

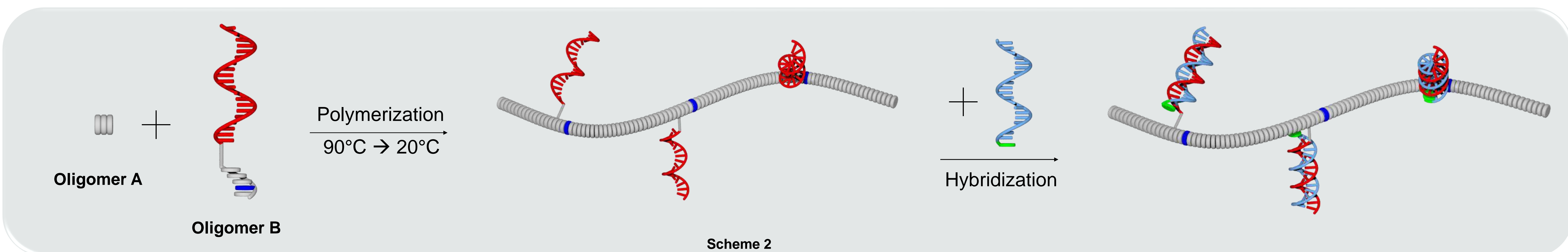
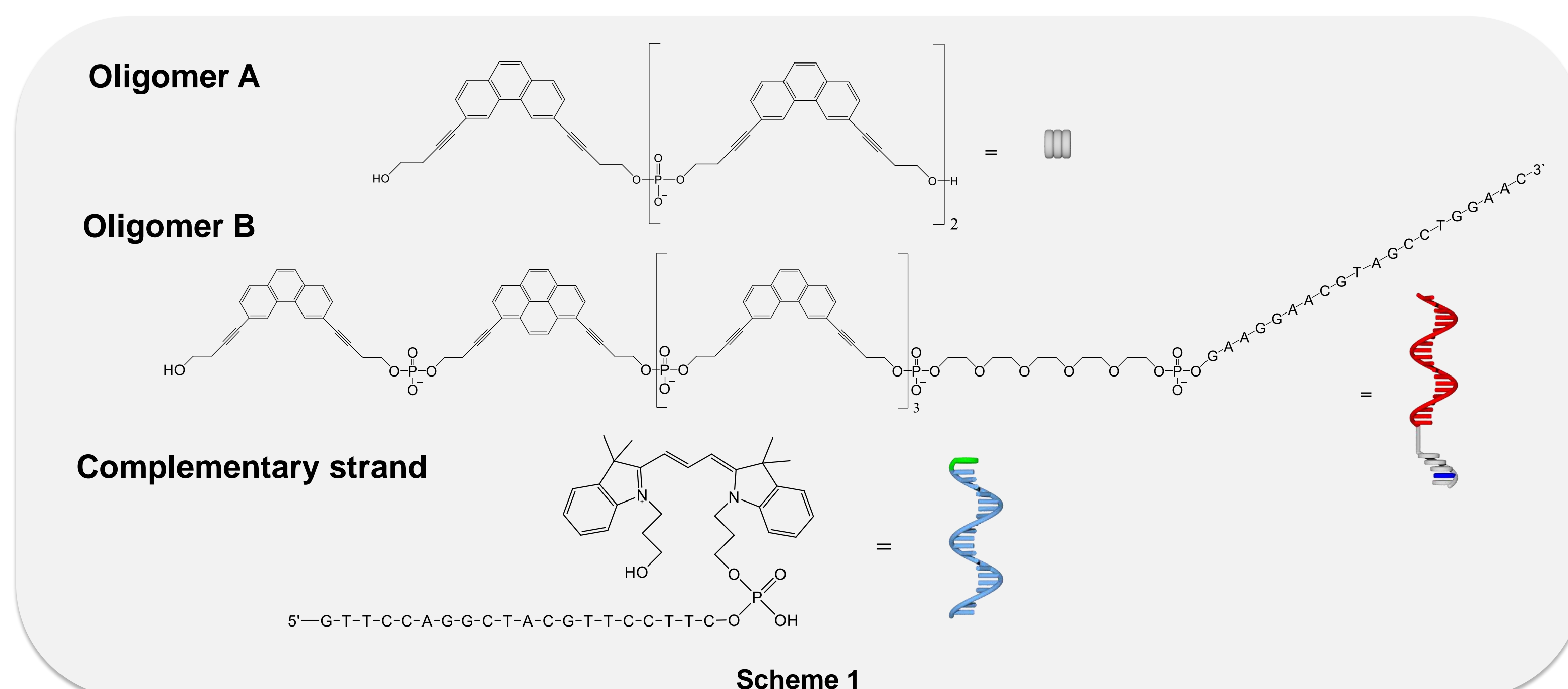
Assembly of Light Harvesting Antennas through Supramolecular Polymerization of Amphiphilic Phenanthrene Oligomers

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ABSTRACT

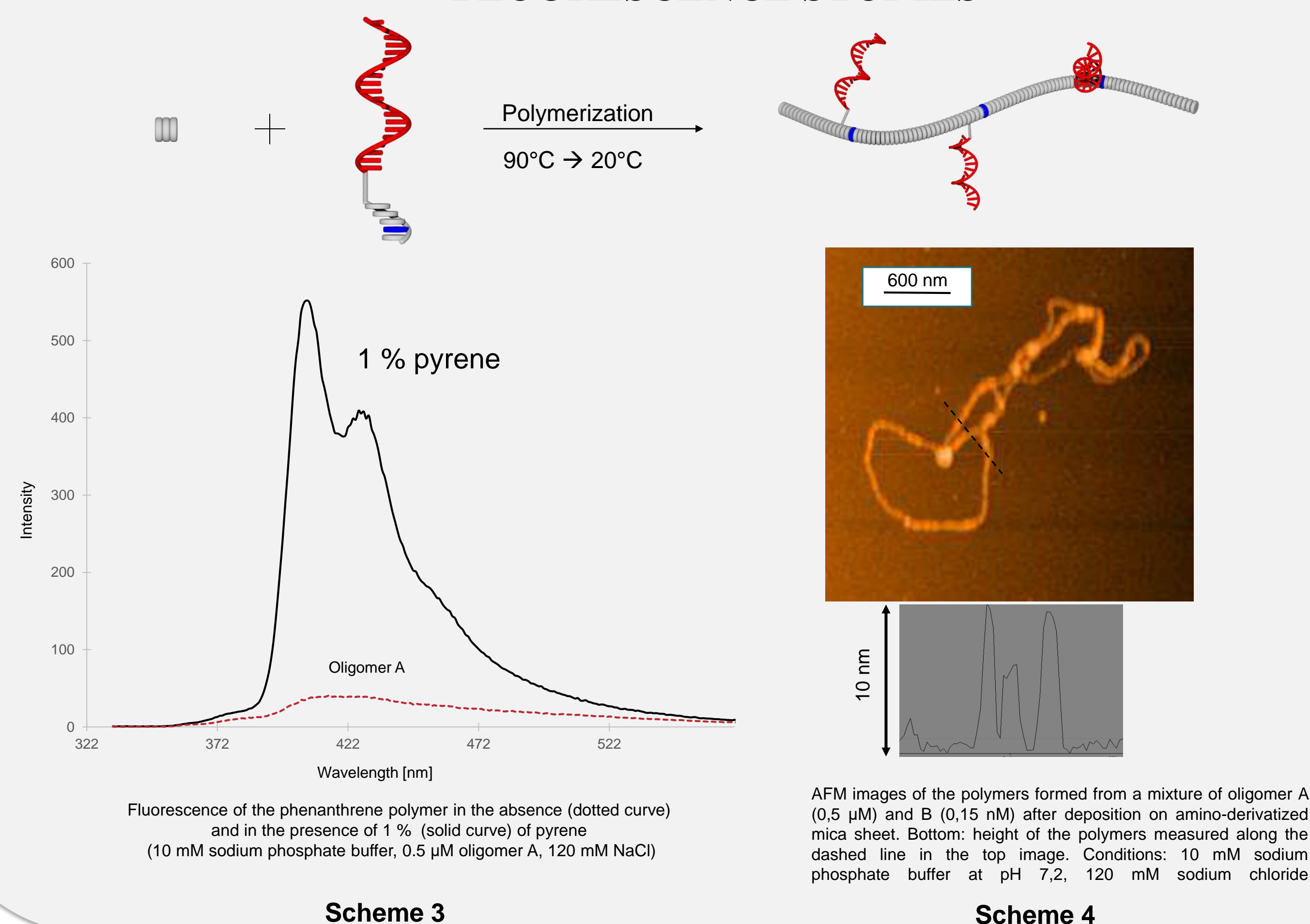
Efficient artificial light-harvesting antennas composed of multichromophoric array in a DNA scaffold are nowadays a key aspect in the supramolecular photochemistry [1]. Recently it was reported that the phenanthrene-pyrene supramolecular polymers can efficiently absorb photons which are transferred to the pyrene collection centre [2]. To expand this idea, 3,6-dialkynylphenanthrene trimer and new pyrene related oligomers were synthesized. As the DNA scaffolds are ideal platforms to organize chromophores the interesting point due to energy transfer is to introduce another acceptors in well-defined interchromophore distance from pyrene. This approach can be done by introducing complementary strand which contains Cy3 dye in different distance from pyrene. Such a supramolecular light harvesting complexes were investigated with different spectroscopic methods to prove efficient energy transport. From phenanthrene to the Cy3 acceptor core through the intermediate donor-acceptor pyrene derivative.



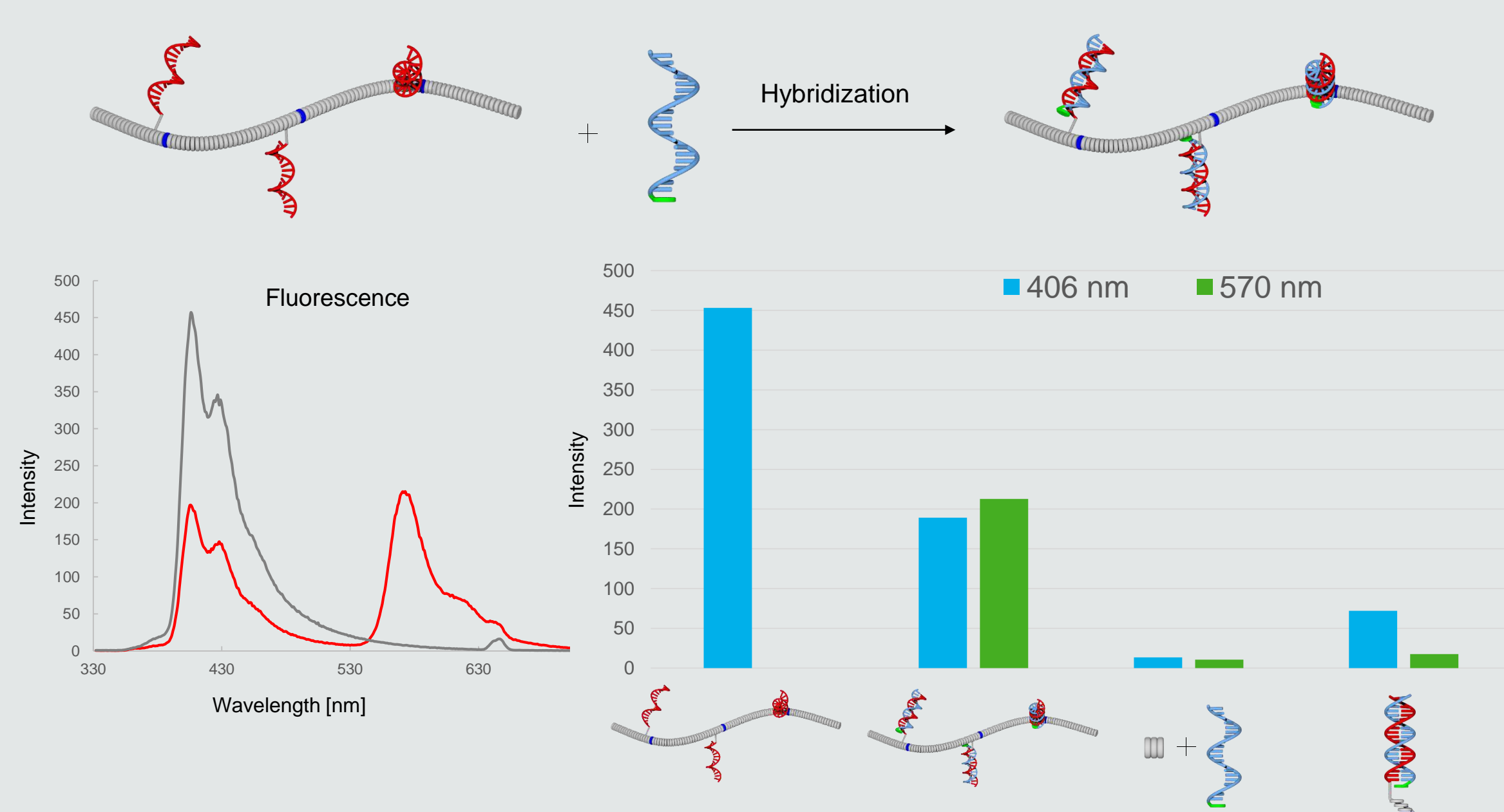
RESULTS

Light-harvesting complexes design, its sequences and chromophores were shown in Scheme 1 and 2. Oligomer **A** is composed of three phosphodiester-linked phenanthrene units, while oligomer **B** contains an additional pyrene and PEG linker building block as well as DNA strand. After polymerization process DNA strand in supramolecular polymer is hybridized with complementary strand which contains Cy3 dye. The energy transfer effectiveness of LHCs were investigated by fluorescence spectroscopy. For polymerization experiments 0.5 μM oligomer **A** solution doped with 15 nM oligomer **B** in 10 mM sodium phosphate buffer in the presence of 120 mM NaCl at pH 7.2 was used. The solution is heated to 90°C and cooled down to room temperature, assembly takes place below 60°C and leads to the formation of supramolecular polymers [2]. Upon the hybridization of the DNA strand (containing the exchangeable Cyanine acceptor), the energy can be transferred from phenanthrene-pyrene polymer to Cy3 acceptor what leads to the cyanine fluorescence emission. Polymers composed exclusively of phenanthrenes (only oligomer A) are weakly fluorescent upon phenanthrene excitation. Polymers doped with 1 % of pyrene results in drastical increase of pyrene fluorescence emission (scheme 3). Obtained polymers were visualized by AFM image (scheme 4). Differences in ET depending on the distance between chromophores are visualized by graphs (scheme 6). As well as controls energy transfer studies (scheme 5).

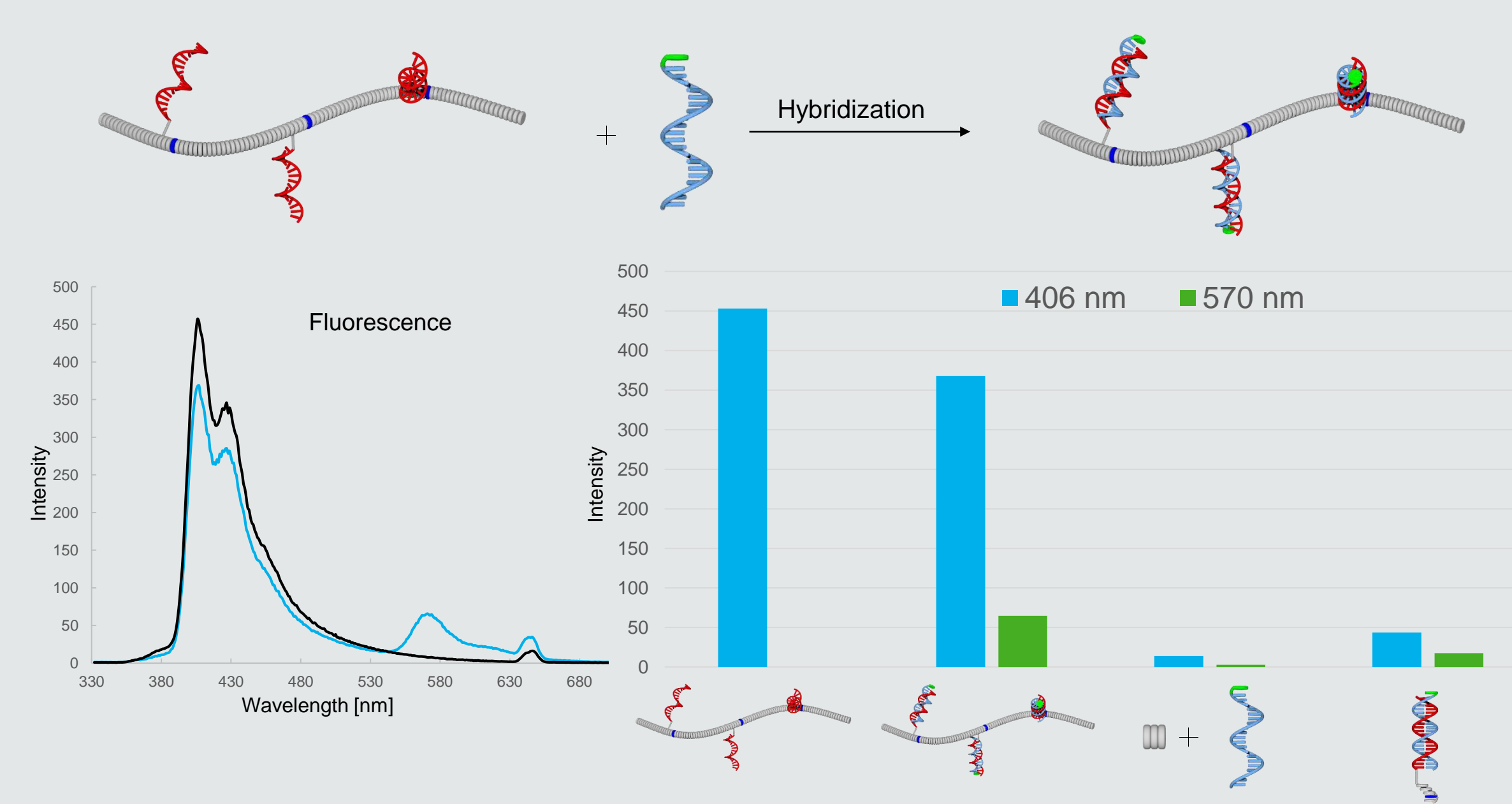
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CONCLUSIONS

Designed supramolecular assemblies of amphiphilic phenanthrene - pyrene oligomers show attractive light harvesting properties. Phenanthrene supramolecular polymer behaves as the light absorbing element. The energy transport to the cyanine 3 acceptor placed in the close proximity to phenanthrene polymer is up to 5 times more efficient in comparison to Cy3 at the end of complementary strand. This kind of energy transfer might be explain by FRET.

REFERENCES

1. Dutta, P. K., Varghese R., Nangreave J., Lin S., Yan H., Liu Y. *J. Am. Chem. Soc.*, 133, p. 11985-11993, **2011**.
2. Winiger C. B., Li S., Kumar G.R., Langenegger S. M., Häner R., *Chem. Int. Ed.*, 53, p. 13609-13613, **2014**.
3. Probst M., Langenegger S. M., Häner R., *Chem. Commun.*, 50, 159-161, **2014**

FRET

