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Electronic Supplementary Information

Surfactant-mediated control of CBPQT^{4+}- dialkoxynaphthalene complexation.

Jeremie Louisy,[a,b] François Delattre,[c] Joel Lyskawa,[b] Aurélie Malfait,[b] Catherine E. Maclean,[a] Léna Sambe,[b] Ning Zhu,[b,d] Graeme Cooke,[a]* Patrice Woisel[b]*

[a] *GCPOC, WestCHEM, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK.*
[b] *Université Lille Nord de France, Unité matériaux et Transformations, UMR -CNRS 8207Université des Sciences et Technologies de Lille 1, C6 59655 Villeneuve d'Ascq Cedex, France.*
[c] *UCEIV (Unité de Chimie Environnementale et Interactions sur le Vivant), EA 4492, Université du Littoral Côte d'Opale,Av. M. Schumann 59140 Dunkerque, France.*
[d] *Department of Polymer Science and Engineering, Key Laboratory of Macromolecular Synthesis and Functionalization of the Ministry of Education, Zhejiang University, Hangzhou 310027, China.*

1.General Information

Materials. All reagents were purchased from Aldrich and were used as received unless otherwise mentioned.

Instrumentation and Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Mass spectrometry was carried out on a Micromass Platform II spectrometer with an electrospray ionization source. UV/vis turbidity measurements were carried out on a Varian Cary 50 Scan UV/vis spectrophotometer equipped with a single cell Peltier temperature controller. IR spectra were recorded using a Spectrum One PerkinElmer spectrometer. Isothermal titration calorimetry (ITC) experiments were performed at 20 °C using a nano-ITC titration calorimeter from TA Instruments with a standard sample cell volume of 1mL, following standard procedures. A 250 µL injection syringe was used with stirring at 400 rpm. Samples were dissolved in deionised water and the solutions were degassed gently under vacuum before use. Each titration comprised an initial 1µl pre-injection followed by 25 x 10 µl injections of (3.5 mM) into host solution (0.06 mM). Control experiments with identical injections of CBPQT(4 Cl^-) into water alone were used to correct titration data.

2. Synthesis and characterization

Compound **3**[1] was prepared according to the literature methods.

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Synthesis of **4**

Triphenylphosphine (1.56 g, 5.96 mmol, 1 eq.) was added to a solution of carbon tetrabromide (1.98 g, 5.96 mmol, 1eq.) and **3** (2 g, 5.96 mmol, 1eq.) in dry acetonitrile (200 mL). The mixture was stirred at room temperature under nitrogen for 24h. The solvent was evaporated to afford a crude product which was subjected to column chromatography (SiO_2: Dichloromethane / Ethyl Acetate, 3:1). The product was obtained as a white solid in 45 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J=8.4 Hz, 2H, H-4,8), 7.29 (t, J=8 Hz, 2H, H-3,7), 6.77 (d, J=7.6 Hz, 2H, H-2,6), 4.23 (t, J=4.6 Hz, 4H, 2×CH_2O), 3.95-3.87 (m, 6H, 3×CH_2O), 3.68 (m, 4H, 2× CH_2O, 3.45 (t, J=6 Hz, 2H, CH_2Br).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.30, 154.28 (aromatic C-1,5), 126.78 (Aromatic C-9,10), 125.24, 125.18 (Aromatic (C-7,3), 114.74, 114.63 (Aromatic C-4,8), 105.83, 105.79 (Aromatic C-2,6), 72.64, 71.51, 69.79, 69.77, 67.96, 67.92, 61.86 (*C*H_2O), 30.47 (*C*H_2Br).

Synthesis of **1 :**

To a solution of **4** (500 mg, 1.25 mmol, 1 eq.) in methanol (70 mL) was added dropwise trimethylamine 31-35 % in ethanol (4.5 mL, 18.8 mmol, 15 eq.). The mixture was stirred at reflux overnight. The mixture was concentrated under reduce pressure to a volume of 10 mL and diethyl ether (250 mL) was slowly added. The precipitate was filtered and washed with diethyl ether. The product was obtained as a white solid in 95 % yield. Mpt. 51-53 ^{o}C (dec).

^{1}H NMR (300 MHz, D_2O): δ = 7.77 (d, J= 8.4 Hz, 1H, H-4), 7.71 (d, J=8.4 Hz, 1H, H-8), 7.34 (t, J= 8.1 Hz, 2H, H-3,7), 6.95 (d, J= 8.1 Hz,1H, H-6), 6.92 (d, J= 8.1 Hz,1H, H-2), 4.30-4.19 (m, 4H, CH_2O), 3.86 (m, 6H, CH_2O), 3.61 (m, 4H, CH_2O), 3.38 (t, J = 4.8 Hz, 2H, N-CH_2), 2.90 (s, 9H, N-CH_3).

^{13}C NMR (100 MHz, D_2O): δ = 153.7, 153.6, 126.2 ,125.9, 125.8, 114.4, 114.1, 107.1, 106.8, 72.6, 71.5, 69.8, 69.77, 68.0, 67.9, 61.9, 30.5, 53.7, 53.6, 53.6

MS (ESI$^+$): 378 (M^+, 100).

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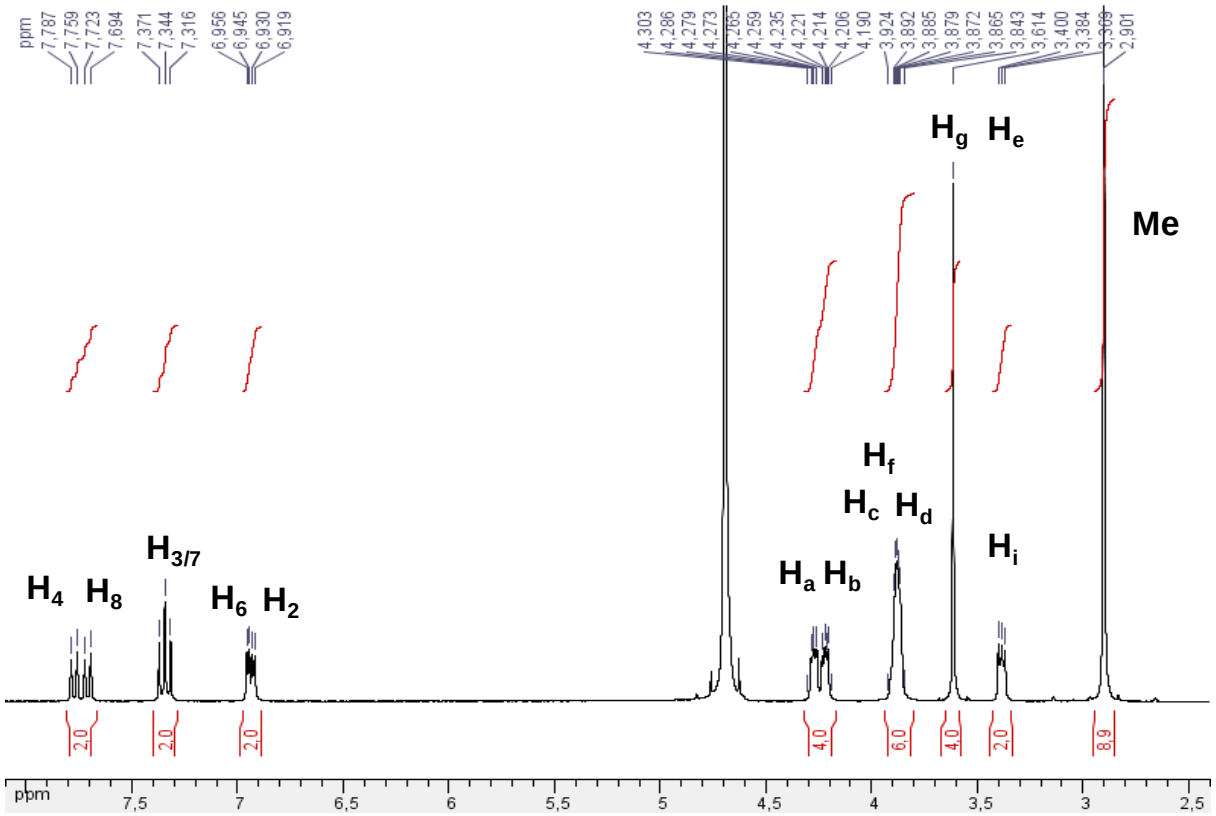

Fig S1. Partial ^{1}H NMR spectrum of **1** recorded in D_2O.

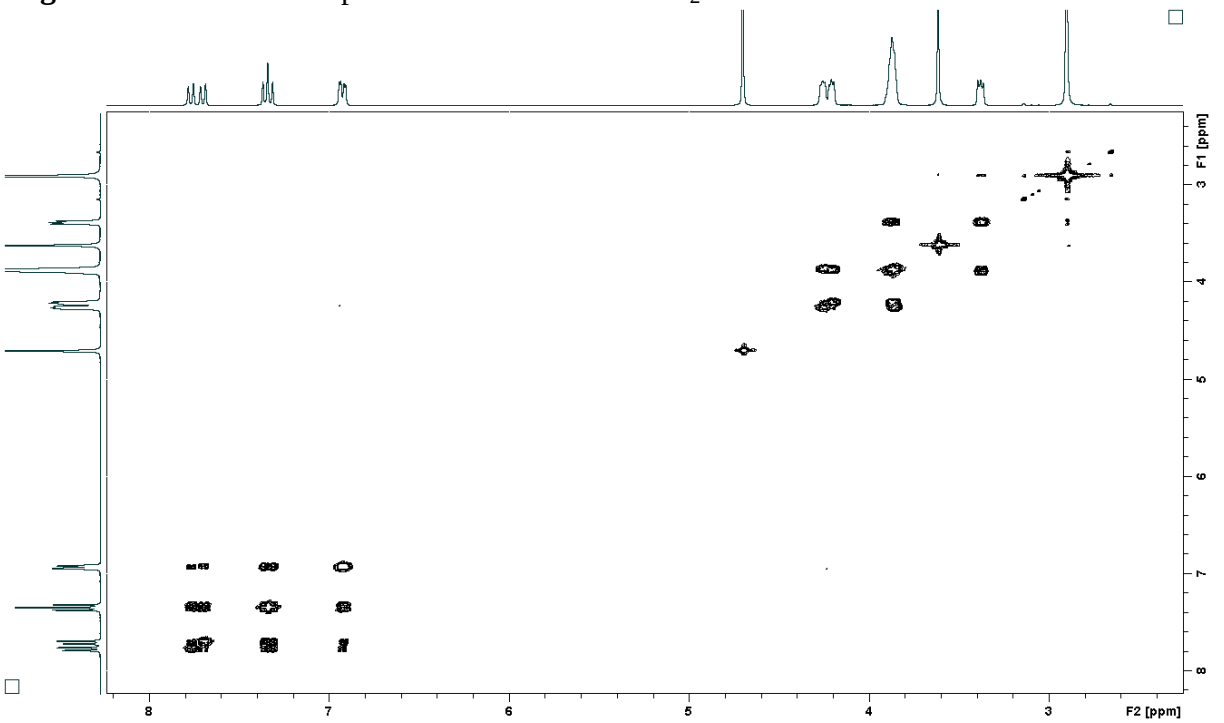

Fig S2. Partial ^{1}H- ^{1}H COSY spectrum of compound **1** recorded in D_2O.

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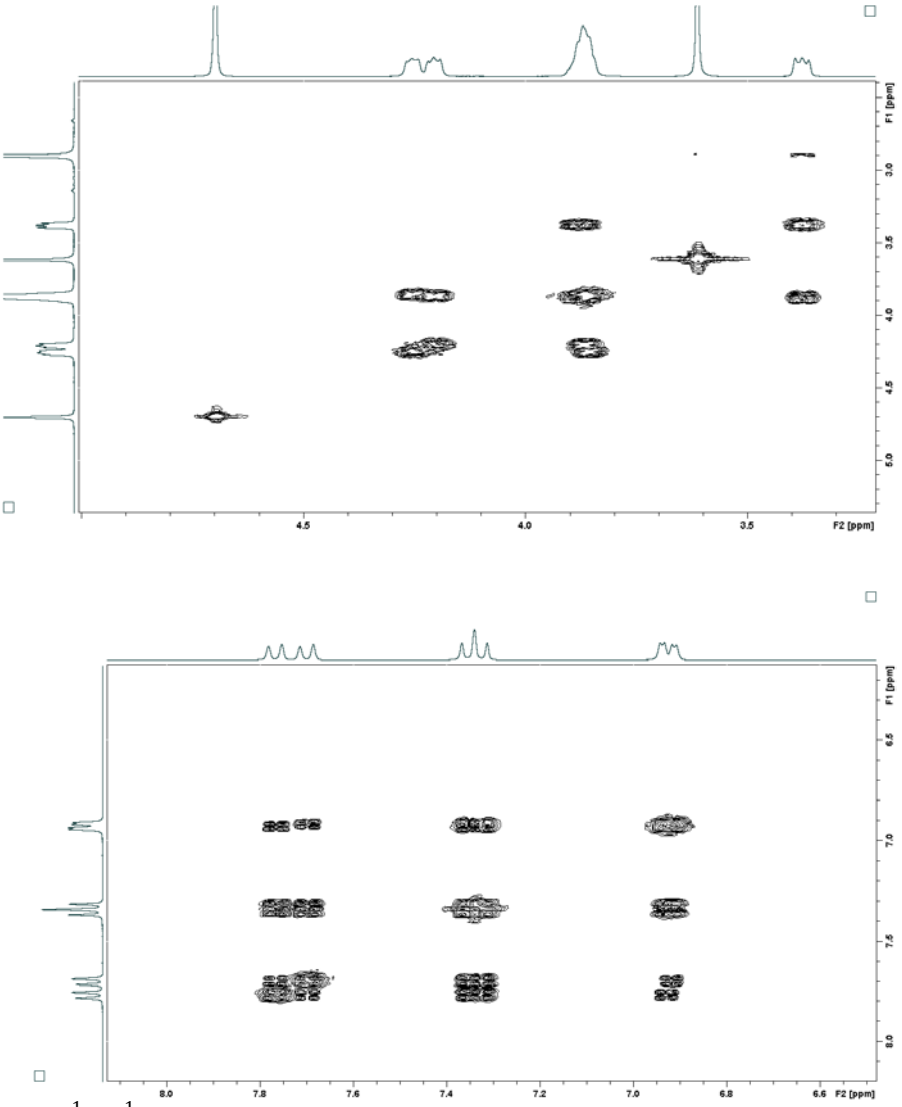


Fig S3. Partial ^{1}H- ^{1}H COSY spectra of compound **1** recorded in D_2O**.**

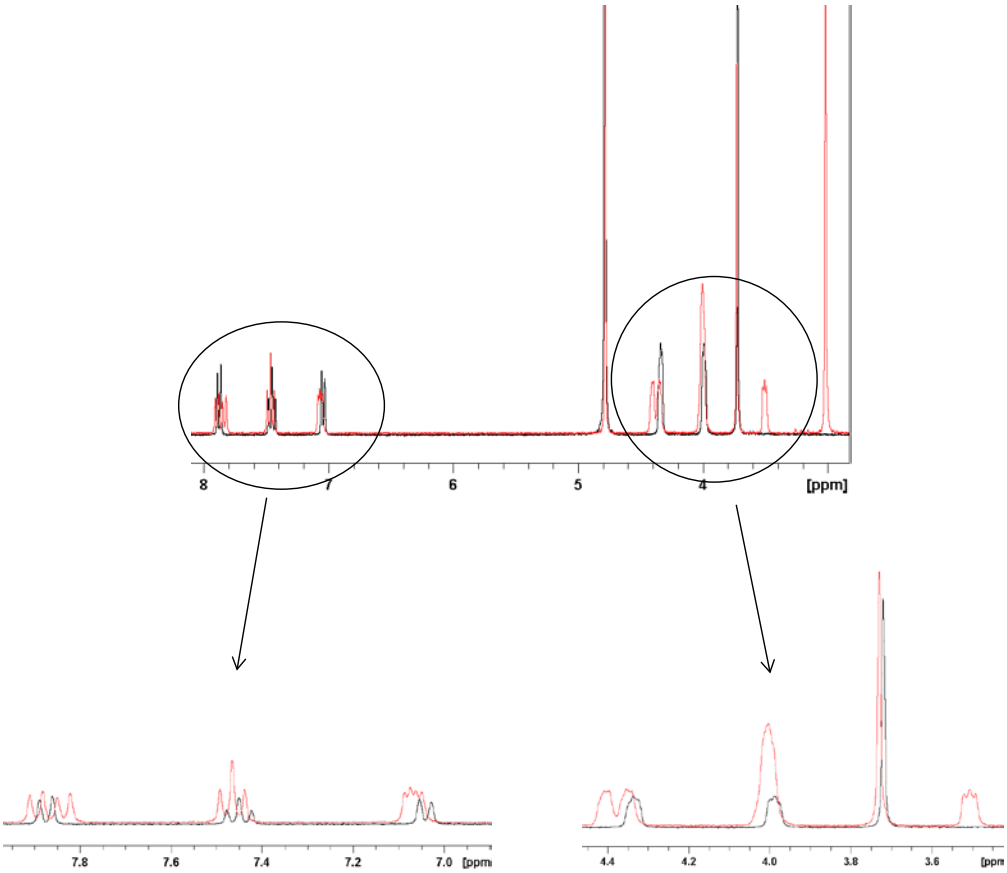
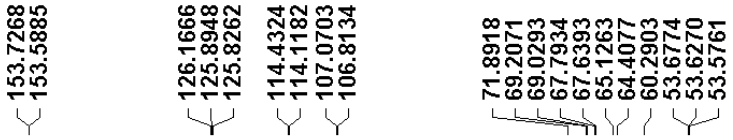


Fig S4. Partial ^{1}H NMR spectrum of **1** (red curve) and **3** (dark curve) recorded in D_2O



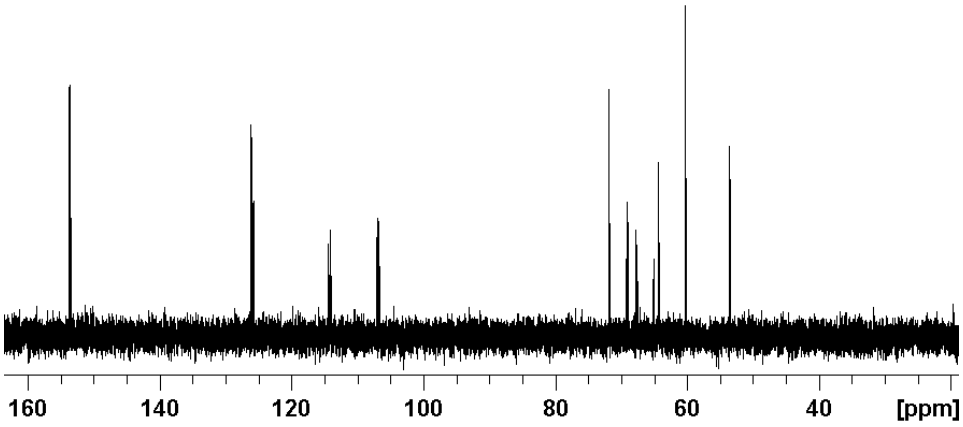


Fig S5. Partial ^{13}C NMR spectrum of **1** recorded in D_2O

[1] P. R. Ahston, R. Ballardini, V. Balzani, S. E. Boyd, A. Credi, *Chem. Eur. J.* 1997, **3**, 152-170.

3. Complexation studies

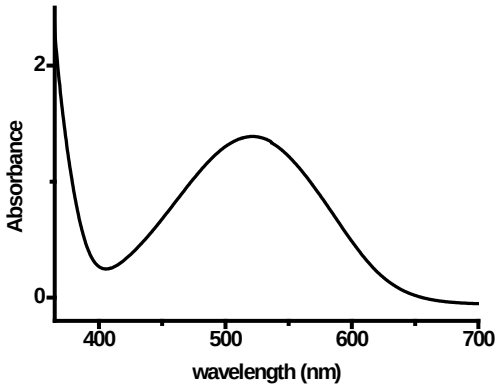


Fig. S6. UV-vis spectra of **1.2** (~10^{-4} M). Recorded in D_2O solution at 25°C.

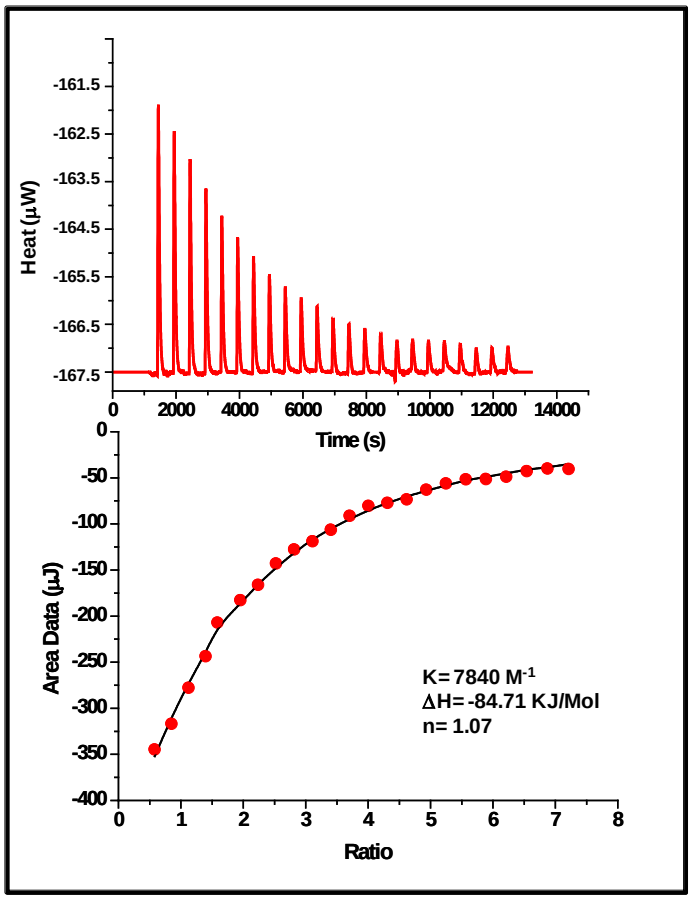


Fig S7. Isothermal titration calorimetry data for the addition of aliquots of **1** to **2**. Recorded in H_2O at 25°C.

4. Micellization studies.

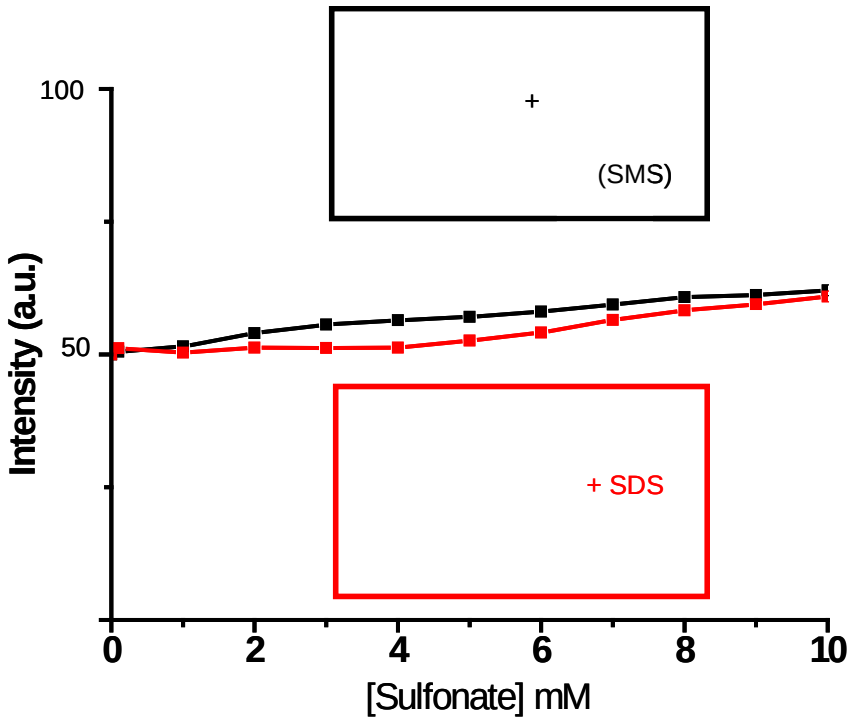


Fig S8. Graph showing the intensity of fluorescence emission of **1** and **3** as a function of the SMS and SDS concentration, respectively. λ_{ex}= 295nm. λ_{em} = 329 nm. Recorded in H_2O at 25°C

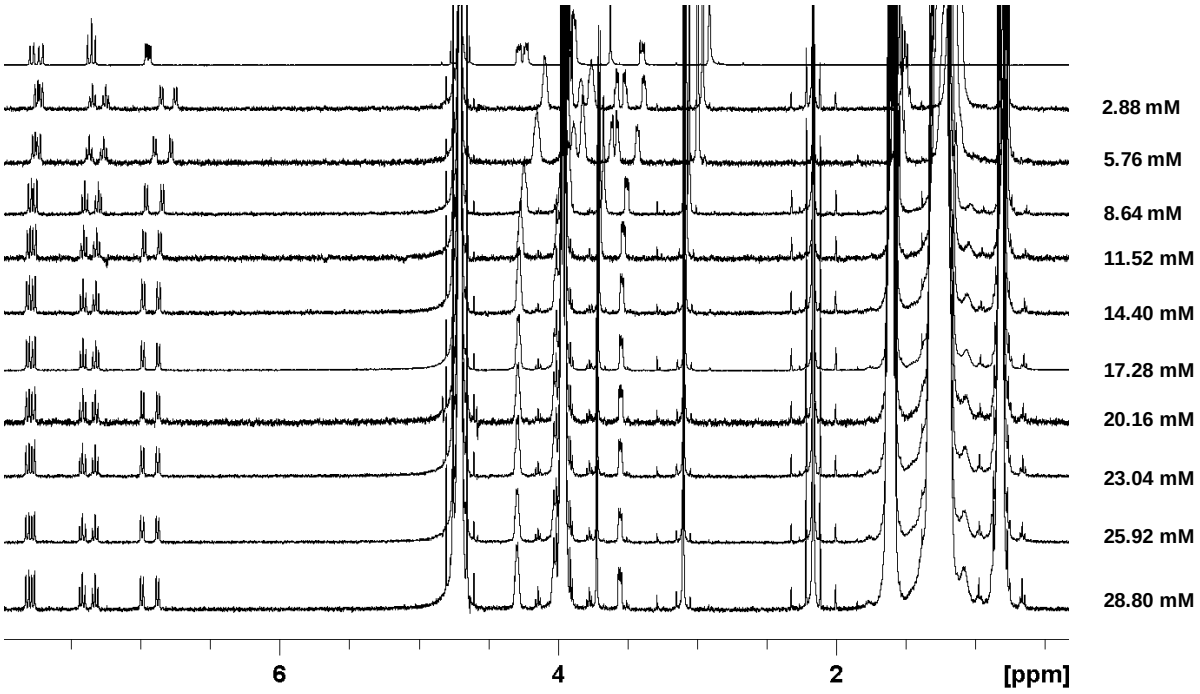


Fig S9. Partial ^{1}H NMR spectrum of **1** (3.6 mM) with various concentrations of SDS recorded in D_2O.

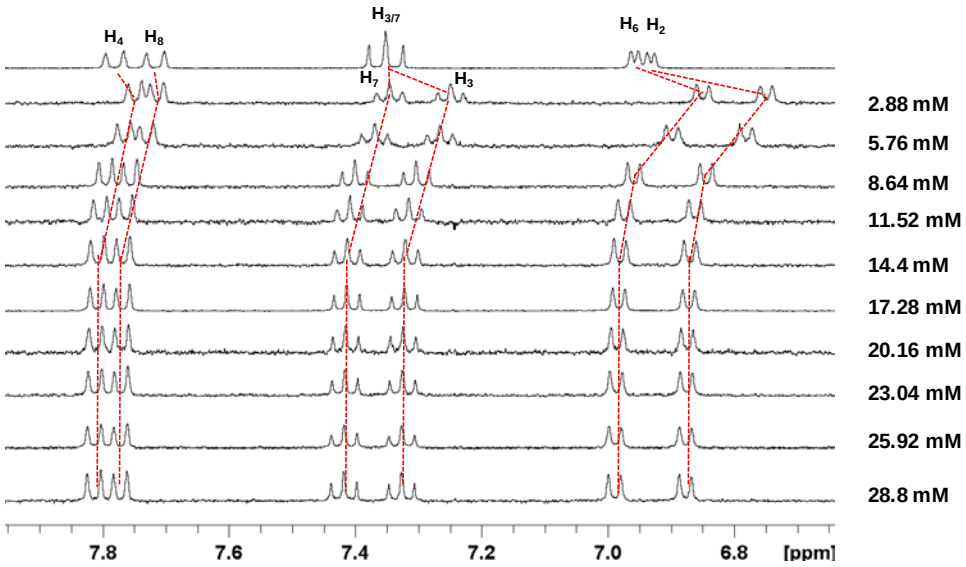


Fig S10. Partial ^{1}H NMR spectrum of **1** (3.6 mM) with various concentrations of SDS recorded in D_2O

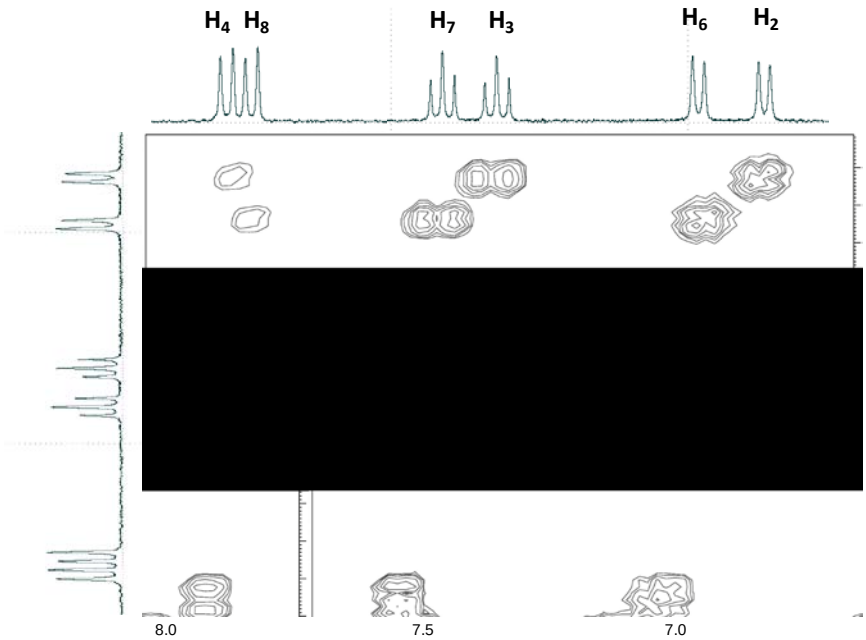


Fig S11. Partial ^{1}H-^{1}H COSY spectrum of **1** (3.6 mM) with SDS (17.28 mM) recorded in D_2O.

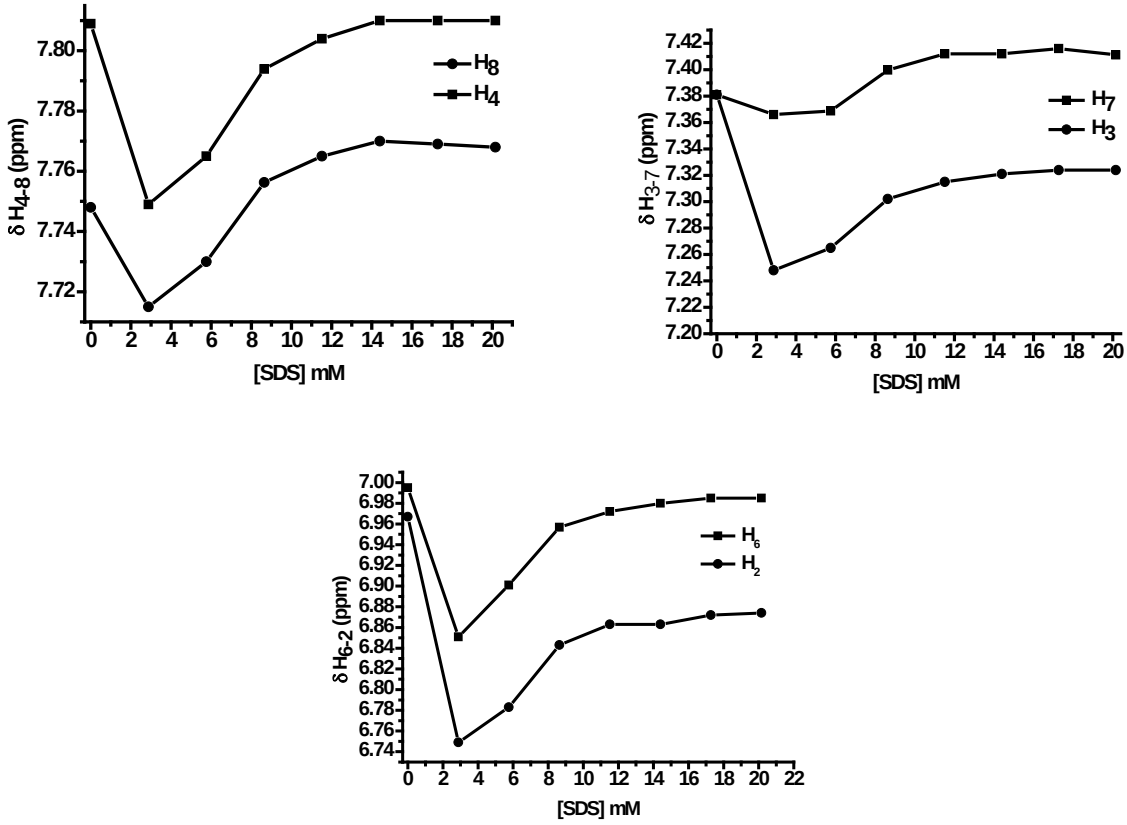


Fig S12. Incorporation of **1** into micelles of SDS: Graphs showing the effect of SDS concentration on the chemical shift of protons $H_{4/8}$, $H_{3/7}$ and $H_{2/6}$.

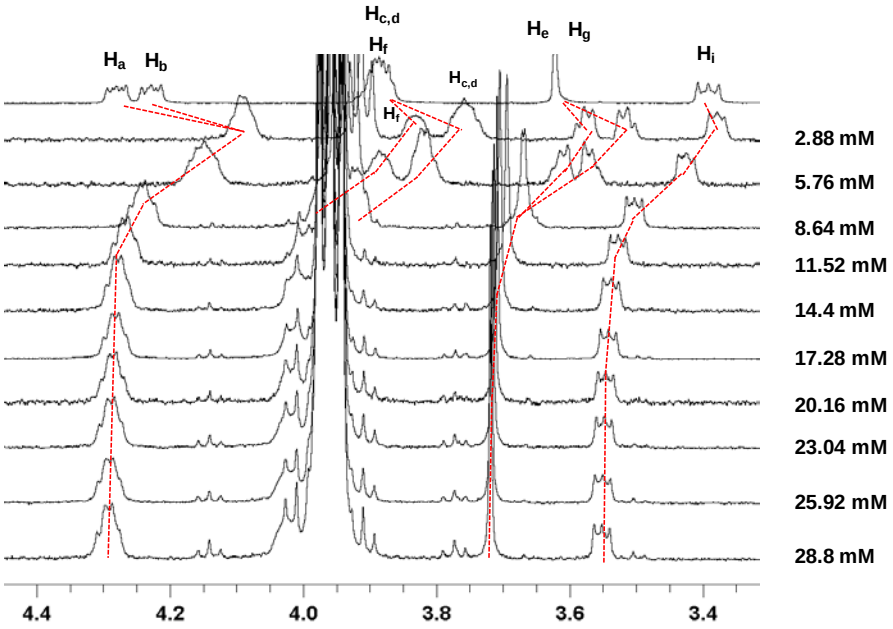


Fig S13. Partial ^{1}H NMR spectrum of **1** (3.6 mM) recorded in the presence of various concentrations of SDS. Recorded in D_2O.

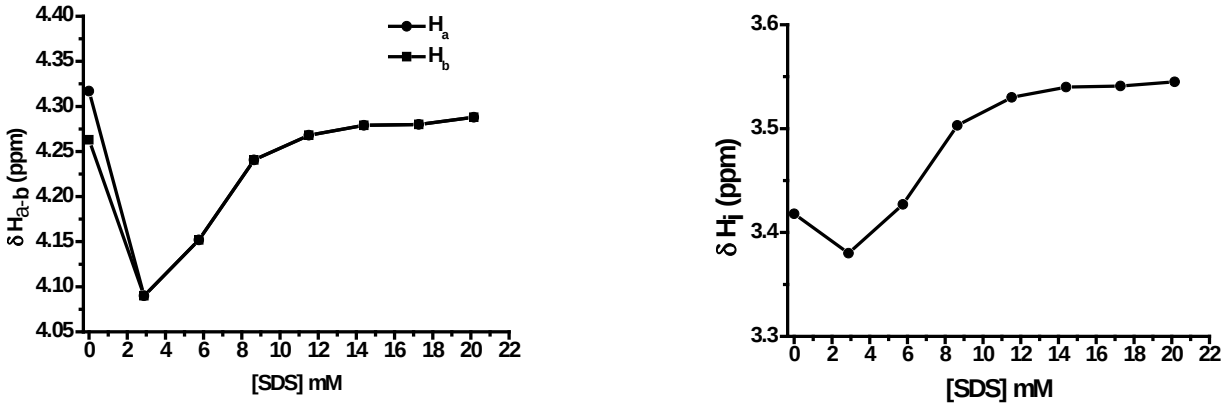


Fig S14. Incorporation of **1** into micelles of SDS: Graphs showing the effect of SDS concentration on the chemical shift of protons $H_{a/b}$, H_i.

5. Control of the complexation between 1.2

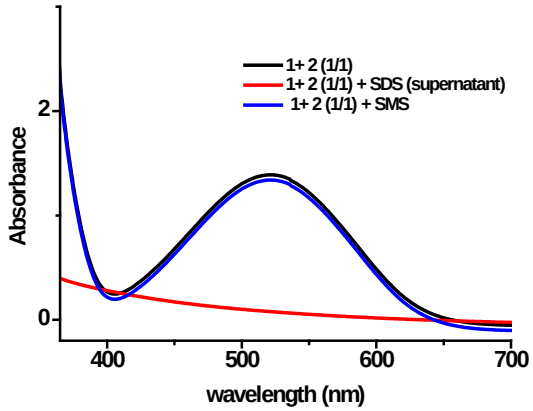
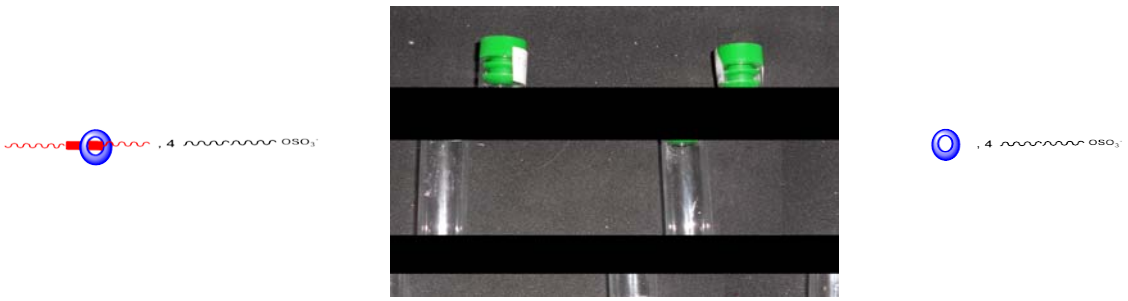


Fig S15. UV-vis spectra of: **1.2** (black curve), **1.2** +SDS (supernatant, red curve), **1.2** +SMS (blue curve). (~10^{-4} M) at 25°C. Recorded in H_2O.



2.3 +**SDS** (after centrifugation) **1.2** +**SDS** (after centrifugation)

Fig S16. Photographs of the solids recovered (following centrifugation) upon the addition of SDS to **2.3** and **1.2**.

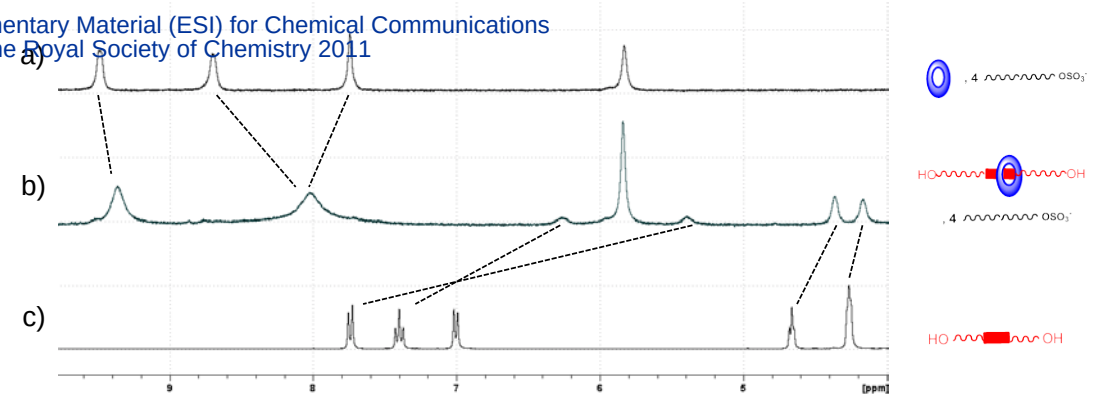


Fig S17. Partial ^{1}H NMR spectra of: (a)CBPQT^{4+},4DS (1mM); (b) CBPQT^{4+},4Cl^{-}/**3** + SDS (precipitate) and (c) **3** in DMSO-d_6. Recorded at 25°C.

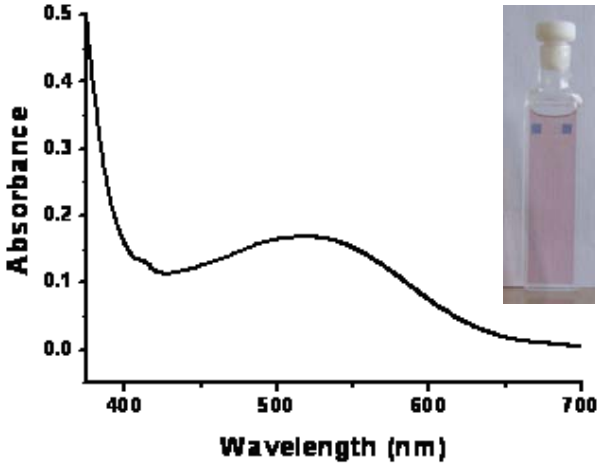


Fig S18. UV-vis spectrum of **2.3**, (4DS^{-}) (~10 $^{-4}$ M). Recorded in DMSO at 25°C

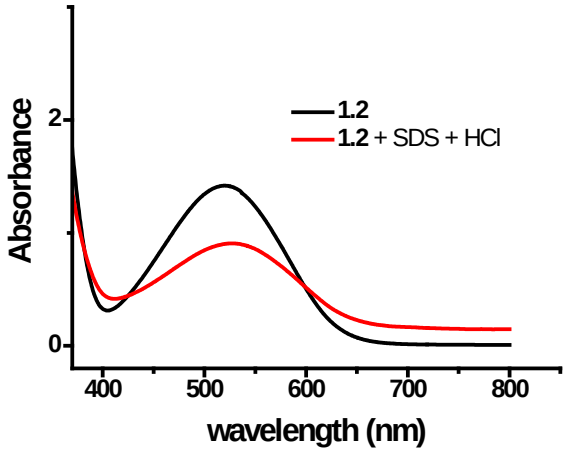


Fig S19. UV-vis spectra of **1.2** (~5 mM) (black curve) and **1.2** + **SDS** + HCl $_{conc}$ in excess (red curve). (final concentration of **1.2**, (4DS^{-}) ~2.7 mM). Recorded in H_2O at 25°C