

Fast exciton diffusion in chiral stacks of conjugated *p*-phenylene vinylene oligomersL. M. Herz,¹ C. Daniel,¹ C. Silva,¹ F. J. M. Hoeben,² A. P. H. J. Schenning,² E. W. Meijer,² R. H. Friend,¹
and R. T. Phillips¹¹*Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom*²*Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

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The ultrafast dynamics of photoexcitations have been studied in chiral stacks of conjugated *p*-phenylene vinylene molecules functionalized with hydrogen-bonding groups. The results indicate that in solution, π - π interactions between the molecules give rise to fast exciton diffusion along the stacking axis of the assemblies. The chiral nature of the assemblies is found to cause a rotation of the dipole moment of excitons propagating along the stacks as indicated by time-resolved measurements of the photoluminescence polarization anisotropy. The observed exciton diffusion and energy relaxation dynamics in the molecular stacks are shown to be very similar to those found in conjugated polymer films. Moreover, it is demonstrated that through changes in the temperature of the surrounding solvent, the stacks can be dissociated reversibly as shown by a marked reduction in the diffusivity of excitons.

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I. INTRODUCTION

Conjugated polymers¹ and molecules² are finding increasing use as materials in optoelectronic devices. Each system offers distinctly different advantages. π -conjugated oligomers with well-defined chemical structure and conjugated length allow a precise ordering into crystalline layers with high charge-carrier mobility. Conjugated polymers, on the other hand, are easier to synthesize and process into a device structure. One major drawback of conjugated polymer films is the energetic and positional disorder of its chromophores induced by structural defects and entanglement of the extended chains. Such films often contain domains of aggregated chains which constitute low-energy trapping sites with a diminished luminescence efficiency.^{3,4} Much effort has been devoted to reducing the extent to which such aggregated domains form, e.g., through means of bulky side chains attached to the polymer backbone^{5,6} or the introduction of disorder via *cis* linkages.⁷ However, increasing the spacing between chains reduces the average overlap between their respective π orbitals, resulting in a trade-off between charge-carrier mobility and electroluminescence efficiency in conjugated polymer films.⁸ One solution to this problem is offered by the use of supramolecular chemistry to build well-defined extended structures through self-assembly of molecules, thus combining high molecular order with ease of processing.^{9,10} Prime examples of such systems are discotic liquid crystalline materials which organize into columnar stacks with a high charge carrier mobility along the stacking direction.^{11–15} Alternatively, hydrogen-bonding motifs have been employed to construct reversible, self-assembling polymer systems.^{16–18} In monothiophene and bithiophene bisurea compounds hydrogen bonding between urea groups was shown to cause the formation of lamellar fibres with efficient intermolecular charge transport.^{19,20} Recently, π -conjugated oligo(*p*-phenylene vinylene) molecules with chiral side chains and hydrogen-bonding ureidotriazine units (MOPV4) were found to assemble into chiral supramolecular stacks in an apolar solvent.²¹ In this paper, we demonstrate that the π

stacking of these molecules results in a delocalization of excitons across more than one oligomer, ensuring efficient exciton diffusion along the stacking direction. We explore electronic processes in these model systems on the molecular lengthscale and find that in solution, the stacks have optoelectronic properties strikingly similar to those encountered in thin films of conjugated polymers. However, the advantages of these stacks lie in the reversibility of the assembly and the easy construction of supramolecular complexes with specific functionality.

II. EXPERIMENT

The synthesis of MOPV4 has been described elsewhere.²¹ All data shown were taken for solutions of MOPV4 in anhydrous dodecane at a concentration of 2.5×10^{-4} mol l⁻¹. The solution was held in a Spectrosil cuvette mounted in a temperature-controlled holder. All time-resolved photoluminescence measurements displayed were conducted using the femtosecond up-conversion technique. MOPV4 was excited with the frequency-doubled output from a mode-locked Ti: Sapphire laser supplying 200-fs pulses at an energy of 3.06 eV and a repetition rate of 76 MHz. To set the polarization of the exciting beam, it was passed through a $\lambda/2$ plate and a Glan-Thompson polarizing prism. At the excitation power of 0.7 mW a single pulse created an average of 1.7×10^{-5} excitons per MOPV4 molecule within the solution region from which luminescence was measured. Photoluminescence emerging at a right angle to the exciting beam was collected with a pair of off-axis parabolic mirrors, and up-converted in a β -barium-borate crystal using the fundamental laser beam at 1.53 eV as a gate. Sum-frequency photons were dispersed in a monochromator, and detected by a cooled photomultiplier tube using photon counting techniques. The overall resolution of the system was approximately 350 fs. Since only vertically polarized light could be up-converted, the excitation polarization was rotated to measure luminescence polarized either parallel or perpendicular to the polarization of the exciting light. To take time-

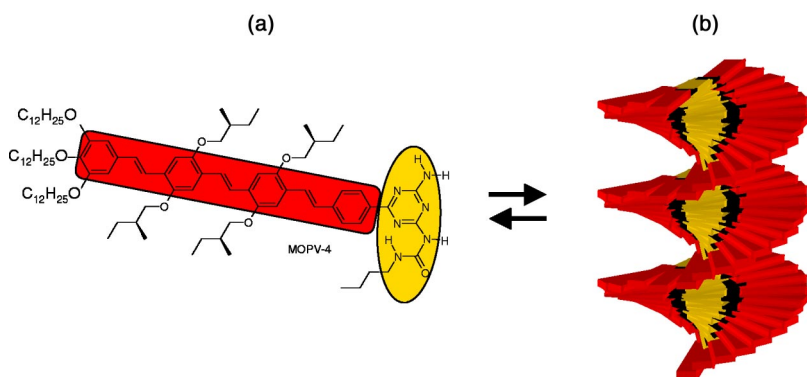


FIG. 1. (a) Chemical structure of MOPV4 comprising a tetra(*p*-phenylene vinylene) derivative (marked by a rectangle) with homochiral side chains and end chains conferring solubility, and a ureido-s-triazine unit (marked by an ellipse). (b) Schematic representation of helical MOPV4 stacks formed from dimerized MOPV4 molecules.

integrated photoluminescence spectra the vertical polarization component was selected using a second Glan-Thompson polarizing prism and dispersed in a double-grating spectrometer (Spectramate 1680) after which it was detected with a Si photodiode using a lock-in technique. Both time-resolved and time-integrated spectra were corrected for spectral response. To measure the decay dynamics of MOPV4 in dodecane at long (>4 ns) times after excitation, time-correlated single photon counting was implemented. The MOPV4 solution was excited with a pulsed (20 MHz, 70-ps full width at half maximum) diode laser at a wavelength of 407 nm (PicoQuant LDH 400) and the luminescence detected with a microchannel plate photomultiplier (Hamamatsu) coupled to a monochromator and time-correlated single photon counting (TCSPC) electronics (Lifespec-ps and VTC900 PC card, Edinburgh Instruments). A decay curve was taken at 2.21 eV for a solution temperature of 14 °C, and the decay time was extracted from the curve by a monoexponential fitting within the time range of 4–10 ns.

III. DISCUSSION

Figure 1 displays the chemical structure of MOPV4 comprising a tetra(*p*-phenylene vinylene) derivative with homochiral side-chains and end-chains conferring solubility, and a ureido-s-triazine unit. Schenning *et al.* have conducted a detailed study of the associative properties of MOPV4 in solvents with varying degree of polarity.²¹ They showed that in chloroform and dodecane, MOPV4 molecules dimerize via quadruple hydrogen bonding between ureidotriazine units. Moreover, in the apolar solvent dodecane a combination of solvophobic effects and π - π interactions between the MOPV4 molecules lead to stacking of MOPV4 dimers into supramolecular columns. In these stacks, a helical arrangement of chromophores was found to be induced by their chiral sidechains [see Fig. 1(b)]. Small angle neutron scattering experiments performed at 10 °C on a solution of MOPV4 in deuterated dodecane (4.1×10^{-3} mol l⁻¹) have indicated the existence of columnar structures with a minimum length of 200 nm and a radius of approximately 3.0 nm.²² The stacking of MOPV4 dimers was demonstrated to be reversible: with increasing temperature the assemblies began to dissociate, as deduced from changes in circular dichroism, luminescence and absorption spectra. Most of the changes occurred within a temperature range of approximately ± 10 °C about a “transition temperature” T_c indicating the existence of two phases for MOPV4 in dodecane: supramo-

lecular assemblies at low ($\ll T_c$) temperatures and dissolved monomeric and dimeric species at high temperatures.²¹ The transition temperature was found to increase with increasing MOPV4 concentration c ; the results presented here were obtained for $c = 2.5 \times 10^{-4}$ mol l⁻¹, for which a transition temperature of approximately 65 °C should be expected.²² In Fig. 2(a) the time-integrated photoluminescence spectra of MOPV4 in dodecane solution are given for a range of temperatures. The molecules were excited with 200-fs laser pulses at an energy of 3.06 eV and only the luminescence component polarized parallel to the polarization of the exciting light was detected. With decreasing temperature supramolecular stacks begin to form and the average energy of the emitted photons shifts to the red while the spectrally integrated photoluminescence intensity decreases. Previous measurements have indicated that with decreasing solution

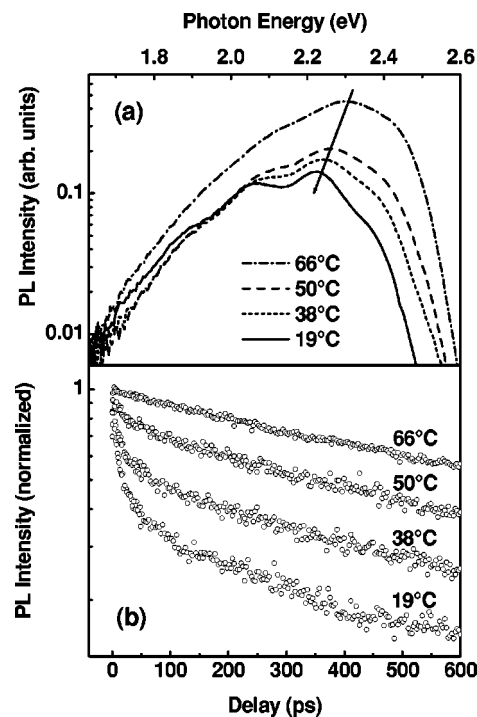


FIG. 2. Changes in the luminescence spectra and decay dynamics of MOPV4 solutions with temperature. (a) Time-integrated photoluminescence spectra. (b) Photoluminescence decay dynamics at 2.226 eV. All data shown were taken for copolarized exciting and detected light.

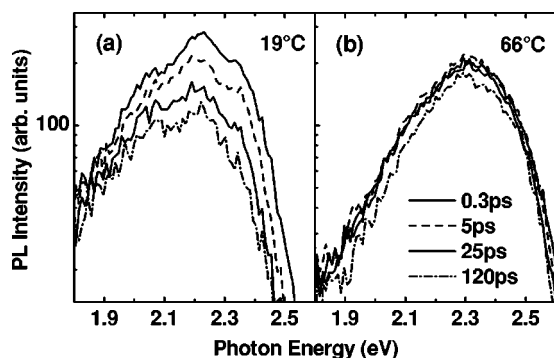


FIG. 3. Photoluminescence spectra of MOPV4 in dodecane at different times after excitation, (a) at a solution temperature of 19 °C (assembled phase) and (b) at a solution temperature of 66 °C (dissociated phase).

temperature a low-energy (≈ 2.5 eV) tail appears in the absorption of MOPV4 in dodecane in accordance with the formation of molecular assemblies.²¹ These changes illustrate that π stacking of MOPV4 in dodecane leads to a delocalization of the exciton across more than one molecule, resulting in a splitting of the excitonic energy levels. The distribution of oscillator strength across these levels depends on the exact stacking geometry, i.e. the angle and the separation between the dipole moments of adjacent chromophores.⁴ Figure 2(b) displays the decay of the photoluminescence from MOPV4 in dodecane at 2.226 eV with time after excitation (under the same experimental conditions as outlined above). At the temperature of 66 °C MOPV4 assumes to a large extent a dissolved monomeric or dimeric form and the luminescence decays almost exponentially to 1/e of its maximum value within approximately one nanosecond. However, strong changes are evident in the decay dynamics for lower temperatures. As supramolecular assemblies begin to form, a fast (≈ 20 ps) initial decay is introduced which is followed by a long-lived decay over a few hundred picoseconds. With the reduction of solution temperature the ratio of the short-lived to the long-lived components increases and both decay rates increase. These observations are further illustrated by the photoluminescence spectra of MOPV4 in dodecane taken at various times after excitation (Fig. 3). At 19 °C, the photoluminescence from MOPV4 assemblies displays a fast decay across the whole spectrum, accompanied by a small redshift [Fig. 3(a)]. In contrast, luminescence from dissociated MOPV4 at 66 °C [Fig. 3(b)] remains almost unchanged during the first one hundred picoseconds after excitation. The decay dynamics observed for supramolecular assemblies of MOPV4 are reminiscent of those found in thin films of poly (*p*-phenylene vinylene) (PPV), one of the most widely studied conjugated polymers. For such films it was found that the introduction of chemical defects led to a quenching of the luminescence due to charge separation of the exciton.^{23–25} These defects were formed as a result of carbonyl (C=O) substitution on the vinyl group which may occur under exposure of the compound to oxygen. Diffusion and subsequent trapping of excitons within the PPV films was shown to cause a temporal decay of luminescence on a timescale dependent on the diffusivity of the exciton and the defect

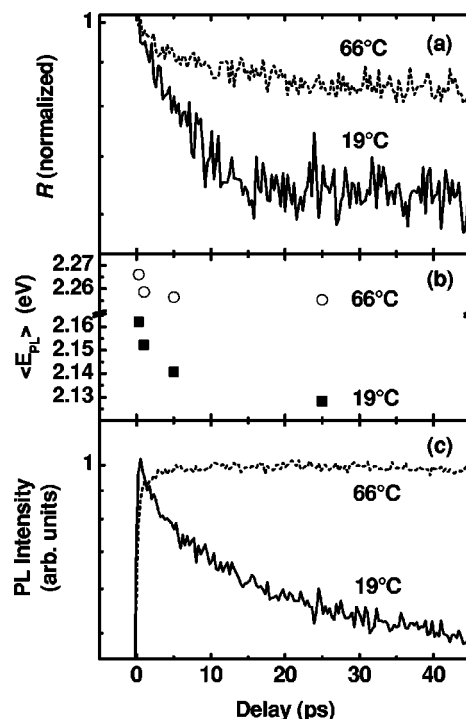


FIG. 4. Photoluminescence depolarization and energy relaxation for MOPV4 in dodecane. (a) Normalized polarization ratio R for MOPV4 stacks (19 °C) and dissolved MOPV4 (66 °C) as a function of time after excitation. (b) Average photoluminescence energy $\langle E_{PL} \rangle$. (c) Polarization-independent decay of the luminescence from MOPV4, taken as the sum of the copolarized luminescence component and twice the measured cross-polarized component.

concentration.²³ At the low excitation density employed for our measurements (on average, 1.7×10^{-5} excitons are created per MOPV4 molecule) we can rule out that the fast initial decay we observe in the luminescence of MOPV4 stacks is due to bimolecular effects such as exciton-exciton annihilation. This is supported by the identical decay dynamics observed when the excitation intensity is changed over an order of magnitude. We therefore suggest that the fast decay is caused by diffusion-assisted trapping of excitons at defect sites indicating a high mobility of excitons along the supramolecular stacks. As the solution temperature is increased, the dissociation of the assemblies causes a reduction of the effective exciton diffusion length, concomitant with a reduced trapping probability and an increase in the photoluminescence efficiency. These arguments are underlined by our study of the photoluminescence depolarization and energy relaxation of excitons in MOPV4 assemblies (Fig. 4). Excitation of a stack of MOPV4 molecules using linearly polarized light propagating along the stacking direction will result in an excitation probability which varies approximately sinusoidally along the stacking axis. This is a direct consequence of the helical nature of the assemblies: assuming the dipole moment of MOPV4 to be parallel to the long axis of the molecule, the transition probability will vary periodically with the angle formed between the excitation polarization and the orientation of successive MOPV4 molecules. Linearly polarized light will consequently create an

anisotropic distribution of excitations in the MOPV4 stacks and the luminescence emitted immediately after excitation will also be polarized (albeit not fully, due to the random orientation of the stacks in solution). However, as excitons diffuse along the chiral stacks, their dipole moments will turn about the stacking axis resulting in a depolarization of the emitted luminescence with time. This is indeed what we observe. Figure 4(a) displays the normalized polarization ratio R for light emitted at 2.226 eV from the solution of MOPV4 in dodecane. (Here, R is defined as the luminescence emitted with polarization parallel to the excitation polarization, divided by the luminescence polarized perpendicular to the excitation polarization.) For supramolecular assemblies of MOPV4 (at 19 °C) the polarization ratio decreases rapidly within the first 15 ps by 36% of its initial value, followed by a much slower decrease by an additional 8.6% over the subsequent 600 ps (not shown). At the solution temperature of 66 °C, depolarization occurs to a much smaller extent indicating that the stacks have largely dissociated. Interestingly, the measured depolarization dynamics correlate closely with the shifts occurring in the average photoluminescence energy with time after excitation [Fig. 4(b)]. These values were obtained by fitting the sum of four Gaussians to each luminescence spectrum taken at a particular time after excitation and extracting the average energy from the energetic positions of and areas under the Gaussians (alternative averaging methods gave almost identical results). The redshift of the photoluminescence from MOPV4 assemblies is again reminiscent of those observed in conjugated polymer films. In these films energetic disorder is induced by structural defects resulting in the presence of a range of conjugation lengths. Photoexcitation of the films is followed by migration of excitons to chain segments of longer conjugation length and a concomitant redshift of the emitted luminescence.^{26–28} In assembled stacks of MOPV4 energetic disorder may similarly be introduced by small local variations in the stacking geometry (e.g., the angle and the offset between adjacent chromophores). Migration of excitons along the stacking direction will as a result not only cause depolarization but also a redshift of the photoluminescence. The amount by which the luminescence of MOPV4 shifts to the red within the first fifty ps (≈ 30 meV) compares favorably with the values found for films of typical conjugated polymers under excitation conditions well above the localization threshold (30–60 meV).^{26,29,30} These results therefore show that the energetic disorder resulting from imperfect stacking in MOPV4 assemblies is lower than or comparable to that encountered in conjugated polymer films due to structural defects, indicating the effectiveness of supramolecular chemistry as a means of achieving molecular order.

The dynamics of the luminescence depolarization may also be compared to those encountered in conjugated polymer films. Anisotropic films have shown luminescence depolarization within the first picosecond after excitation²⁹; however, this is largely due to a relatively small correlation between the orientations of dipole moments on adjacent chromophores. The situation in MOPV4 stacks may hence be more similar to that in films whose chains are partly oriented and for which the polarization ratio was found to decay over

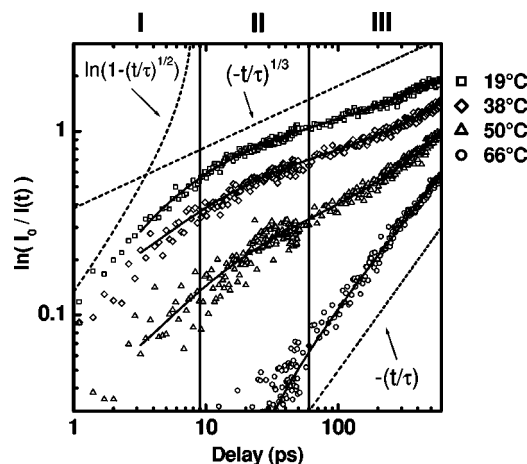


FIG. 5. Photoluminescence decay dynamics at 2.226 eV in a KWW plot together with fitting curves based on a model for one-dimensional diffusion and trapping of photoexcitations (see the text).

a timescale of one hundred picoseconds.³⁰

Figure 4(c) shows the polarization-independent decay of the photoluminescence from MOPV4 in dodecane at 2.226 eV (given by the sum of the copolarized component and twice the measured cross-polarized component). The fast initial decay of the luminescence from MOPV4 stacks (at 19 °C) indicates that the decay of the copolarized luminescence (shown in Fig. 2) is not solely due to depolarization but is also caused by quenching due to exciton diffusion to nonradiative traps.

In the following we aim to give a more quantitative description of the decay dynamics in the helical assemblies formed by MOPV4. Incoherent transfer in random media has often been described by a stretched exponential form, i.e.,

$$I(t) = I_0 \exp\left(-\left[\frac{t}{\tau}\right]^\beta\right), \quad (1)$$

which has proved to be the output of a variety of theoretical models within certain temporal regimes of the transfer process.^{27,31,32} While stretched exponentials provide the asymptotic solutions to the survival probability of excitations on a lattice containing randomly distributed traps,^{31,32} they may, under certain conditions, also adequately describe the trapping of excitations in systems with energetic disorder. In the latter case the stretched exponential decay dynamics are related to the dispersive nature of the diffusion process: as the system relaxes energetically, the diffusivity and consequently the trapping probability decreases.²⁸ In order to investigate whether stretched exponential behavior may also play a role in the exciton dynamics in MOPV4 assemblies, we have displayed the photoluminescence intensity $I(t)$ in a double-logarithmic plot of $\ln[I(0)/I(t)]$ versus time t after excitation (Fig. 5). In such a Kohlrausch-Williams-Watt (KWW) representation, the stretched exponential form given in Equation 1 should yield a straight line with slope β allowing an insight into the nature of the dispersive exciton transfer. In Fig. 5 three regimes can clearly be identified: at early times (regime I) a fast initial decay of excitations is observed

(corresponding to a fast increase in the KWW representation of the data). This behavior is followed by a stretched exponential decay (regime II) with an exponent β approximating 1/3 up to a solution temperature of 50 °C. Finally, in the third regime a transition occurs to a stretched exponential behavior whose exponent depends strongly on the solution temperature: as the temperature is increased, the exponent varies from $\beta \approx 1/3$ at 19 °C to an almost exponential form ($\beta \approx 1$) at 66 °C. We have also investigated the excitation dynamics in a fourth regime between 4 and 10 ns after excitation, using time-correlated single photon counting (not shown). At these delay times the photoluminescence (PL) decay is found to be monoexponential ($\beta = 1$) with a lifetime of 2.94 ns independent of the solution temperature. We therefore attribute this value to the natural lifetime of the energetically fully relaxed exciton which is largely immobile due to its location in a minimum of the potential surface of the disordered medium, and consequently evades encounter with non-radiative traps. This observation bears resemblance to the exponential ($\beta = 1$) decay found at the low energy end of the photoluminescence from poly(phenylphenylenevinylene) (PPPV) for times ≥ 0.8 ns after excitation²⁷ for which these excitons can be assumed to be localized. In thin films of conjugated polymers the PL quenching dynamics due to exciton migration to nonradiative traps has often been described successfully^{33,23,30} using the model developed by Balagurov and Vaks for the survival probability of an exciton on a one-dimensional walk with randomly situated traps.³¹ The success of this description has been surprising considering that while a single polymeric chain may well be viewed as a one-dimensional system, exciton migration in a polymeric film is expected to be dominated by interchain transfer (i.e., three-dimensional processes) due to the larger electronic wavefunction overlap between closely packed conjugated segments of adjacent chains.³⁴ The model by Balagurov and Vaks³¹ yields the following asymptotic solution for the exciton survival probability $W(t)$ on a one-dimensional lattice:

$$W(t) \sim \begin{cases} 1 - \left(\frac{4}{3\pi}\right)^{3/2} \left(\frac{t}{\tau_d}\right)^{1/2} & \text{for } t \lesssim \tau_d \\ \left(\frac{t}{\tau_d}\right)^{1/2} \exp\left[-\left(\frac{t}{\tau_d}\right)^{1/3}\right] & \text{for } t \gtrsim \tau_d, \end{cases} \quad (2)$$

with a diffusion time τ_d related to the one-dimensional effective density of traps c and the exciton diffusion constant D through $\tau_d = [2\pi^2(3/2)^3 c^2 D]^{-1}$. For times much longer than the diffusion constant the asymptotic solution will be dominated by the stretched exponential and should therefore resemble a line in the KWW plot with slope of 1/3. We have indicated these asymptotic solutions in Fig. 5 with dashed lines (using arbitrary time constants selected for ease of viewing). Up to a solution temperature of 50 °C the PL decay dynamics in regimes I and II closely match the asymptotic solutions, indicating that the fast PL decay within the first 60 ps can be well described by the model by Balagurov and Vaks. Within the range of ≈ 60 –100 ps the decay dynamics change abruptly over to a much slower decay regime [seen more clearly in Fig. 2(b)]. We attribute this long-lived emission to excitons located near the energetic minima of the

TABLE I. Parameters extracted from best fits to the photoluminescence decay displayed in Fig. 5.

T (°C)	τ_d (ps)	τ_h (ps)	n	I_d/I_h
19	0.10 ± 0.02	356 ± 120	0.36 ± 0.05	1.78 ± 0.13
26	0.15 ± 0.03	797 ± 204	0.39 ± 0.07	1.30 ± 0.14
38	0.22 ± 0.04	1173 ± 54	0.62 ± 0.09	1.32 ± 0.07
50	0.35 ± 0.10	1364 ± 71	0.84 ± 0.12	0.63 ± 0.11
66	–	1926 ± 53	0.80 ± 0.02	0 (set)

surrounding potential landscape where their diffusivity is much reduced compared with that of excitons created near the energetic maxima. Detailed simulations of the survival probability of excitons in a three-dimensional lattice with a Gaussian energy distribution have shown that the trapping probability depends strongly on the initial energy of an exciton undertaking a random walk,²⁸ with a critical energy E below which excitons may become almost immobilized. The existence of such a “localization energy” in conjugated polymer films has been demonstrated repeatedly using site-selective photoluminescence spectroscopy.^{35,36} In the case of MOPV4 assemblies this effect should be much more pronounced due to the reduced dimensionality of the system and is therefore likely to be the cause of the PL decay occurring on two very distinctly different time scales. Including all these considerations given above, we have chosen the following fitting functions to model the PL decay $I(t)$ in MOPV4 assemblies within the time range of 3.2–600 ps after excitation:

$$I = \left[I_d \sqrt{\frac{t}{\tau_d}} \exp\left(-\left[\frac{t}{\tau_d}\right]^{1/3}\right) + I_h \exp\left(-\left[\frac{t}{\tau_h}\right]^n\right) \right] \exp\left(-\frac{t}{\tau_0}\right). \quad (3)$$

Here, the first part describes the initial fast decay of highly mobile excitons created well above the localization energy, while the second term represents the slower decay of more localized excitons. While the highly mobile excitons are subject to fast trapping at nonradiative defects and PL depolarization, they may also relax sufficiently in energy to contribute to the long-lived decay component. However, since the highly mobile and the partly localized excitons cause PL in roughly the same spectral region (as evident from the small redshift of the PL observed as a function of time) a transfer from the former to the latter cannot be observed in the decay dynamics and will therefore be neglected in this very simple model. Both terms have been multiplied with an exponential to account for the natural lifetime of the exciton, τ_0 , taken to be 2.94 ns from the long-lived (> 4 ns) exponential decay as mentioned above. The values determined for the fitting parameters are given in Table I with the corresponding best fitting curves displayed in Fig. 5 together with the data. As the temperature of the MOPV4 solution is increased, both the fast diffusion time τ_d and the longer time τ_h increase, while the relative amplitudes I_d/I_h of the short- and long-lived components decrease. These changes can be understood considering that an increase of the solution temperature breaks the coherence of the stacks inducing further

disorder and shorter segments over which the exciton can diffuse. As a result, excitons are more likely to become localized in local potential minima and the overall diffusivity is much reduced. For models describing the trapping of excitations on a lattice with randomly situated traps (but without consideration of energetic disorder) the exponent β in the stretched exponential form of the asymptotic decay has been linked with the dimensionality of the system d with $\beta = d/(d+2)$.³² Within the framework of this model the decay behavior we observe therefore implies that the initial diffusion of mobile excitons is governed by one-dimensional processes while the slower diffusion of partly localized excitons is linked to transfer processes of higher dimensionality. This seems plausible considering that the early migration of excitons created close to the energetic maxima of the potential surface will be dominated by nearest neighbor interactions. As the center-to-center distance of the chromophores in a hydrogen-bonded MOPV4 dimer should be of the order of 3 nm, while the separation of the π -stacked chromophores on one side of the double-stranded helical assemblies is of the order of a few Å, the early migration dynamics of mobile excitons will occur predominantly on one side of the helix. Furthermore, considering the sufficiently large π - π overlap between adjacent molecules, the pitch of the helix cannot be too large, leading to an initial diffusion which is quasi-one-dimensional. In contrast, for excitons partly localized near the potential minima of the potential surface, lower-energy sites will be located much further away. Diffusion to a suitable site may therefore also involve transfer to the other side of the helix, leading to a higher dimensionality of the diffusion process. We should finally point out that while these considerations seem very plausible, care has to be taken when applying models to these systems which do not explicitly take into account energetic disorder. Since the data presented in Fig. 5 are the copolarized luminescence component, the decays are not only governed by trapping of excitations but also by photoluminescence depolarization as described previously. However, as can be seen in Figs. 4(a) and 4(c), the PL depolarization and the exciton trapping dynamics in the MOPV4 assemblies are very similar, allowing us to model both processes with the same fitting function. While random walk models based solely on a statistical distribution of traps may be expected to describe exciton trapping in these systems adequately, the PL depolarization dynamics should rely on a somewhat different mechanism. Here, the nonexponential decay dynamics are most likely related to the statistical fluctuations in the angle between adjacent molecules and the variation in the local potential. The former is closely related to the latter due to the strong effect which the stacking angle between two adjacent chromophores has on the delocalization of the excitonic wave

function across the molecules and consequently on the excitonic energy levels at this site.⁴ The nonexponential PL depolarization dynamics thus indicate that energy relaxation should generally be taken into account when describing these molecular assemblies. For a more complete description of these helical assemblies it will be necessary to include the exact stacking geometry, and its statistical variations, into a model which relates these parameters to the potential energy landscape an exciton will encounter in these systems. Further work is currently being undertaken to determine these parameters, which are as yet unknown, and to establish a link between the geometry of the stacked chromophores and the corresponding excitonic energy level structure.

IV. CONCLUSION

In conclusion, we have demonstrated that the assembly of oligo(phenylene vinylene) molecules into chiral stacks using hydrogen-bonding motifs leads to fast exciton diffusion along the stacking axis. The relatively high degree of intermolecular order achieved emphasizes the effectiveness of supramolecular chemistry for the formation of well-defined molecular assemblies. The exciton diffusion dynamics in the MOPV4 stacks are very similar to those encountered in conjugated polymer films. However, one advantage of supramolecular stacks lies in the reversibility of the assembly, e.g., through changes in type of solvent or solution temperature. Moreover, through attachment of specific hydrogen-bonding motifs to different categories of molecules the construction of supramolecular complexes becomes viable, which can be tailored to display efficient light-harvesting or charge-separating properties. The quasi-one-dimensional nature of the MOPV4 assemblies may also allow their implementation in nanometer-scale molecular electronics. Additional effort is required to ensure that the high degree of order present in dodecane solutions of MOPV4 can be fully maintained in solid films. This work is in progress.

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¹R.H. Friend *et al.*, Nature (London) **397**, 121 (1999).

²M.D. Watson, A. Fechtenkötter, and K. Müllen, Chem. Rev. (Washington, D.C.) **101**, 1267 (2001).

³J.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).

⁴J. Cornil, D.A. dos Santos, X. Crispin, R. Silbey, and J.L. Brédas, J. Am. Chem. Soc. **120**, 1289 (1998).

- ⁵S. Setayesh, A.C. Grimsdale, T. Weil, V. Enkelmann, K. Müllen, F. Meghdadi, E.J.W. List, and G. Leising, *J. Am. Chem. Soc.* **123**, 946 (2001).
- ⁶L.M. Herz, C. Silva, R.T. Phillips, S. Setayesh, and K. Müllen, *Chem. Phys. Lett.* **347**, 318 (2001).
- ⁷S. Son, A. Dodabalapur, A.J. Lovinger, and M.E. Galvin, *Science* **269**, 376 (1995).
- ⁸T.-Q. Nguyen, I.B. Martini, J. Liu, and B. Schwartz, *J. Phys. Chem. B* **104**, 237 (2000).
- ⁹E.W. Meijer and A.P.H.J. Schenning, *Nature (London)* **419**, 353 (2002).
- ¹⁰V. Percec *et al.*, *Nature (London)* **419**, 384 (2002).
- ¹¹D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, and K. Siemensmeyer, *Phys. Rev. Lett.* **70**, 457 (1993).
- ¹²D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K.H. Etbach, H. Ringsdorf, and D. Haarer, *Nature (London)* **371**, 141 (1994).
- ¹³A.M. van de Craats, J.M. Warman, A. Fechtenkötter, J.D. Brand, M.A. Harbison, and K. Müllen, *Adv. Mater. (Weinheim, Ger.)* **11**, 1469 (1999).
- ¹⁴A.M. van de Craats and J.M. Warman, *Adv. Mater. (Weinheim, Ger.)* **13**, 130 (2001).
- ¹⁵L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R.H. Friend, and J.D. MacKenzie, *Science* **293**, 1119 (2001).
- ¹⁶R.P. Sijbesma, F.H. Beijer, L. Brunsveld, B.J.B. Folmer, J.H.K.K. Hirschberg, R.F.M. Lange, J.K.L. Lowe, and E.W. Meijer, *Science* **278**, 1601 (1997).
- ¹⁷F. Würthner, C. Thalacker, and A. Sautter, *Adv. Mater. (Weinheim, Ger.)* **11**, 754 (1999).
- ¹⁸J.H.K.K. Hirschberg, L. Brunsveld, A. Ramzi, J.A.J.M. Veekmans, R.P. Sijbesma, and E.W. Meijer, *Nature (London)* **407**, 167 (2000).
- ¹⁹F.S. Schoonbeek, J.H. van Esch, B. Wegewijs, D.B.A. Rep, M.P. de Haas, T.M. Klapwijk, R.M. Kellogg, and B.L. Feringa, *Angew. Chem., Int. Ed. Engl.* **38**, 1393 (1999).
- ²⁰D.B.A. Rep, R. Roelfsema, J.H. van Esch, F.S. Schoonbeek, R.M. Kellogg, B.L. Feringa, T.T.M. Palstra, and T.M. Klapwijk, *Adv. Mater. (Weinheim, Ger.)* **12**, 563 (2000).
- ²¹A.P.H.J. Schenning, P. Jonkheijm, E. Peeters, and E.W. Meijer, *J. Am. Chem. Soc.* **123**, 409 (2001).
- ²²P. Jonkheijm, A. Gequire, F.J.M. Hoeben, J.v. Herrikhuyzen, A.H.J. Schenning, R. Kleppinger, S. de Feyter, F.C. de Schryver, and E.W. Meijer (unpublished).
- ²³M. Yan, L.J. Rothberg, F. Papadimitrakopoulos, M.E. Galvin, and T.M. Miller, *Phys. Rev. Lett.* **73**, 744 (1994).
- ²⁴N.T. Harrison, G.R. Hayes, R.T. Phillips, and R.H. Friend, *Phys. Rev. Lett.* **77**, 1881 (1996).
- ²⁵L.J. Rothberg, M. Yan, F. Papadimitrakopoulos, M.E. Galvin, E.W. Kwock, and T.M. Miller, *Synth. Met.* **80**, 41 (1996).
- ²⁶R. Kersting, U. Lemmer, R.F. Mahrt, K. Leo, H. Kurz, H. Bässler, and E.O. Göbel, *Phys. Rev. Lett.* **70**, 3820 (1993).
- ²⁷B. Mollay, U. Lemmer, R. Kersting, R.F. Mahrt, H. Kurz, H.F. Kauffmann, and H. Bässler, *Phys. Rev. B* **50**, 10769 (1994).
- ²⁸B. Movaghar, M. Grünwald, B. Ries, H. Bässler, and D. Würtz, *Phys. Rev. B* **33**, 5545 (1986).
- ²⁹G.R. Hayes, I.D.W. Samuel, and R.T. Phillips, *Phys. Rev. B* **52**, R11569 (1995).
- ³⁰L.M. Herz and R.T. Phillips, *Phys. Rev. B* **61**, 13 691 (2000).
- ³¹B.Y. Balagurov and V.G. Vaks, *Zh. Éksp. Teor. Fiz.* **65**, 1939 (1973) [*Sov. Phys. JETP* **38**, 968 (1974)].
- ³²J. Klafter, G. Zumofen, and A. Blumen, *J. Phys. (France) Lett.* **45**, L49 (1984).
- ³³G.S. Kanner, X. Wei, B.C. Hess, L.R. Chen, and Z.V. Vardeny, *Phys. Rev. Lett.* **69**, 538 (1992).
- ³⁴D. Beljonne, G. Pourtois, C. Silva, E. Hennebicq, L. M. Herz, R. H. Friend, G. D. Scholes, S. Setayesh, K. Müllen, and J. L. Brédas, *Proc. Natl. Acad. Sci. USA* **99**, 10982 (2002).
- ³⁵H. Bässler and B. Schweitzer, *Acc. Chem. Res.* **32**, 173 (1999).
- ³⁶S.P. Kennedy, N. Garro, and R.T. Phillips, *Phys. Rev. B* **64**, 115206 (2001).