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Supporting Information

for

DNA-Induced Chirality in Water-Soluble Poly(cobaltoceniumethylene)

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1. Experimental details

General Comments

Deoxyribonucleic acid sodium salt from salmon testes (*ca*. 2000 bp), deoxyribonucleic acid sodium salt from herring testes (type XIV, *ca*. 700 bp) and deoxyribonucleic acid from herring sperm (degraded, crude oligonucleotides, < 50 bp) were purchased from Sigma. The deoxyribonucleic acid from herring sperm (degraded, crude oligonucleotides, < 50 bp) was transformed to its sodium salt form by adding one equivalent of sodium hydroxide when the aqueous solution was prepared. The preparation of dicarba[2]cobaltocenophane **1** and poly(cobaltoceniumethylene) nitrate **PCE-NO$_3$** (M_w ~ 55,000, DP_w ~ 198) have been reported elsewhere.[1,2]

Cryogenic transmission electron microscopy: Samples for cryo-TEM experiments were prepared using a controlled environment vitrification system where the relative humidity was kept close to saturation at *ca.* 30 °C. A 10 µL drop of each solution analyzed was placed on a carbon-coated copper grid and the excess sample was gently blotted away leaving a thin film of solution covering the grid. The grid was then plunged into liquid ethane at -180 °C to allow rapid vitrification of the specimen (avoiding crystallization of water). Images were digitally recorded using a Tecnai 20 FEI twin lens scanning transmission electron microscope, operated at 200 kV, equipped with a FEI Eagle CCD camera. To minimize beam damage, all samples were imaged under minimal electron dose conditions.

Drop-cast transmission electron microscopy: The samples were prepared by drop-casting one drop (*ca*. 10 µL) of the solution onto a carbon-coated copper grid which was placed on a piece of filter paper to remove excess solvent. Bright field TEM images were

obtained on a JEOL1200EX II microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. No staining of the samples was necessary.

Atomic force microscopy: Tapping mode height images were obtained using a Multimode V atomic force microscope equipped with a Nanoscope V controller (Veeco Instruments Ltd, Santa Barbara, USA). Nanosensors (Neuchatel, Switzerland) PPP NCHR10 cantilevers with a rotated monolithic silicon probe with a tip radius of approximately 10 nm were employed. The samples were prepared by drop-casting one drop (*ca.* 10 µL) of the solution onto a piece of cleaned silicon wafer (washed with acetone and methanol sequentially). Imaging was conducted in air at ambient temperature. Images were analyzed using Gwyddion, an open source program designed for AFM image (www.gwyddion.net).

Dynamic light scattering: DLS experiments were performed using a nano series Malvern zetasizer instrument equipped with a 633 nm red laser and a detector oriented at 173° to the incident radiation. The results of DLS studies are reported as apparent hydrodynamic radius ($R_{H,app}$), acknowledging that the particles have been modelled as spheres in the experiments conducted.

Circular dichroism spectroscopy: CD measurements were performed on a JASCO J-815 spectrophotometer. Typically, the spectra were acquired in a 5 mm path-length quartz cuvette at room temperature (*ca*. 25 °C). Three scans were averaged per spectrum to improve the signal-to-noise ratio, operating from 200 to 400 nm at a scan rate of 100 nm/min and a bandwidth of 1 nm. Measurements were performed under constant nitrogen flow, which was used to purge the ozone generated by the light source of the instrument.

UV-vis spectroscopy: UV-vis data were obtained on a Thermo Scientific NanoDrop 2000c UV-vis spectrophotometer from 200 to 400 nm at a scan rate of 100 nm/min.

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Raman spectroscopy: Raman spectra were recorded on a Bruker Sentarra Dispersive Raman microscope and were excited with a 785 nm laser (100 mW) in order to minimize the fluorescence of the sample. Direct analysis of the aqueous samples sealed in capillary tubes was not successful because of the intense background signals. The measurements were eventually conducted on freeze-dried powders placed on glass slides. The spectra were recorded from two to five different points for each sample to check for the representative nature of the spectra. The fluorescence background was subtracted with an appropriate *n*th order polynomial. Control experiments based on freeze-dried **PCE-NO$_3$** powder did not yield useful data as a result of a very strong fluorescence background.

Formation of DNA/PCE complexes

Aqueous solutions of DNA (0.1 mg/mL) and **PCE-NO$_3$** (0.1 mg/mL) were mixed and stirred for 1 min at room temperature (*ca*. 25 °C). The volumetric ratio of the two solutions was varied while their sum was constant to 1 mL. Upon mixing the solutions of DNA and **PCE-NO$_3$**, stable cloudy colloidal solutions formed immediately. The resulting solutions were stored statically at room temperature and tested within one week.

Mass ratios of DNA to **PCE-NO$_3$** have been given rather than mole ratios as the sequence structure of the DNA was not known. This approach has been used elsewhere: *e.g*., J. O. Rädler, I. Koltover, T. Salditt, C. R. Safinya, *Science*, 1997, **275**, 810.

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2. Additional results

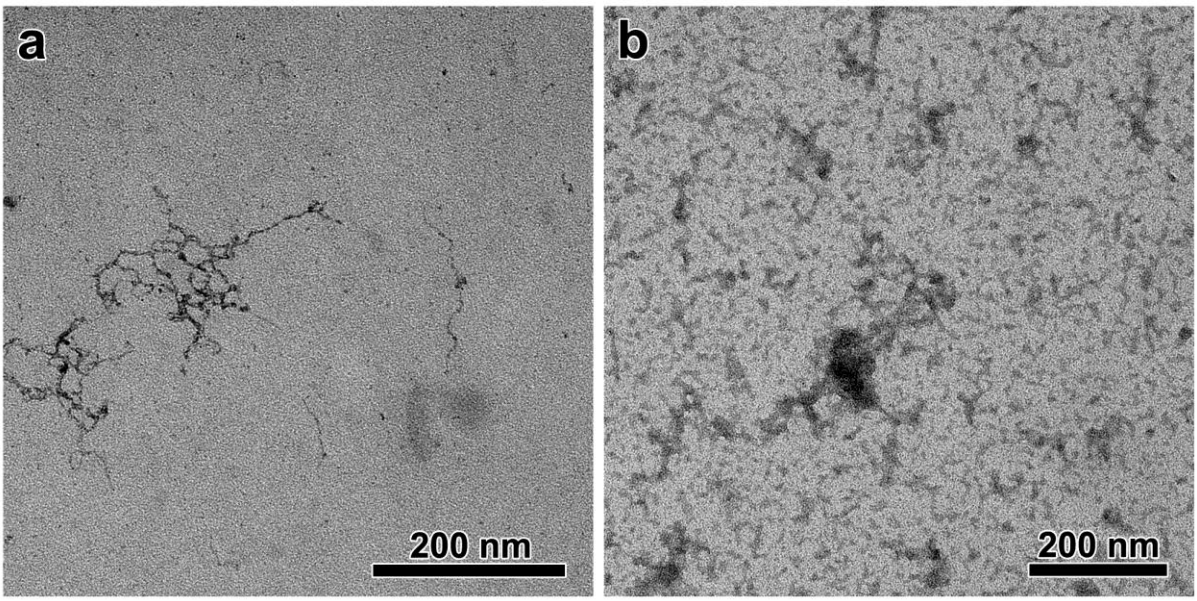

Fig. S1 Drop-cast TEM images of (a) DNA (deoxyribonucleic acid sodium salt from salmon testes, *ca*. 2000 bp) and (b) **PCE-NO_3** from 0.1 mg/mL aqueous solutions.

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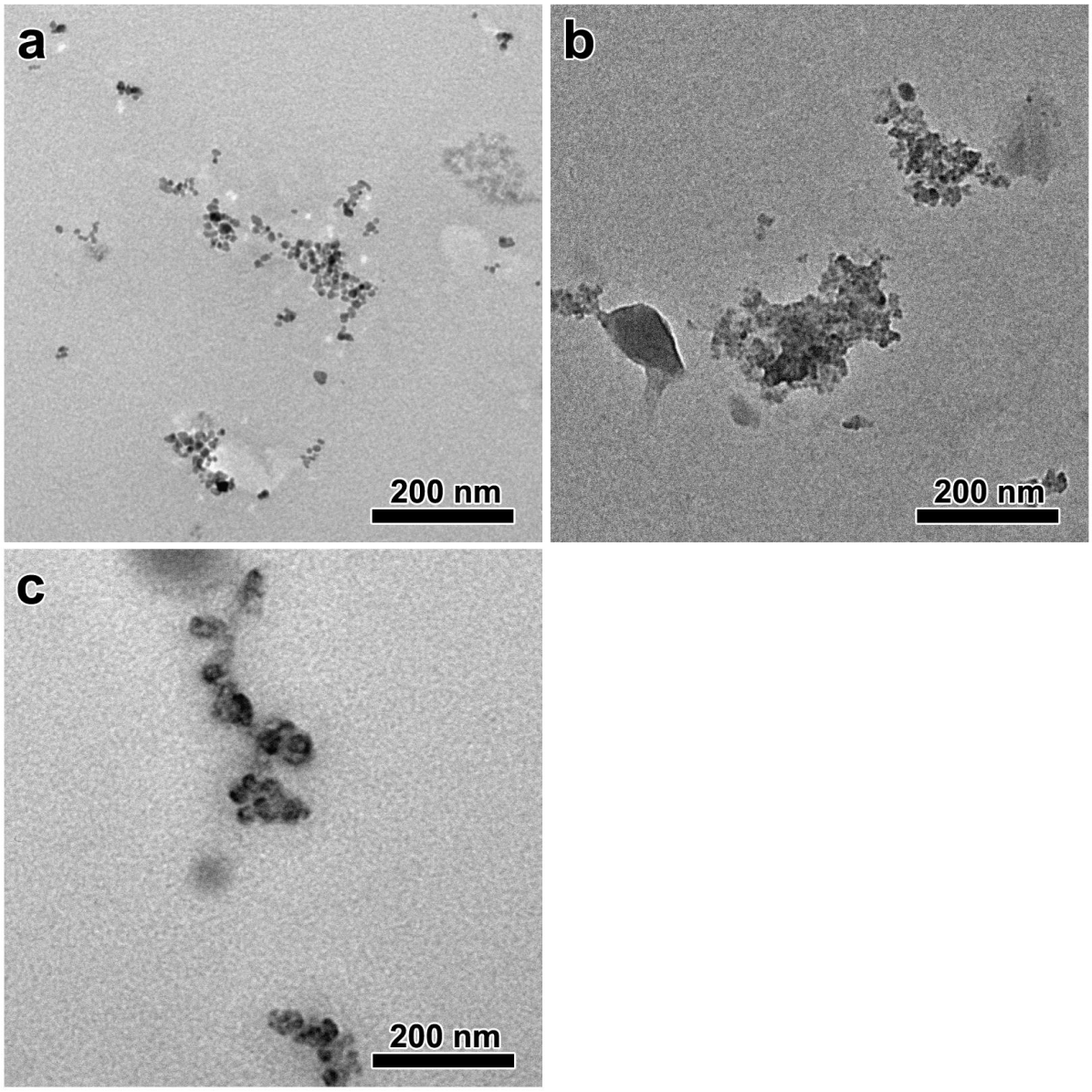

Fig. S2 Drop-cast TEM images of the DNA/PCE complexes formed with DNA (deoxyribonucleic acid sodium salt from salmon testes, *ca*. 2000 bp) to **PCE-NO_3** mass ratios of (a) 4:1, (b) 2:1 and (c) 1:1.

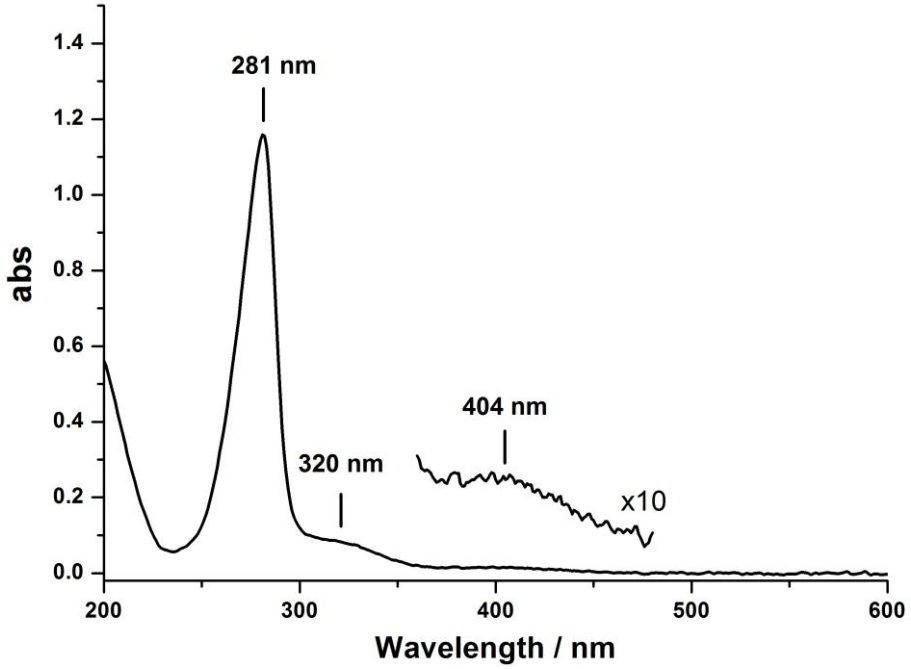

Fig. S3 UV-vis spectra of **PCE-NO_3** (0.1 mg/mL in deionized water).

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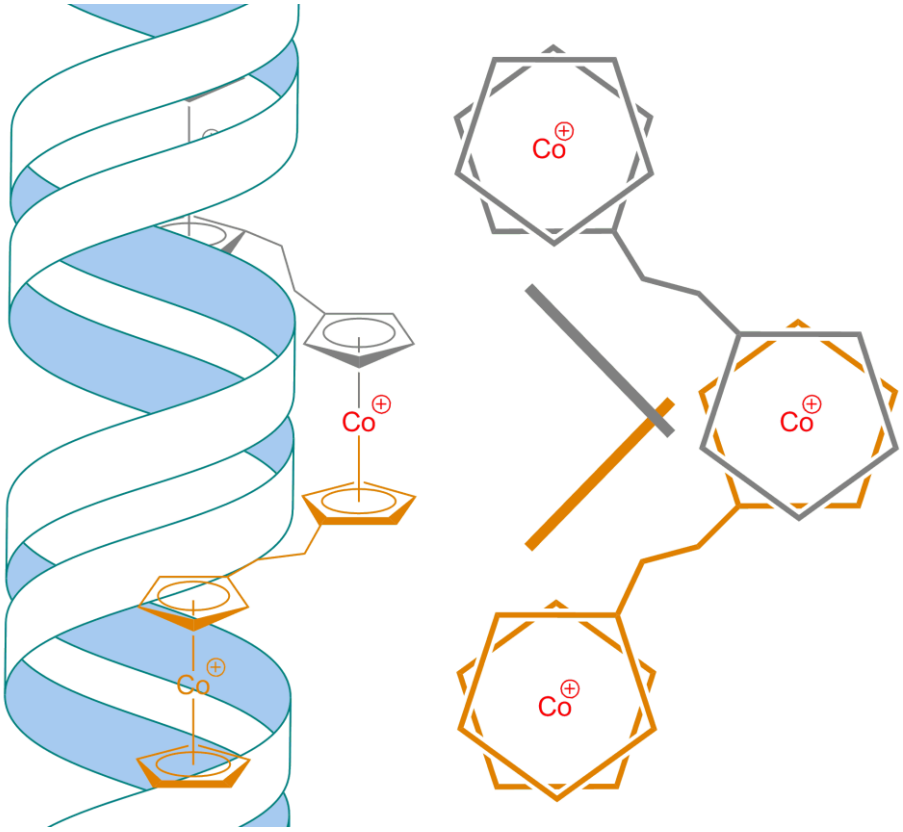

Fig. S4 A possible binding model for the DNA/PCE complex.

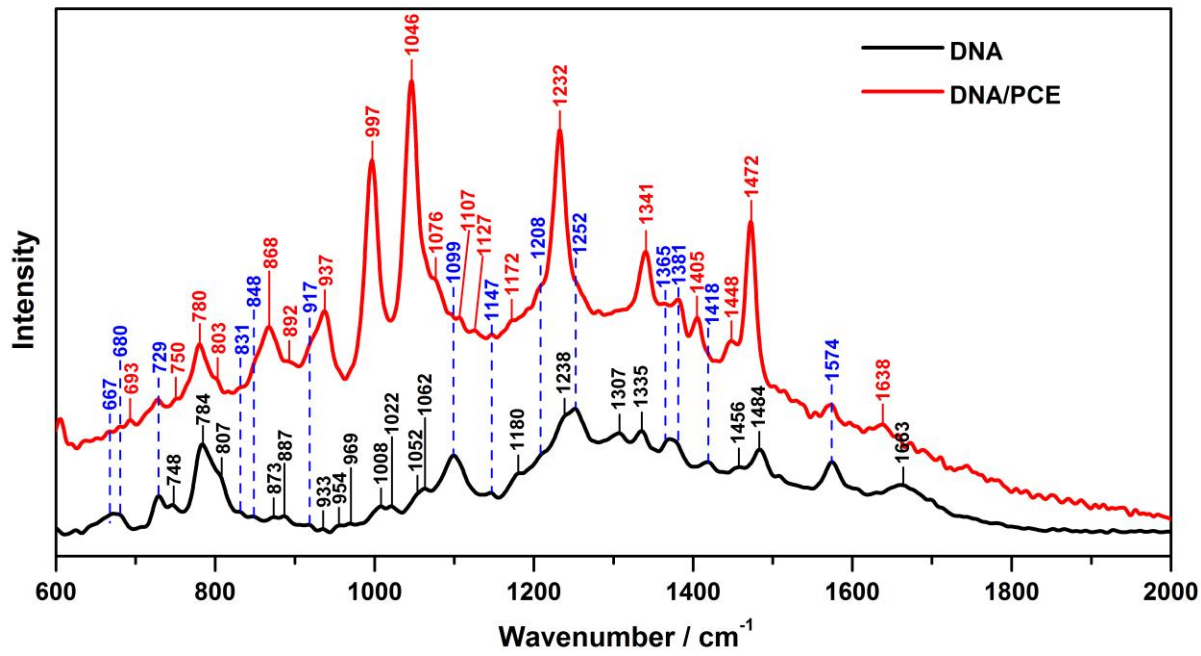

Fig. S5 Raman spectra of freeze-dried DNA (black line) and freeze-dried 1:1 DNA/PCE complex (red line). DNA: deoxyribonucleic acid sodium salt from salmon testes, *ca*. 2000 bp.

Raman spectra of freeze-dried DNA (black line) revealed a peak at 807 cm^{-1} typically assigned to A-DNA (υ_{as} of the O-P-O diester group), indicating a B- to A-form transformation during dehydration.[3]

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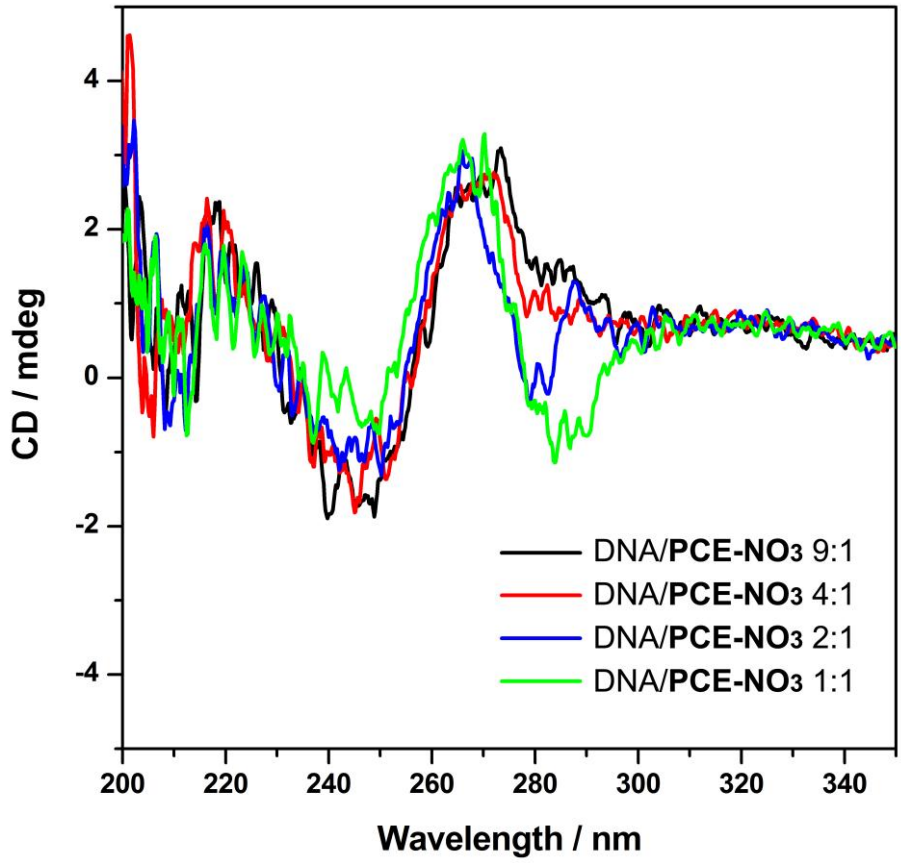

Fig. S6 CD spectra of the complexes formed by mixing **PCE-NO_3** and deoxyribonucleic acid sodium salt from herring testes (type XIV, *ca*. 700 bp) with different DNA to **PCE-NO_3** mass ratios. The spectra were acquired in a 1 mm path-length quartz cuvette at room temperature (*ca*. 25 °C).

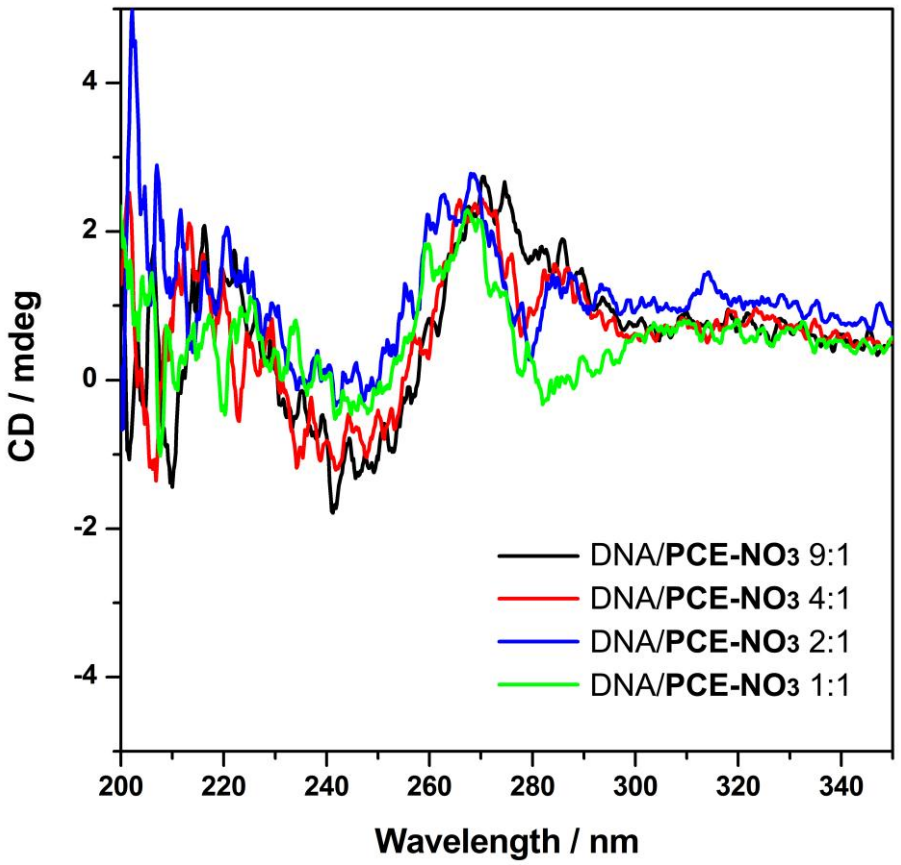

Fig. S7 CD spectra of the complexes formed by mixing **PCE-NO$_3$** and deoxyribonucleic acid sodium salt from herring testes (degraded, crude oligonucleotides, < 50 bp) at different DNA to **PCE-NO$_3$** mass ratios. The spectra were acquired in a 1 mm path-length quartz cuvette at room temperature (*ca*. 25 °C).

3. References

[1] U. F. J. Mayer, J. P. H. Charmant, J. Rae, I. Manners, *Organometallics*, 2008, **27**, 1524.

[2] U. F. J. Mayer, J. B. Gilroy, D. O'Hare, I. Manners, *J. Am. Chem. Soc.*, 2009, **131**, 10382.

[3] B. Prescott, W. Steinmetz, G. J. Thomas, JR., *Biopolymers*, 1984, **23**, 235.