Functionalized Two-Dimensional Supramolecular Polymers

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Abstract: 2D supramolecular polymers may find application as functional platforms. Previously it was shown that the phosphodiester-linked trimers of 1,6-dialkynyl-substituted pyrene **Py_3** self-assembled into supramolecular nanosheets in aqueous medium [1]. Here we doped the supramolecular nanosheets with pyrene DNA conjugates to functionalize the nanosheets. Further the functionalized nanosheets were hybridized with Au nanoparticles modified with the complementary DNA strand. The two-dimensional supramolecular nanosheets were characterized by UV-vis spectroscopy and atomic-force microscopy (AFM).

Introduction

In this study four different monomers were used (see Table 1). The monomers consist of one, two or three parts with different chemical characters. All of them have pyrene (Py) units which are modified with alkynyl-linkers in the 1- and 6-position, and are linked by a phosphodiester; the next part of the monomer are ten respectively twenty nucleobases. Two of the oligomers have hexaethylene glycol (HEG) attached to the pyrene, as reported in other research [2], the hydrophilic HEG will change the self-assembly process.

As a previous study revealed the trimers of 1,6-dialkynyl-substitueted pyrene **Py_3** formed two-dimensional supra-molecular polymers [1]. In this study additional investigations showed that the **$(Py)_3$-$(HEG)_1$** also self-assembled into supra-molecular nanosheets in aqueous medium, however, higher salt concentration is needed.

Both monomers **Py_3** and **$(Py)_3$-$(HEG)_1$** were used as a template for arrangement of the DNA modified strands. The addition of the pyrene DNA conjugates to the **Py_3** respectively **$(Py)_3$-$(HEG)_1$** leads to an aggregation of monomers in aqueous medium and self-assembly into two-dimensional (2D) nanosheets.

Table 1: Monomers used in this study.

Monomers
3'-GAG TGC CTT C – $(HEG)_1$ – $(Py)_3$
5'-CAA GGT CCG ATG CAA GGA AG – $(Py)_5$
$(Py)_3$ – $(HEG)_1$
Py_3

Spectroscopic characterisation

The aggregation was also investigated by UV-vis spectroscopy (see Figure 1), the absorption spectra showed absorptions at λ_{max} = 305 nm (J-band) and λ_{max} = 335 nm (H-band), which were already observed in the previous study [1].

In both cases the monomers formed supramolecular polymers in aqueous medium although the monomers had different units and different conditions.

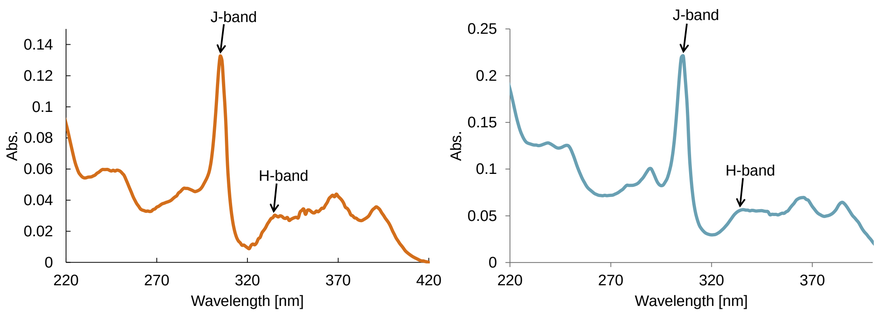
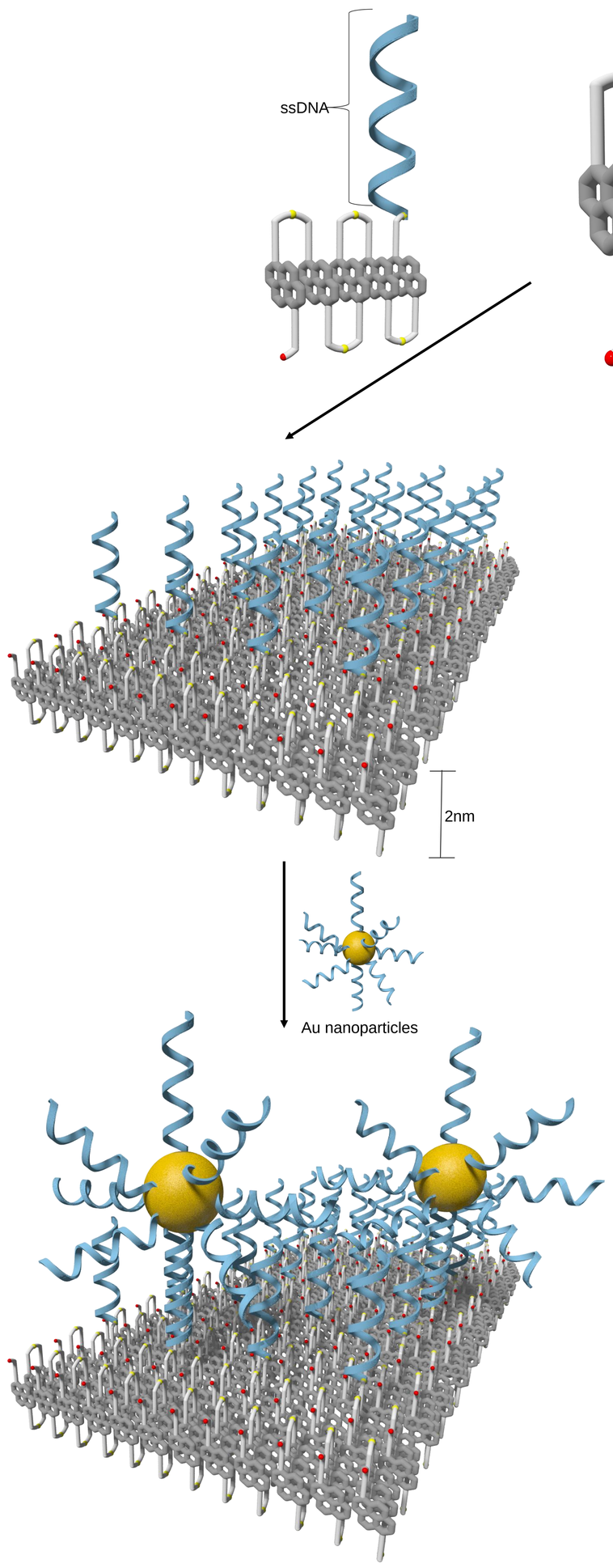


Figure 1: UV-vis absorption spectra of the $(Py)_3$-$(HEG)_1$ with DNA-$(HEG)_1$-$(Py)_3$ in 10 mM PB buffer and 500 mM NaCl (orange). UV-vis absorption spectra of the Py_3 with DNA-$(Py)_5$ in 10 mM PB buffer, 10 mM NaCl and 15% ethanol (blue).



Microscopic characterisation

The two-dimensional (2D) nanosheets were investigated by atomic-force microscopy (AFM). The measured height of the two-dimensional polymers was about 2 nm. The hybridization of the Au nanoparticles with the complementary DNA single strand of the pyrenes DNA conjugates allow to identify the doped supramolecular polymers.

The AFM images showed a high accumulation of the Au nanoparticles on the edges of the two-dimensional polymers (see Figure 2).

Therefore, doping the **$(Py)_3$-$(HEG)_1$** with **DNA-$(HEG)_1$-$(Py)_3$** results in the aggregation of the pyrenes DNA conjugates on the edges of the nanosheets.

Hybridization of the Au nanoparticles with the two-dimensional **Py_3** doped with **DNA-$(Py)_5$** showed no accumulation at a specific location (see Figure 3).

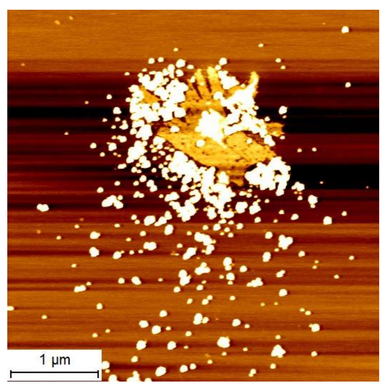


Figure 2: AFM images of the mixture of 2 µM $(Py)_3$-$(HEG)_1$ and 0.3 µM DNA-$(HEG)_1$-$(Py)_3$ with modified Au nano-particles, deposited on APTES-modified mica from aqueous solution containing 10 mM PB buffer and 500 mM NaCl.

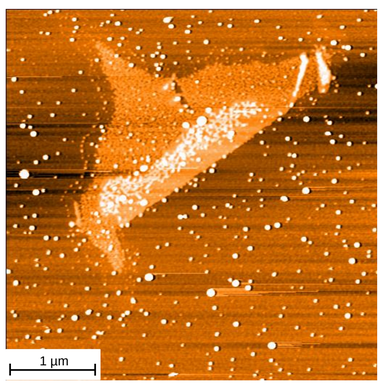


Figure 3: AFM images of the mixture of 2 µM Py_3 and 0.2 µM DNA-$(Py)_5$ with modified Au nanoparticles, deposited on APTES-modified mica from aqueous solution containing 10 mM PB buffer, 10 mM NaCl and 15% ethanol.

Conclusions

UV-vis absorption spectra revealed the aggregation of the monomers. Investigation by AFM experiments confirmed the formation of the two-dimensional (2D) supramolecular polymers. The AFM image showed that **$(Py)_3$-$(HEG)_1$** doped **DNA-$(HEG)_1$-$(Py)_3$** results in high accumulation of the pyrenes DNA conjugates at the edges of the nanosheets. In contrast doping the **Py_3** polymers with **DNA-$(Py)_5$** showed no accumulation of the Au nanoparticles at a specific location. This result shows, it is possible to functionalize two-dimensional polymers at different locations.

References

[1] M. Vybornyi, A. V. Rudnev, S. M. Langenegger, T. Wandlowski, G. Calzaferri and R. Häner, *Angew. Chem. Int. Ed.*, 2013, **52**, 11488–11493.

[2] T. G. Edwardson, K. M. Carneiro, C. J. Serpell and H. F. Sleiman, *Angew. Chem. Int. Ed.*, 2014, **53**, 4567–4571.