

**DNA as a supramolecular scaffold for the helical arrangement
of a stack of 1-ethynylpyrene chromophores**

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Supporting Information

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Materials and Methods.

MALDI-TOF analysis was performed in the analytical facility of the department on a Bruker Biflex III spectrometer using 3-hydroxypicolinic acid in aqueous ammonium citrate as the matrix. C18-RP analytical and semipreparative HPLC columns (300 Å) were purchased from Supelco. All spectroscopic measurements were performed in quartz glass cuvettes (1 cm) and using Na-P_i-buffer (10 mM). The melting temperatures (260 nm, 20-90 °C, interval 1°C, scan speed 1°C / min) were recorded on a Varian Cary Bio 100 spectrometer. The fluorescence spectra were measured on a Fluoromax-3 fluorimeter (Jobin-Yvon) at an excitation wavelength of 360 nm and corrected for Raman emission from the buffer solution. All emission spectra were recorded with a bandpass of 2 nm for both excitation and emission and are intensity corrected. CD-measurements were performed on a JASCO J-715 Spectropolarimeter (200-500 nm, 5 accumulations, 0.5 sec response, band width 2 nm).

Preparation and Characterization of Oligonucleotides (General Procedure).

The oligonucleotides were prepared on an Expedite 8909 DNA synthesizer (Applied Biosystems) via standard phosphoramidite protocols using CPGs (1 µmol) and chemicals from ABI and Glen Research. After preparation, the trityl-protected oligonucleotide was cleaved off the resin and was deprotected by treatment with conc. NH₄OH at 55°C for 10 h. The oligonucleotides were dried and purified by HPLC using the following conditions: A=NH₄OAc buffer (50 mM), pH=6.5; B= MeCN; gradient=0-15% B over 50 min. The oligonucleotides were lyophilised and quantified by their absorbance at 260 nm (see: J. D. Puglisi, I. Tinoco, *Meth. Enzymol.*, 1989, **180**, 304-325.) on a Varian Cary Bio 100 spectrometer. Duplexes were formed by

heating of pyrene-modified oligonucleotides in the presence of 1 equiv. unmodified complementary strand to 90 °C (10 min), followed by slow cooling to r.t.

Preparation and Characterization of Py- \equiv -dU-Modified Oligonucleotides.

The oligonucleotides were prepared on an Expedite 8909 DNA synthesizer (Applied Biosystems) via standard phosphoramidite protocols using CPGs (1 μ mol) and chemicals from ABI and Glen Research. The Py- \equiv -dU building block was synthesized according to literature (see: A. D. Malakhov, E. V. Malakhova, S. V. Kuznitsova, I. V. Grechishnikova, I. A. Prokhorenko, M. V. Skorobogaty, V. A. Korshun, Y. A. Berlin, *Russ. J. Bioorg. Chem.*, 2000, **26**, 39-44.) The coupling time for the Py- \equiv -dU phosphoramidite was extended to 15 min. After preparation, the trityl-off oligonucleotide was cleaved off the resin and was deprotected by treatment with conc. NH₄OH at 55 °C for 10 h, protected from light. The oligonucleotide was dried and purified by HPLC on a semipreparative RP-C18 column (300 Å, Supelco) using the following conditions: A=NH₄OAc buffer (50 mM), pH=6.5; B= MeCN; gradient=10-50% B over 45 min. The oligonucleotides were lyophilised and quantified by their absorbance at 260 nm (see: J. D. Puglisi, I. Tinoco, *Meth. Enzymol.*, 1989, **180**, 304-325.) on a Varian Cary Bio 100 spectrometer, using ϵ (260 nm)=12.700 M⁻¹ cm⁻¹ for the Py- \equiv -dU unit.

Table S1

Mass spectrometry of the single stranded(ss)-**DNA1 - DNA4**.

Oligonucleotide	mass calc.	mass exp.
ss-DNA1	6213	6213
ss-DNA2	6423	6430
ss-DNA3	6633	6636
ss-DNA4	6843	6845

Fig. S1 UV/Vis spectra of **DNA1-DNA4a** (2.5 μ M in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

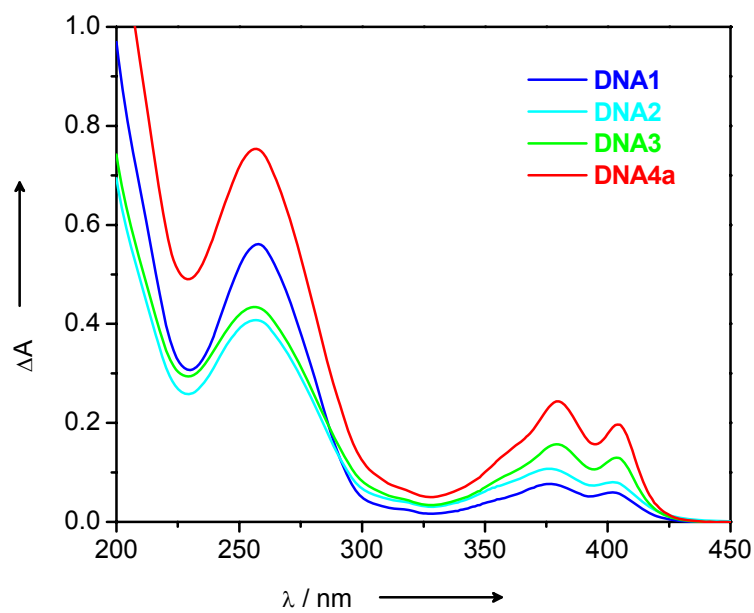


Fig. S2: UV/Vis spectra of **DNA4a-DNA4d** (2.5 μ M in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

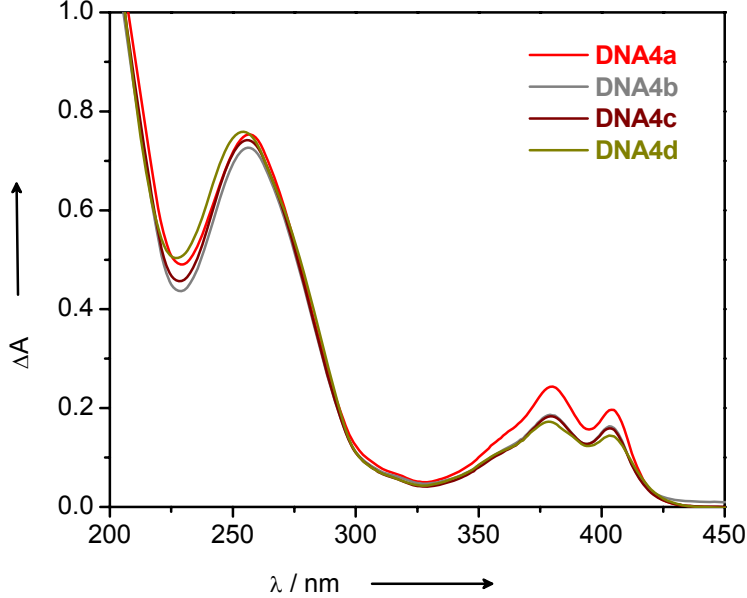


Fig. S3: Temperature-dependent UV/Vis spectra of **DNA3** (2.5 μ M in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

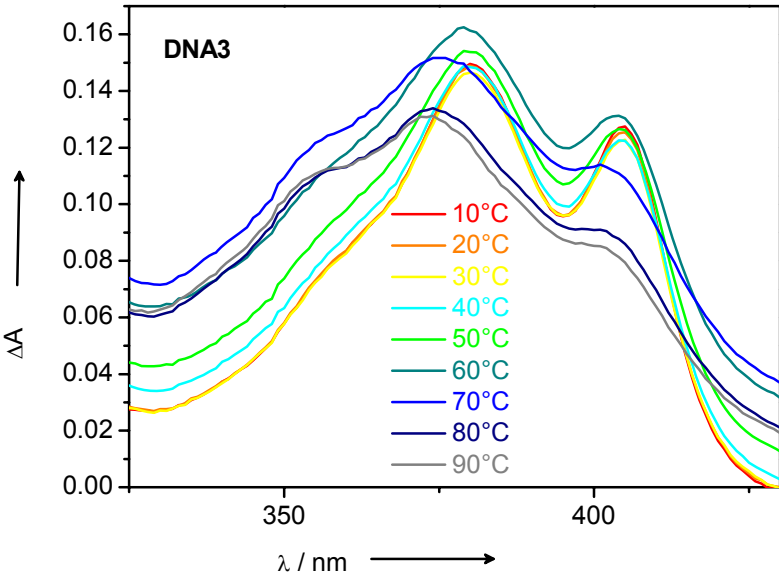


Fig. S4: Temperature-dependent UV/Vis spectra of **DNA4b** (2.5 μM in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

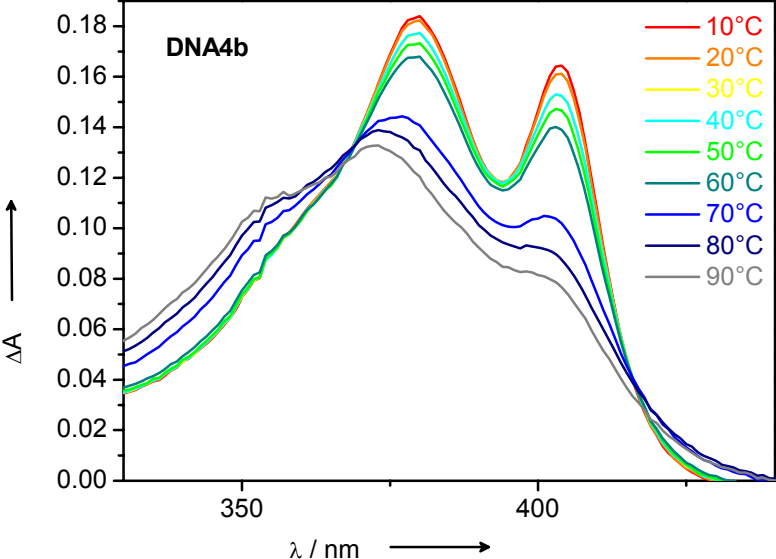


Fig. S5: Temperature-dependent UV/Vis spectra of **DNA4c** (2.5 μM in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

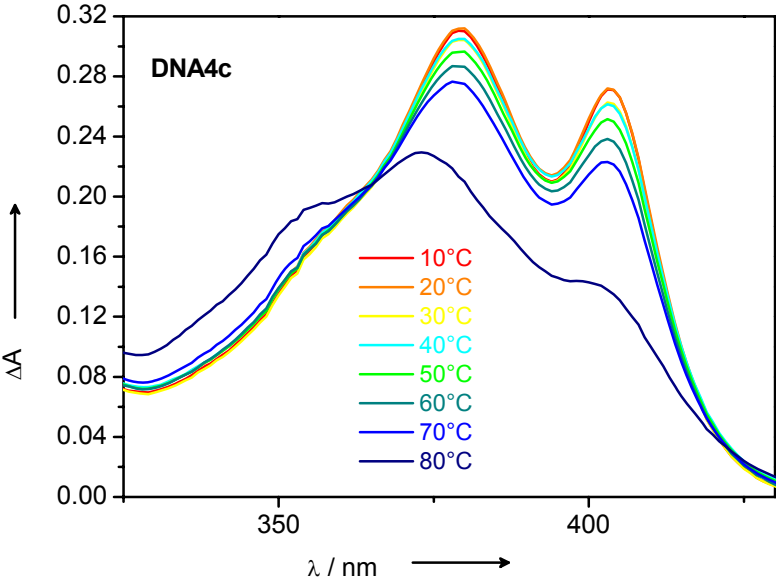


Fig. S6: Temperature-dependent UV/Vis spectra of **DNA4d** (2.5 μM in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

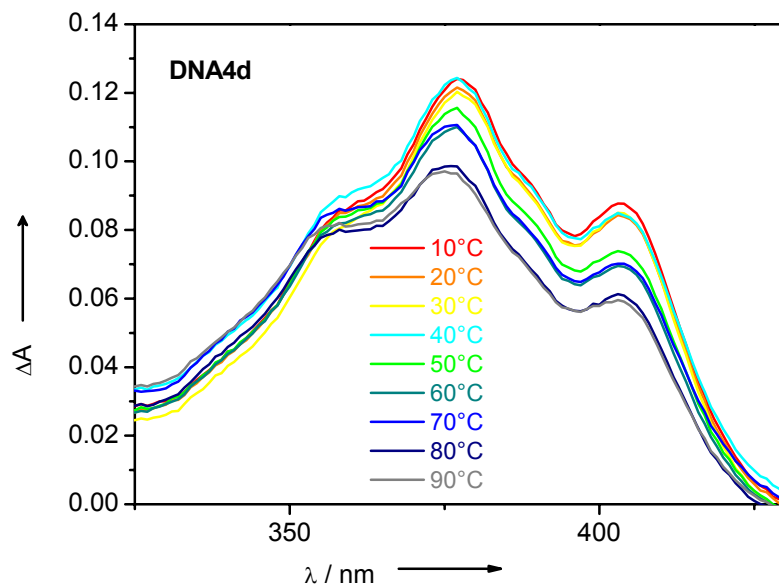


Fig. S7: Temperature-dependent CD spectra of **DNA3** (2.5 μM in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

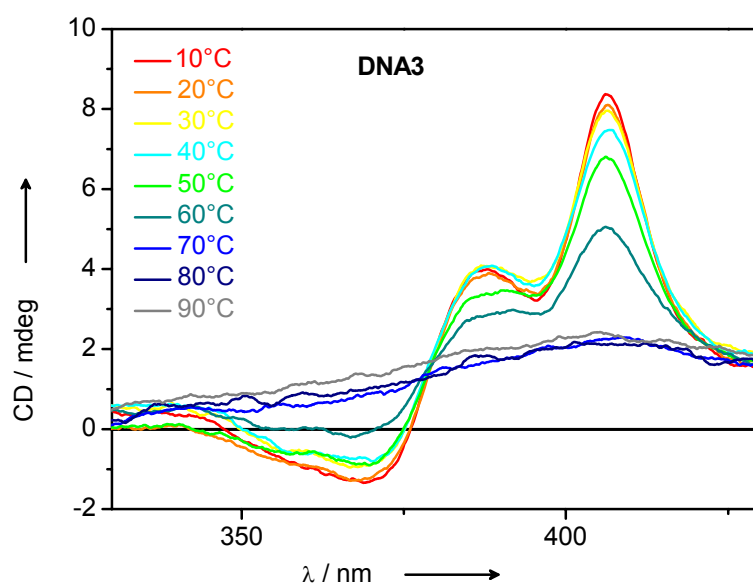


Fig. S8: Temperature-dependent CD spectra of **DNA4b** (2.5 μM in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

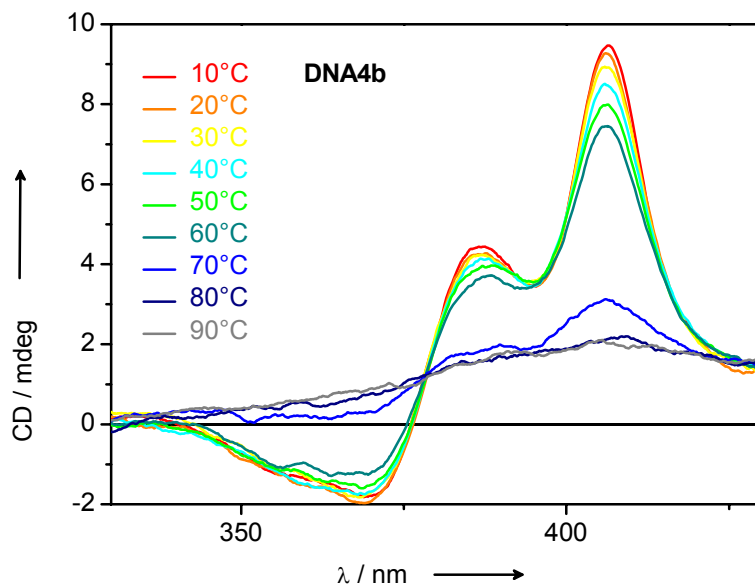


Fig. S9: Temperature-dependent CD spectra of **DNA4c** (2.5 μM in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

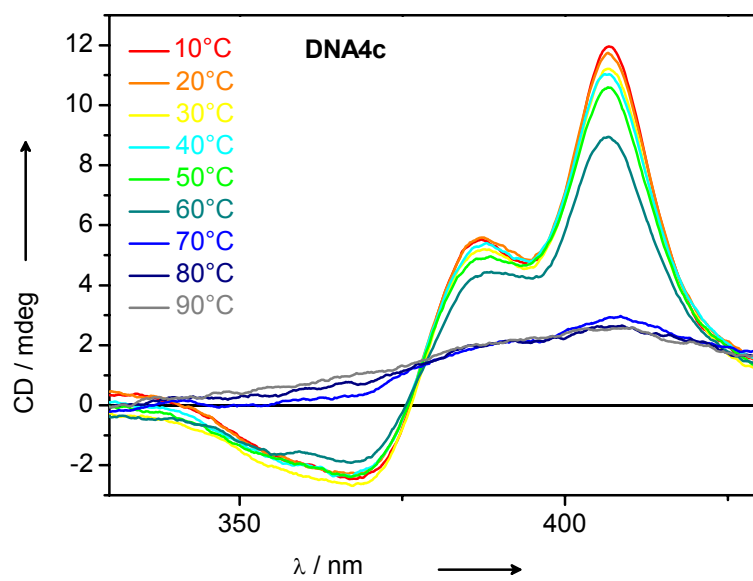


Fig. S10: Temperature-dependent CD spectra of **DNA4d** (2.5 μM in 10 mM Na-P_i-buffer, 250 mM NaCl, pH 7).

