Supramolecular polymerization of oligopyrenotides - stereochemical control by single, natural nucleotides

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General procedures

The required pyrene building block\(^1\) and the oligomers were synthesized and purified according to a published procedures.\(^2\)

Spectroscopic methods

Unless otherwise indicated, all experiments were performed in sodium phosphate buffer (10 mM, 1M NaCl, pH 7.0) for 5 µM oligomer concentration, \(\varepsilon_{350} = 20'000 \text{ dm}^3\text{mole}^{-1}\text{cm}^{-1}\) was used for pyrene units.

**Temperature dependent UV/VIS spectra** were collected with an optic path of 1 cm over the range of 200-500 nm at 10-90 °C with a 10 °C interval on *Varian Cary-100 Bio-UV/VIS* spectrophotometer equipped with a *Varian Cary*-block temperature controller. The cell compartment was flushed with N\(_2\).

**Thermal melting experiments** were carried out on *Varian Cary-100 Bio-UV/VIS* spectrophotometer equipped with a *Varian Cary*-block temperature controller and data were collected with Varian WinUV software at 354 nm (cooling-ramp in the temperature range of 10-90°C, temperature gradient of 0.5°C/min). Data are normalized at maximum of absorbance (at high temperature).

**Temperature dependent fluorescence** data were collected on a *Varian Cary Eclipse* fluorescence spectrophotometer equipped with a *Varian Cary*-block temperature controller (excitation at 350 nm; excitation and emission slit width of 2.5 nm) using 1 cm x 1 cm quartz cuvettes. *Varian Eclipse* software was used to investigate the fluorescence of the oligopyrenes at a wavelength range of 370-700 nm in the temperature range of 10-90 °C.

**CD spectra** were recorded on a *JASCO J-715* spectrophotometer using quartz cuvettes with an optical path of 1 cm. (Scanning speed: 100 nm/min; data pitch: 0.5 nm; band width: 1.0 nm; response: 1 sec).


The calculation of the g-factor was done with the equation \( G = \frac{CD(\text{mdeg})}{32980 \times \text{Abs}} \) using the absorbance and CD values in mdeg recorded by the JASCO-J-715.

Amplification experiment using 10% chiral information. Oligomer 1 (5 \( \mu \text{M} \) building block concentration) was mixed together with phosphate buffer and sodium chloride and heated to 90°C (10 mM, 1M NaCl, pH 7.0). After cooling and equilibration of 1 week, 10% (0.5 \( \mu \text{M} \) building block concentration) of the corresponding oligomers of 3, 5, 7 and 11 were added to the preformed supramolecular polymers. From then on data points were taken after 2 hours, 1 day, 4 days and then every week until one month was passed.

Mass spectrometry of oligomers was performed with a Sciex QSTAR pulsar (hybrid quadrupole time-of-flight mass spectrometer, Applied Biosystems). ESI-TOF MS (negative mode, CH\(_3\)CN/H\(_2\)O/TEA) data of compounds are presented in Table 1. LC-MS was performed with a Shimadzu LCMS-2010EV high-performance liquid chromatograph/ mass spectrometer.

Table 1. Mass spectrometry data of synthesized oligomers (ESI-TOF MS, negative mode, CH\(_3\)CN/H\(_2\)O/TEA).

<table>
<thead>
<tr>
<th>Oligonucleotide</th>
<th>Molecular Formula</th>
<th>Calc. average mass</th>
<th>Found mass</th>
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<tbody>
<tr>
<td>1 SSS SSS S</td>
<td>C(<em>{168})H(</em>{156})N(<em>{14})O(</em>{40})P(_{6})</td>
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<td>3492.0</td>
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<tr>
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<td>3531.0</td>
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<tr>
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<tr>
<td>7 (5') GSS SSS SSG</td>
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Figure 1. MS and LC-MS data of oligomer Py₇ (1); MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 230 nm and 254 nm.
Figure 2. MS and LC-MS data of oligomer Py7-C (2); MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 230 nm,
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Figure 11. MS and LC-MS data of oligomer Py7-A (11): MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm.
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Figure 14. Temperature variable absorbance spectra of oligomers 2, 3, 4 (left) and co-aggregates 1*2, 1*3, 1*4 in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH = 7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
Figure 15. Temperature variable absorbance spectra of oligomers 5, 6, 7 (left) and co-aggregates 1*5, 1*6, 1*7 in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH = 7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
Figure 16. Temperature variable absorbance spectra of oligomer 8, 9, 10 (left) co-aggregates 1*8, 1*9, 1*10 in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
Figure 17. Temperature variable absorbance spectra of oligomers 11, 12, 13 (left) and co-aggregates 1*11, 1*12, 1*13 in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
**Figure 18.** Temperature variable fluorescence spectra of oligomer 2, 3, 4 (left) and co-aggregates 1*2, 1*3, 1*4 in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
Figure 19. Temperature variable fluorescence spectra of oligomer 5, 6, 7 (left) and co-aggregates 1*5, 1*6, 1*7 in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH = 7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
Figure 20. Temperature variable fluorescence spectra of oligomer 8, 9, 10 (left) and co-aggregates 1*8, 1*9, 1*10 in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH = 7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
Figure 21. Temperature variable fluorescence spectra of oligomer 11, 12, 13 (left) and co-aggregates 1*11, 1*12, 1*13 in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
The effect of nucleobase complementarity

Figure 22. Temperature variable absorption spectra (left) and fluorescence spectra (right) of oligomer 2, 3, 4 and its complementary base. Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
Figure 23. Temperature variable absorption spectra (left) and fluorescence spectra (right) of oligomer 8, 9, 10 and its complementary base. Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.
Figure 24. Normalized absorbance (left) and fluorescence (right) spectra of 2*6 (Py7-C)* (G-Py7), 3*5 (C-Py7)* (Py7-G), 4*7 (C-Py7-C)* (G-Py7-G). Conditions: sodium phosphate buffer, pH = 7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.

Figure 25. CD-spectra of 2*6 (Py7-C)* (G-Py7), 3*5 (C-Py7)* (Py7-G), 4*7 (C-Py7-C)* (G-Py7-G). Conditions: see Fig. 11.
Figure 26. Normalized absorbance (left) and fluorescence spectra (right) of 8*12 (Py7-T)\textsuperscript{*} (A-Py7), 9*11 (T-Py7)\textsuperscript{*} (Py7-A), 10*13 (T-Py7-T)\textsuperscript{*} (A-Py7-A). Conditions: see Fig. 11.

Figure 27. CD-spectra of pyrene oligomer 8*12 (Py7-T)\textsuperscript{*} (A-Py7), 9*11 (T-Py7)\textsuperscript{*} (Py7-A), 10*13 (T-Py7-T)\textsuperscript{*} (A-Py7-A). Conditions: see Fig. 11.
**Figure 28.** Melting profile of the co-aggregates $2^*6$, $3^*5$, $4^*7$, $8^*12$, $10^*13$ in a 1:1 ratio. Conditions: see Fig. 11.