SUPPORTING INFORMATION

Reversible DNA Compaction Induced by Partial Intercalation of 16-Ph-16 Gemini Surfactants: Evidences of Triple Helices Formation

Elia Grueso[*a], Emilio Roldan[a], Pilar Perez-Tejeda[a], Edyta Kuliszewska[b] B. Molero[a], Lothar Brecker[c] and R. M. Giráldez-Pérez.[a]

Contribution from:

a) Department of Physical Chemistry, Faculty of Chemistry, University of Seville.

C/ Profesor García González, s/n, 41012, Sevilla, Spain.

b) Innovia s. p. z. o. o. Chemtra, 47-300 Krapkowice, Poland.

c) Institute of Organic Chemistry, University of Vienna, Währingerstrasse 38, A-1090 Wien, Austria

* Author to whom correspondence should be addressed. Tel: +34-954557175 (ext. 215); Fax: +34-954557174; e-mail address: elia@us.es

NMR Characterization

For NMR spectroscopic measurements, the two compounds (see Fig. S1 for the structure) were dissolved in 99.95% $CDCl_3$ (~10 mg in 0.7 mL) and transferred into 5 mm NMR sample tubes (Promochem, Wesel, Germany). Spectra were measured on a Bruker DRX-400 AVANCE spectrometer at 400.13 MHz (^1H) or 100.62 MHz (^{13}C) using the Topspin 1.3 (Bruker, Rheinstetten, Germany). For 1D spectra 32k data points were recorded and Fourier transformed to spectra with a range of 15 ppm (^1H) and 240 ppm (^{13}C). Two dimensional COSY, TOCSY, NOESY, HMQC and HMBC spectra were measured with 128 experimental runs, each having 1024 data points each. Appropriate linear forward prediction, sinusoidal multiplication and Fourier transformation led to 2D-spectra with ranges of 12 ppm and 220 ppm for ^1H and ^{13}C, respectively. Residual $CHCl_3$ was used as internal standard for ^1H (δ_H 7.24) and $CDCl_3$ for ^{13}C (δ_C 77.0) spectra. Measurement temperature was 298.1 K +/-0.1 K.

1. ***N,N'*-Di-*n*-hexadecyl-*N,N,N',N'*-tetramethyl-phenylene-1,4-dimethylenammonium dibromide (p-16-Ph-16).** ^1H-NMR (400 MHz, $CDCl_3$, δ in ppm): 7.79 (s,br, 4 H, H-2 (4x)); 5.10 (s,br, 4 H, H-1' (2x)); 3.51 (s,br, 4 H, H-1'' (2x)); 3.21 (s,br, 12 H, CH_3 (4x)); 1.80 (s,br, 4 H, H-2'' (2x)); 1.35 (s,br, 4 H, H-3'' (2x)); 1.24_c (m,br, 48 H, H-4'' to H-15'' (2x)); 0.68 (t, 6 H, *J*=7.0 Hz, H-16'' (2x)). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 133.6 (d, C-2 (4x)); 128.7 (s, C-1 (2x)); 66.6 (t, C-1' (2x)); 65.1 (t, C-1'' (2x)); 49.6 (q, CH_3 (4x)); 31.4 (t, C-14'' (2x)); 29.7-29.4 (t (10x), C-4'' to C-13'' (2x)); 28.5 (t, C-3'' (2x)); 26.4 (t, C-2'' (2x)); 22.7 (t, C-15'' (2x)); 14.1 (q, C-16'' (2x)).

2. ***N,N'*-Di-*n*-hexadecyl-*N,N,N',N'*-tetramethyl-phenylene-1,3-dimethylenammonium dibromide ((m-16-Ph-16).** ^1H-NMR (400 MHz, $CDCl_3$, δ in ppm): 8.45 (s,br, 1 H, H-4); 7.76 (d,br, 2 H, *J*=6.4 Hz, H-2 (2x)); 7.45 (t,br, 1 H, *J*=6.4 Hz, H-3); 4.99 (s,br, 4 H, H-1'

(2x)); 3.47 (s,br, 4 H, H-1'' (2x)); 3.20 (s,br, 12 H, CH_3 (4x)); 1.79 (s,br, 4 H, H-2'' (2x)); 1.32 (s,br, 4 H, H-3'' (2x)); 1.24$_c$ (m,br, 48 H, H-4'' to H-15'' (2x)); 0.85 (t, 6H, J=7.0 Hz, H-16'' (2x)). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 138.8 (d, C-4); 135.1 (d, C-2 (2x)); 129.9 (d, C-3); 128.8 (s, C-1); 66.9 (t, C-1' (2x)); 65.0 (t, C-1'' (2x)); 49.9 (q, CH_3 (4x)); 31.3 (t, C-14'' (2x)); 29.7-29.4 (t (10x), C-4'' to C-13'' (2x)); 29.3 (t, C-3'' (2x)); 26.4 (t, C-2'' (2x)); 23.3 (t, C-15'' (2x)); 14.1 (q, C-16'' (2x)).

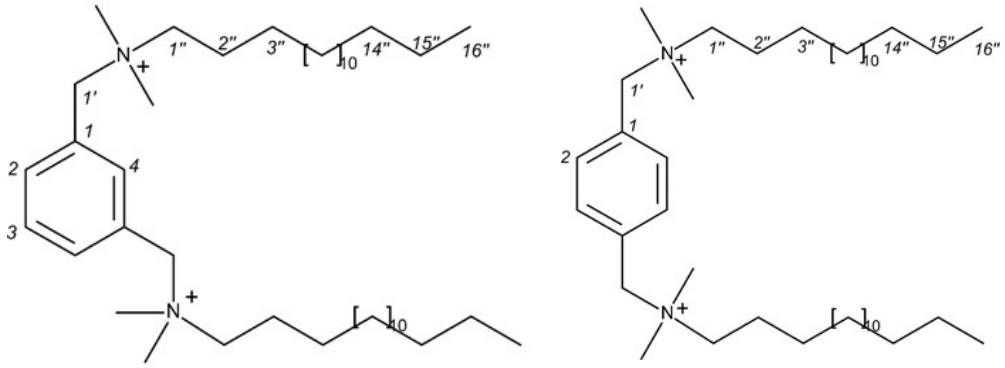

Figure S1. Structures of compounds m-16-Ph-16 and p-16-Ph-16. The numbering is accordance with those used in for the NMR shift data. It is not in accordance to the IUPAC nomenclature, but allows an easy comparison of different shifts in the two compounds.

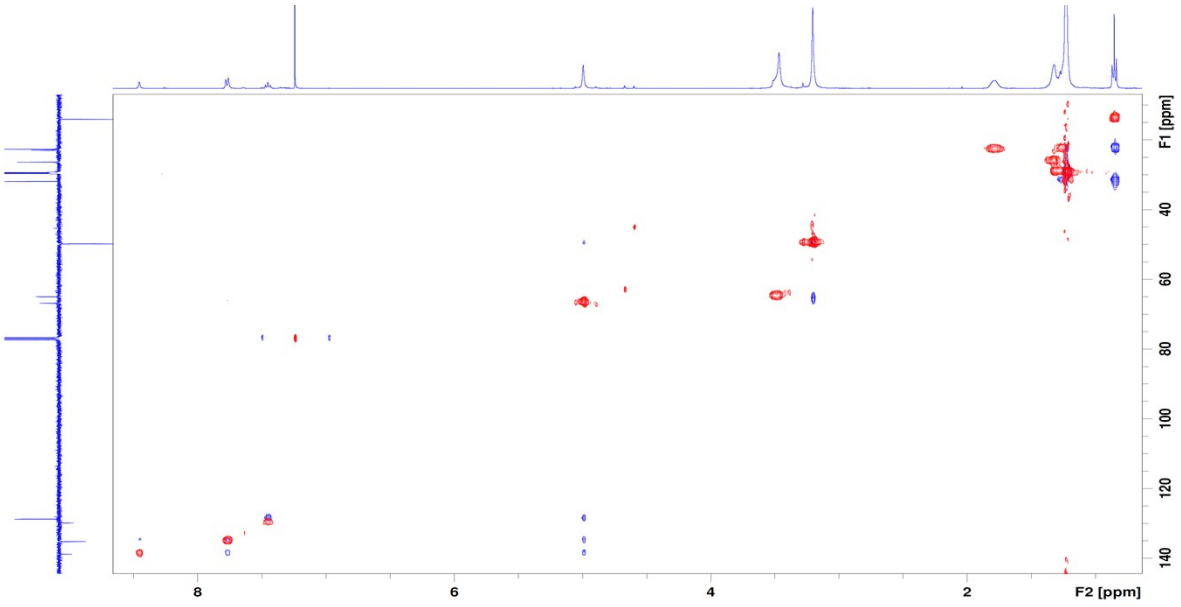

Figure S2. Combined HSQC (red) and HMBC (blue) spectra of compound m-16-Ph-16, together with the respective ^{1}H and ^{13}C NMR spectra on the axes.

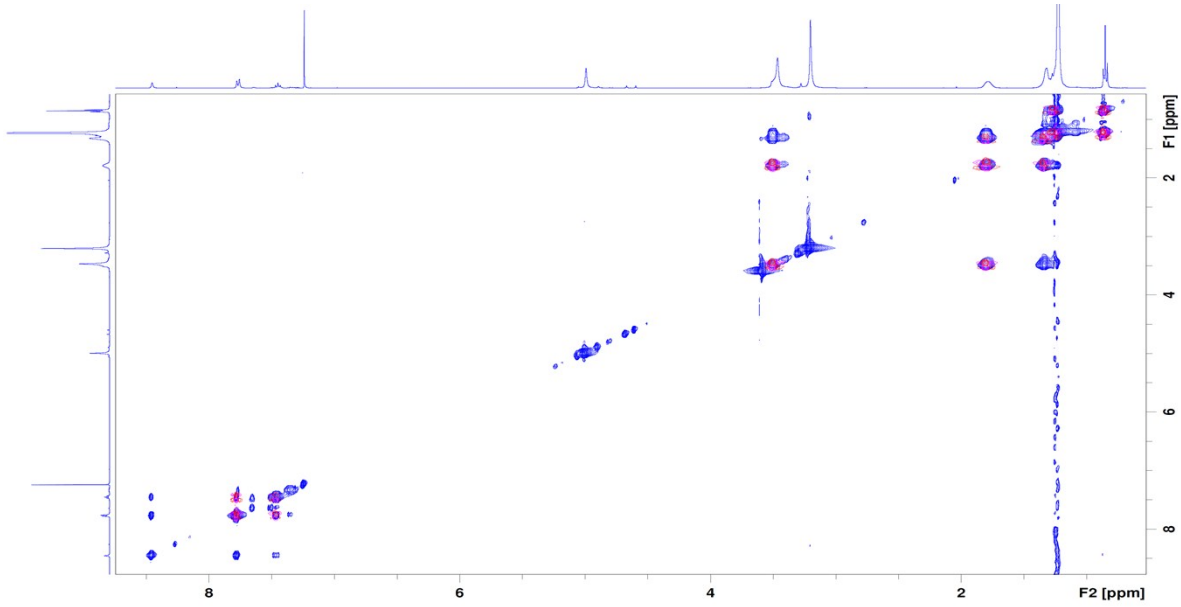

Figure S3. Combined COSY (pinc) and TOCSY (blue) spectra of compound m-16-Ph-16 together with the respective ^{1}H NMR spectrum on both axes.

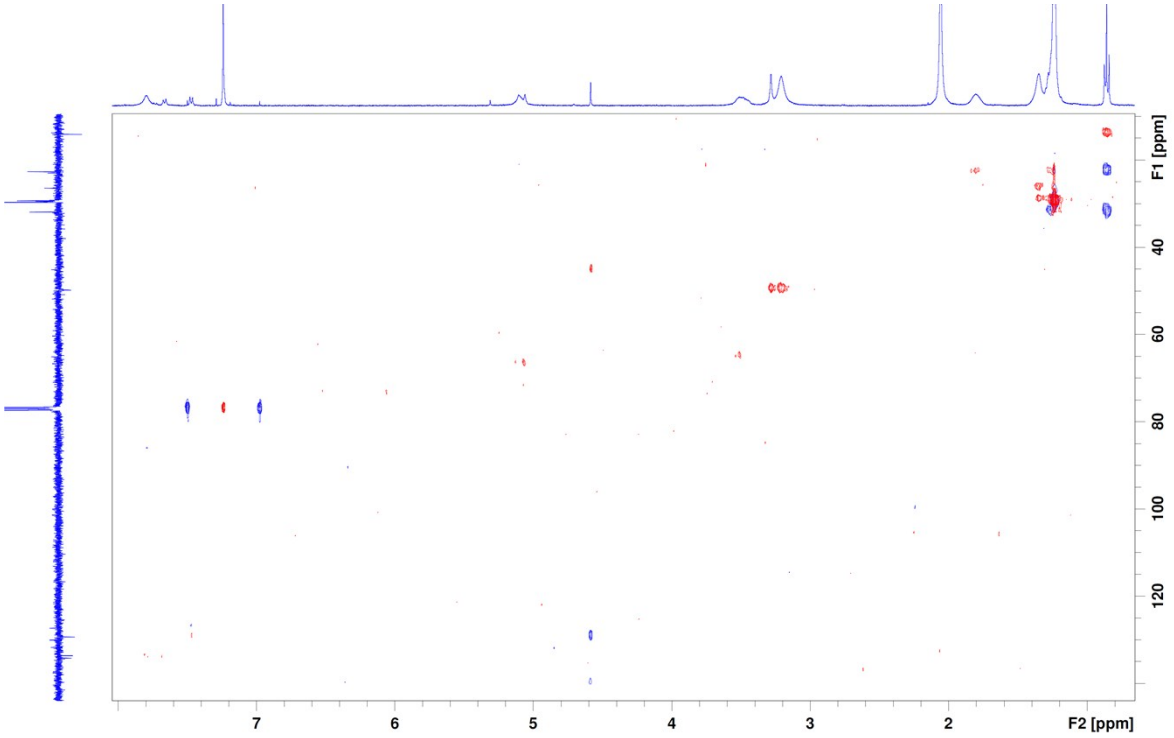

Figure S4. Combined HSQC (red) and HMBC (blue) spectra of compound p-16-Ph-16, together with the respective ^{1}H and ^{13}C NMR spectra on the axes.

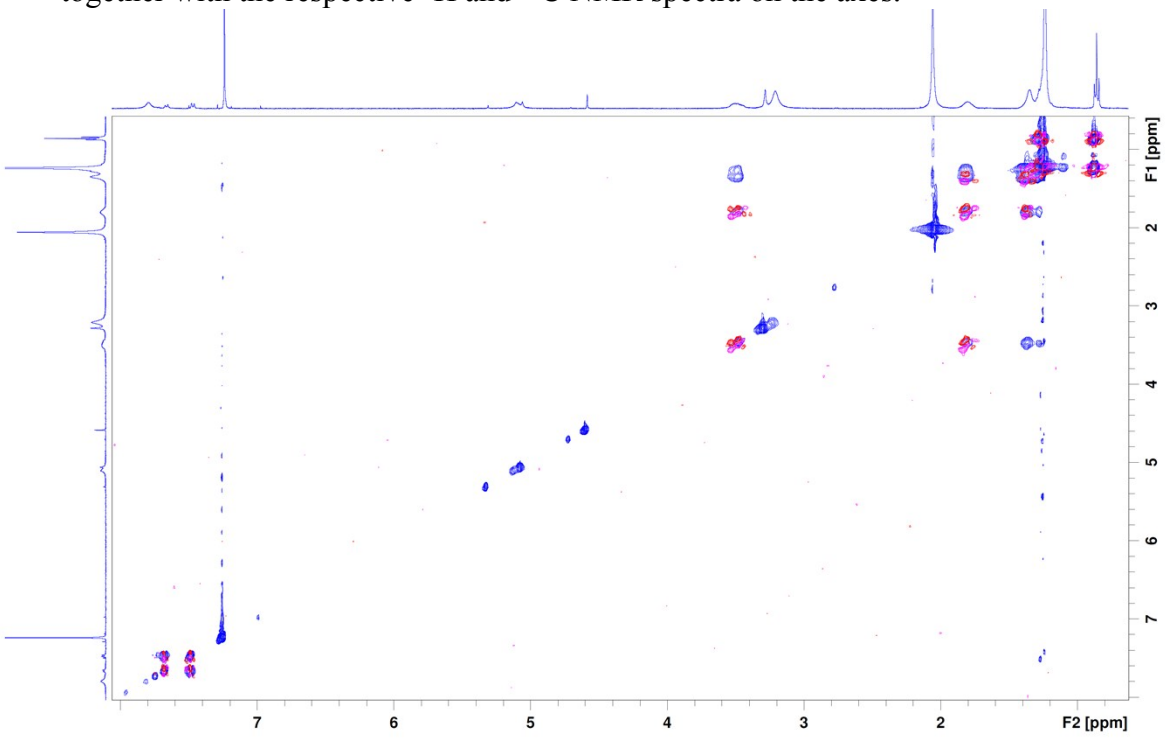

Figure S5. Combined COSY (pinc) and TOCSY (blue) spectra of compound p-16-Ph-16 together with the respective ^{1}H NMR spectrum on both axes.

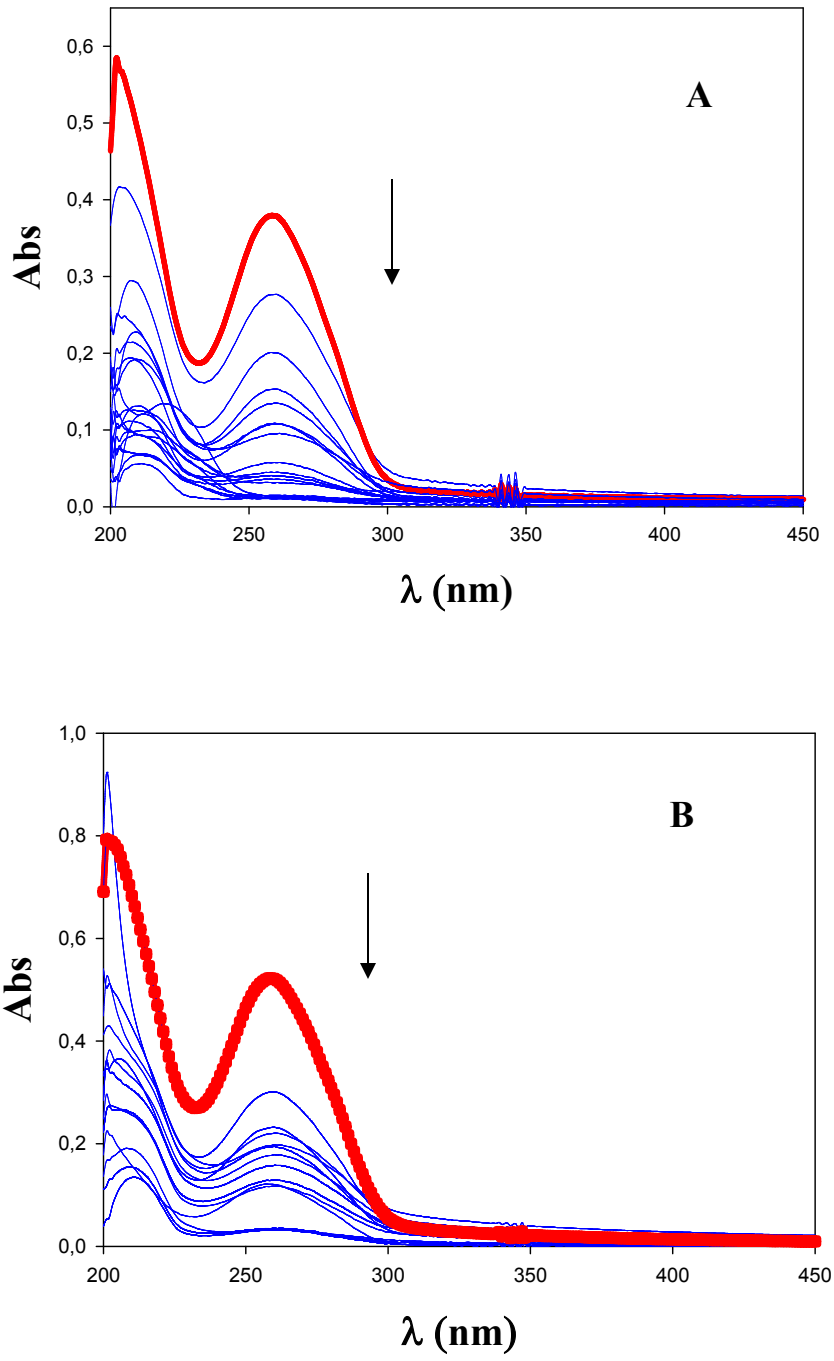

Figure S6. Absorbance spectra of 16-Ph-16/DNA systems (A) $C_{m\text{-}16\text{-}Ph\text{-}16}$ = 5 μM; C_{DNA} = 0.2, 0.3, 0.5, 0.8, 1.0, 2.0, 3.0, 4.0, 5.0, 7.5, 10.0, 12.5, 15.0, 20.0, 25.0, 32.5 and 75.0 μM. (B) $C_{p\text{-}16\text{-}Ph\text{-}16}$ = 7.5 μM; C_{DNA} = 0.15, 0.19, 0.25, 0.38, 1.25, 1.50, 1.87, 3.75, 7.50, 12.5, 18.7, 25.0, 37.5 and 75.0 μM.

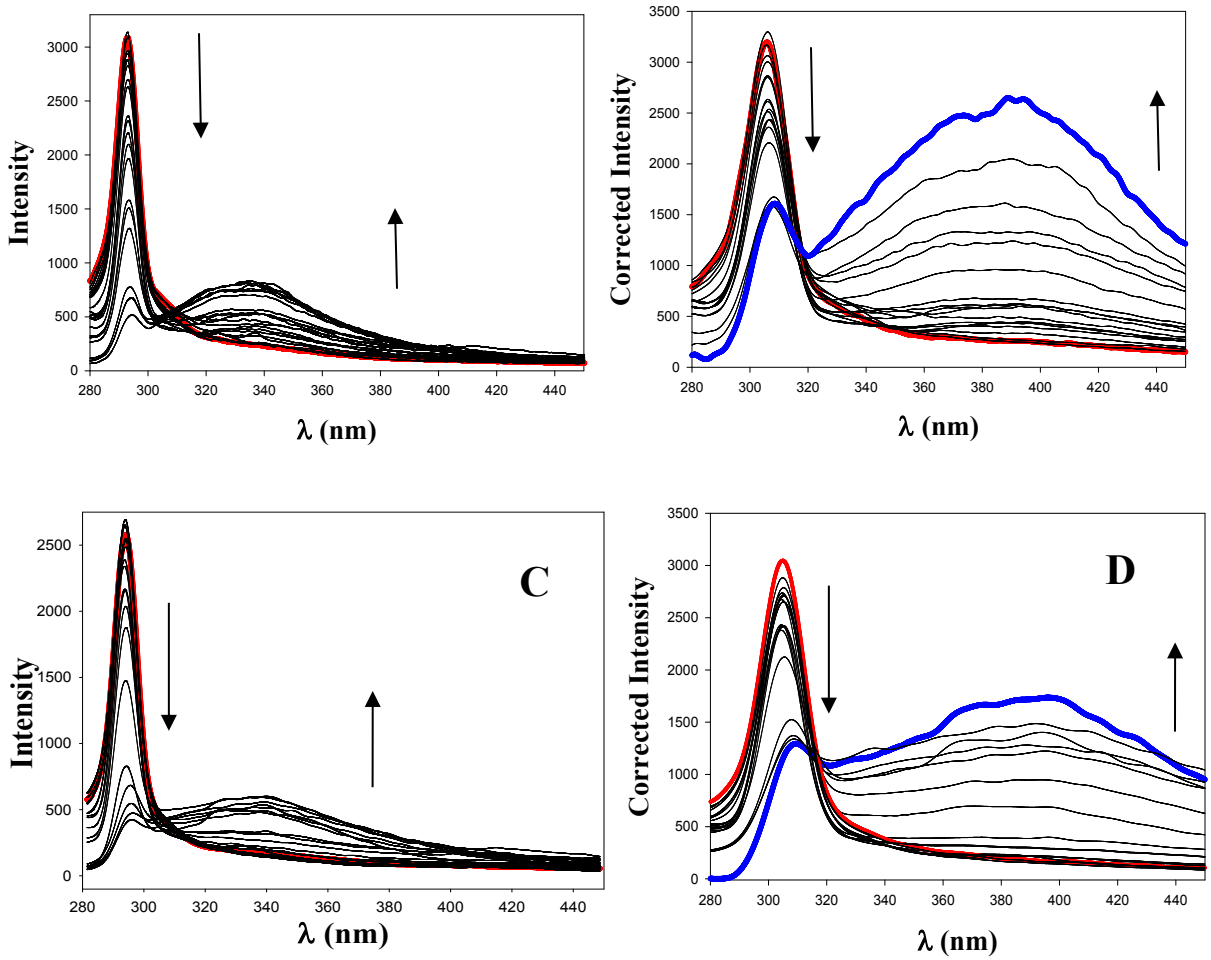

Figure S7. Fluorescence spectra (A, C) and the corresponding corrected fluorescence emission spectra (B, D) of 16-Ph-16/DNA systems. (A-B) $C_{m\text{-}16\text{-}Ph\text{-}16}$ = 5 μM, C_{DNA} = 0.15, 0.20, 0.5, 0.8, 1.0, 2.0, 3.0, 4.0, 5.0, 7.5, 10.0, 20.0, 30.0, 40.0, 50.0, 75.0, 100.0 μM. (C-D) $C_{p\text{-}16\text{-}Ph\text{-}16}$ = 5 μM, C_{DNA} = 0.15, 0.20, 0.5, 0.8, 1.0, 2.0, 3.0, 4.0, 5.0, 7.5, 10.0, 20.0, 30.0, 40.0, 50.0, 75.0, 100.0 μM.

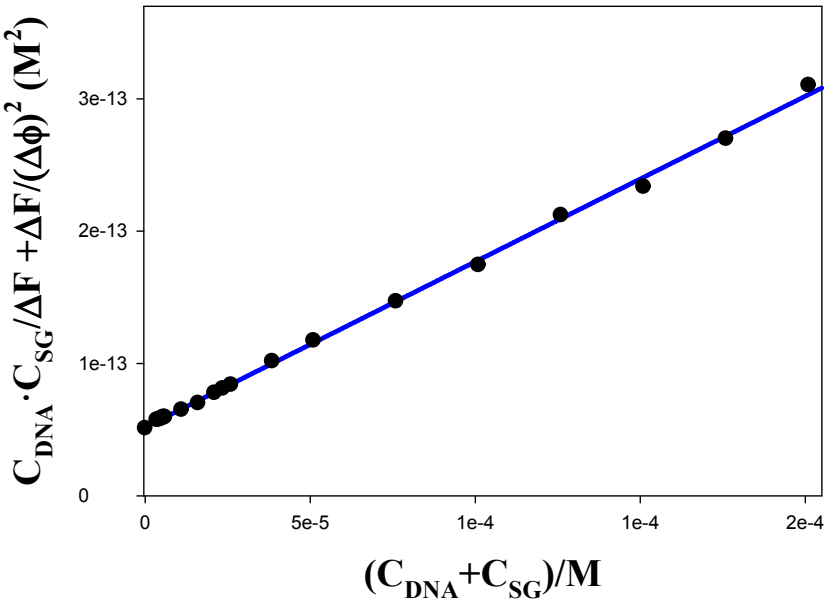

Figure S8. Analysis of the fluorescence titration data for the SG/DNA system in cacodilate buffer. λexc = 484 nm; λem = 520 nm. $C_{SG} = 5 \cdot 10^{-6}$ M.

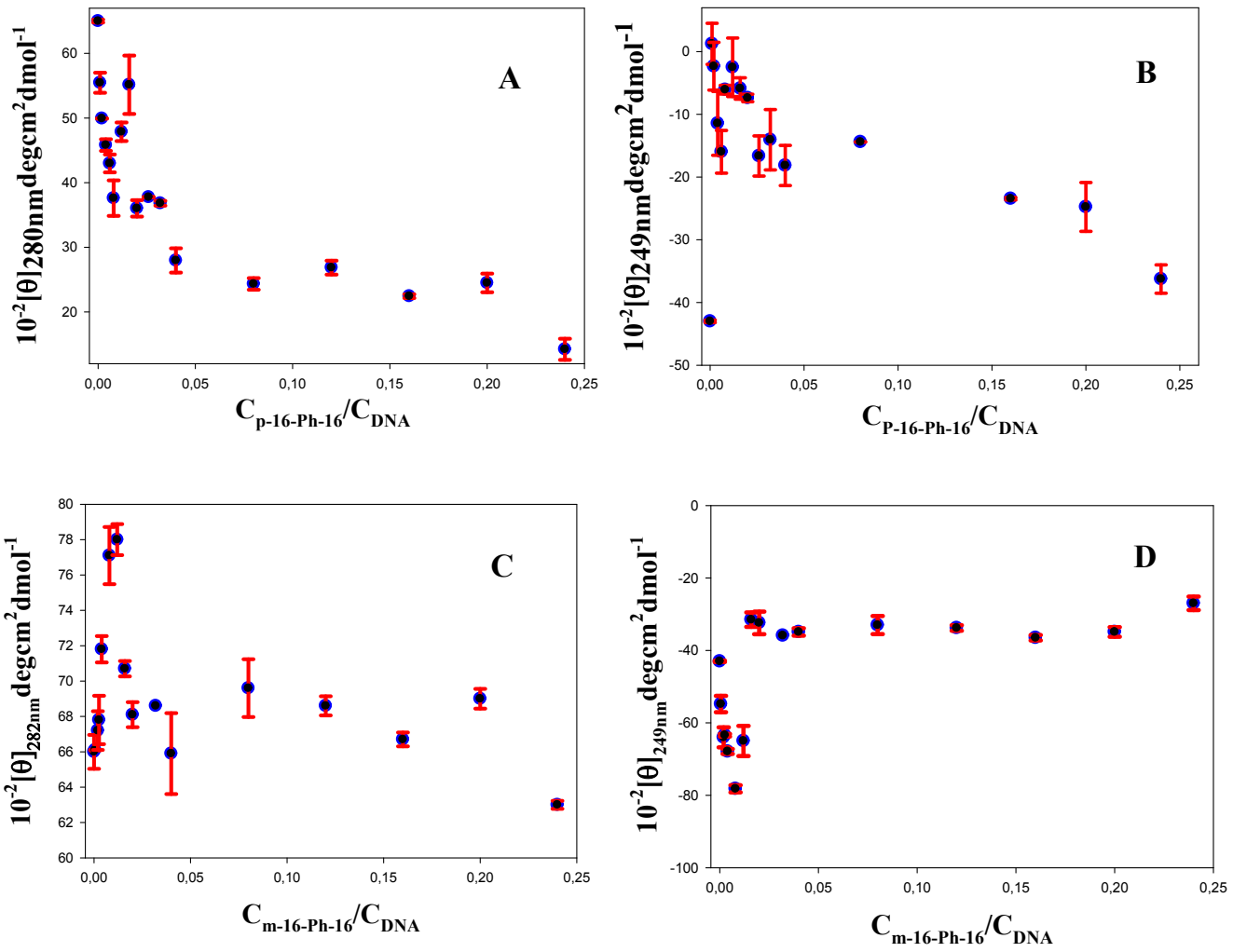

Figure S9. Representation of the molar ellipticity as a function of the R ratio at the maximum of the positive and negative CD band for (A, B) p-16-Ph-16/DNA system and (C, D) m-16-Ph-16/DNA system. The error bars represent the 95% confidence intervals of the fit to the mean data obtained from 5 cumulated CD spectra.

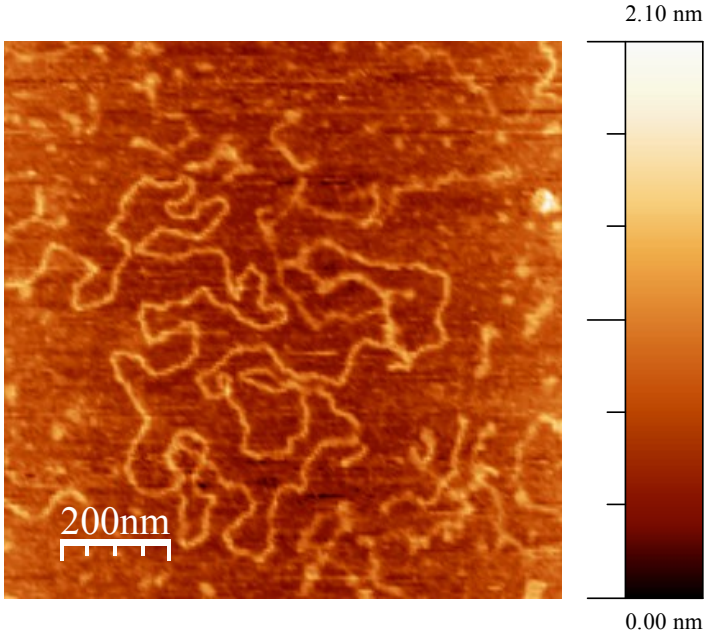

Figure S10. AFM topographic images of CT-DNA in extended-coil conformation, $C_{DNA} = 3 \cdot 10^{-7}$ M.

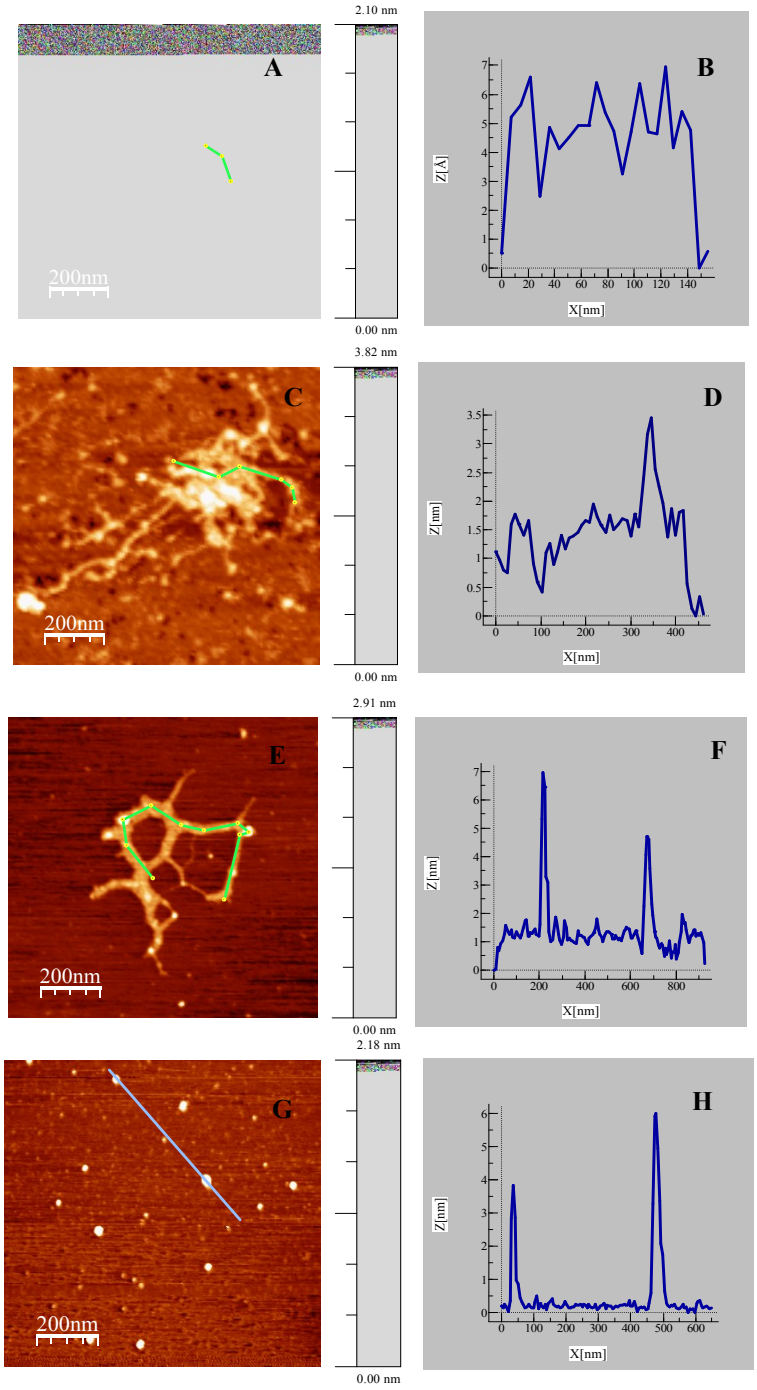

Figure S11. Analysis of AFM topographic images in Fig. 9, S10 and surfactant micelles. (A) DNA, $C_{DNA} = 3 \cdot 10^{-7}$ M, R = 0.0; (C) p-16-Ph-16/DNA system, $C_{DNA} = 3 \cdot 10^{-7}$ M, R = 10.0; (E) m-16-Ph-16/DNA system, $C_{DNA} = 3 \cdot 10^{-7}$ M, R = 10.0; (F) p-16-Ph-16 micelles, $C_{p\text{-}16\text{-}Ph\text{-}16} = 5 \cdot 10^{-5}$ M. Figures B, D, F and H correspond to cross sectional analysis of the heights along the selected line for images A, C, E and G, respectively.