Light-Harvesting Nanotubes

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Light-Harvesting Nanotubes Formed by Supramolecular Assembly of Aromatic Oligophosphates

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Abstract: *A 2,7-disubstituted phosphodiester-linked phenanthrene trimer forms tubular structures in aqueous media. Chromophores are arranged in H-aggregates. Incorporation of small quantities of pyrene results in the development of light-harvesting nanotubes in which phenanthrenes act as antenna chromophores and pyrenes as energy acceptors. Energy collection is most efficient after excitation at the phenanthrene H-band. Fluorescence quantum yields up to 23 % are reached in pyrene doped, supramolecular nanotubes.*

The construction of artificial light-harvesting complexes has received much attention in recent years.[1–11] In light-harvesting systems, energy is absorbed by numerous chromophores and transferred to an acceptor. Polymers[12–19] and dendrimers[20–26] were used to arrange multiple organic chromophores around acceptor molecules. Efficient transport of the excitation energy is a key aspect for the construction of effective light-harvesting systems.[27] The degree of structural order determines the level of electronic coupling and, thus, the efficiency of energy transfer in chromophore arrays.[2,3,28,29] One way of assembling highly organized molecular arrays is provided by supramolecular polymerization.[30–36] Inspired by the unique electronic properties of carbon nanotubes,[37,38] supramolecular organic nanotubes appear as particularly attractive scaffolds for the molecular organization of chromophore aggregates. Owing to the non-covalent nature of interaction, supramolecular polymers offer a high degree of modularity and, hence, flexibility for their construction and potential functionalization. The assembly of supramolecular nanotubes with light-harvesting properties has been shown for amphiphilic monomers[39–41] and aromatic peptides.[42] In previous work we described the formation of one-dimensional, light-harvesting supramolecular polymers from aromatic oligophosphates.[43] These linear polymers were formed of 3,6-substituted phenanthrene oligomers. The use of 2-dimensional (2D) polymers would allow extending considerably the number of structurally organized, energy collecting chromophores. The assembly of 2D polymers was demonstrated with 1,6- and 2,7-linked pyrene oligomers.[44–46] Here, we describe the formation of light-harvesting supramolecular nanotubes from 2,7-linked oligophenanthrenes doped with pyrene acceptor chromophores.

Oligomers **1** and **2** (Figure 1) were assembled on a phenanthrene-derived solid support using phosphoramidite chemistry. The required phenanthrene and pyrene phosphoramidites were synthesized from 2,7-dibromophenanthrene,[47] or the commercially available 2,7-dibromopyrene (see Supporting Information). Trimer **1** consists of three phenanthrene units joined by phosphodiester groups attached via butynol linkers in positions 2 and 7. The structure of **2** is similar to **1**, except that the phenanthrene in the central position has been replaced by a 2,7-substituted pyrene.

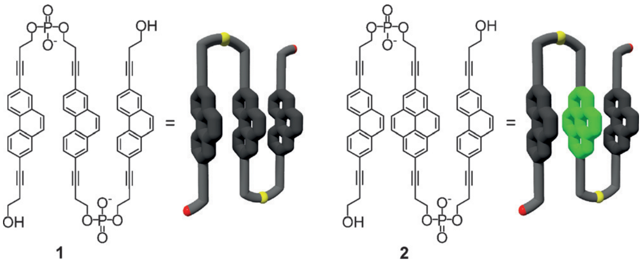

Figure 1. Chemical structure and illustrative model representations of trimers **1** and **2**. Pyrene is highlighted in green.

The effect of solvent polarity on the aggregation behavior of **1** is shown by changes in the absorption spectra (Figure 2). In ethanol, the oligomer is very soluble and the spectrum closely resembles that of the phenanthrene monomer (Supporting Information). In a more polar, aqueous environment (see Figure 2 for experimental details), phenanthrenes exhibit strong aggregation behavior as revealed by a substantial hypochromism, especially at 270 and 316 nm, and the characteristic changes in the vibronic structure.[48–53] Phenanthrene aggregation leads to the disappearance of the 270 nm

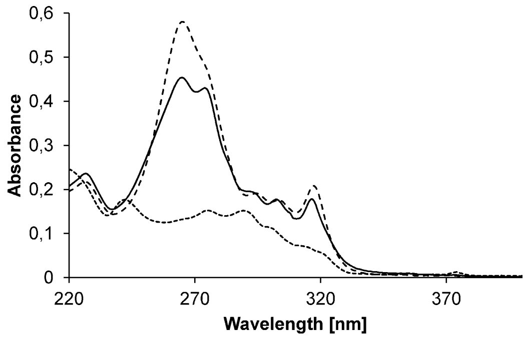

Figure 2. Absorption spectra of **1** in aqueous 10 mM sodium phosphate buffer pH 7.0, 10% ethanol (•••• at 20 °C, ––– at 80 °C) and in ethanol at 20 °C (——). Concentration of **1**: 1 μM.

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band and the occurrence of an H-band (243 nm).[48,54] This suggests that oligomer **1** forms supramolecular polymers in which the phenanthrenes are arranged in extended H-aggregates. Heating of the aqueous solution to 80°C leads to disassembly of the polymers, with concomitant disappearance of the H-band.

Trimer **1** forms tubular structures in aqueous solution. Atomic force microscopy (AFM, Figure 3A) reveals elongated objects reaching a length of several micrometers. The measured height of the polymers after deposition on $NiCl_2$-treated mica[55] is in the range of 4–4.5 nm. This corresponds to a double-layer of π-stacked phenanthrenes formed by the deposition of supramolecular tubes on the surface.[46] The diameter of the nanotubes varies in the range of 50–150 nm (Supporting Information). The tubular morphology of the nanostructures was confirmed by transmission electron microscopy (TEM) experiments (Figure 3B). Notably, polymerization of oligomer **1** exclusively results in the formation of tubular objects. This is in contrast to findings with trimers of the *iso*-structural 2,7-pyrene,[46] which leads to the simultaneous formation of nanosheets and nanotubes.

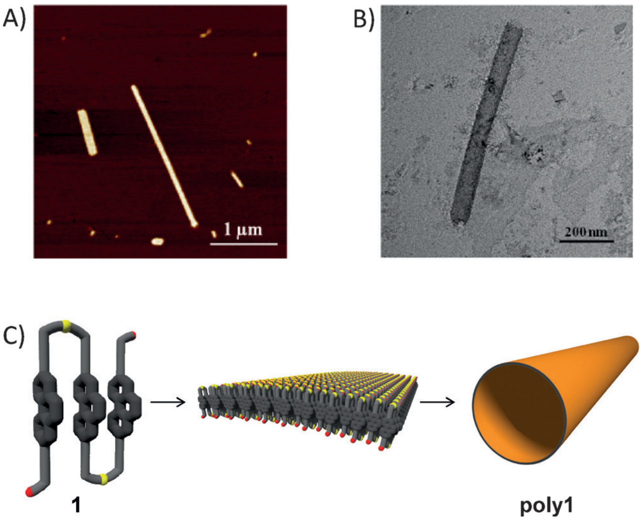

Figure 3. A) AFM image of supramolecular polymers (**poly1**) assembled in aqueous solution and deposited on mica using $NiCl_2$ as surface binding agent. Formation of the nanotubes is accomplished by slow cooling of a 1 µM solution of trimer **1** from 80°C to room temperature in water (10 mM sodium phosphate buffer, pH 7.0) containing 10% v/v of ethanol. B) TEM image of a phenanthrene nanotube. C) Illustration of the self-assembly of phenanthrene oligomers **1**. Hydrophobic phenanthrene units are arranged in a sheet-like manner with hydroxyl-groups (red) and phosphates (yellow) located on its inner and outer surfaces.

The fluorescence spectrum of **poly1** measured in aqueous medium shows a structured emission band with maxima at 371 and 391 nm when excited at 316 nm (Figure 4A). Excitation at 243 nm (H-band) leads to changes in the shape of the emission band. The maxima are shifted by 5 nm to the red (376 and 396 nm) and a broad band newly appears around 425 nm, which most likely arises from excimer formation.[56] The excitation wavelength dependence of phenanthrene fluorescence has been reported previously and was attributed to solvation effects.[57] The fluorescence quantum yield (Φ) also depends significantly on the excitation wavelength. For excitation at 316 nm, a value of 7% was obtained (see the Supporting Information for details), whereas excitation at 243 nm (H-band) renders a value of only 3%. A red-shifted fluorescence and a low quantum yield are well-known features of H-aggregates.[58] Excitation spectra (Figure 4B) further demonstrate the strong dependence of the fluorescence on the excitation wavelength. The spectrum obtained by recording the emission at 391 nm resembles the absorption spectrum of oligomer **1** dissolved in ethanol. Monitoring of the emission at 412 nm gives a spectrum with a peak at 243 nm, which coincides with the H-band in the absorption spectrum of **poly1**. Finally, the excitation spectrum recorded at 437 nm is comparable to the absorption spectrum of **poly1** obtained in aqueous medium exhibiting again the characteristic band at 243 nm and a comparatively reduced intensity at 275 and 316 nm. Thus, H-aggregation leads to a red-shifted fluorescence.

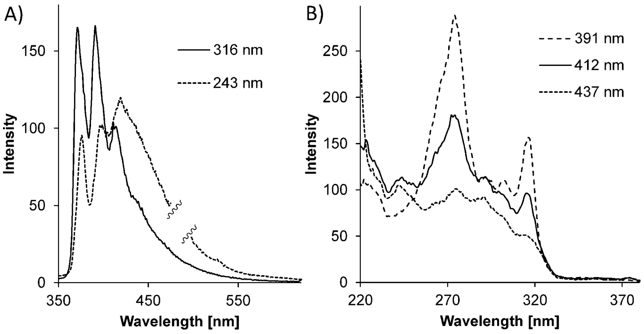

Figure 4. A) Fluorescence and B) excitation spectra of **poly1**. Conditions: 1 µM in 10 mM sodium phosphate buffer pH 7.0, 10% ethanol; excitation slit: 5 nm, emission slit: 5 nm; (λ_{ex} and λ_{em} as indicated).

We previously observed efficient energy transfer from 3,6-disubstituted phenanthrenes to acceptor pyrenes in light-harvesting supramolecular polymers fibers.[43] To test if the present nanotubes formed of 2,7-dialkynyl phenanthrenes also possess light-harvesting properties, polymerization of **1** was carried out in the presence of small quantities of the pyrene containing oligomer **2**. This leads to the formation of pyrene-doped supramolecular nanotubes, as illustrated in Figure 5.

A comparison of the fluorescence spectra of nanotubes consisting exclusively of phenanthrenes and nanotubes containing 1.2% of pyrene molecules is displayed in Figure 6A. Already small quantities of pyrene acceptor lead to a substantial increase in the fluorescence intensity upon irradiation at 243 nm, which corresponds to the H-band in the spectrum of the phenanthrene polymer. The effect of increasing pyrene content in the nanotubes on the intensity of pyrene fluorescence is displayed in Figure 6B. The maximum intensity is reached with a pyrene content of about 7%. This confirms that the supramolecular nanotube functions as a light-harvesting antenna in which the excitation energy is transferred from phenanthrenes to pyrene acceptor moieties. Phenanthrene excitation at 316 nm also leads to a steady increase of pyrene emission, although not as much as excitation at the H-band

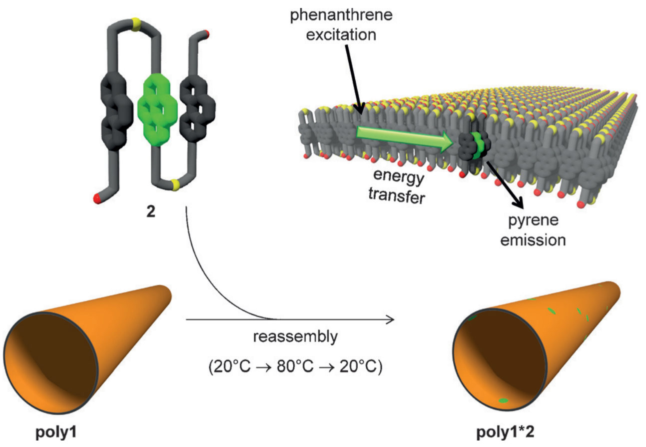

Figure 5. Illustration of light-harvesting nanotubes: supramolecular polymerization of aromatic oligophosphates leads to the formation of pyrene-doped phenanthrene nanotubes. Excitation of phenanthrene (gray) is followed by energy transfer to pyrene acceptor molecules (green).

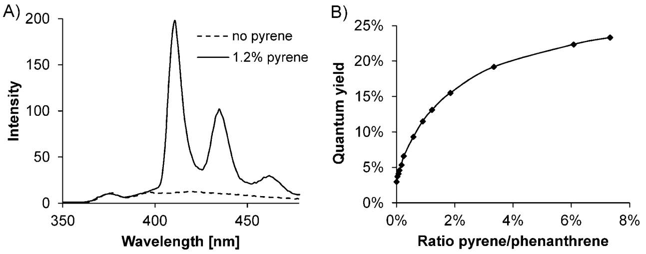

Figure 6. A) Fluorescence spectra of assembled phenanthrene nanotubes in the absence (-----) and in the presence of 1.2% of pyrene (——). B) Quantum yield of light-harvesting supramolecular nanotubes as a function of the pyrene/phenanthrene ratio. Concentration of **1** = 0.5 μM in 10 mM sodium phosphate buffer pH 7.0, 10% ethanol. λ_{ex} 243 nm; excitation slit: 2.5 nm, emission slit: 5 nm.

(Supporting Information). The ratio of pyrene/phenanthrene emission is higher if the antenna is excited at 243 nm. This is in agreement with the theory that the increased radiative lifetime for the relaxed excited state in H-aggregates is beneficial for efficient energy transfer.[59] The quantum yield of the light-harvesting antenna containing 7.3% pyrene, however, is the same (23%) for both of these excitation wavelengths.

It is important to note that incorporation of oligomer **2** into the nanotubes takes place only if the polymerization process (heating of the oligomer solution to 80 °C and then cooling to 20 °C) is carried out in the presence of **2**. No incorporation is observed upon addition of **2** to preformed nanotubes **poly1** at ambient temperature. Furthermore, oligomer **2** alone does not exhibit light-harvesting properties, which is demonstrated by titration experiments carried out with solutions not containing oligomer **1** (Supporting Information). Finally, the presence of small quantities of oligomer **2** has no effect on the morphology of the supramolecular polymers. AFM samples that were prepared using a solution containing 0.5 μM **1** and 0.5 nM **2**, yielding a ratio pyrene/phenanthrene of 0.1%, revealed only objects of identical shape as those formed of oligomer **1** alone (Supporting Information).

In conclusion, the self-assembly of aromatic oligomers into nanotubes with light-harvesting properties was demonstrated. Phosphodiester-linked phenanthrene trimers form H-aggregated, supramolecular polymers in aqueous medium. AFM and TEM imaging reveals tubular objects with a length of up to several micrometers. Nanotubes assembled entirely from phenanthrenes exhibit weak fluorescence. Incorporation of small quantities of pyrene units, however, leads to a strong increase of fluorescence. The supramolecular nanotubes function as light-harvesting antennae in which the excitation energy is transferred from phenanthrenes to pyrene acceptor moieties. The observed antenna effect is highest when the nanotubes are excited at the phenanthrene H-band. Fluorescence quantum yields reach 23% for nanotubes containing about 7% pyrene.

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Keywords: energy transfer · H-aggregates · light-harvesting antenna · nanotubes · supramolecular polymers

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