Extended Columnar Aggregates

Efficient Energy Transfer in Mixed Columnar Stacks of Hydrogen-Bonded Oligo(*p*-phenylene vinylene)s in Solution**

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Long-range ordering in well-defined aggregates of π-conjugated structures is the key feature in energy-transfer processes in photosynthetic systems[1] as well as electronic devices based on organic compounds.[2] All the studies on artificial antenna–target systems[3] have indicated the need for precise control of distance and orientation. However, detailed insight into the subtleties of the organizational demands of these artificial systems is lacking. Dynamic structures in solution are not shape persistent, while semi-crystalline bulk samples lack the uniform positioning of chromophores. Our design of a modular supramolecular approach enables us to create molecular stacks which are both dynamic and well-defined.[4]

Previously, we synthesized and fully characterized mono-functionalized oligo(*p*-phenylene vinylene)s **MOPV3** and **MOPV4**, which are essentially the same molecules but with a different conjugation length.[4] Temperature-dependent UV/Vis, circular dichroism (CD), and fluorescence measurements in dodecane show that these oligomers are helically aggregated at low temperatures and molecularly dissolved at high temperatures, with melting temperatures of T_m = ca. 33 °C (1.6×10^{-5} M) for **MOPV3** and T_m = ca. 53 °C (1.4×10^{-5} M) for **MOPV4** (Figure 1 a). Small angle neutron scattering (SANS) and atomic force microscopy (AFM) measurements[5] have demonstrated that the aggregates are composed of stacked hydrogen-bonded dimers.

The presence of highly ordered columnar structures in solution provides an attractive scaffold for studying energy transfer between the two oligomers if mixed stacks of oligomers can be formed (Figure 1 b).

Temperature-dependent fluorescence measurements were performed on a dilute dodecane solution with 1.2 mol % **MOPV4** in **MOPV3**. The addition of **MOPV4** to **MOPV3** at low temperatures results in the spectrum closely resembling the spectrum of aggregated **MOPV3** (λ_{em} = 483 nm and λ_{em} = 513 nm). This result is to be expected since the solution consists mainly of **MOPV3**, and no exchange is possible between the two different oligomeric stacks at temperatures below the melting transition of the **MOPV3** aggregates. Raising the temperature results in the aggregates breaking up into molecularly dissolved species and the total fluorescence intensity increasing (Figure 2). The spectrum now displays the characteristics of molecularly dissolved **MOPV3** (λ_{em} = 471 nm and λ_{em} = 495 nm). The peaks characteristic of molecularly dissolved **MOPV4** can not be distinguished because of the excess of **MOPV3**. Cooling the solution results in the appearance of new peaks (λ_{em} = 512 nm and λ_{em} = 548 nm) which are ascribed to molecularly dissolved **MOPV4**. This behavior suggests that the **MOPV4** oligomers have now been incorporated into the **MOPV3** stacks and that their presence becomes apparent as a consequence of a highly efficient energy transfer to the lowest lying electronic state. The shape of the spectrum at low temperatures is representative of molecularly dissolved acceptor **MOPV4**, thus indicating its isolated existence inside the donor **MOPV3** aggregates. Residual **MOPV3** fluorescence is expressed as a small shoulder around λ_{em} = 470 nm, which indicates there is incomplete energy transfer because of the exciton diffusion length being smaller than the donor–acceptor distance. As shown in more detail below, incorporation of **MOPV4** into **MOPV3** assemblies occurs only when the samples have been heated above the melting temperature of the aggregates, that is, energy transfer is not observed if this thermal cycling is omitted.

Titration experiments were performed in dodecane solution to determine how the number of acceptor molecules in the donor stack influences the excitation transfer. Measurements were carried out at 80 °C and 10 °C (Figure 3), that is, above and below the melting temperature of the **MOPV3** aggregates [**MOPV3** = 1.9×10^{-5} M], respectively. Energy transfer to **MOPV4** was monitored by measuring the fluorescence spectra as a function of **MOPV4** concentration. To study the energy-transfer process accurately, excitation was performed either at the top or at the high-energy edge of the **MOPV3** absorption band, because of the strong spectral overlap of both components.

At 80 °C, in the molecularly dissolved state, the quenching behavior at low **MOPV4** concentration (up to about 3×10^{-6} M) can be described by using the Stern–Volmer equation[6] as a consequence of formation of a donor–acceptor heterodimer ($K_{SV} = 1.8\times10^{5}$ M^{-1}).[7] The Stern–Volmer equation does not suffice in describing the quenching at 10 °C because of the presence of aggregated structures.[7] The fluorescence drastically changes at this temperature upon addition of **MOPV4**. The fluorescence of **MOPV3** is strongly quenched (λ_{em} = 483 nm), while signals characteristic of isolated **MOPV4** start to appear (λ_{em} = 512 and λ_{em} = 548 nm). In contrast to the behavior in the molecularly dissolved state, the initial decrease at λ = 483 nm is very strong in the aggregated state. Apparently, the supramolecular assemblies present at 10 °C provide an effective pathway for the transfer of excitation energy. Further addition of **MOPV4** results in its fluorescence reaching a maximum and then decreasing again while simultaneously displaying a bathochromic shift (λ_{em} = 524 nm and λ_{em} = 553 nm), which is caused by interaction between its oligomers. This result indicates that at low **MOPV4** incorporations (up to about 2 mol %) it exists as isolated energy traps in **MOPV3** stacks. At high incorporation ratios the trap molecules are able to interact, thus making it more difficult to distinguish between energy transfer from **MOPV3** to **MOPV4** and direct excitation of **MOPV4**.

The resonance energy transfer process in mixed **MOPV** stacks (2.6 mol % **MOPV4** in **MOPV3**) displays a very fast

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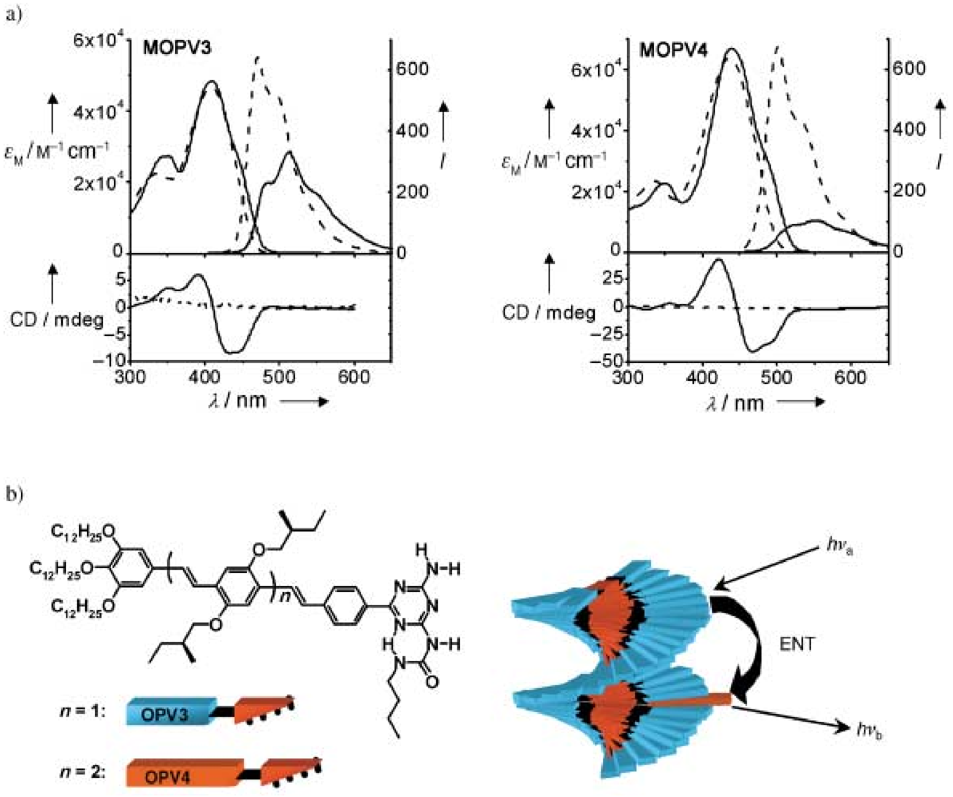

Figure 1. a) Thermochromic behavior of **MOPV3** (1.6×10^{-5} M) and **MOPV4** (1.4×10^{-5} M) in dodecane solution, as monitored by UV/Vis, photoluminescence, and CD spectroscopy (solid line 10 °C, dotted line 80 °C. b) Mixed columnar stacks of MOPV dimers in an apolar environment. The formation of mixed stacks is enabled by the identical hydrogen-bonded motif of both molecules. Energy transfer (ENT) within mixed stacks is studied from **MOPV3** (blue) to **MOPV4** (red).

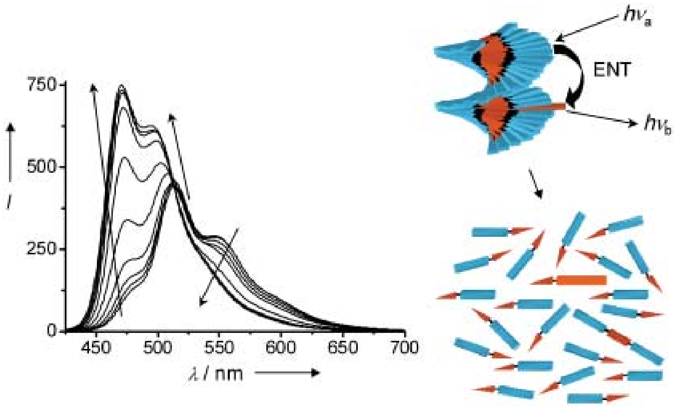

Figure 2. Temperature-dependent photoluminescence spectra ($\lambda_{exc}=412$ nm) of a solution of **MOPV3** (blue) in dodecane with 1.2 mol% trap molecules of **MOPV4** (red). The arrows indicate a temperature rise from 0–90 °C. At high temperatures, when the oligomers are molecularly dissolved, the presence of **MOPV4** can not be distinguished. At low temperatures, when mixed stacks are present, the spectrum resembles a spectrum of molecularly dissolved **MOPV4**. This is a consequence of very efficient energy transfer from **MOPV3** to the isolated trap molecules in the ordered assembly.

(Figure 4) component which is absent when the stacks are dissociated at higher temperature. We have recently shown that excitons undertake fast diffusion along **MOPV4** stacks in the first 50 ps before becoming localized in local potential minima.[8] The diffusion of the exciton over the chiral structure was found to cause a decay of the photoluminescence polarization anisotropy.[8] We are able to relate the previously measured anisotropy decay time to the distance travelled by the excitons along the stacks by using a simple MonteCarlo scheme.[9] From these calculations we estimate that, for the given concentration of acceptors, around 17% excitons will have reached an acceptor site within the first 20 ps after excitation. These predictions are consistent with the experimentally observed relative decay of the donor luminescence with time (Figure 4).

Such a fast diffusion process can be exploited to achieve efficient resonance energy transfer in artificial light-harvesting nanostructures. It has been demonstrated that intermolecular electronic coupling can be comparable to the intramolecular relaxation energy in oligo(phenylene vinylene) assemblies with controlled intermolecular order.[10] We consider that our observation of an early, fast energy-transfer component is compatible with such an exciton transfer in an intermediate coupling regime.

The localization of excitons by configurational and energetic disorder at later times leads to weaker electronic coupling between chromophores and a significant reduction of the transfer rate. The transfer dynamics of localized excitons at timescales greater than a few hundred picoseconds is most likely dominated by direct Förster energy transfer to the guest chromophores (Figure 4 and Figure 5a). Energy

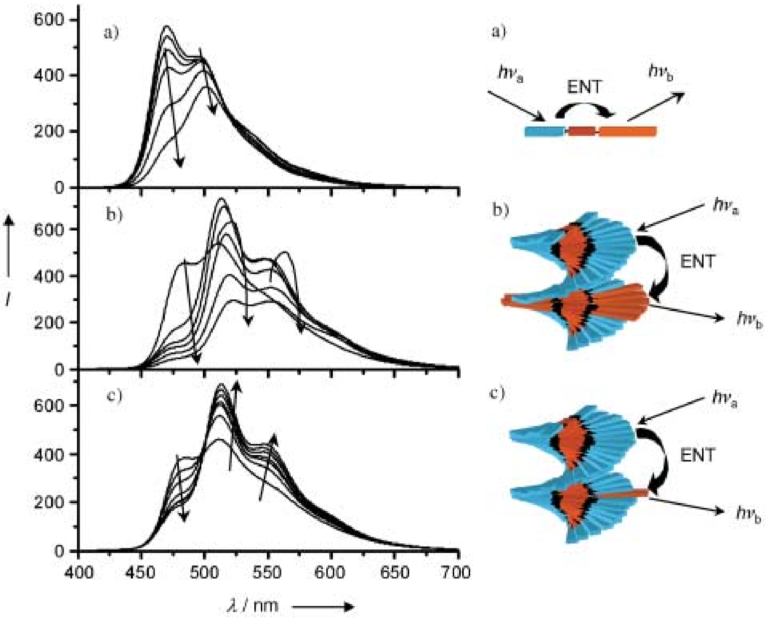

Figure 3. Photoluminescence spectra for mixtures of **MOPV4** and **MOPV3** in dodecane solution ($\lambda_{exc}=412$ nm). The **MOPV3** concentration is fixed at 1.9×10^{-5} M: a) at 80 °C, 0—30 mol% **MOPV4**; b) at 10 °C, 0—30 mol% **MOPV4**; c) at 10 °C, 0–1.2 mol% **MOPV4**. The quenching at 80 °C can be described by using the Stern–Volmer equation. At 10 °C, **MOPV3** fluorescence is quenched instantly, in favor of enhanced **MOPV4** luminescence. This is most visible at low incorporation ratios. The luminescence is strongly diminished at 10 °C, but this is veiled by the fact that different slit widths were used in the experiments.

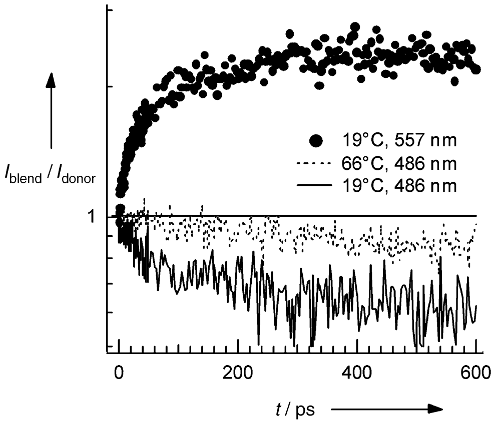

Figure 4. Relative changes in the photoluminescence decay dynamics caused by the introduction of 2.6% molefraction of **MOPV4** into **MOPV3**. For supramolecular stacks formed in the cold (19 °C) solution, a fast relative increase is observed in the spectral region where the **MOPV4** guest emits ($\lambda_{em}=557$ nm), with a corresponding decay in the region where the **MOPV3** host emits ($\lambda_{em}=486$ nm). In contrast, the relative decay of the host in the dissociated phase (66 °C) occurs to a much smaller extent and over a timescale of more than one nanosecond. The curves were obtained by dividing the photoluminescence decay measured for **MOPV3** containing 2.6% molefraction **MOPV4** by the decay curves obtained from **MOPV3** without **MOPV4**.

transfer is not observed if thermal cycling (as described previously) is not undertaken (Figure 5b). Hence, the electronic properties of the assemblies can be tailored reliably by altering the environmental parameters.

In conclusion, ultrafast energy transfer has been observed in mixed supramolecular stacks of oligo(phenylene vinylene)s in solution. Extended columnar aggregates of **MOPV3** incorporating **MOPV4** show a very efficient quenching of the **MOPV3** fluorescence, which indicates that energy transfer occurs within the supramolecular stacks from the shorter oligomer to the longer one. We have demonstrated that control of nanoscale order provides a strategy for tailoring macroscopic electronic properties of organic semiconductor systems. To achieve these objectives, we make use of a comprehensive set of processing variables, such as temperature, blend composition, functional side groups, and solvent. In addition, we aim to extend this concept to longer oligomers in the near future.

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[1] a) W. Kühlbrandt, D. N. Wang, Y. Fujiyoshi, *Nature* **1994**, *367*, 614–621; b) G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell, N. W. Isaacs, *Nature* **1995**, *374*, 517–521.

[2] a) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, P. Herwig, D. M. De Leeuw, *Nature* **1999**, *401*, 685–688; b) L. Schmidt-Mende, A. Fechtenkötter, K.

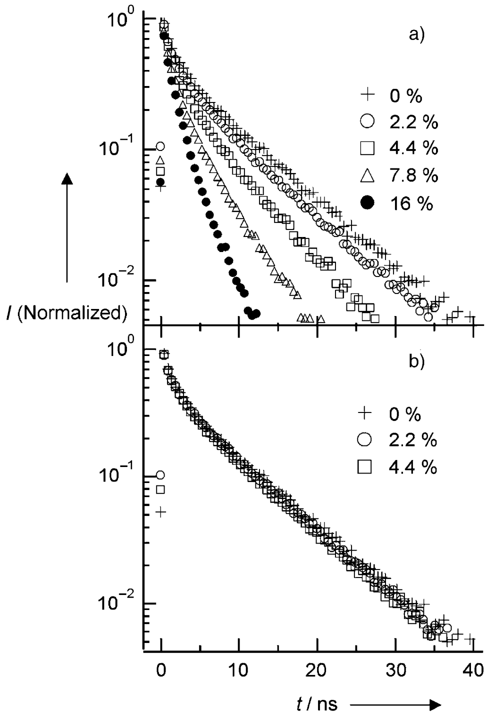

Figure 5. Fluorescence decay of **MOPV3** and blends of **MOPV4** in **MOPV3** at 14 °C and $\lambda_{em}=475$ nm. The **MOPV3** concentration was kept around 1.4×10^{-4} M while the mole fractions of **MOPV4** were varied as shown). The decays displayed in (a) were obtained by heating the solutions to 80 °C prior to measurement, while for the decays displayed in (b), the thermal cycling was omitted.

Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119–1122; c) 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. Hudson, H. Duan, *Nature* **2002**, *419*, 384–387.

[3] a) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40–48; b) M.-S. Choi, T. Aida, T. Yamazaki, I. Yamazaki, *Angew. Chem.* **2001**, *113*, 3294–3298; *Angew. Chem. Int. Ed.* **2001**, *40*, 3194–3198; c) R. A. Garoff, E. A. Litzinger, R. E. Connor, I. Fishman, B. A. Armitage, *Langmuir* **2002**, *18*, 6330–6337; d) V. I. Prokhorenko, A. R. Holzwarth, M. G. Müller, K. Schaffner, T. Miyatake, H. Tamiaki, *J. Phys. Chem. B* **2002**, *106*, 5761–5768; e) A. de la Escosura, M. V. Martínez-Díaz, P. Thordarson, A. E. Rowan, R. J. M. Nolte, T. Torres, *J. Am. Chem. Soc.* **2003**, *125*, 12300–12308.

[4] A. P. H. J. Schenning, P. Jonkheijm, E. Peeters, E. W. Meijer, *J. Am. Chem. Soc.* **2001**, *123*, 409–416.

[5] a) P. Jonkheijm, F. J. M. Hoeben, R. Kleppinger, J. Van Herrikhuyzen, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2003**, *125*, 15941–15949; b) SANS experiments show that the shape of the aggregates does not change upon addition of 2 mol% **MOPV4** to pure **MOPV3** aggregates.

[6] J. Wang, D. Wang, E. K. Miller, D. Moses, G. C. Bazan, A. J. Heeger, *Macromolecules* **2000**, *33*, 5153–5158.

[7] See Supporting Information.

[8] 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**, *68*, 045203/1–045203/7.

[9] Our scheme models the diffusion of excitons on a chiral structure consisting of 350 chromophores with a cofacial angle of 12° (molecular mechanics calculations, based on the Dreiding force field [S. L. Mayo, B. D. Olafson, W. A. Goddard, *J. Phys. Chem.* **1990**, *94*, 8897–8909] lead to angles ranging from 6° to 12° in a stack of 16 molecules). An effective hopping rate is used to define the time interval, so that at every time step every exciton has to hop up or down along the structure. Long-range transfer and correlation effects are not taken into account. The probability for exciton creation is taken to be proportional to the square of the cosine between the excitation polarization and each chromophore orientation. The anisotropy at any time is calculated using the orientation of the chromophores supporting an exciton and integration over a large number of stack orientations and exciton paths (typically 10000). The anisotropy, defined as $(I_{\parallel}-I_{\perp})/(I_{\parallel}+2I_{\perp})$, where $I_{\parallel(\perp)}$ is the photoluminescence intensity parallel (perpendicular) to the excitation polarization, decays from 0.4 to 0.1 and is compared to the experimental value of the anisotropy. This simple simulation allows the temporal evolution of the exciton diffusion to be obtained.

[10] F. C. Spano, *J. Chem. Phys.* **2002**, *116*, 5877–5891.