

Self-Assembly of Phenanthrene Oligomers into Nanotubes with Light-Harvesting Properties

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Abstract: A 2,7-disubstituted phosphodiester-linked phenanthrene trimer was synthesised which forms tubular structures in aqueous medium. The chromophores are arranged in H-aggregates. In combination with an acceptor the assembled phenanthrene units act as an antenna which transfers its excitation energy to the acceptor. The efficiency depends on excitation wavelength. Direct excitation of the H-band leads to a higher increase of fluorescence intensity.

Structure

The investigated phenanthrene trimer consists of three phenanthrene units which are modified with alkynyl-linkers in the 2- and 7-position, and are connected by phosphodiesters. It was synthesised on a phenanthrene-modified solid support using phosphoramidite chemistry. In aqueous medium those phenanthrene trimers aggregate and form tubular structures which were revealed by TEM and AFM (Figure 2). The measured height of the polymers is in the range of 4-4.5 nm. This corresponds to a double-layer of phenanthrenes, as the tubes flatten on the surface.

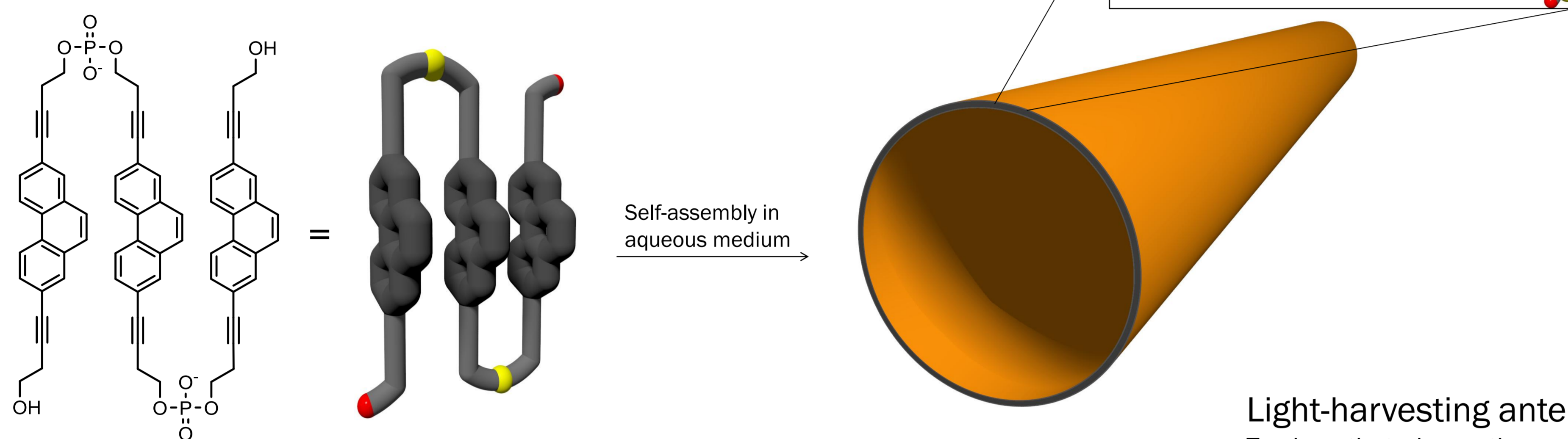


Figure 1: Chemical structure and illustrative model representation of 2,7-disubstituted phenanthrene trimer and its self-assembly.

Spectroscopic data

Aggregation of the phenanthrene trimer can be observed indirectly by UV-vis absorption spectroscopy (Figure 3). In ethanol (black) the oligomer is well-soluble and it has a similar absorption band as the monomer (not shown here). In aqueous medium (blue) changes are observed. A large hypochromism, especially at 270 and 316 nm, indicates strong aggregation of the phenanthrene units. Further, there appears a new band at 243 nm (H-band), concluding that the oligomer forms supramolecular polymers in aqueous medium in which the phenanthrenes are stacked in H-aggregates. When the aqueous sample is heated to 80 °C (red), the absorption band looks like the one measured in ethanol due to disassembly of the supramolecular polymer.

Fluorescence measurements in aqueous solution shows phenanthrene monomer emission if excited at 316 nm, and additional red-shifted (excimer) emission if excited at 243 nm (Figure 4). The quantum yield was measured to be 7% if excited at 316 nm, and 3% if excited at 243 nm (H-band).

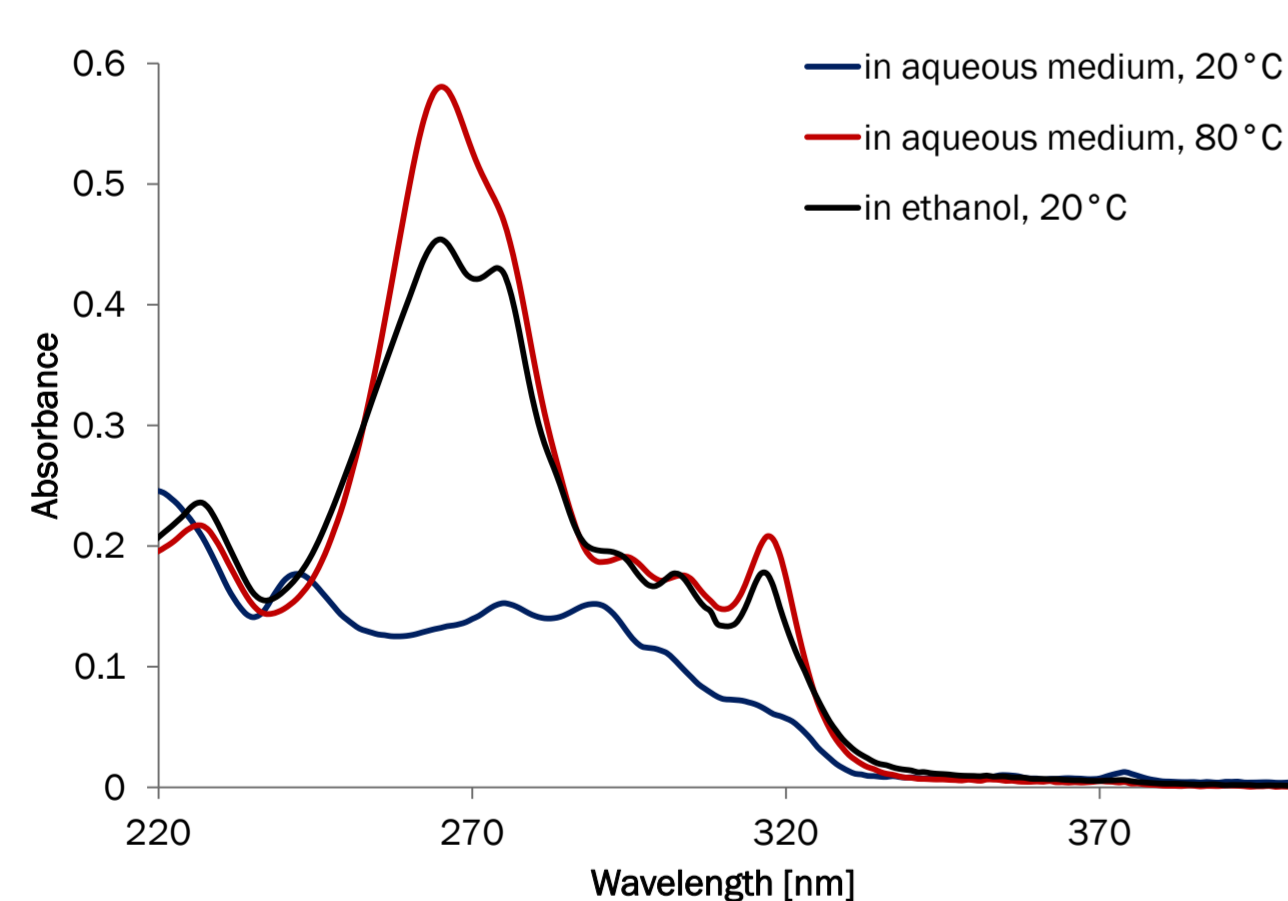


Figure 3: Absorption spectra of phenanthrene trimer, conditions: 1 μ M in 10 mM sodium phosphate buffer pH 7.0, 10% ethanol (blue: 20 °C, red: 80 °C), 1 μ M in ethanol (black).

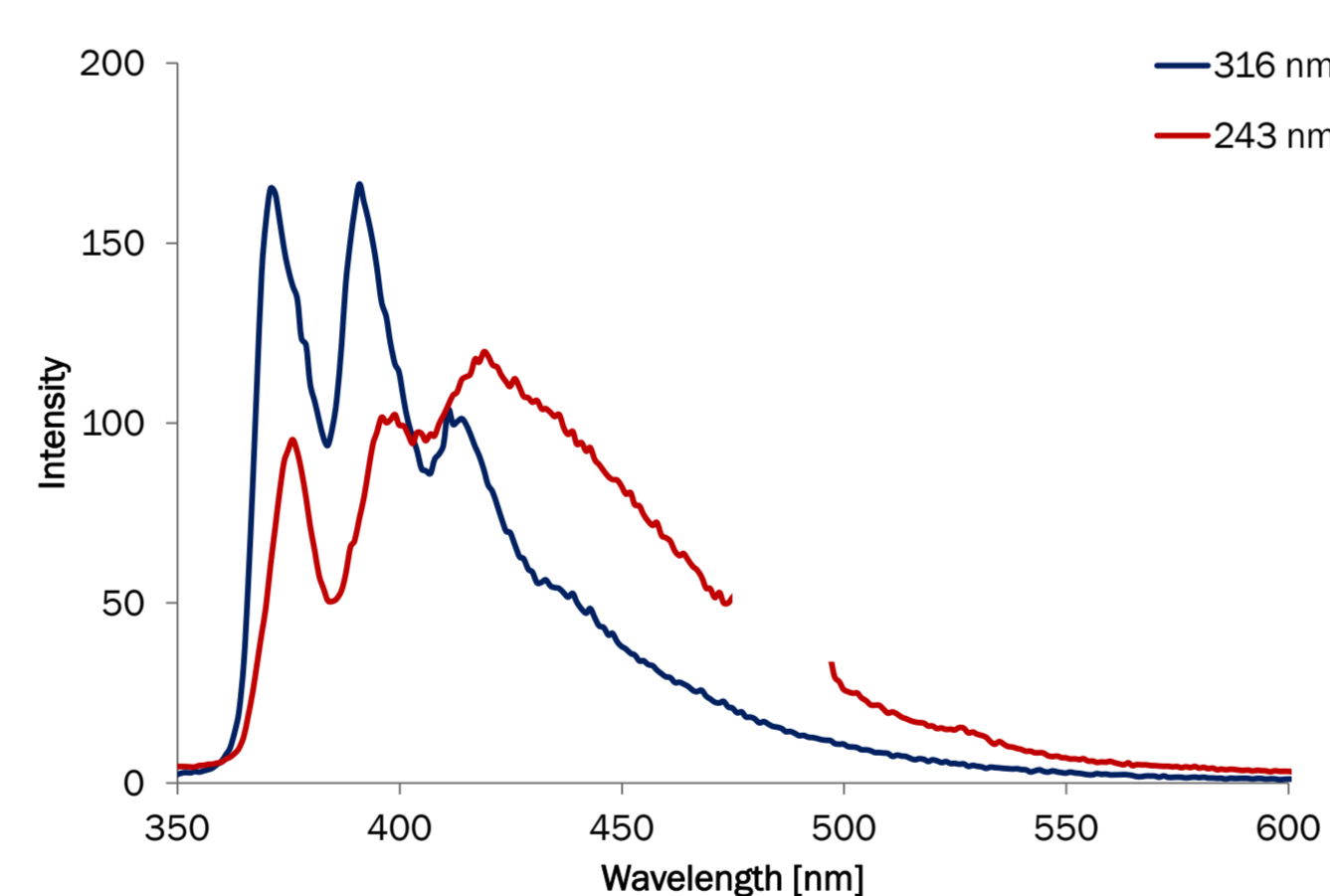


Figure 4: Fluorescence spectra of phenanthrene trimer for two excitation wavelengths, conditions: 1 μ M in 10 mM sodium phosphate buffer pH 7.0, 10% ethanol; excitation slit: 5 nm, emission slit: 5 nm.

Light-harvesting antenna

To show that phenanthrene nanotubes are able to act as light-harvesting antennae, an acceptor was chosen that consists of two phenanthrene and one pyrene (Figure 5). In a titration experiment, small amounts of the acceptor were added to the phenanthrene nanotube. Fluorescence measurements show a sharp increase in intensity after irradiation of the H-band (Figure 6). Excitation at 316 nm also leads to an increase of pyrene emission, although not as much as direct excitation of the H-band (Figure 7). The ratio of pyrene/phenanthrene emission is higher when excited at 243 nm. N.B.: Pyrene itself does not absorb appreciably at those excitation wavelengths, especially not at such low concentrations. After addition of ~7% of pyrene, the intensity does not increase remarkably anymore. The maximal quantum yield of the light-harvesting antenna (with 7.3% pyrene) is the same for both excitation wavelengths (23%).

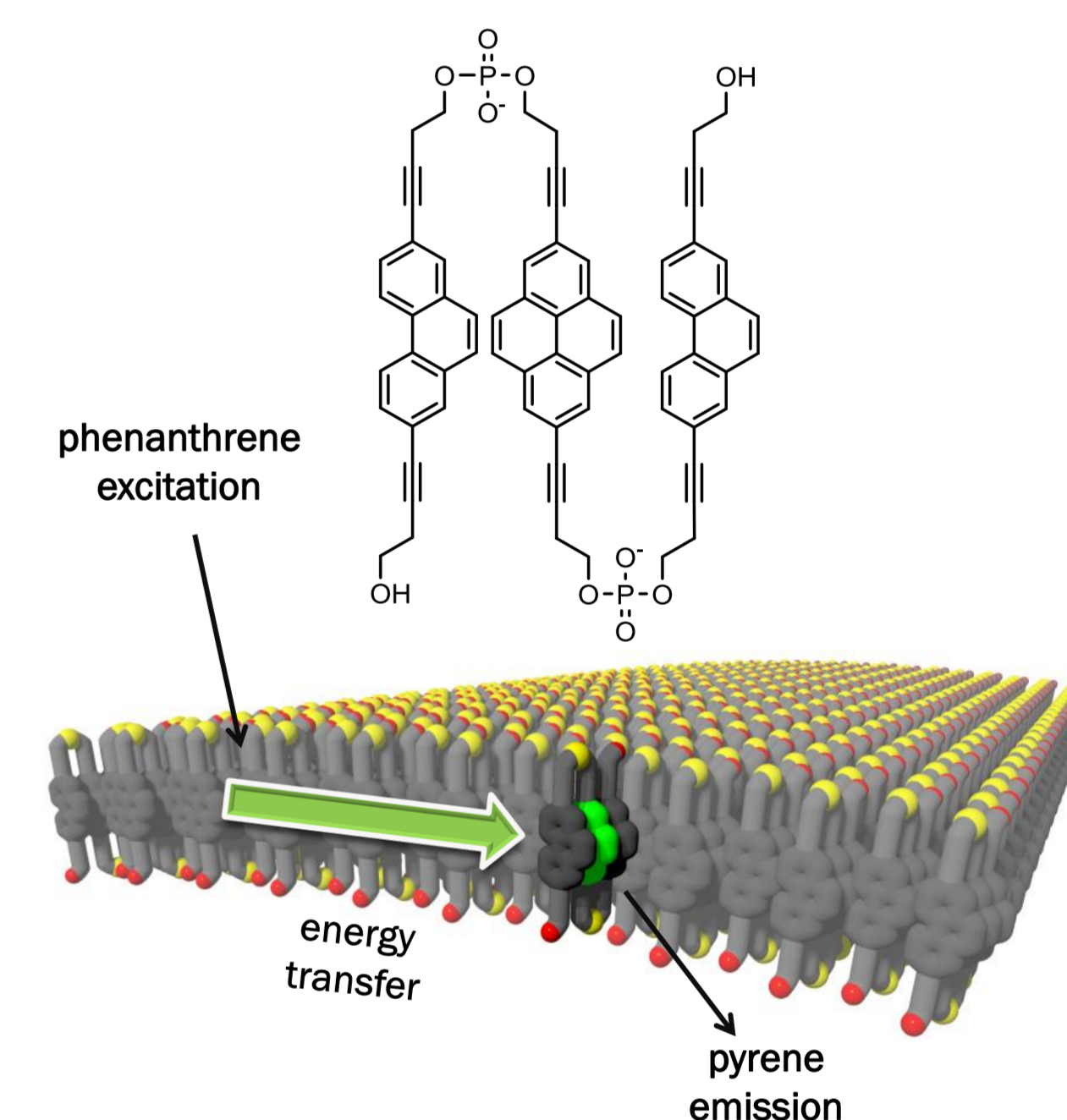


Figure 5: Chemical structure of acceptor oligomer and illustrative model representation of its incorporation into the nanotube.

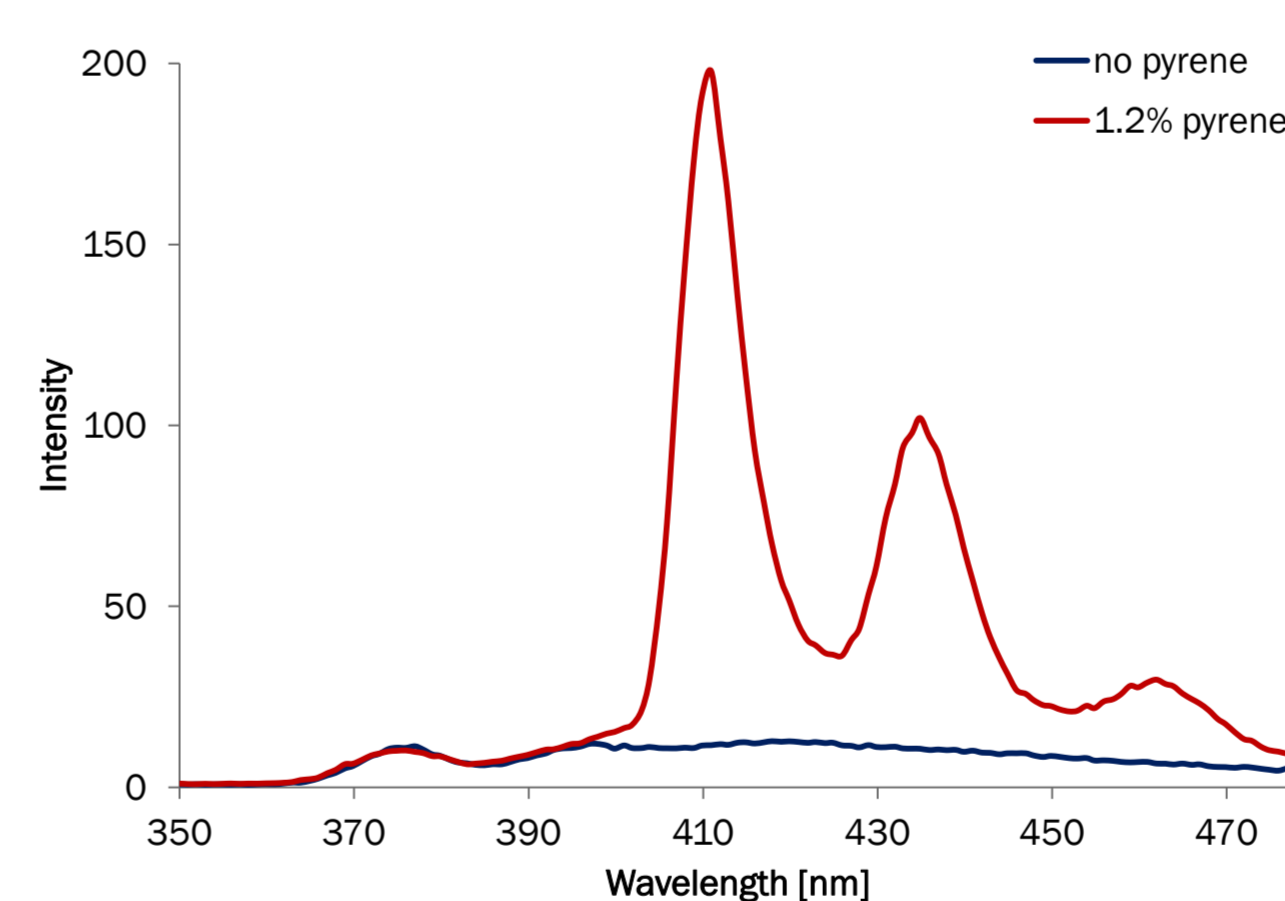


Figure 6: Fluorescence spectra of light harvesting antenna with 1.2% pyrene. Concentration of phenanthrene trimer 0.5 μ M in 10 mM sodium phosphate buffer pH 7.0, 10% ethanol. λ_{exc} 243 nm; excitation slit: 2.5 nm, emission slit: 5 nm.

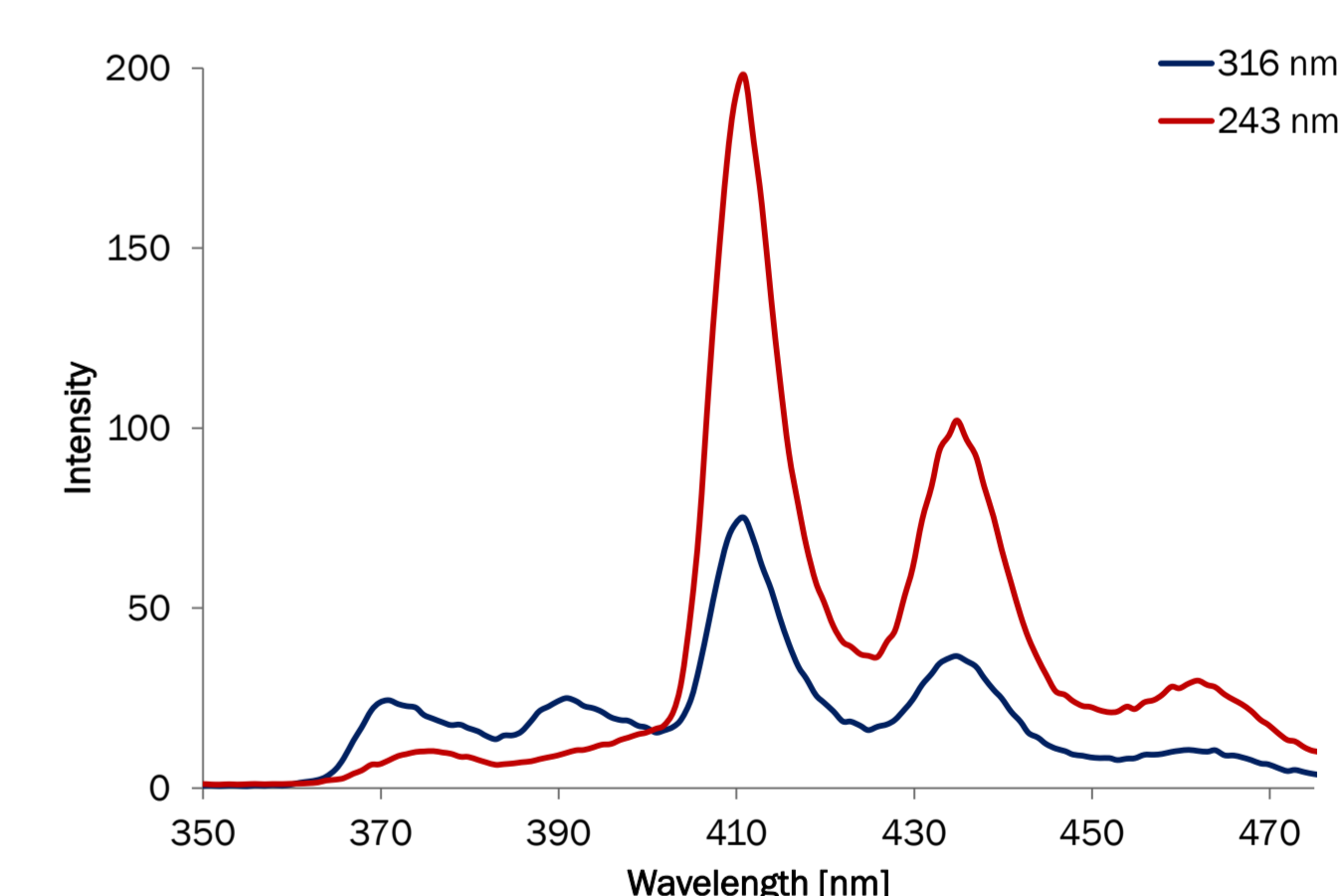


Figure 7: Fluorescence spectra of light-harvesting antenna for two excitation wavelengths, conditions as in Figure 4.

Conclusions

The self-assembly of aromatic oligomers into nanotubes with light-harvesting properties was demonstrated. TEM and AFM images show elongated objects with lengths of several micrometers. Those phenanthrene nanotubes exhibit only weak fluorescence. By incorporating minute amounts of acceptor, an increase of the corresponding acceptor fluorescence is observed. The π -stacked phenanthrene units function as light-harvesting antennae in which the excitation energy is efficiently transferred to the acceptor. By exciting the phenanthrene H-band directly, a higher increase of acceptor fluorescence is observed. In the case of pyrene, this is illustrated with a higher increase in quantum yield and a higher ratio of pyrene emission to phenanthrene emission.

References

- [1] C.D. Bösch, S.M. Langenegger, R. Häner, *Angew. Chem. Int. Ed.*, 2016, **55**, DOI: 10.1002/anie.201604508.
- [2] C.B. Winiger, S. Li, G.R. Kumar, S.M. Langenegger, R. Häner, *Angew. Chem. Int. Ed.*, 2014, **53**, 13603-13613.

Further, acridine orange and rhodamine 6G were tested for their acceptor efficiency. Both are positively charged, fluorescent dyes which are known as DNA intercalators. Figure 8 shows the fluorescence measurements with the addition of 1% of the respective dyes. In both cases the intensity does not increase as much as in the case with pyrene, but again, the intensities are higher when the phenanthrenes are excited at the H-band. The maximal values are already reached with concentration of 1.7% of dye (quantum yields of 10% with excitation wavelength 243 nm).

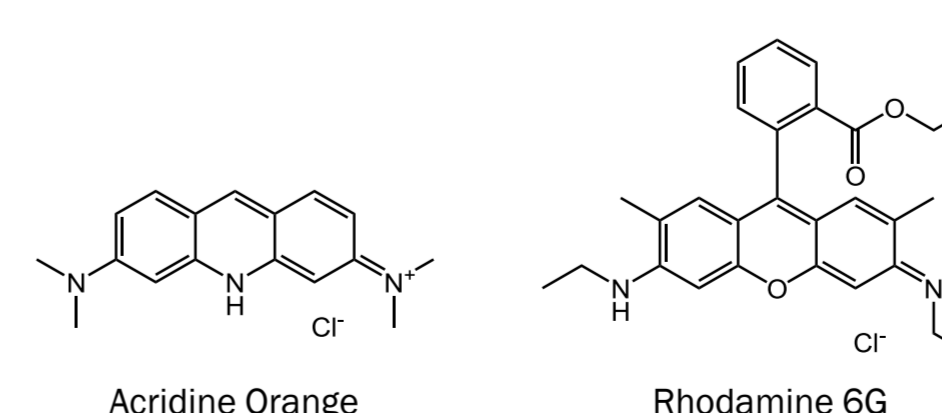


Figure 7: Chemical structures of acridine orange and rhodamine 6G.

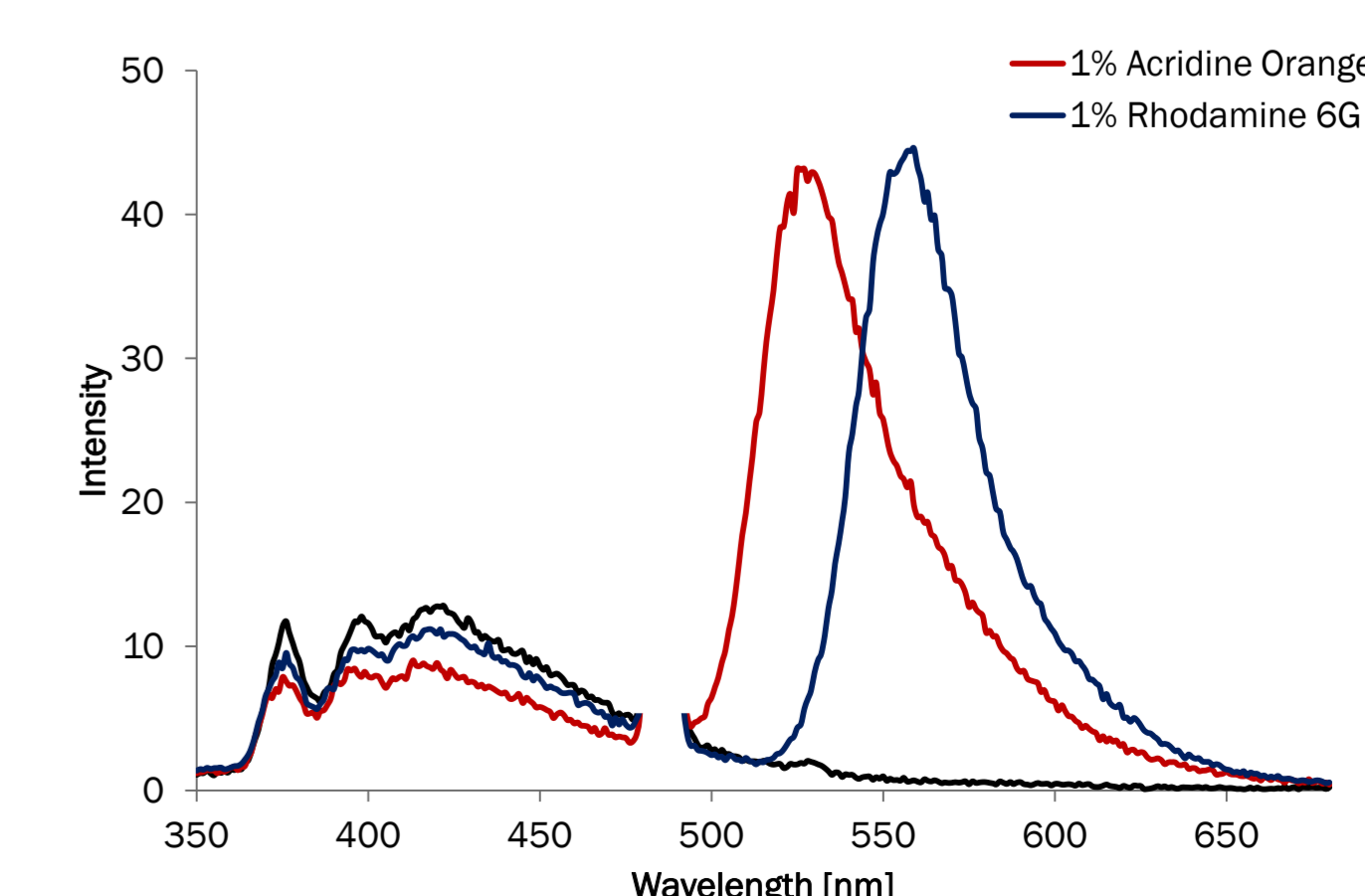


Figure 8: Fluorescence spectra of phenanthrene nanotube without acceptor (black), with 1% acridine orange (red), and with 1% rhodamine 6G (blue), conditions as in Figure 4.