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Photoinduced Electron Transfer in Hydrogen-Bonded Oligo(*p*-phenylene vinylene)−Perylene Bisimide Chiral Assemblies

Albertus P. H. J. Schenning,*,† Jeroen v. Herrikhuyzen,† Pascal Jonkheijm,† Zhijian Chen,‡
Frank Würthner,*,‡ and E. W. Meijer*,†

*Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands, and the Department of Organic Chemistry II, University of Ulm,
Albert-Einstein-Allee 11, D-89081 Ulm, Germany*

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Organized dye assemblies play an important role in biological electron-transfer processes and hydrogen bonding has been recognized as crucial for structural and functional reasons. To shed light into these processes photoinduced electron-transfer has been studied for numerous electron donor (D)−electron acceptor (A) dyads that are connected by hydrogen bonds.[1] In the given work we extend these studies to the next level of hierarchy by combining hydrogen-bonding and $\pi-\pi$-interactions to give extended multichromophoric assemblies containing electron donor and acceptor dyes. This self-assembly process is not only important for addressing fundamental questions in chemical biology but also of great interest in the field of solar cells.[2]

Previously, our groups have independently shown that well-defined superstructures can be obtained of electron-acceptor associates (cylindrical strands of hydrogen-bonded perylene bisimide derivatives)[3] or electron-donor associates (helical supramolecular stacks of chiral π-conjugated oligo(*p*-phenylene vinylenes) containing ureidotriazine hydrogen-bonding units).[4] Here, we report the collective and hierarchical self-assembly of these two functional dyes, that is, oligo(*p*-phenylene vinylene) **1** and perylene bisimide **2**, into chiral fibers that show photoinduced electron transfer. Perylene bisimide acceptor **2** has two complementary binding sites for the diaminotriazine hydrogen-bonded moiety of donor **1**. Although the binding constant of the **1**−**2**−**1** complex is expected to be rather low in chloroform,[5] a significant increase will be found in more apolar solvents, like methylcyclohexane.[3] Moreover, the binding strength will further increase when additional $\pi-\pi$ stacking interactions during the process of superstructure formation come into play.[6]

UV/vis, fluorescence, and CD titration experiments in methylcyclohexane (MCH) were performed to study the interactions of **1** and **2**. A bathochromic shift from $\lambda_{max} = 562$ to 604 nm was observed for the perylene absorption maximum of the S_0−S_1 electronic transition upon adding aliquots of **1** to **2**. This shift is much larger than for all perylene aggregates studied so far,[3,6] and it suggests that the perylenes pack tightly in a J-type aggregate. Ordinary J-aggregated dyes show intense fluorescence but, here the fluorescence of the perylene was heavily quenched ($\lambda_{ex} = 575$ nm, $\lambda_{em,max} = 591$ nm) which is rationalized by an electron-transfer process from the OPV-donor to the perylene-acceptor chromophore. Optimal quenching of fluorescence was obtained when all bisimide binding sites of **2** are hydrogen-bonded to **1** at a ratio of 1:2. A Stern−Volmer constant of 6.5×10^5 M^{-1} was calculated from the Stern−Volmer plot. In addition to these changes in the absorption and photoluminescence properties a strong negative Cotton effect of the perylene chromophore was developed upon adding **1** that indicates that the chirality of the side chain of the OPV-unit is expressed in the bisimide chromophore.[7] Likewise, if the concentration of **1** was taken constant and **2** was added, a bathochromic shift was observed for the OPV absorption from $\lambda_{max} = 436$ to 450 nm, while in the CD experiment a bisignated Cotton effect at the position of the $\pi-\pi^*$ band of the OPV moiety appeared upon adding **2**. Analysis of both titrations shows the formation of a 2:1 hydrogen-bonded complex of the individual compounds. The optical activity found in all absorptions provides clear evidence that the complex **1**−**2**−**1** further stacks into J-aggregates with a helical screw sense, similar as for extended π-conjugated oligomers.[8]

To further shed light into the self-assembly process between the two chromophoric building blocks, concentration- and temperature-dependent optical spectroscopy was carried out for the 1:2 complex. In the concentration-dependent UV−vis spectra we saw a red-shift of the absorption maximum for both **1** and **2** with increasing concentration and a well-defined transition from nonaggregated species at concentrations $<10^{-7}$ M to aggregated species at concentrations $>10^{-5}$ M. Evaluation of the self-assembly process in a simplified model assuming a one-dimensional growth process of preformed **1**−**2**−**1** affords an aggregation constant of 10^7 M^{-1} which is about 1 order of magnitude higher than the value for a simple tetra(*p*-*tert*-butylphenoxy)-substituted perylene bisimide dye[6]—an increase which we attribute to a favorable contribution of the associated OPV moieties. The same spectral changes took place in temperature-dependent UV−vis spectra at a constant concentration (Figure 1). At temperatures higher than 60 °C, the absorption spectra were similar to those of the separate compounds in methylcyclohexane at room temperature. Coinciding with the changes in the UV−vis spectra, the CD intensity of **1** and **2** decreases at temperatures higher than 40 °C and was completely lost at 60 °C. Upon cooling, the CD spectrum was fully recovered, indicating full reversibility. Further proof for the existence of two different phases of the **1**−**2**−**1** assembly in methylcyclohexane solutions comes from the increase of the photoluminescence of **2** at $\lambda = 591$ nm ($\lambda_{ex} = 575$ nm) upon disassembly at elevated temperature.

The three techniques prove the existence of two phases for the **1**−**2**−**1** complex in solution, that is, aggregates at low temperatures and molecularly dissolved monomeric species at high temperatures (Figure 1). The phase transitions take place at a “melting” temperature of about 50 °C, demonstrating a remarkably stable assembly. Atomic force microscopy (AFM) on a glass substrate revealed that the assemblies are also chiral (Figure 2). Helical rodlike aggregates were observed with a length of several mi-

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* To whom correspondence should be addressed. E-mail: E.W.Meijer@tue.nl.
† Eindhoven University of Technology.
‡ University of Ulm.

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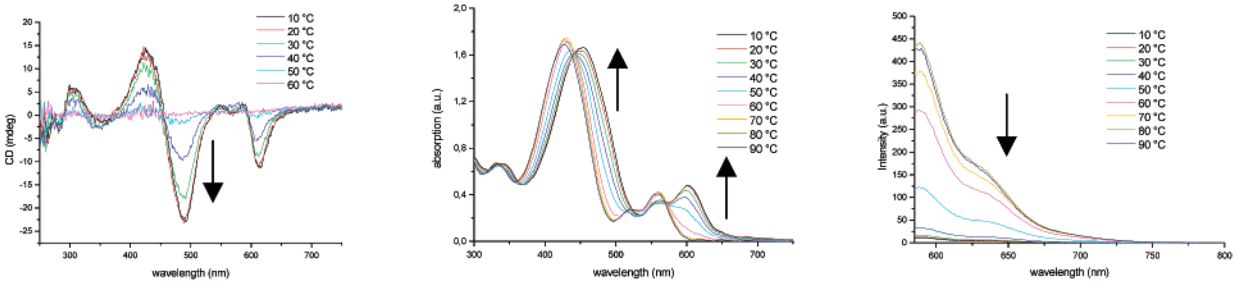


Figure 1. Temperature-dependent CD (left), UV−vis (middle), and fluoresence spectra (right) of the **1−2−1** triad ($c = 3.7\ 10^{-5}$ mol/L) in MCH (arrows indicate the changes upon cooling).

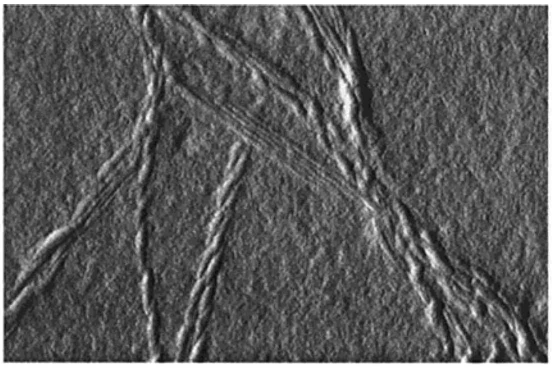
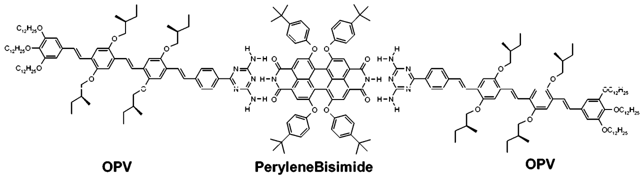


Figure 2. Tapping mode AFM image (715 nm × 475 nm) of the **1−2−1** complex upon spin-coating from MCH ($c = 1$ wt %) on a glass slide.

Chart 1. 2:1 Assembly of OPV **1** and Perylene Bisimide **2**



crometers and a width of the smallest resolved fibers of about 7 nm. The large fibers are presumably composed of multilayers having a width of multiples of 7 nm, that coil into chiral aggregates.

On the basis of the information sofar, we favor a model of hydrogen-bonded complexes (Chart 1), which further self-assemble into long fibers that have a width of 7 nm. To explain the large bathochromic shift of the perylene absorption and the strong negative CD of the dye assemblies, winding of the complex in a chiral screw sense as shown in Figure 3 seems to be a reasonable possibility. For such an assembly each molecule of **2** is coordinated by hydrogen-bonding to two molecules of **1** and all polar parts (e.g., the hydrogen-bonding sites and the π-surfaces) are covered in the interior while the alkyl parts direct into the aliphatic solvent or interpenetrate to neighboring fibers at the glass surface.

Femtosecond pump−pulse spectroscopy measurements were performed in MCH to determine the charge-transfer rate in the complex. When excited at 450 nm where mainly **1** absorbs, the OPV radical cation becomes visible at 1450 nm, indicating a photoinduced electron-transfer process.[9] At room temperature this charge-separated state is formed within a few picoseconds, while the recombination is within 60 ps. At 80 °C where only monomers and small hydrogen-bonded complexes are present the charge formation is again within picoseconds, but the recombination takes now more then 300 ps. Presumably, the charge-separated state lives longer at high temperature because after charge transfer the complex may dissociate.

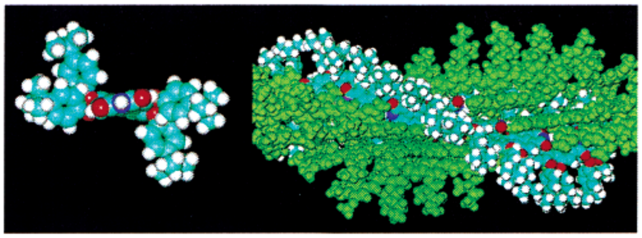


Figure 3. Top view on one atropisomer of **2** (left) and possible helical arrangement for **1−2−1** (right; OPVs are shown in green color).

In conclusion, well-defined chiral fibers incorporating donor and acceptor chromophores could be realized by self-assembly. Upon photoillumination of these fibers electron transfer takes place, leading to charge separation within the aggregated dyes. The application of these bichromophoric assemblies in photovoltaic and nanoscale devices is in progress.

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