitons created by the pump pulse [15], that is, the measured transients reflect the time-dependence of the exciton population in the high density regime. At high (65 °C) solution temperatures, the transients show very little variation with exciton density (Fig. 3, right column). However, at a solution temperature of 19 °C, at which MOPV4 forms helical assemblies (Fig. 3, left column) the shape of the transients changes markedly with excitation power. As the density of excitons is increased, a fast initial decay is observed which we attribute to bimolecular exciton annihilation. The formation of MOPV4 stacks should increase the occurance of bimolecular interactions both through an enhancement of the diffusivity of the excitons due to the π-stacking of molecules and through closer proximity of molecules in the stacks supporting exciton annihilation via the Förster transfer mechanism [16,17]. A detailed model of the mechanisms involved in the exciton bimolecular annihilation is in progress.

4. Conclusion

We have studied the dynamics of photoexcitations in supramolecular stacks of a *p*-phenylenevinylene derivative, both in the high and the low density regime. In both cases, the measured transients are indicative of fast exciton diffusion along the MOPV4 stacks. In the low density regime, exciton diffusion is found to result in photoluminescence depolarization and the trapping of excitons at chemical defects, while in the high density regime, in addition, bimolecular exciton annihilation occurs. In both density regimes, the exciton dynamics observed in MOPV4 stacks are reminiscent of those encountered in thin films of poly(phenylenevinylene) [13,17].

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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] M.D. Watson, A. Fechtenkötter, K. Müllen, Chem. Rev. 101 (2001) 1267.
[3] L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R.H. Friend, J.D. MacKenzie, Science 293 (2001) 1119.
[4] V. Percec, M. Glodde, T.K. Bera, Y. Miura, I. Shiyanovskaya, K.D. Singer, V.S.K. Balagurusamy, P.A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S.D.H.H. Duan, Nature 419 (2002) 384.
[5] D.B.A. Rep, R. Roelfsema, J.H. van Esch, F.S. Schoonbeek, R.M. Kellogg, B.L. Feringa, T.T.M. Palstra, T.M. Klapwijk, Adv. Mater. 12 (2000) 563.
[6] J.H.K.K. Hirschberg, L. Brunsveld, A. Ramzi, J.A.J.M. Vekemans, R.P. Sijbesma, E.W. Meijer, Nature 407 (2000) 167.
[7] A.P.H.J. Schenning, P. Jonkheijm, E. Peeters, E.W. Meijer, J. Am. Chem. Soc. 123 (2001) 409.
[8] L.M. Herz, R.T. Phillips, Phys. Rev. B 61 (2000) 13691.
[9] L.M. Herz, C. Silva, R.T. Phillips, S. Setayesh, K. Müllen, Chem. Phys. Lett. 347 (2001) 318.
[10] P. Jonkheijm, A. Gequire, F.J.M. Hoeben, J.V. Herrikhuyzen, A.H.J. Schenning, R. Kleppinger, S. de Feyter, F.C. de Schryver, E.W. Meijer, manuscript in preparation.
[11] J. Cornil, D.A. dos Santos, X. Crispin, R. Silbey, J.L. Brèdas, J. Am. Chem. Soc. 120 (1998) 1289.
[12] L.M. Herz, C. Daniel, C. Silva, F.J.M. Hoeben, A.P.H.J. Schenning, E.W. Meijer, R.H. Friend, R.T. Phillips, Phys. Rev. B, (2003) in press.
[13] M. Yan, L.J. Rothberg, F. Papadimitrakopoulos, M.E. Galvin, T.M. Miller, Phys. Rev. Lett. 73 (1994) 744.
[14] N.T. Harrison, G.R. Hayes, R.T. Phillips, R.H. Friend, Phys. Rev. Lett. 77 (1996) 1881.
[15] V.I. Klimov, D.W. McBranch, N.N. Barashkov, J.P. Ferraris, Chem. Phys. Lett. 277 (1997) 109.
[16] M.A. Stevens, C. Silva, D.M. Russel, R.H. Friend, Phys. Rev. B 63 (2001) 165213.
[17] A. Dogariu, D. Vacar, A.J. Heeger, Phys. Rev. B 58 (1998) 10218.