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Influence of mesoscopic ordering on the photoexcitation transfer dynamics in supramolecular assemblies of oligo-*p*-phenylenevinylene

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Abstract

We have investigated the influence of molecular arrangement on the transfer rates of photoexcitations along supramolecular assemblies of hydrogen-bonded oligo-*p*-phenylenevinylene (OPV) molecules for two different packing geometries. For well-defined, helical stacks of monofunctional OPVs fast (≈50 ps) photoluminescence depolarization and excitation transfer to dopants was observed, in agreement with semi-coherent exciton diffusion. For disordered assemblies of bifunctional OPVs incorporating a spacer to link adjacent molecules, depolarization and energy transfer dynamics occur on a longer time scale (≈nanosecond). This strongly suggests that such spacers need to be tuned carefully as they may otherwise interfere with the π-stacking thereby reducing the intermolecular electronic coupling.

1. Introduction

Organic π-conjugated systems have become increasingly popular as active materials in optoelectronic devices such as light-emitting diodes [1], field-effect transistors [2] and solar cells [3]. One of their most compelling features is that they may be processed very easily from solution opening the possibility for cheap, large-area production of devices using, e.g., inkjet printing techniques [4]. While intramolecular electronic properties can now be tailored routinely through chemical synthesis [5], control of intermolecular interactions from solution casting remains a challenge. Achieving the latter is important, since mesoscopic order is strongly linked to charge-carrier mobilities and exciton diffusivities in the material [2,6]. As a result, device performance is often more strongly related to the precise packing geometry of the active molecules or polymer chains in the solid than to their intramolecular electronic properties [7]. A promising approach to control of intermolecular interactions is supramolecular chemistry [8], which may draw on a combination of tools, as for example, solvophobic, solvophilic or π–π interactions, and ionic or hydrogen bonding. Well-defined supramolecular structures of π-conjugated molecules may then self-assemble in solution and the intermolecular arrangement may be maintained through the casting process [9].

One recent example for such materials are mono- and bi-functional oligo(*p*-phenylene vinylene) molecules functionalized with ureido-*s*-triazine units (MOPV and BOPV, respectively) [10,11]. The chemical structures of these oligomers (with three benzene rings – MOPV3 and BOPV3) are given in Fig. 1. In a polar solvent (e.g., chloroform), complementary hydrogen bonding between ureidotriazine units leads to the formation of dimers for MOPV, and random

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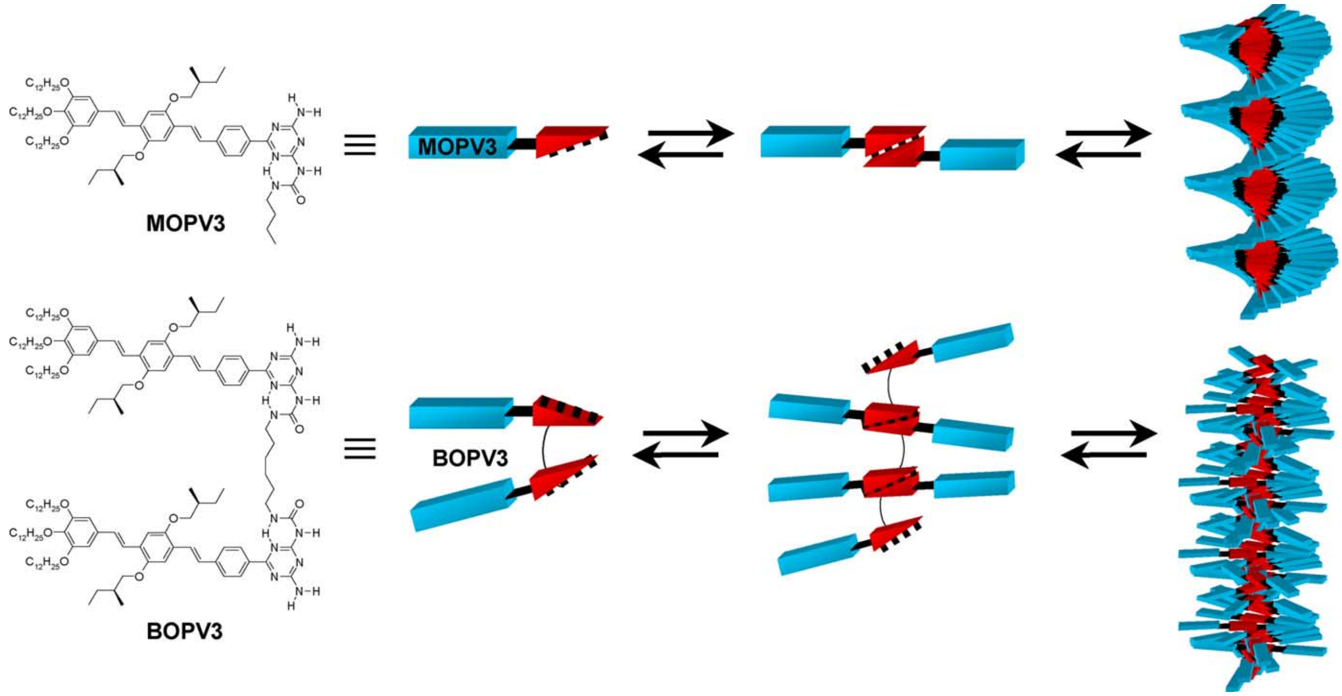

Fig. 1. Chemical structure of MOPV3 and BOPV3 molecules (left) and schematic representation of their presumed stacking geometries in dodecane solution at low temperatures (right).

coil polymers for BOPV as a result of its hexamethylene spacer linking pairs of hydrogen-bonded units [10]. In an apolar solvent (e.g., dodecane) and at low temperatures (≈10 °C) solvophobic and π–π interactions cause the formation of molecular aggregates of MOPV and BOPV, as evident from changes in the absorption spectra and small-angle neutron scattering experiments [9–11]. These assemblies may be dissociated by raising the solution past a certain transition temperature, which depends on the molecular concentration. For MOPVs, a bisignate Cotton effect was observed in the circular dichroism (CD) spectra [9], indicating that the chiral side chains induce molecular packing with a preferred helicity. Dreiding force field and photophysical modelling suggest that the angle between adjacent dimers in stacks of the four-ring MOPV4 is of the order of 6–12° [12]. Small-angle neutron scattering measurements are consistent with the existence of columnar stacks in dodecane with length of the order of 100 nm depending on oligomer length [9]. These observations point towards the existence of extended, well-ordered helical stacks of MOPV molecules in an apolar solvent below the transition temperature, as pictured schematically in Fig. 1. BOPVs, on the other hand, only display a very weak Cotton effect in the CD spectra in an apolar solvent. It has, therefore, been suggested [10] that the hexyl spacer linking the ureidotriazine units in BOPV may interfere with the packing leading to the formation of frustrated stacks with no preferred helicity, as indicated in Fig. 1. In the study reported here, we have investigated the implications of the distinctly different packing geometries for the photophysical properties of MOPV and BOPV assemblies. In particular, we have examined how disorder in these model systems affects the electronic coupling between chromophores by measuring the diffusion dynamics of photoexcitations along the stacks. We find that while photoexcitations in MOPV stacks undertake a random diffusion process that is initially very fast, indicative of semi-coherent motion along the stacks, this component is almost entirely absent for BOPV assemblies. These results suggest that while linker chains between chromophores may assist film processing through higher solution viscosities, the linker has to be tuned carefully as it may otherwise interfere with π-stacking and strongly reduce the electronic coupling between chromophores.

2. Experimental

The chemical synthesis of BOPV3, MOPV3 and MOPV4 has been described elsewhere [10,11]. The molecules were dissolved in anhydrous dodecane at concentrations of 1.3×10^{-4}, 2.6×10^{-4} and 2.6×10^{-4} mol/l, respectively, to ensure that the concentration of actual OPV chromophores was comparable for all three samples. To permit study of the exciton transfer rate along the stacks, a small fraction of MOPV4 molecules (4.8% of all OPV chromophore) was incorporated into BOPV3 and MOPV3 stacks. Blending was carried out by adding a certain amount of MOPV4 solution to either MOPV3 or BOPV3 solutions, heating the mixture to 90 °C to dissociate the stacks and inducing the formation of mixed stacks by cooling it to 15 °C. Previous examination of the Cotton effect for BOPV/MOPV blends [10,11] and STM images of

MOPV/MOPV blends [13] suggest that heterodimers form between the different blend components so that good intermixing should be expected for low dopant concentrations. To examine the excitation transfer dynamics along the stacks, photoluminescence upconversion (PLUC) experiments were conducted on solutions kept in a quartz cuvette mounted in a temperature-controlled holder. Samples were excited with the frequency-doubled output of a mode-locked Ti:Sapphire laser providing pulses of 100-fs duration at photon energy of 3.06 eV and a repetition rate of 80 MHz. The emerging photoluminescence (PL) was collected by a pair of off-axis parabolic mirrors and focused onto a β-barium-borate (BBO) crystal mounted on a rotation stage to allow tuning of the phase-matching angle. An intense vertically polarized gate beam of 1.53 eV arriving at the BBO crystal at adjustable time delays was used to upconvert the PL at given times after excitation. The resulting sum-frequency photons were collected, dispersed in a monochromator and detected by a liquid-nitrogen cooled CCD. Only the vertical polarization component of the PL was upconverted in this set-up, therefore, either the parallel or perpendicular luminescence polarizations with respect to the excitation polarization could be selected by changing the polarization of the excitation beam through rotation of a $\lambda/2$ plate and a polarizer. The vertically polarized component of the time-integrated photoluminescence was measured by using the same spectrometer and replacing the BBO crystal with a polarizer. Both time-integrated and time-resolved spectra were corrected for instrumental response using a filament lamp of known emissivity. At the average excitation power of 1 mW the exciton density on the stacks was sufficiently low to exclude the possibility of non-linear effects such as bimolecular exciton annihilation [14].

3. Results and discussion

To investigate the diffusivity of excitons in BOPV3 and MOPV3 assemblies the energy transfer to small amount of incorporated MOPV4 units was measured. MOPV4 is chemically identical to MOPV3 apart from an additional unit of the central phenylene vinylene derivative. As a result the MOPV4 emission and absorption is shifted by approximately 0.2 eV towards the red [15] so that efficient energy transfer from OPV3 assemblies to MOPV4 dopants should be expected. Fig. 2 shows time-integrated PL spectra for MOPV3 (left) and BOPV3 (right) assemblies formed in dodecane at 15 °C both for the doped (solid line) and the undoped (dashed line) case. At the chosen excitation energy (3.06 eV) and for the low dopant concentration used, excitons are most likely to be initially located on the OPV3 chromophores. For both systems doping results in a red shift of the emission indicative of excitation transfer to MOPV4, however, for BOPV3 assemblies the transfer efficiency is significantly lower than for MOPV3 assemblies. These findings are in agreement with recent titration experiments on MOPV3 and BOPV3 assemblies doped with the five-ring oligomer MOPV5, for which classical Stern–Volmer plots against the dopant concentration revealed a Stern–Volmer constant higher by a factor of 3.5 for MOPV3 compared to BOPV3 [11]. In order to assess the influence of the packing geometry on the dynamics of the excitation transfer we measured the photoluminescence decay from doped and undoped assemblies both in the region where the dopant emits (2.226 eV) and in the region where only the pure assemblies emit (2.55 eV). To determine the relative changes in the assembly emission caused by the incorporation of the dopants we then divided the PL measured for the doped assemblies by that measured at the same energy for the undoped assemblies, as shown in Fig. 3. For MOPV3 stacks a strong relative increase of the emission at the low-energy end of the spectrum can be observed (Fig. 3, top) which is accompanied by a relative decrease at the high-energy end (Fig. 3, bottom). These results are consistent with the existence of efficient energy transfer along MOPV assemblies [16,15] assisted by the diffusion of excitations along the MOPV stacking direction. At the low-energy end the dynamics are complicated by overlapping contributions from both assemblies and dopants. However, at the high-energy end (2.55 eV) only assembly emission is observed, therefore the relative assembly decay $I(t)$ can be directly linked to the time-dependent excitation transfer rate $k(t)$ through [17]:

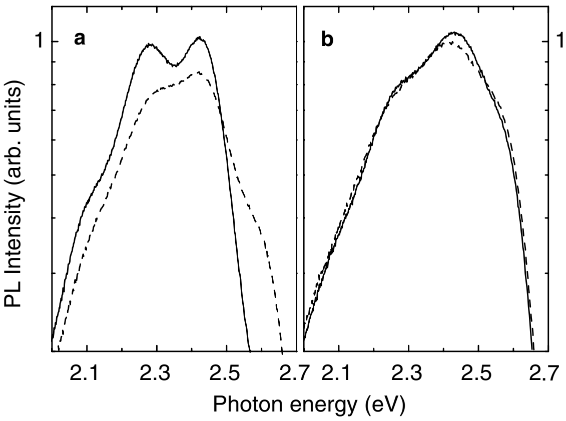

Fig. 2. Time-integrated photoluminescence spectra of (a) MOPV3 and (b) BOPV3 assemblies in dodecane at 15 °C for the undoped case (dashed line) and for the case of incorporation of 4.8% MOPV4 per chromophore (solid line).

$$k(t) = -\frac{\mathrm{d}}{\mathrm{d}t}\ln I(t). \tag{1}$$

Beljonne et al. [12] have modelled the exciton diffusion rate along MOPV stacks using quantum-chemical calculations coupled to a Pauli master equation formalism. The results indicate that sufficient agreement with experimental data may only be achieved if delocalization of the excitonic wavefunction of the acceptor state across more than one MOPV molecule is taken into account. The donor exciton, on the other hand, is assumed to be self-localized as a result of rapid lattice relaxation. The resulting semi-coherent motion induces a faster decay than would be expected for fully

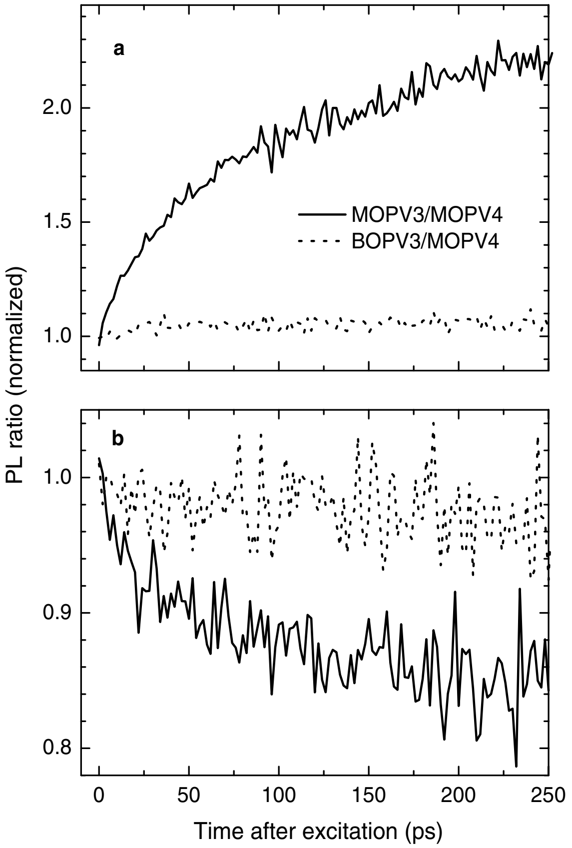

Fig. 3. Photoluminescence emitted from MOPV3 (solid line) and BOPV3 (dashed line) incorporating 4.8% MOPV4 dopants (per OPV chromophore) divided by that for the respective undoped assemblies, as a function of time after excitation. The curves were taken at 15 °C for (a) 2.226 eV, where both the host and the dopant emit, and (b) 2.55 eV, where only the host (MOPV3 or BOPV3) emits.

incoherent hopping transport. Sufficient electronic coupling between adjacent molecules in the stack therefore appears to be a prerequisite for efficient excitation transfer. Fig. 3 also displays the relative energy transfer data taken for BOPV3 stacks. Both the relative increase at the low-energy end and the relative decrease at the high-energy end are significantly reduced compared to MOPV3 stacks. While for MOPV3 the relative emission at 2.226 eV more than doubles over the first 250 ps, it only increases by ≈6% for BOPV3. Similarly, at 2.55 eV we find a relative decrease in the assembly emission for MOPV3 of 16% compared to ≈3% for BOPV3 over the same time window. These findings indicate that the hexyl spacer linking adjacent hydrogen-bonding units in BOPV3 (see Fig. 1) disrupts the π-stacking of units in the assemblies. As a result, adjacent chromophores are only weakly coupled leading to slow incoherent transfer of excitations along the assemblies. Direct excitation transfer from the BOPV3 assemblies to MOPV4 dopants located nearby may of course still occur. However, diffusive motion of excitations along the assemblies, which makes a significant contribution to the overall excitation transfer for the case of MOPV3, is significantly slower for the case of BOPV3 leading to an overall inefficient energy transfer.

While direct excitation transfer from the BOPV3 assemblies to MOPV4 dopants located near by may still occur to some extent, diffusive motion of excitations along the BOPV3 assemblies is less likely to assist the overall transfer than for MOPV3 stacks. To explore the differences in excitation transfer dynamics for the two stacking geometries further we have conducted additional measurements on the undoped assemblies. Fig. 4 shows the average energy of a photon, $\langle E \rangle$ emitted from MOPV3 (left) and BOPV3 (right) as a function of time. The values were obtained by integration over the time-resolved, calibrated PL spectra using:

$$\langle E \rangle = \frac{\int f(E) E \, \mathrm{d}E}{\int f(E) \mathrm{d}E}, \tag{2}$$

where $f(E)\mathrm{d}E$ is the number photons emitted in the energy interval $\mathrm{d}E$. At 85 °C both MOPV3 and BOPV3 exist as molecularly dissolved (monomeric and dimeric) species in dodecane, with little aggregate signature present in their absorption spectra [11]. MOPV3 forms homodimers at this solution concentration while BOPV3 may exist as random coil supramolecular polymer. At this temperature, a small (32 meV for MOPV3, 36 meV for BOPV3) energy shift is observed over the first 100 ps after excitation, which may be caused by intramolecular relaxation upon excitation [18] or exciton transfer across the hydrogen bridge [12]. Cooling the solution to 15 °C results in the formation of aggregated assemblies and a general red shift of the PL emission energy for both MOPV3 and BOPV3. Again the average PL energy decreases with time after excitation, but now to a larger extent. Similar observations for the time-dependence of the average PL energy from OPV assemblies have previously been explained [16] and modelled [12] invoking a random walk of excitons through an inhomogeneously broadened density of states (DOS) present in the assemblies e.g., as a result of variation in stacking

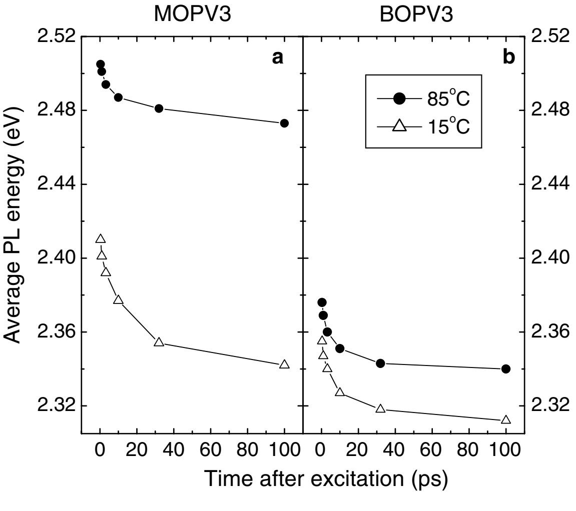

Fig. 4. Average energy of a photon emitted from (a) MOPV3 and (b) BOPV3 in dodecane at a solution temperature of 85 °C (closed circles) and 15 °C (open triangles) as a function of time after excitation.

geometry. For MOPV3 we observe an additional red-shift (w.r.t. the initial energy) of 68 meV over the first 100 ps while only a modest increase of 43 meV is found for BOPV3. The small red-shift for the average emission of BOPV3 within a given time window may be either explained by a smaller extent of energetic disorder present in the system, or a much longer relaxation time compared to MOPV3, the latter being consistent with our observations of reduced energy transfer for BOPV3.

To obtain a third indicator of excitation transfer along the OPV assemblies we have examined the depolarization dynamics for MOPV3 and BOPV3 assemblies in dodecane at 15 °C. Fig. 5 displays the PL polarization ratio (at 2.55 eV) for both systems, defined as the ratio of the PL intensity emitted with polarization parallel to the excitation polarization divided by that emitted with polarization perpendicular to the excitation polarization. The dominant optical dipole moment of the OPV chromophores is directed along the long axis of the molecule [19]; excitation of stacks will therefore occur preferentially for molecules whose long axis is oriented parallel to the polarization of the exciting light. The resulting emission will therefore also be partly polarized until excitation transfer to molecules with different orientation has led to a loss of the polarization memory. For MOPV3 the helical nature of the assembly leads to a fast initial polarization (see Fig. 5) until exciton localization at energetic minima of the DOS has led to a reduction of exciton migration rates, similar to previous observations for MOPV4 assemblies [16]. In contrast, the data displayed in Fig. 5 suggests that for BOPV3 the PL depolarization occurs on a much longer timescale. The fact that some PL depolarization occurs for BOPV3 even though energy transfer to dopants is hardly observed (see Fig. 3) might indicate that the average angle between chromophores is somewhat larger in BOPV3 than in MOPV3, as would be expected for weakly coupled chromophores. In this case, even a single hop to a neighbouring molecule in BOPV3 could results in a significant PL depolarization. More detailed modelling of the exciton migration in BOPV assemblies, similar to those conducted previously for MOPVs [12], will need to be conducted to allow a clearer picture on relative stacking angles to be deduced from these data.

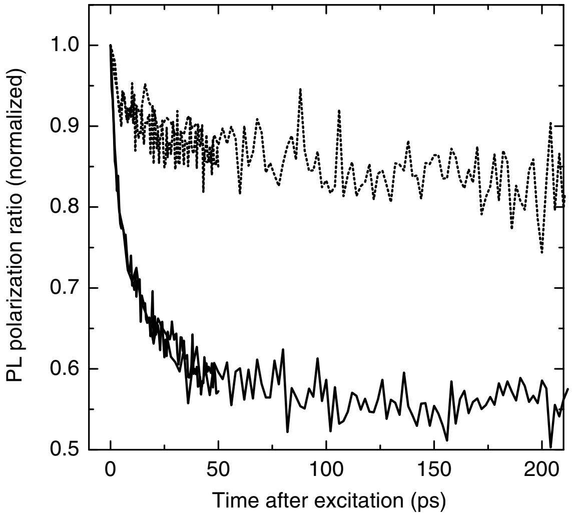

Fig. 5. Photoluminescence polarization ratio for MOPV3 (solid line) and BOPV3 (dotted line) assemblies in dodecane at 15 °C.

4. Conclusion

We have demonstrated that the mesoscopic ordering within supramolecular assemblies of π-conjugated molecules has a strong influence on the transfer rate of photoexcitations along the assemblies. For the ordered, chiral stacks of MOPV3 fast (≈50 ps) initial photoluminescence depolarization and excitation transfer to dopants was observed, in agreement with semi-coherent exciton diffusion along the stacks. For BOPV3 assemblies, both depolarization and energy transfer dynamics occur on a much longer time scale (≈nanosecond). This strongly suggests that the included hexyl spacer, which joins pairs of hydrogen-bonding units, interferes with the π-stacking of OPV molecules. The resulting drastic reduction of the intermolecular electronic coupling leads to a slow incoherent motion of excitations along the BOPV stacks. Inclusion of an aliphatic spacer has the advantage of increasing solution viscosity so that devices may more easily be fabricated [11]. However, our results indicate that unless the spacer is carefully optimized it will interfere with the formation of ordered π-stacks, leading to a substantial reduction in the mobility of excitations in the assembly.

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