Electronic Supplementary Information

LCST: A Powerful Tool to Control Complexation Between a Dialkoxynaphthalene functionalised Poly(*N*-isopropylacrylamide) and $CBPQT^{4+}$ In Water.

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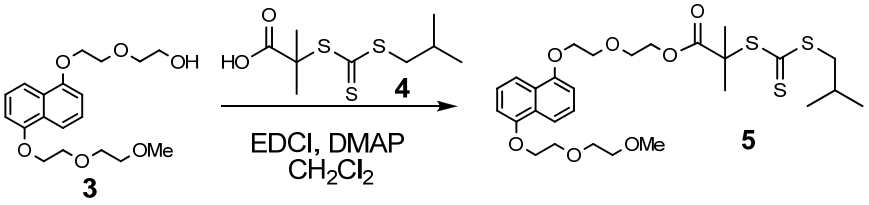
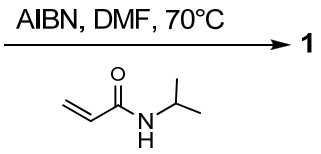
I/General information

Materials. All reagents were purchased from Aldrich and were used as received unless otherwise mentioned. *Tert*-butyl acrylate (tBA) monomer was distilled over calcium hydride before use.

Instrumentation and Measurements. Size exclusion chromatography (SEC) measurements were performed on a Waters 515 GPC system with a Waters 1410 refractive index detector. Three columns (PL Gel 5 mm, Styragel HR3, Styragel HR4) placed in series were employed for the chromatography. The system was calibrated against linear polystyrene (PS) standards ranging molecular weight from 580 to 377 400 Da. Experiments were performed at 35°C in THF eluent with a flow rate 1.0 mL/min. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Due to the complexity of the 2D NMR spectra of the polymeric complexes, only tentative assignment of the naphthalene and cyclophane protons was possible. Mass spectrometry was carried out on a Micromass Platform II spectrometer with an electrospray ionization source. UV/vis turbidity measurements were carried out for lower critical solution temperature (LCST) determination on a Varian Cary 50 Scan UV/vis spectrophotometer equipped with a single cell Peltier temperature controller. Dynamic light scattering experiments (DLS) were undertaken using a Malvern Zetasizer Nano ZS instrument using a light scattering apparatus equipped with a He-Ne (633 nm) laser and a thermoelectric Peltier temperature controller. The measurements were made at a scattering angle of $\theta = 173°$ ("back scattering detection"). The samples were filtered through 0.2 micron filters below their critical temperature. IR spectra were recorded using a Spectrum One PerkinElmer spectrometer.

II/Polymer synthesis and characterization





Synthesis of **1**

Compound **3**[1], **4**[2] were prepared according to the literature methods.

Synthesis of **5**

A solution of the alcohol **3,** 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionic acid **4** (1.43g, 6.03 mmol), EDCI (1.57 g, 8.23 mmol) and DMAP (1.00 g, 8.23 mmol) in dry DCM (100 mL) was stirred for 12 h at 0°C under nitrogen. The organic solution was subsequently washed with HCl (0.1 M, 100 mL), $NaHCO_3$ (0.1 M, 100 mL), brine (100 mL) and dried over Na_2SO_4. The solvent was evaporated to afford a crude product which was subjected to column chromatography (SiO_2: diethyl ether / petroleum spirit, 3:17). The fractions containing the product were combined and the eluent was removed in vacuum, affording the product **5** as yellow oil.

^{1}H NMR ($CDCl_3$) : δ = 0.89 (d, *J=6.9Hz,*6H, ($\underline{CH_3}$)$_2$CH-CH_2-S-), 1.61 (s, 6H, C(O)C($\underline{CH_3}$)$_2$-), 1.85 (m, 1H, (CH_3)$_2\underline{CH}$-CH_2-S-), 3.09 (d, *J=6.9Hz,* 2H, (CH_3)$_2$CH-$\underline{CH_2}$-S-), 3.34 (s, 3H, OCH_3), 3.53 (m, 2H, -$\underline{CH_2}$-O-), 3.74 (m, 4H, -$\underline{CH_2}$-O-), 3.92 (m, 4H, -$\underline{CH_2}$-O-), 4.22 (m, 6H, -$\underline{CH_2}$-O-), 6.76 (d, *J=8.1Hz*, 2H, $H_{2/6}$), 7.27 (t, *J=8.1Hz*, 2H, $H_{3/7}$), 7.79 (d, *J=8.1Hz*, 2H, $H_{4/8}$). ^{13}C NMR ($CDCl_3$): δ = 21.9, 25.2, 27.8, 45.0, 56.0, 59.2, 65.2, 68.0, 69.1, 69.7 (x2), 70.8 (x2), 71.9, 105.7 (x2), 114.6 (x2), 125.1 (x2), 126.6 (x2), 154.2 (x2), 172.7 (C=O), 221.5 (C=S). MS (ESI): m/z 607 (M + Na+). Found: %C: 57.62, H: 7.09 required for $C_{28}H_{40}O_7S_3$ C: 57.51, H: 6.89.

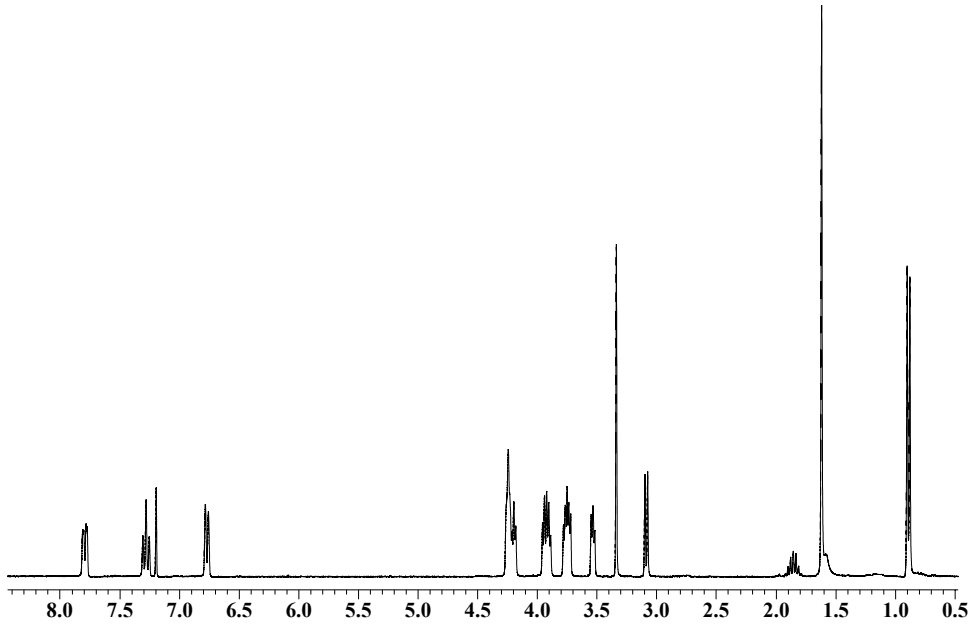


Figure S1: ^{1}H NMR spectrum of **5** recorded in $CDCl_3$

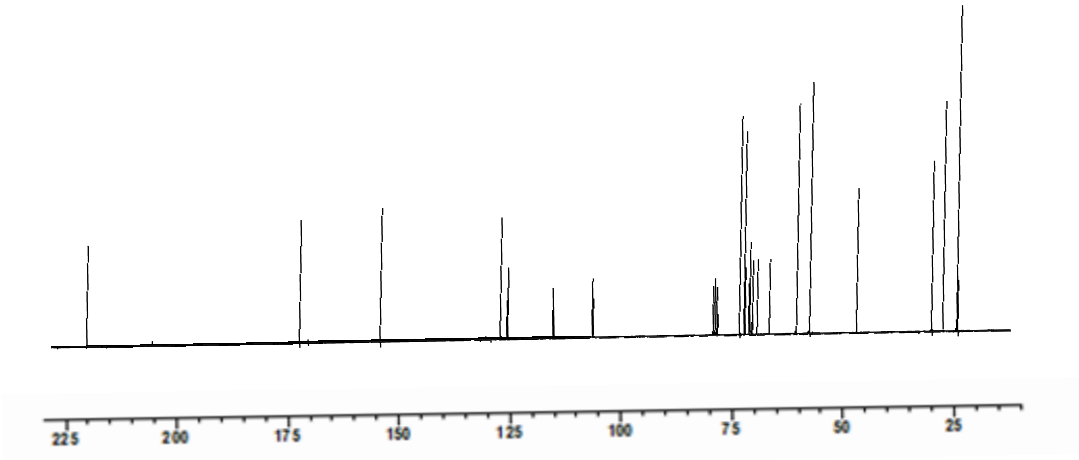


Figure S2: ^{13}C NMR spectrum of **5** recorded in $CDCl_3$

Synthesis of **1**

A solution of the **5** (0.05 g, $8.77.10^{-5}$mol), AIBN (3.6 mg, $2.19.10^{-5}$ mmol) and freshly recrystallised NIPAM (0.99 g, 8.77 mmol) in DMF (5 mL) was deoxygenated by bubbling nitrogen for 30 min at room temperature. The reaction flask was placed in an oil bath preheated to 70°C. The polymerisation was allowed to proceed for 4 h under constant magnetic stirring. At the end of polymerisation, the solution was cooled to room temperature. The polymer was isolated by precipitation in diethyl ether. It was purified further by two consecutive precipitations from THF into diethyl ether.

^{1}H NMR (D_2O) : δ = 0.96-1.21 (brm, ($\underline{CH_3}$)$_2$CH-NH), 1.29-2.15 (brm, CH_2CH backbone), 3.31 (s, OCH_3), 3.59 (brm, OCH_2), 3.69-3.94 (brm, $(CH_3)_2\underline{CH}$-NH + OCH_2), 3.95-4.03 (brm, OCH_2), 4.34 (brm, OCH_2), 7.02 (brm, $H_{2/6}$), 7.02 (brm, $H_{2/6}$), 7.44 (brm, $H_{3/7}$), 7.84 (brm, $H_{4/8}$).

IR (KBr pellet) (cm^{-1}): 3440, 3304, 3074, 2974, 2942, 1646, 1548, 1460, 1386, 1369, 1265, 1174, 1132.

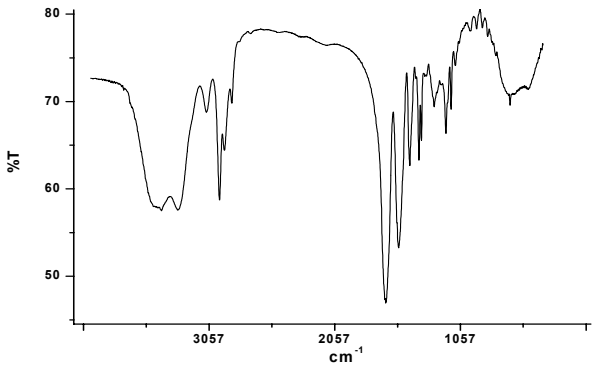


Figure S3: FT-IR spectrum of polymer **1** cast onto a KBr pellet.

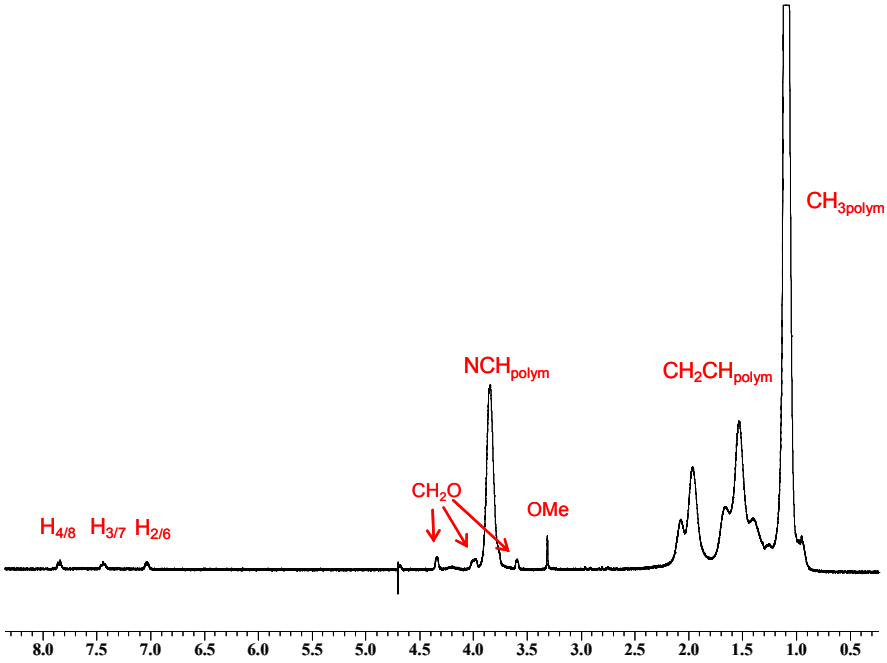


Figure S4: ^{1}H NMR spectrum of **1** recorded in D_2O

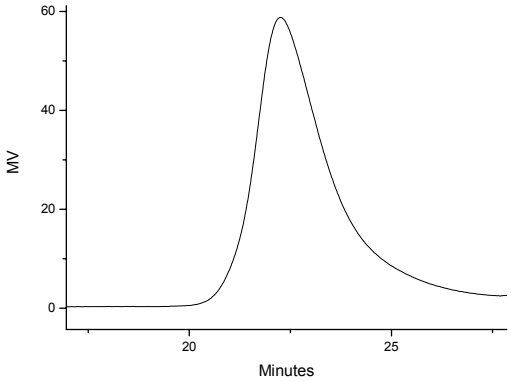
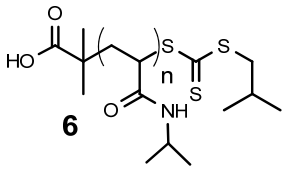


Figure S5: GPC data for polymer **1**. Eluent = THF. Calibrated using PS standards. Mn = 5160 $g.mol^{-1}$ and PDI =1.33.

Synthesis of **6**



6

Compound **6** was prepared in an analogous manner to that compound **1** using 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionic acid **4** (0.25 g, 1.05 mmol), AIBN (8.6 mg, $5.25.10^{-5}$ mol) and NIPAM (11,89 g, 105 mmol).

^{1}H NMR (D_2O): δ = 0.98-1.15 (brm, $(\underline{CH_3})_2$CH-NH), 1.45-1.68 (brm, CH_2 backbone), 1.86-2.14 (brm, CH backbone), 3.94 (1H, m, $\underline{CH}$-$(CH_3)_2$).

IR (KBr disk) (cm^{-1}): 3432, 3304, 3076, 2972, 2936, 1652, 1546, 1458, 1384, 1172, 1132, 1028.

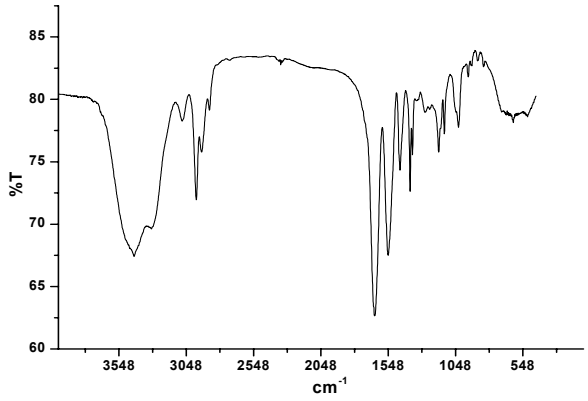


Figure S6: FT-IR spectrum of polymer **6** cast onto a KBr pellet.

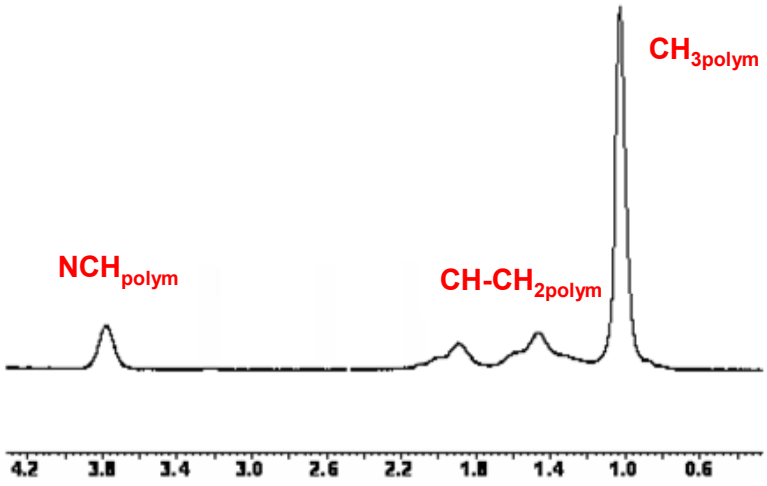


Figure S7: ^{1}H NMR spectrum of **6** recorded in D_2O

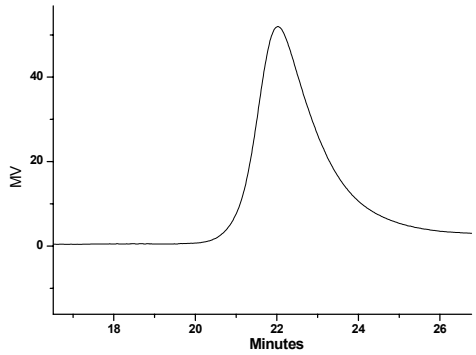
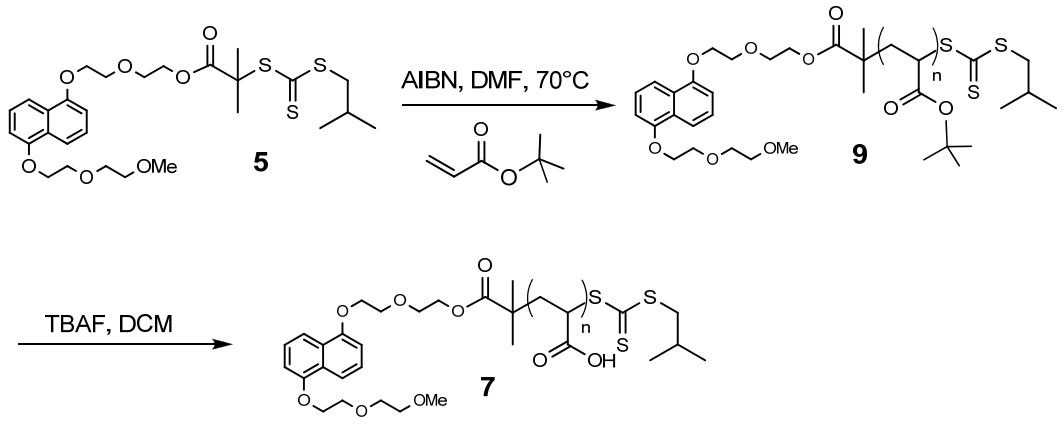


Figure S8: GPC data for polymer **6**. Eluent = THF. Calibrated using PS standards. Mn = 7060 g.mol^{-1}and PDI = 1.17.

Synthesis of **7**



Synthesis of **9**

A solution of the **5** (0.1 g, 0.17 mmol), AIBN (1.5 mg, 8.5.10^{-6} mol) and a freshly distilled *tert*-butyl acrylate (4.85 mL, 34.0 mmol) in toluene (3 mL) was deoxygenated by bubbling nitrogen for 30 min at room temperature. The reaction flask was placed in an oil bath preheated to 70°C. The polymerisation was allowed to proceed for 12 h under constant magnetic stirring. At the end of polymerisation, the solution was cooled to room temperature. The polymer was isolated by precipitation in water. It was purified further by two consecutive precipitations from THF into water.

^{1}H NMR (CD_3CN): δ = 1.23- 2.31 (brm, ($\underline{CH_3}$)$_3$C + CH_2-CH backbone), 3.34 (s, 3H, OCH_3), 3.51-4.34 (brm, 16H, OCH_2), 6.97 (brm, 2H, $H_{2/6}$), 7.40 (brm, 2H, $H_{3/7}$), 7.83 (brm, 2H, $H_{4/8}$).

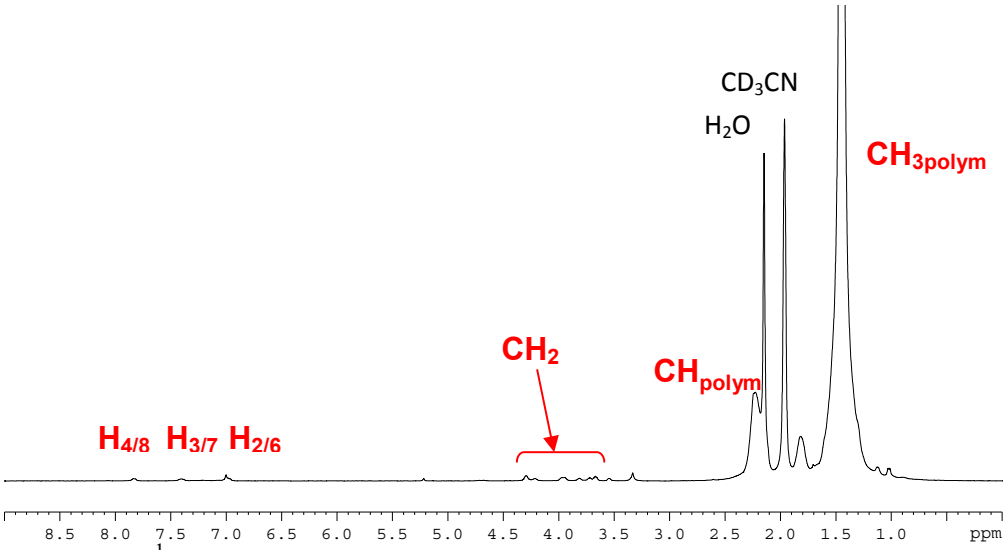


Figure S9: ^{1}H NMR spectrum of **9** recorded in CD_3CN

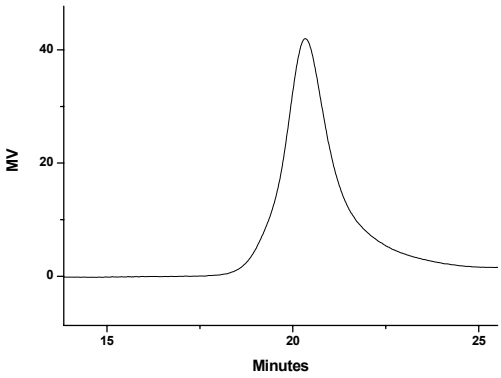


Figure S10: GPC data for polymer **9**. Eluent = THF. Calibrated using PS standards. Mn = 19650 g.mol^{-1}and PDI =1.13. Mn (NMR) = 19600 g/mol

Hydrolysis of **9**:

To a solution of **9** (2 g, 13 mmol) in dichloromethane (15 mL) was added TFA (5 mL, 65 mmol). The mixture was allowed to stir at room temperature for 12 h. The solvent and the excess of TFA were removed by evaporation under vacuum without heating. Finally, **8** was dried under high vacuum for 24 h.

^{1}H NMR (CD_3OD): δ = 1.40-1.90 (brm, $CH_{2polymer}$), 2.18-2.41 (brm, $CH_{polymer}$), 3.03 (s, 3H, OCH_3), 3.43-4.30 (br m, OCH_2), 6.92 (2H, br m), 7.34 (2H, br m), 7.78 (2H , br m).
IR (KBr pellet) (cm^{-1}): 3444, 2958, 2620, 1710, 1456, 1419, 1241, 1170, 804.

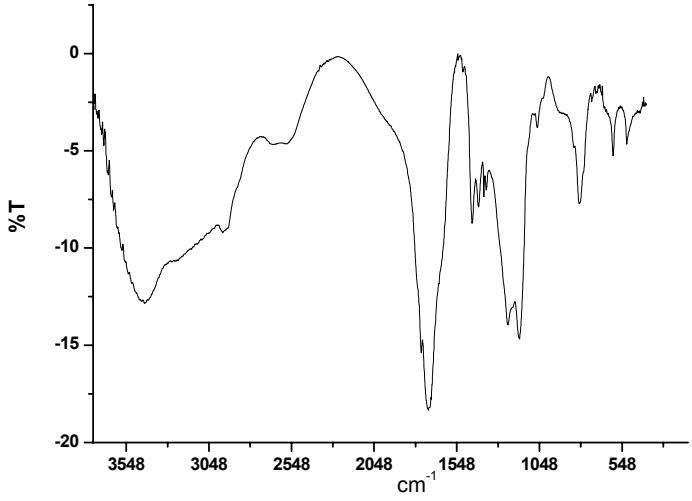


Figure S11: FT-IR spectrum of polymer **7** cast onto a KBr pellet.

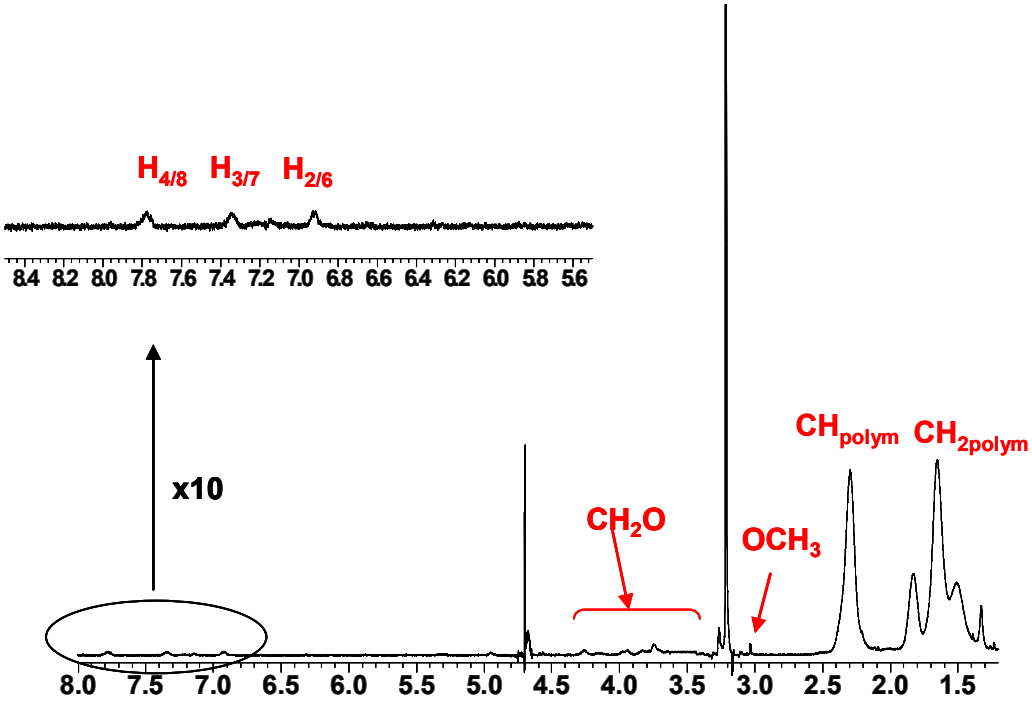


Figure S12: ^{1}H NMR spectrum of **7** recorded in CD_3OD

[1] P. R. Ahston, R. Ballardini, V. Balzani, S. E. Boyd, A. Credi, *Chem. Eur. J.* **1997**, 3, 152-170.
[2] X. P. Qiu, F. Tanaka, F. M. Winnik, *Macromolecules* **2007**, 40, 7069-7071

III/ Complexation studies

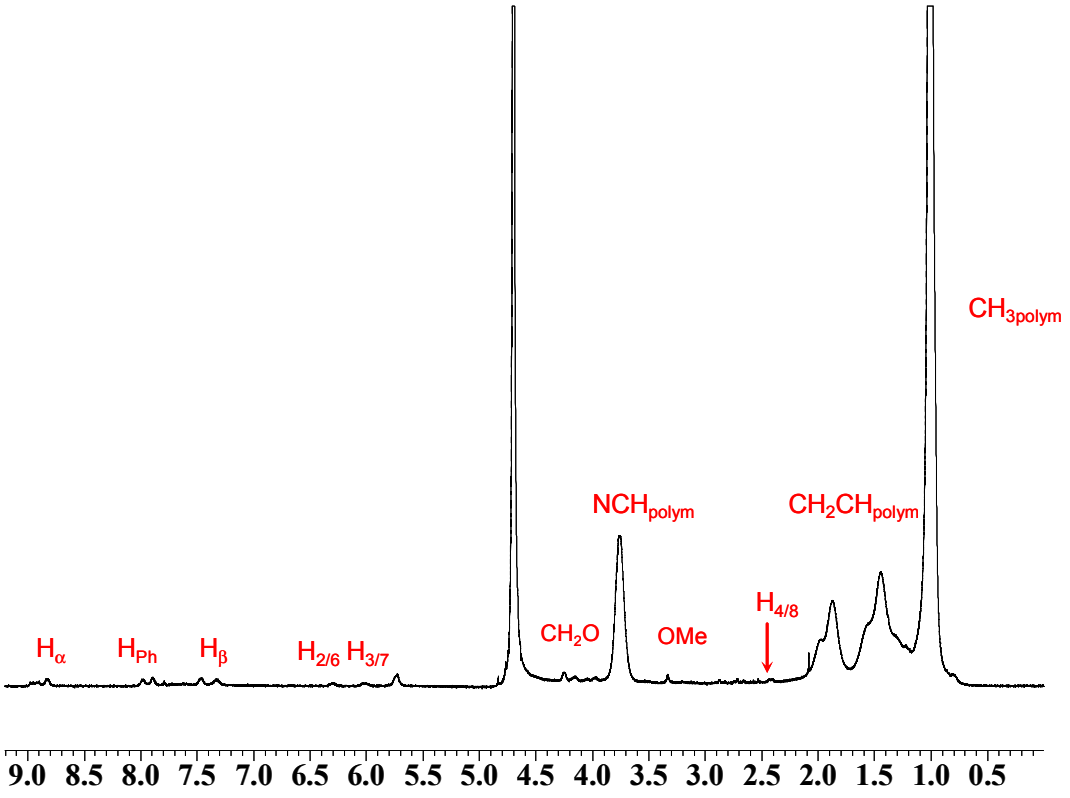


Figure S13: ^{1}H NMR spectrum of **1.2** recorded in D_2O at 25°C. The cyclophane and naphthalene protons of the complex are tentatively assigned.

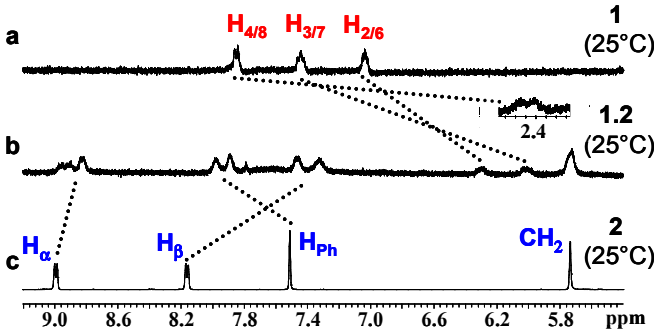


Figure S14: Partial ^{1}H NMR spectra of: (a) **1** (3 x 10^{-3} M) and (b) upon the addition of 1.0 equivalent of **2**, (c) **2** alone. Recorded in D_2O at 25°C. The cyclophane and naphthalene protons of the complex are tentatively assigned.

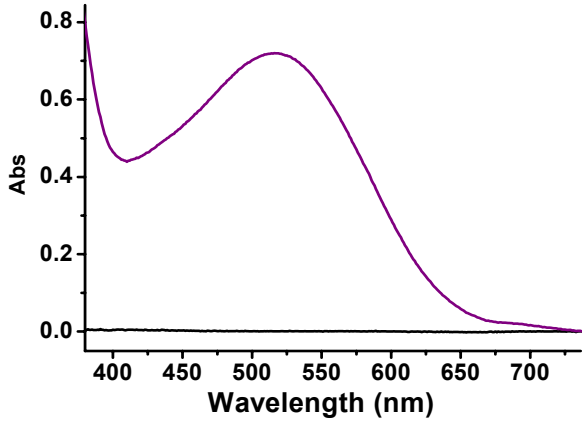


Figure S15: UV-vis spectra of **1** (black curve) and **1.2** (1.3 x 10^{-3}M)(purple curve) recorded in H_2O at 25°C

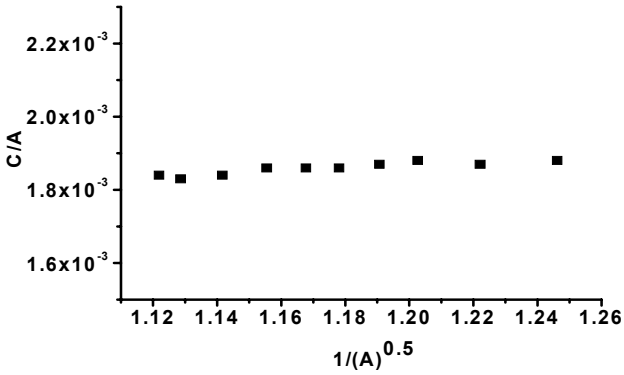


Figure S16: Plot of the ratio between the concentration C and absorbance A against $1/\sqrt{A}$ for equimolar solutions of **1** and **2**. (Concentration range 1 x 10^{-2} to 5 x 10^{-4} M). Recorded in H_2O at 25 °C.

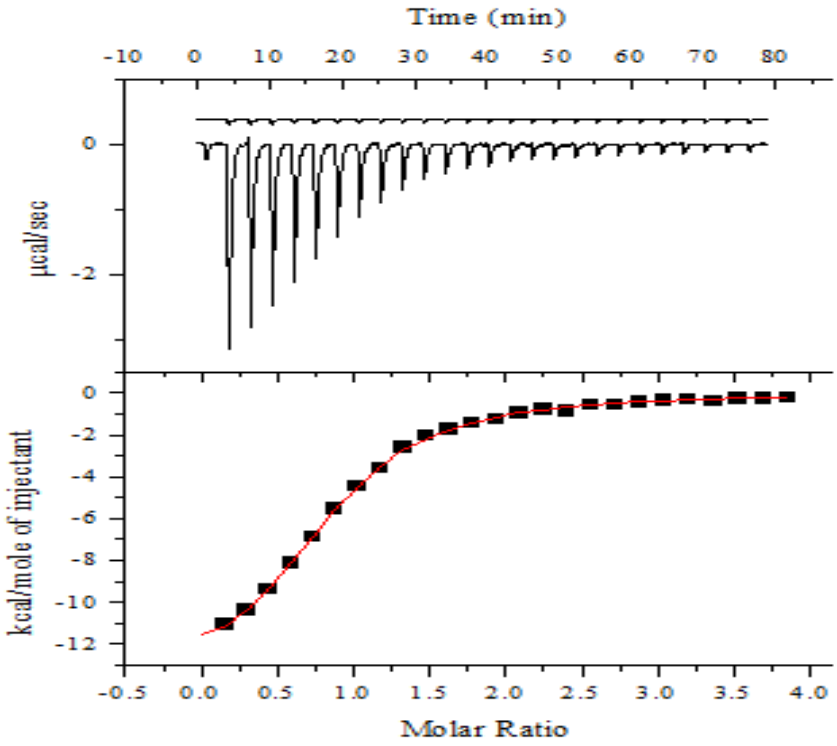


Figure S17: Isothermal titration calorimetry data for the addition of aliquots of **1** to **2**. Recorded in H_2O at 25°C.

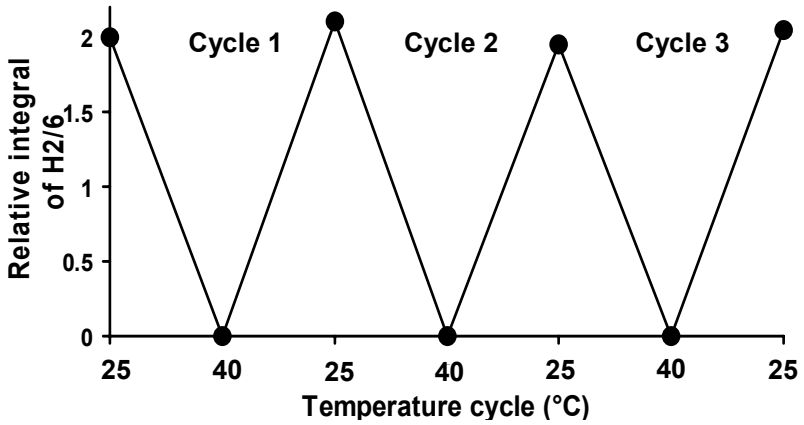


Figure S18: Graph showing the change in the relative intensity of the integral of $H_{2/6}$ of the naphthalene moiety of the ^{1}H NMR spectrum of **1.2** upon cycling between 25°C and 40°C.

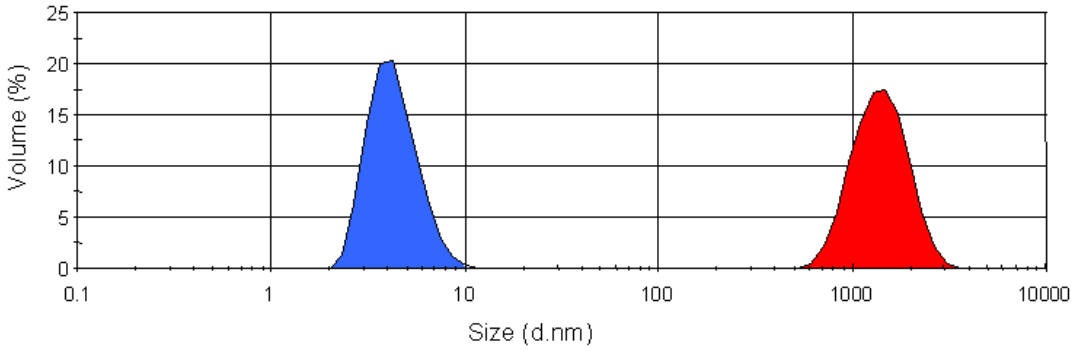
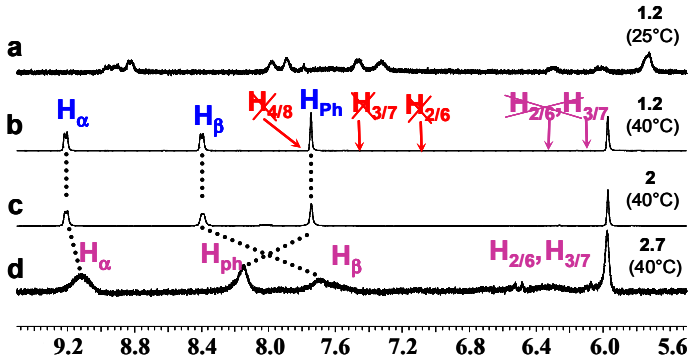


Figure S19: DLS data for **1.2** (0.2 mmol in water) recorded at 25°C (blue shaded curve) and 40°C (red shaded curve).



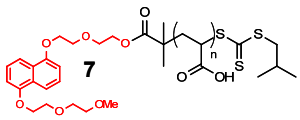


Figure S20: Partial ^{1}H NMR spectra of: (a) **1.2** (3 x 10^{-3}M) at 25°C; (b) **1.2** (3 x 10^{-3}M) at 40°C; (c) **2** alone at 40°C ; (d) **2.7** (3 x 10^{-3}M) at 40°C. Recorded in D_2O. The cyclophane and naphthalene protons of the complex are tentatively assigned.

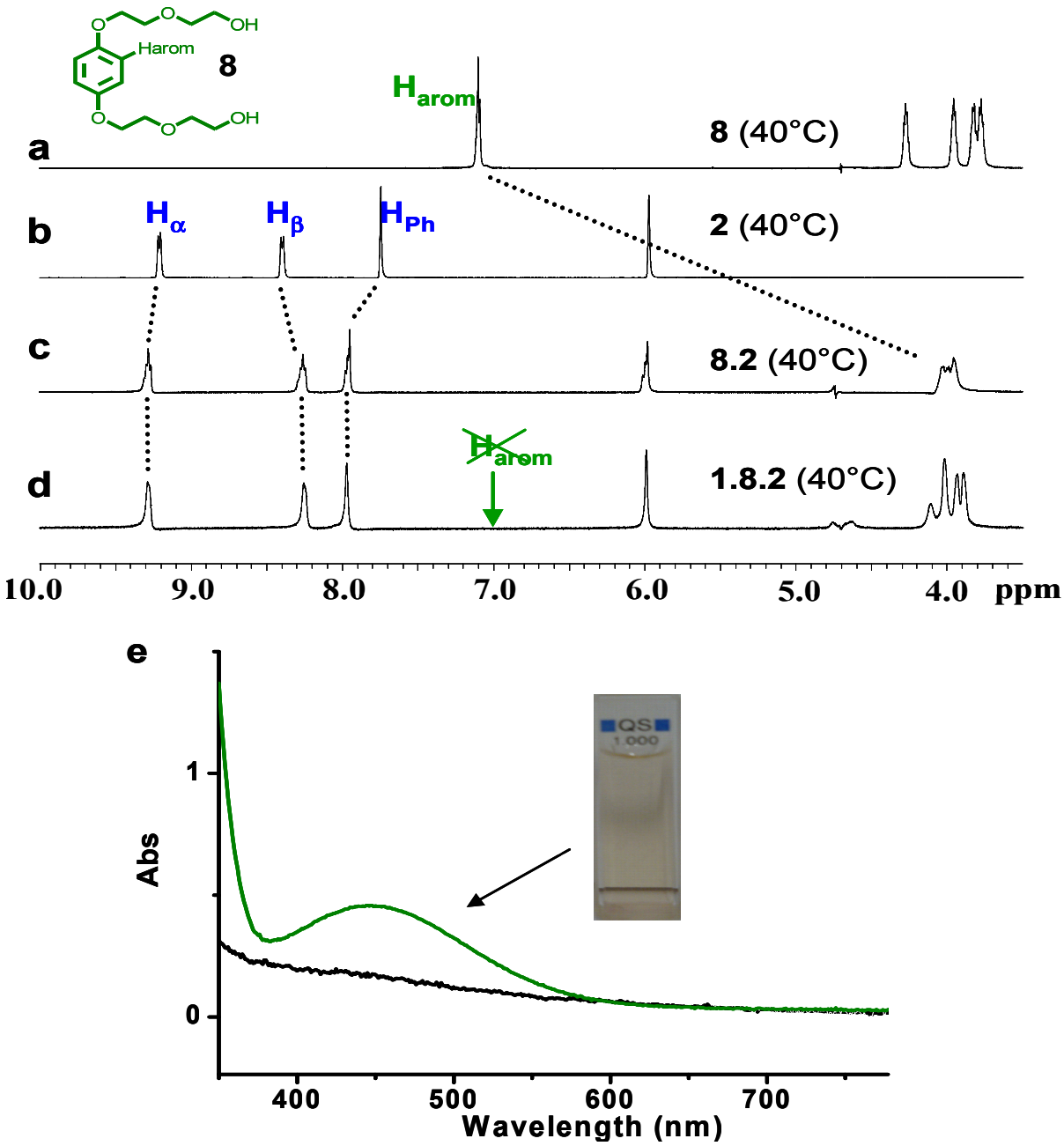


Figure S21: Partial ^{1}H NMR spectra of: (a) **8**; (b) **2**; (c) **2.8**; (d) **1.2.8** (3 x 10^{-3} M) at 40°C. (e) UV-vis spectra of supernatant of **1.2** (black line) and **1.2.8** (green line)(~10^{-4} M) at 40°C.

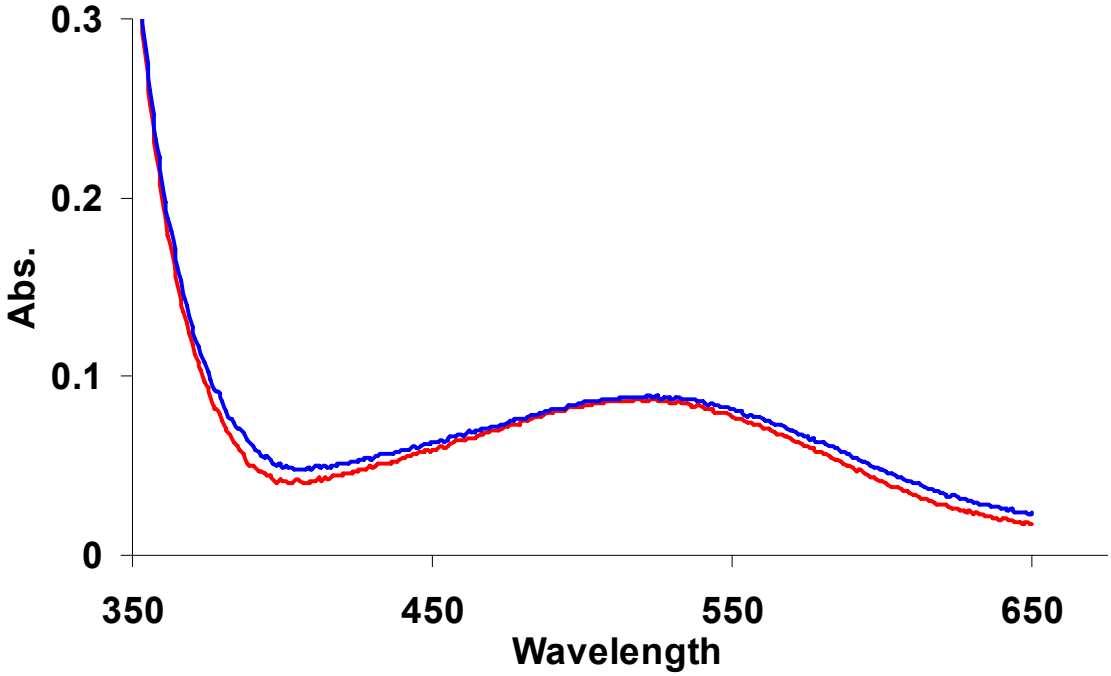


Figure S22: UV-vis spectra of **2.7** (~10^{-4} M) at 25°C (blue curve) and 40°C (red curve).

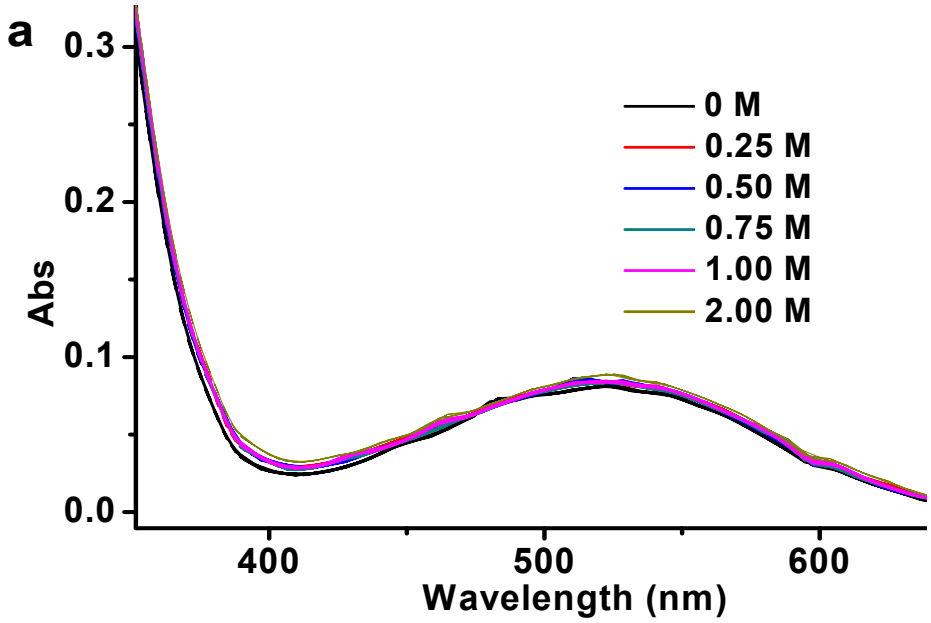


Figure S23: UV-vis spectra of **1.2** with different salt (NaCl) concentrations.