Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2017

# **Supporting information**

# Functional DNA-grafted supramolecular polymers –

# chirality, cargo binding and hierarchical organization

Yuliia Vyborna, Mykhailo Vybornyi and Robert Häner\*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern,

Switzerland.

### Synthesis and purification of oligophosphates

Chemicals required for the organic and solid-phase DNA synthesis were purchased from commercial suppliers (Aldrich, Glen Research or TCI) and used without further purification. The pyrene phosphoramidite building block required for the solid-phase synthesis was synthesized according to the published procedure.<sup>1</sup> All oligonucleotide sequences were prepared on a 1  $\mu$ M scale using a standard cyanoethyl phosphoramidite protocol on an ABI 394 (Applied Biosystems Instruments) automated DNA synthesizer. dG-CPG 500 was used as solid support for sequences **Py-a** and **S-b**. 5'-thiol-modifier C<sub>6</sub> S-S (Glen Research) was used for the **S-b** synthesis as a 5'-end modifier. Cleavage and deprotection of the sequences was achieved by treatment of solid support beads with 0.8 ml of 27% ammonia at 55 °C in a closed vial for 16 hours. The supernatant was separated by centrifugation and lyophilized. The samples were dissolved in mobile phase A, passed through 0.45  $\mu$ m syringe filters, and purified by HPLC using a Reprosil 100 C<sub>8</sub> 250 x 4 mm column (mobile phase A=(Et<sub>3</sub>NH)OAc (0.1 M, pH 7.0)/CH<sub>3</sub>CN in 80/20 v/v and mobile phase B = CH<sub>3</sub>CN; gradient 0–40% B over 22 min, then 40–100% B over 5 min). The purity of the sequences was confirmed by HPLC traces and mass spectroscopy.

### Sample preparation

Solutions of supramolecular polymers were prepared according to the following procedure: aliquots of corresponding stock solutions were mixed in a cuvette to yield a mixture containing 10 mM phosphate buffer solution (PBS), 150 mM NaCl and 2  $\mu$ M **Py-a** (or 2+6  $\mu$ M of **Py-a+b**), the cuvette was heated to 95 °C and consequently cooled to 15 °C at a rate of 0.1 °C/min.

### Spectroscopic measurements

Absorption spectra were recorded on a Varian Cary-300 Bio-UV/VIS. Fluorescence data were collected on a Varian Cary Eclipse fluorescence spectrofluorimeter at an excitation wavelength of 352 nm. For the CD measurements, a JASCO J-715 spectropolarimeter was used. All measurements were performed in 1 cm quartz cuvettes.

#### Transmission Electron Microscopy (TEM) Measurements

Carbon-coated Films on 300 Mesh Copper Grids from Agar Scientific were routinely used. All experiments were performed on an FEI Tecnai Spirit device, using an operating voltage of 80 kV. For the sample preparation, a drop (5 µl) of the solution was placed onto the TEM grid. After 5 minutes, the grid was washed with a drop of distilled water. Afterwards, a drop of aqueous uranyl acetate solution (0.8%) was placed onto the TEM grid. After 1 min, an excess of staining agent was blotted away with filter paper.

#### Atomic Force Microscopy (AFM) Measurements

Mica plates were purchased from Plano GmbH. AFM images were acquired using a Nanosurf FlexAFM equipped with Tap190AI-G cantilevers from BudgetSensors (resonance frequency  $\approx$  190 kHz, force constant = 48 N/m) in a tapping mode. Sample preparation was based on deposing of 15 µl of the supramolecular polymers solution in buffer (10 mM PBS pH=7.0) onto APTES-modified mica plates. After 1 min of incubation, the samples were rinsed with 1 ml of Milli-Q water.

# Synthesis of AuNPs<sup>2</sup>

AuNPs with a diameter of ~5 nm were synthesized by the citrate reduction method in the presence of a tannic acid as a co-reductant. First, 100 ml of a solution of 0.3 mM HAuCl<sub>4</sub> was brought to a boil and mixed with 2 ml of 1% citric acid and 7 ml of 1% tannic acid. After the color of the solution changed to burgundy, the solution was refluxed for another 3 min and cooled to room temperature. The AuNPs solution was filtered through a syringe filter with a pore size of 0.2  $\mu$ m. Next, the citrate coated nanoparticles were stabilized by exchanging the citrate shell for a more stable phosphine ligand. Thus, 11 mg of BSPP (bis(p-sulfonatophenyl)- phenylphosphine dihydrate dipotassium salt) was added to 10 ml of the AuNPs solution and was shaken overnight at low speed. For the precipitation of AuNPs, solid NaCl was added slowly until a color changed from red to grey-blue. The solution was then centrifuged for 15 min at 4400 rpm; the supernatant was removed, and the AuNPs were resuspended in 500  $\mu$ l of an aqueous 0.5 mM BSPP solution. The centrifugation and resuspension were repeated twice. Finally, the concentration was determined photometrically at 520 nm assuming a molar extinction coefficient for the 5 nm AuNP of 1  $\cdot$  10<sup>7</sup> M<sup>-1</sup>  $\cdot$  cm<sup>-1</sup>.

# **AuNPs-DNA** conjugation

The thiol-modified oligonucleotide **S-b** was mixed with AuNPs in a 0.5× TBE (Tris base, boric acid, EDTA, pH 8.0) at a ratio of 1:17 (AuNPs:DNA) and incubated overnight at 20<sup>o</sup>C. The excess of oligonucleotides was removed via centrifugation and resuspension steps. The concentration was determined as described above.



# Mass spectrometry and HPLC traces of the synthesized sequences

*Figure S1*. Mass spectra of *Py-a* (top) and *S-b* (bottom). The inset shows HPLC traces of the purified product on a RP apHera  $C_4$  column.

code	sequence	mass calc.	mass found
Ру-а	(2,7-Py)7 - CTT CCG TGA G -3'	6014.8	6014.3
S-b	(Thiol-Modifier C <sub>6</sub> S-S) -CTC ACG GAA G - 3'	3365.5	3264.6



*Figure S2.* Fluorescence emission spectrum of the supramolecular polymers **Py-a** in aqueous solution at 20 °C ( $\lambda_{ex}$ = 352 nm). Conditions: 10 mM PBS, 150 mM NaCl, pH=7, 2  $\mu$ M **Py-a**.



*Figure S3*. AFM images and cross-section analysis of **Py-a** supramolecular polymers on APTES-modified mica surface from aqueous solutions deposited at 20 °C (A) and at 4 °C (B). Scale bar:  $2 \mu m$ .



*Figure S4. A:* Normalized temperature-dependent absorption curve for **Py-a/b** ( $2\mu$ M/ $6\mu$ M) mixture monitored at 252 nm. The inset shows temperature-dependent UV/Vis absorption for **Py-a/b**. *B:* CD spectra of **Py-a/b** in aqueous solution at different temperatures ( $15^{\circ}$ C,  $20^{\circ}$ C,  $25^{\circ}$ C). *C:* AFM image of networks formed from supramolecular polymers **Py-a** and complementary strand **b**. Conditions: 10 mM PBS, 150 mM NaCl, pH=7. Scale bar:  $2 \mu m$ .



Figure S5. CD spectra of  $2 \mu M \mathbf{a}$  (A) and  $2\mu M/6\mu M \mathbf{a}/\mathbf{b}$  (B) in aqueous solution. Conditions: 10 mM PBS, 150 mM NaCl, pH=7.



*Figure S6.* Size distribution (left) and corresponding TEM image (center) of AuNPs modified with DNA strands. Right: electrophoretic mobility of gold nanoparticles (left band) and DNA-modified NPs conjugates (right band). Samples were loaded on 2.5% agarose gel (0.5 x TBE buffer, pH 8) and run for one hour at 165 V.

# References

- 1. M. Vybornyi, Y. Hechevarria, M. Glauser, A. Rudnev, and R. Häner, *Chem. Commun.*, 2015, **51**, 16191.
- D. A. Handley (1989) Colloidal Gold: Principles, Methods and Applications Vol. 1 (Hayat, M. A., Ed.) pp 13-22, Academic press, San Diego.