Light-Harvesting Polymers

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Long-Distance Electronic Energy Transfer in Light-Harvesting Supramolecular Polymers**

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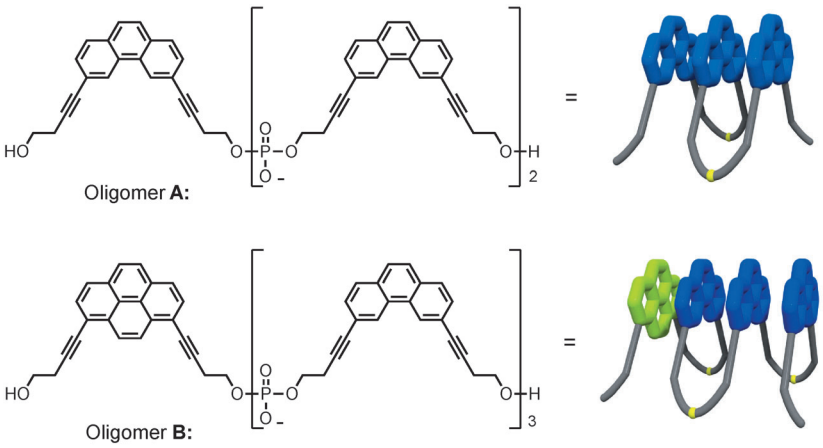
Abstract: *The efficient collection of solar energy relies on the design and construction of well-organized light-harvesting systems. Herein we report that supramolecular phenanthrene polymers doped with pyrene are effective collectors of light energy. The linear polymers are formed through the assembly of short amphiphilic oligomers in water. Absorption of light by phenanthrene residues is followed by electronic energy transfer along the polymer over long distances (>100 nm) to the accepting pyrene molecules. The high efficiency of the energy transfer, which is documented by large fluorescence quantum yields, suggests a quantum coherent process.*

Photosynthesis is the key process that enables life on Earth. In natural light-harvesting complexes (LHC), photons are collected by arrays of protein-bound chromophores.[1–8] After excitation of the chromophores the absorbed energy is transferred to the photosynthetic reaction center. The design and development of artificial light-harvesting systems is a contemporary academic and industrial challenge with economic and ecological implications.[9–23] The structural organization of the light-absorbing molecules is of particular importance for efficient energy harvesting and transfer processes. Polymeric and dendritic materials appear particularly promising in this context, due to the covalent joining of large numbers of light absorbing molecules.[24–36] Alternatively, DNA has been used as a supramolecular scaffold[37–49] for the construction and the study of light-harvesting antenna systems. We have recently reported on the assembly of water soluble linear[50,51] and two-dimensional[52] supramolecular polymers[53–57] from short amphiphilic pyrene oligomers (oligopyrenotides).[58] Herein, we describe the light harvesting properties of linear supramolecular phenanthrene polymers doped with minute amounts of pyrene acceptors.

The two different oligomers used in the present study are shown in Scheme 1. Oligomer **A** is composed of three phosphodiester-linked phenanthrene units, while oligomer **B** contains an additional, terminal pyrene building block. Synthesis of the required 3,6-dibutynylphenanthrene phosphoramidite is summarized in Scheme 2.

Starting from 3,6-dibromophenanthrene (**1**)[59] the alkynyl-linkers were introduced in a Sonogashira reaction using but-3-yne-1-ol to give diol **2**. Subsequent DMT-protection provided alcohol **3**, which was converted into phosphoramidite **4**. Assembly of the oligomers was accomplished by automated oligonucleotide chemistry using **4** and the corresponding 1,8-dibutynyl-substituted pyrene phosphoramidite.[60] Oligomers **A** and **B** were purified by HPLC and characterized by mass spectrometry (see Supporting Information).



Scheme 1. Left: Oligomers **A** and **B**. Right: model representation: phenanthrene units blue (donor), pyrene green (acceptor), linkers gray, and phosphodiester groups yellow spheres.

Polymerization experiments typically involve a 0.5 μM oligomer solution in 10 mM sodium phosphate buffer at pH 7.2. The solution is heated to 90 °C and cooled to room temperature over 10 min. Assembly of the oligomeric building blocks takes place below 60 °C (see below) and leads to the formation of supramolecular polymers, which are readily visualized by atomic force microscopy (AFM). Figure 1 displays a representative sample of polymers obtained from a mixture of oligomers **A** (0.5 μM) and **B** (0.5 nM). The AFM image shows linear polymers of uniform thickness and a length of several micrometers. Individual fibers adopt

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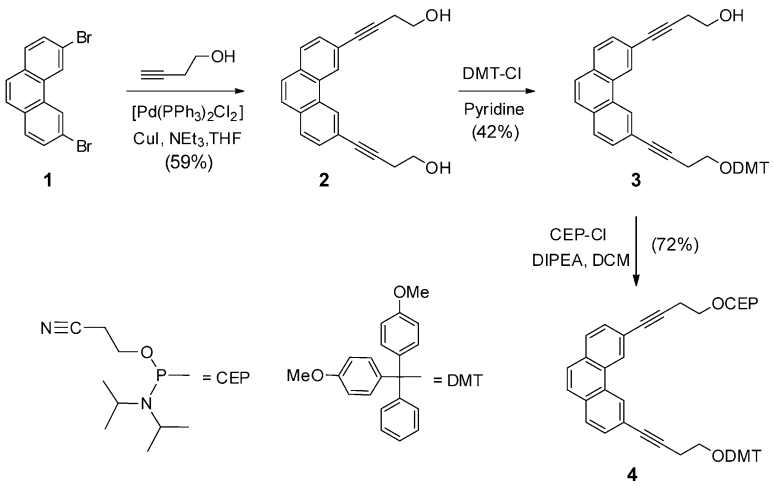


Scheme 2. Synthesis of the 3,6-dialkynylphenanthrene phosphoramidite used for the preparation of phosphodiester-linked oligomers **A** and **B**. DCM = dichloromethane, DIPEA = diisopropylethylamine.

assemblies, as schematically illustrated in Scheme 3. Pyrene units are embedded in the polymer at rare positions.

The assembly process leading to the polymers was studied in more detail by temperature dependent absorption and emission experiments. Figure 2 displays the UV/Vis absorption and the fluorescence spectra of the assembled polymers (at 20 °C) and the oligomers **A** and **B** in their disassembled state (at 90 °C). The UV/Vis spectrum shows a distinct shift of the phenanthrene $S_0 \rightarrow S_1$ band from $\lambda_{abs} = 322$ nm at 20 °C to $\lambda_{abs} = 314$ nm at 90 °C. Furthermore, the band around $\lambda_{abs} = 250$ nm shows changes in intensity and shape. Pronounced temperature-dependent differences are also visible in the fluorescence spectrum upon phenanthrene excitation. A change from pyrene fluorescence in the polymers to phenanthrene emission in the dissociated state is observed. This implies that the energy absorbed

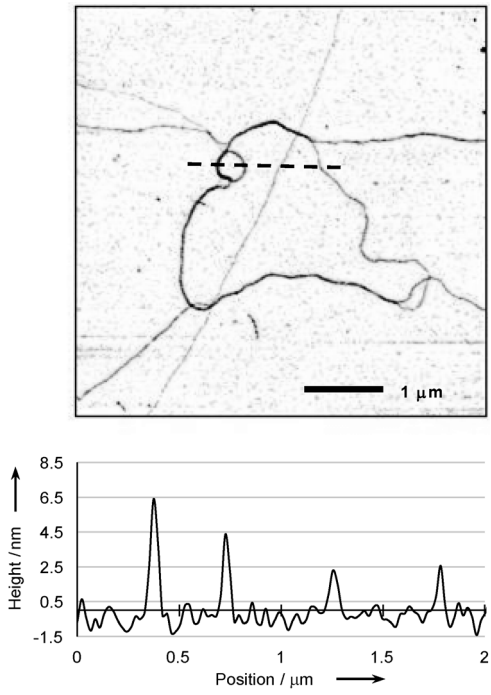
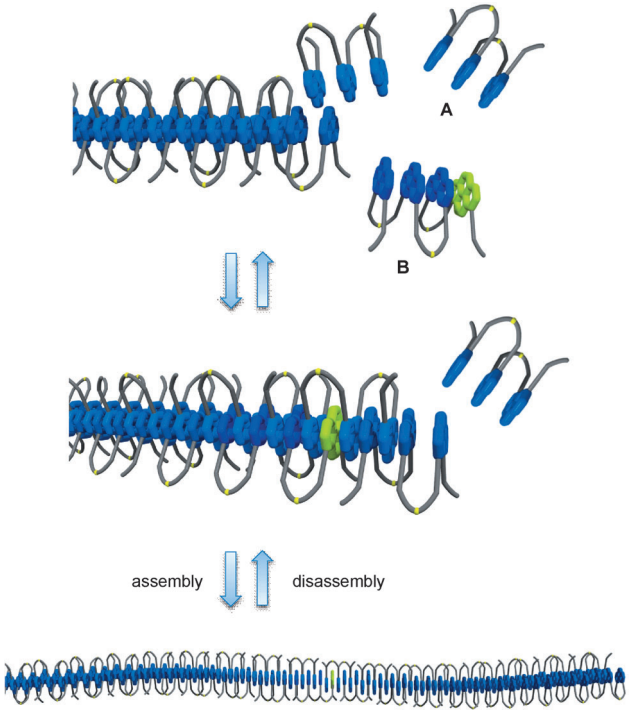


Figure 1. Top: AFM image of the polymers formed from a mixture of oligomer **A** (0.5 µM) and **B** (0.5 nM) after deposition on amino-derivatized mica sheet (see Supporting Information). Bottom: height of the polymers measured along the dashed line in the top image. Conditions: 10 mM sodium phosphate buffer at pH 7.2.



Scheme 3. Graphical illustration of the assembly of supramolecular polymers from short, phosphodiester-linked phenanthrene oligomers (blue, oligomer **A**); pyrene molecules (green, in oligomer **B**) are randomly integrated into growing polymer chain. Butynyl substituents gray, phosphodiesters yellow.

a relatively straight, elongated shape. Regions in which single fibers join to form bundles (measured height up to ca. 6.5 nm, see Figure 1, bottom) are abundant. The thickness of a single polymer strand (2.5 ± 0.3 nm, Supporting Information) is very similar to the value determined for polymers of carboxamide-derived oligopyrenes.[61] This suggests an interdigitated, face-to-face stacked arrangement of dialkynylphenanthrene molecules of different oligomers resulting in long π-stacked

by phenanthrene ($\lambda_{abs} = 322$ nm, see also Figure S10 in the Supporting Information) is transferred to pyrene acceptor molecules in the intact polymers, and this energy transfer is disrupted when the polymers are disassembled. The temperature-controlled assembly–disassembly of the polymers can be followed by monitoring changes in the pyrene fluorescence intensity at $\lambda_{em} = 406$ nm (Figure 3).

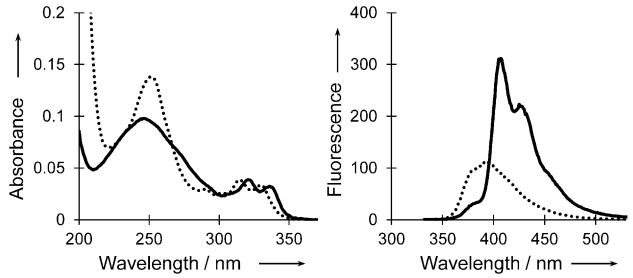


Figure 2. UV/Vis (left) and fluorescence (right) spectra of the assembled polymers (20 °C, solid curve) and the disassembled oligomers (90 °C, dotted curve). Conditions: 10 mM sodium phosphate buffer, pH 7.2; 0.5 μM oligomer **A** and 0.5 nM oligomer **B**; $\lambda_{ex} = 322$ nm.

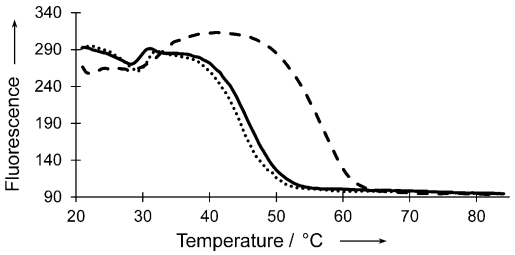


Figure 3. Assembly and disassembly process of supramolecular polymers monitored by temperature dependent changes of pyrene fluorescence. Conditions: 10 mM sodium phosphate buffer, pH 7.2; $\lambda_{ex} = 322$ nm; $\lambda_{em} = 406$ nm temperature gradient 0.3 °C min^{-1}; cooling–heating–cooling: solid–dashed–dotted.

The assembly and disassembly curves show strong hysteresis. A difference of approximately 10 °C indicates that the process is relatively slow under the chosen experimental conditions. Nevertheless, it can be concluded that the assembly–disassembly process takes place between 40 and 60 °C, and that the polymers are stable at room temperature. The same results are obtained in temperature-dependent absorption experiments (see also Figure S9). Furthermore, dynamic light scattering (DLS) experiments[62,63] show a temperature-dependent particle size (see Supporting Information).

Polymers composed exclusively of phenanthrenes (i.e. only of oligomer **A**) are weakly fluorescent upon phenanthrene excitation at $\lambda_{ex} = 322$ nm (Figure 4, dotted curve).

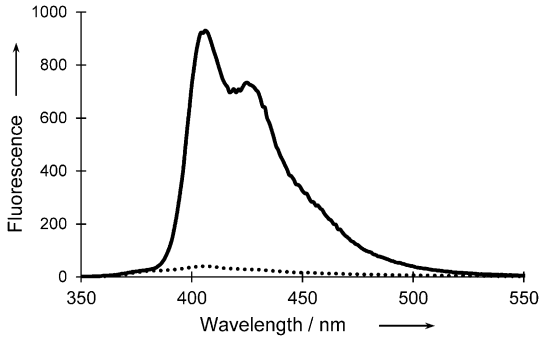


Figure 4. Fluorescence of the phenanthrene polymer in the absence (dotted curve) and in the presence of 1.3 mol% (solid curve) of pyrene. Conditions: 10 mM sodium phosphate buffer, pH 7.2; $\lambda_{ex} = 322$ nm.

This changes drastically when the polymers are formed in the presence of traces of pyrene-containing oligomer **B**. Phenanthrene excitation now results in an emission spectrum that corresponds to pyrene monomer fluorescence (Figure 4, solid curve).[60] Furthermore, the fluorescence quantum yield (ϕ_f) increases sharply. As shown by the doping experiment displayed in Figure 5, already minute amounts of pyrene

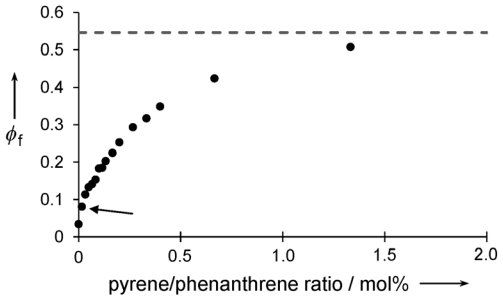


Figure 5. Dependence of the fluorescence quantum yield (ϕ_f) on the fraction of pyrenes present in the phenanthrene polymers. Conditions: 10 mM sodium phosphate buffer, pH 7.2; 0.5 μM oligomer **A**; $\lambda_{ex} = 322$ nm. The dashed line represents the value of the quantum yield of 1,8-dibutynylpyrene monomer (0.55) and the arrow indicates the value taken for calculation of the average distance of energy transfer (D_{ET}) according to Equation (1).

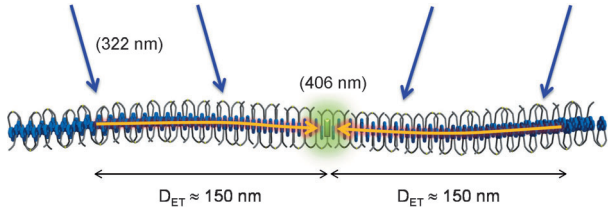
(< 0.1 mol%) result in a substantial increase in ϕ_f, which reaches a value of 0.51 when oligomer **B** is admixed such that the total pyrene content equals 1.33 mol%. Notably, the value of 0.51 is close to the quantum yield of 1,8-dibutynylpyrene monomer fluorescence (0.55, dashed line in Figure 5, see also Supporting Information.

Information on the efficiency of the electronic energy transfer (EET) can be derived from this doping experiment. Polymers formed exclusively of oligomer **A** exhibit only weak fluorescence. Addition of 0.5×10^{-3} equivalents of oligomer **B**, which corresponds to a phenanthrene/pyrene ratio of approximately 6000 (indicated with arrow in Figure 5), results in a sharp increase in ϕ_f (0.080). It can be assumed that, at this ratio, the pyrene accepts and emits the maximum possible amount of excitation energy. The energy absorbed by the phenanthrene molecules is transferred along the polymer over a certain distance to the pyrene acceptor where it is emitted. When the number of pyrenes, which are assumed to be statistically distributed over the polymer chain, increases, they are located more and more densely in the polymer. The fluorescence quantum yield of the polymer grows with an increasing number of pyrenes and eventually approximates the value of 1,8-dibutynylpyrene monomer ($\phi_f^{Py} = 0.55$). Assuming an intrachain energy transfer (ET) and a statistical distribution of pyrene acceptor molecules in the fibers, a rough estimation of the average distance of ET (D_{ET}) can be made according to Equation (1):

$$D_{ET} \approx \frac{N^{Phe} \times \phi_f^{A}}{\phi_f^{Py}} \times 0.5 \times 0.35\,\text{nm} \approx 150\,\text{nm} \quad (1)$$

where N^{Phe} = number of phenanthrene molecules per one pyrene; ϕ_f^{Py} = quantum yield of 1,8-dibutynylpyrene monomer; ϕ_f^{A} = quantum yield of phenanthrene polymers doped with 0.5×10^{-3} mol equivalents of pyrenes; 0.35 nm = distance separating face-to-face stacked polyaromatic compounds; factor 0.5 = geometry factor considering that, in this model, light is collected from both sides of the pyrene (see also the Supporting Information).

A value of approximately 150 nm is thus obtained, which means that the excitation energy is transferred over more than 400 phenanthrene molecules with high efficiency (illustrated in Scheme 4).



Scheme 4. Illustration of light-harvesting antenna. Supramolecular polymers are assembled in aqueous medium from short, negatively charged phenanthrene oligomers and doped with small quantities of pyrene (≤1%). Light is absorbed by phenanthrenes (blue) and transported with high efficiency over an average distance of 150 nm (more than 400 phenanthrene molecules) to the next pyrene (green), where relaxation takes place by emission of pyrene monomer fluorescence.

Considering that the quantum yield of the pyrene-doped antenna is higher than that of the phenanthrene polymer alone, energy transfer over such a long distance cannot be explained by a classical Förster resonance energy transfer mechanism. Newer concepts for the description and understanding of light-harvesting phenomena include theories of coherent energy transfer[27,64–70] and could help to explain the remarkable efficiency of EET observed in the system described herein. It is not inconceivable that electronic coupling of the stacked aromatic molecules in the present polymers, which are formed of hydrophobic phenanthrene units in an aqueous environment, is sufficiently strong to enable coherent energy transfer.

In conclusion, the formation of water soluble, light-harvesting supramolecular polymers with a length of several μm has been demonstrated. Polymers are composed of phosphodiester-linked phenanthrenes that act as energy-collecting donor molecules. Integration of trace amounts (≤ 1%) of pyrene acceptor molecules into the polymer leads to intense pyrene fluorescence upon phenanthrene excitation. At higher pyrene contents (>1%) the fluorescence quantum yield of the light harvesting polymers approximates the one of the monomeric pyrene building block ($\phi_f^{Py} = 0.55$). Model considerations indicate that the energy is transferred with high efficiency over an average distance of approximately 150 nm, making quantum coherent EET more likely than classical Förster resonance energy transfer.

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