Use of anion recognition to control the folding and unfolding of a single chain phosphorescent polymer

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## Electronic Supplementary Information

1. Materials and methods

Carboxylic acid derived-Pt(II) porphyrin **5**[S1] and methacrylate-derived calix[4]pyrrole **3**[S2] were prepared according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a Bruker Advance DMX-400 or a Bruker DMX-500 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AVANCE DMX-400 or a Bruker DMX-500 spectrometer. Molecular weight distributions were measured on a conventional gel permeation chromatography (GPC) system equipped with a Waters 1525 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR1, HR2 and HR4, 7.8 mm × 300 mm). GPC measurements were carried out at 35 °C using THF as the solvent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. Transmission electron microscopy investigations were carried out on a HITACHI HT-7700 instrument. Fluorescence measurements were performed on a Perkin-Elmer Luminescence Spectrophotometer LS 50B or a Gilden Photonics Ltd. instrument.

2. Synthesis and characterization of 1
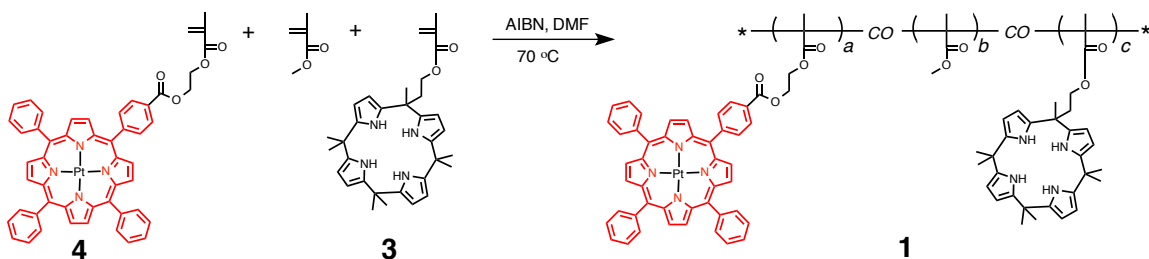
Scheme S1 Synthetic route to **1**.

Polymer **1** was prepared from compounds **3**, **4**, and methyl methacrylate by free radical polymerization. A mixture of compound **4** (50.0 mg, 0.0519 mmol), methyl methacrylate (0.110 mL, 1.04 mmol), compound **3** (54.6 mg, 0.104 mmol), and 1.70 mg (0.0104 mmol) of azobisisobutyronitrile (AIBN) in 2.5 mL of DMF was stirred at room temperature. The mixture was sealed with a rubber septum and subjected to three freeze/pump/thaw cycles. The reaction mixture was then heated to 70 °C and stirred overnight. The associated polymerization reaction was quenched by rapid freezing in liquid nitrogen. The solution was dropped into 50 mL of methanol, and the precipitated solid was collected by vacuum filtration. This process was repeated three times. The resulting dark red product was dried in vacuum; yield 137 mg (65%).
^{1}H-NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): (8.76−7.03, porphyrin pyrrole β-position CH and Phenyl CH), 8.76−8.68 (m, 8H), 8.46 (m, 2H), 8.26 (m, 2H), 8.13 (m, 6H), 7.73 (m, 9H), 7.03 (3H, calix[4]pyrrole NH), 5.89 (12H, calix[4]pyrrole β-CH), 4.70 (2H, porphyrin −CH$_2$O-), 4.43 (2H, porphyrin −CH$_2$O-), 3.90−3.23 (m, 63H, polymer backbone −OCH$_3$), 2.26−0.55 (m, 150H, polymer backbone −CH$_2$-, and −CH$_3$). M_n = 25.8 kDa, PDI = 1.66.
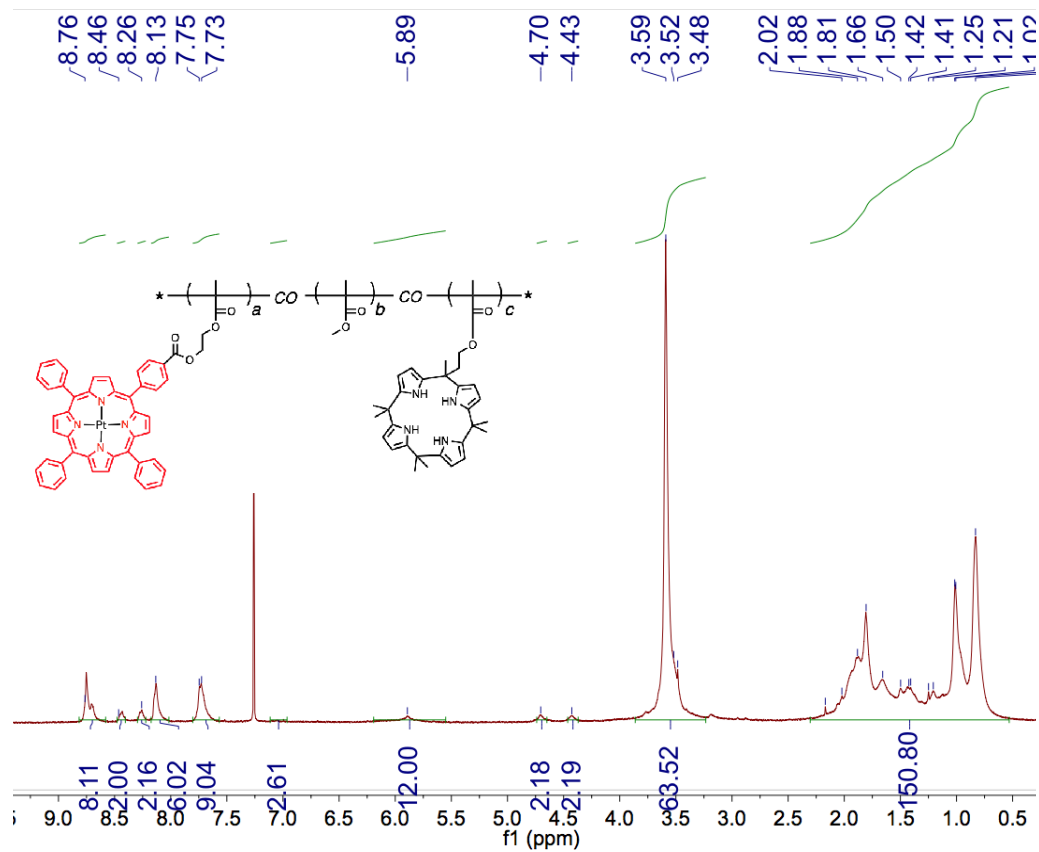
**Fig. S1** ¹H-NMR spectrum (400 MHz, CDCl₃, 298 K) of **1**.
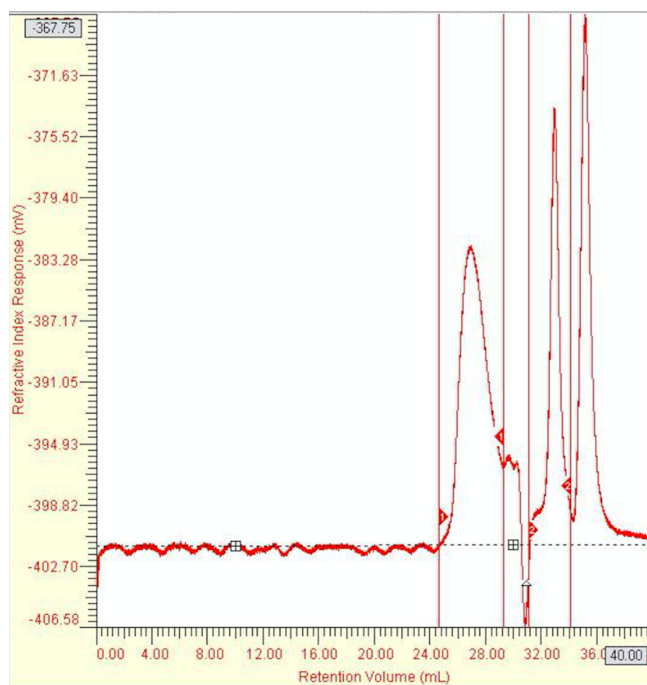
Fig. S2 GPC spectrum of **1**.

The ratio of $a/b/c$ is 1/21/1.5, as calculated from integrations of the proton signals corresponding to the porphyrin, calix[4]pyrrole β-position CH, and polymer backbone $-OCH_3$, respectively, seen in the ^{1}H-NMR spectrum. From the M_n value, this $a/b/c$ ratio, the values of a, b, and c were calculated to be 6.7, 141, and 10, respectively.
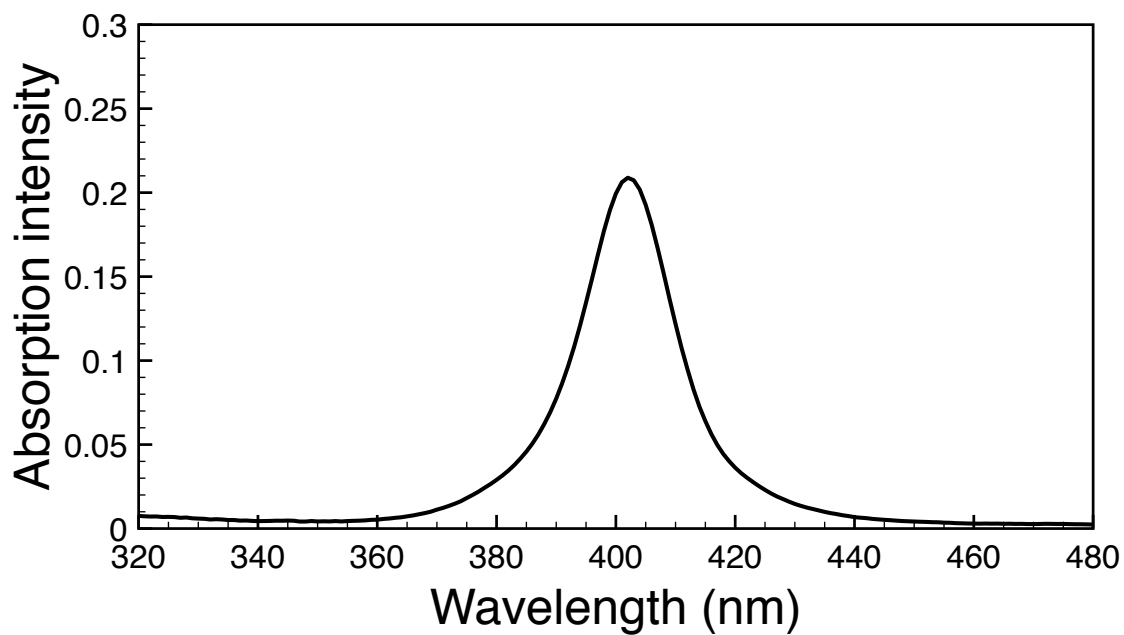
Fig. S3 Absorption spectrum of **1**.

3. Synthesis and characterization of methacrylate-derived Pt(II) porphyrin 4
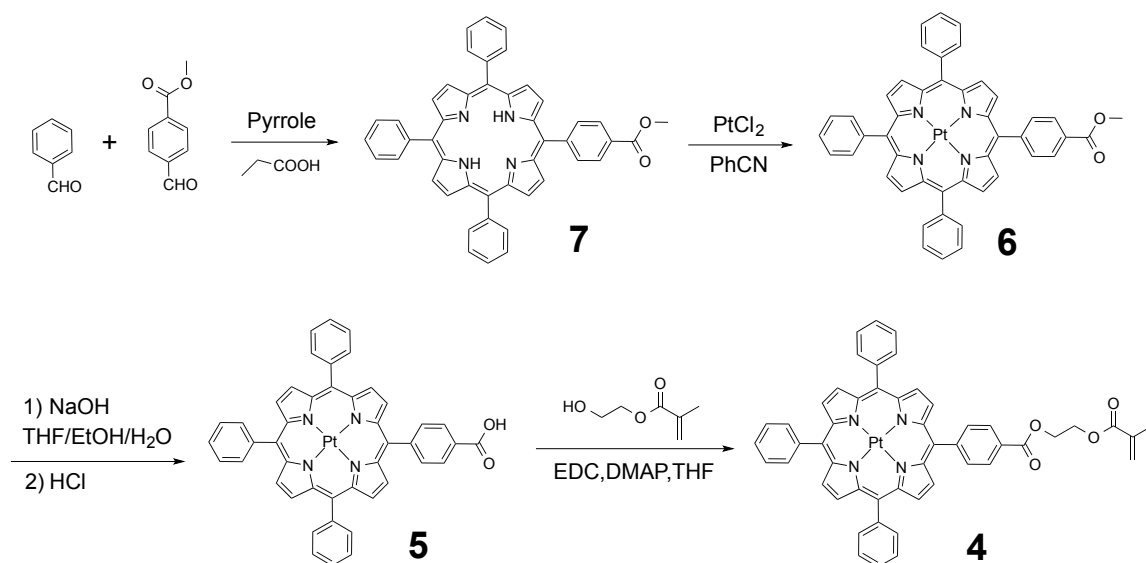

Scheme S2 Synthetic routes to methacrylate-derived Pt(II) porphyrin **4**.

To a solution of propionic acid (500 mL) containing methyl-4-formyl benzoate (4.1 g, 0.25 mol) was added benzaldehyde (7.9 g, 0.75 mol) and pyrrole (6.7 g, 1.0 mol). The mixture was then heated at reflux for 4 h. The solvent was distilled off and the product was first purified over basic alumina in a column using CH_2Cl as the eluent. The resulting crude product was passed through a silica gel column using hexanes/ CH_2Cl (2:1 v/v) as the eluent to give the product **7**: Yield 1.5 g (9%). ^{1}H-NMR (400 MHz, chloroform-*d*) δ 8.86 (m, 6H), 8.79 (d, *J* = 4.8 Hz, 2H), 8.44(m, 2H), 8.31(m, 2H), 8.22(m, 6H), 7.83 − 7.70 (m, 9H), 4.11 (s, 3H), -2.78 (s, 2H).

Intermediate **7** (940 mg, 1.40 mmol) and $PtCl_2$ (924 mg, 3.5 mmol) were suspended in anhydrous benzonitrile. The mixture was purged with N_2 and slowly heated to 180 ºC under N_2 for 30 h. The mixture was cooled to room temperature and the solvent was removed by vacuum distillation. The crude product was purified by column chromatography (silica gel, CH_2Cl /hexanes, 2:1) to afford **6**. (1.0 g, 83%). ^{1}H-NMR (400 MHz, chloroform-*d*) δ 8.79 (m, 6H), 8.72 (d, *J* = 5.0 Hz, 2H), 8.43(m, 2H), 8.26 (m, 2H), 8.17(m, 2H), 7.75(m, 9H), 4.11 (s, 3H).

Intermediate **6** (1.0 g, 1.15 mmol) and KOH (1.0 g, 18.0 mmol) were dissolved in a mixed solution of THF–EtOH–H_2O (1:1:0.1, 100 mL), and the solution was heated at reflux for 12 h. The mixture was cooled to room temperature and acidified with conc. HCl to pH=1. The orange

solid obtained in this way was collected by filtration and then washed with water before being dried under vacuum. This gave **5** (940 mg, 96%). ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.74 (s, 8H), 8.36 (m, 2H), 8.29 (m, 2H), 8.17 (m, 6H), 7.82(m, 9H).
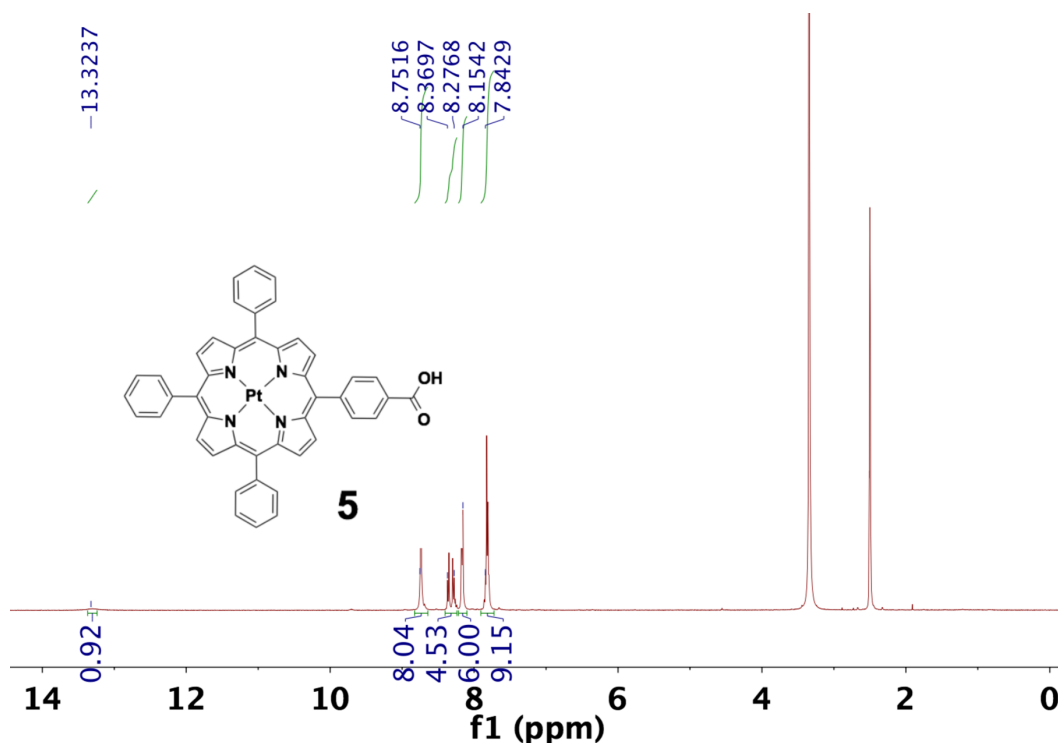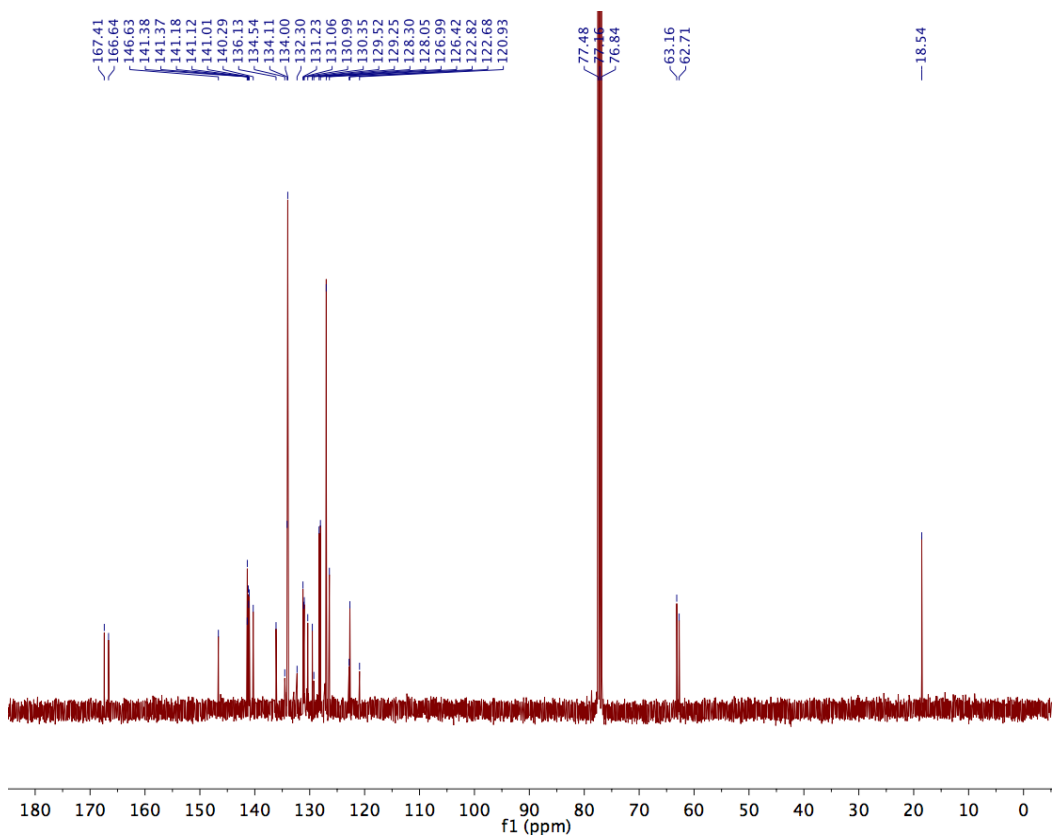

Fig. S4 ^{1}H-NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **5**.

Porphyrin **5** (150 mg, 0.176 mmol), DMAP (65 mg, 0.528 mmol), and EDCI·HCl (68 mg, 0.352 mmol) were dissolved in 50 mL dry THF. 2-Hydroxyethyl methacrylate (344 mg, 2.64 mmol) was added under N_2, after which the mixture was stirred for 2 d at room temperature. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and the mixture was washed with water and brine. The organic layer was separated off and dried over Na_2SO_4 and the solvent was removed by evaporation. The resulting residue was purified by column chromatography over silica gel using CH_2Cl_2 as the eluent to give compound **3** as a red solid (70 mg, 41%). ^{1}H-NMR (400 MHz, chloroform-d) δ 8.76−8.68 (m, 8H), 8.44 (d, J = 5.1 Hz, 2H), 8.27 (m, 2H), 8.15 (m, 6H), 7.75 (m, 9H), 6.26 (m, 1H), 5.66 (m, 1H), 4.76 (m, 2H), 4.64 (m, 2H), 2.02 (m, 3H). ^{13}C-NMR (100 MHz, chloroform-d) δ 167.41, 166.64, 146.63, 141.38, 141.37, 141.18, 141.12, 141.01, 140.29, 136.13, 134.54, 134.11, 134.00, 132.30, 131.23, 131.06, 130.99, 130.35, 129.52, 129.25, 128.30, 128.05, 126.99, 126.42, 122.82, 122.68, 120.93, 63.16, 62.71, 18.54. HRMS (ESI) Calcd for [M + Na]$^+$: 986.2280. Found: 986.2265.
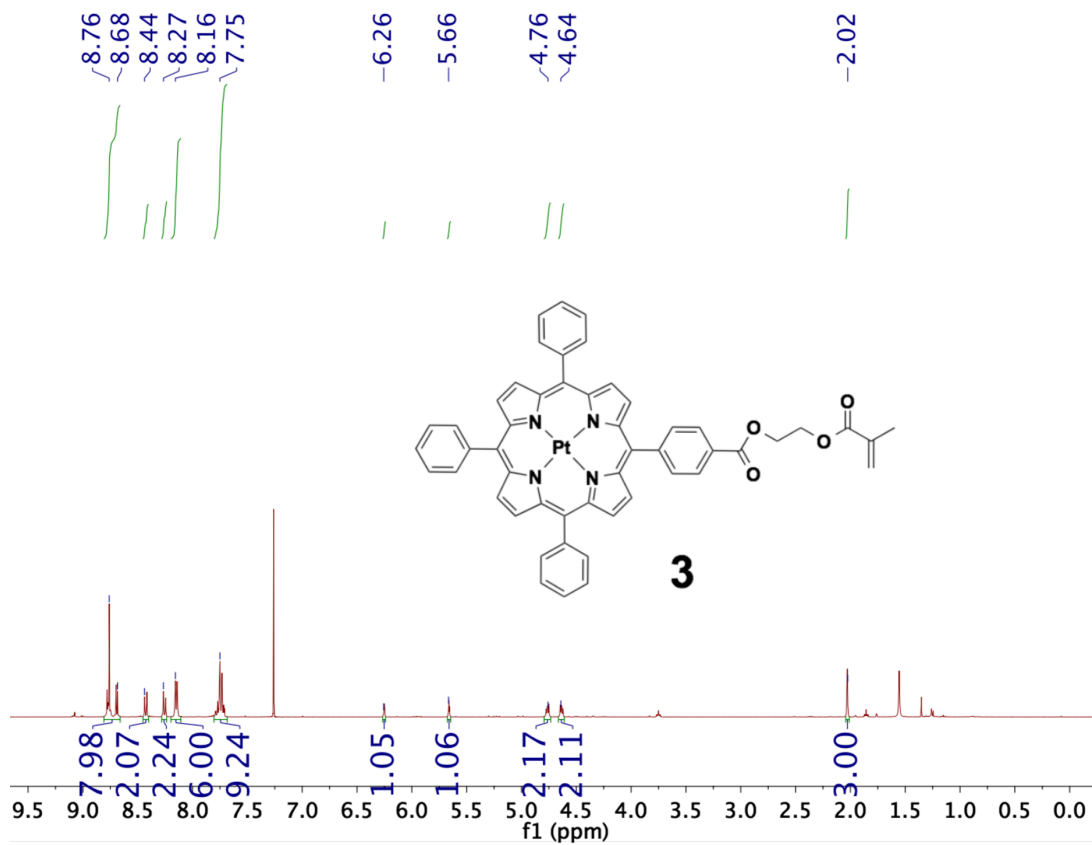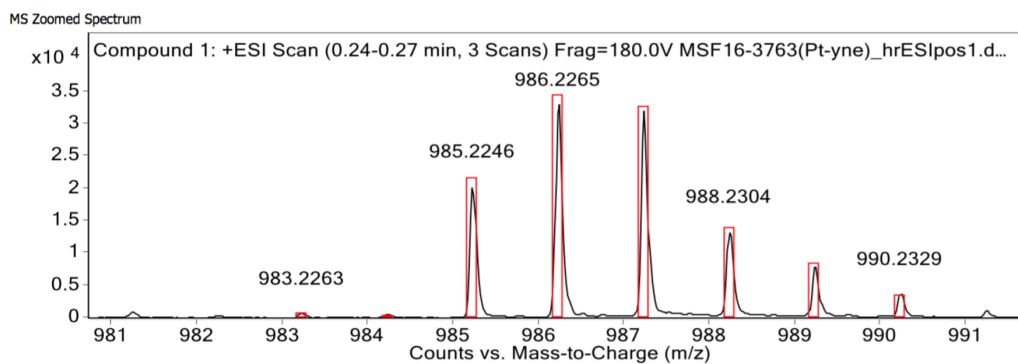
Fig. S5 ^{1}H-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **3**.

**Fig. S6** ^{13}C-NMR spectrum (100 MHz, CDCl$_3$, 298 K) of **3**.

MS Zoomed Spectrum

Compound 1: +ESI Scan (0.24-0.27 min, 3 Scans) Frag=180.0V MSF16-3763(Pt-yne)_hrESIpos1.d...

MS Spectrum Peak List

| Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
466.25660			43458.38			
981.24930	981.22280	1	955.23	C51H36N4O4Pt	(M+Na)+	-26.99
983.22630	983.22390	1	799.67	C51H36N4O4Pt	(M+Na)+	-2.38
985.22460	985.22560	1	20479.37	C51H36N4O4Pt	(M+Na)+	1.01
986.22650	986.22800	1	33367.33	C51H36N4O4Pt	(M+Na)+	1.61
987.22900	987.22940	1	31946.84	C51H36N4O4Pt	(M+Na)+	0.49
988.23040	988.23200	1	13467.14	C51H36N4O4Pt	(M+Na)+	1.66
989.23010	989.23250	1	8010.75	C51H36N4O4Pt	(M+Na)+	2.5
990.23290	990.23470	1	3834.51	C51H36N4O4Pt	(M+Na)+	1.83
991.23600	991.23750	1	1224.46	C51H36N4O4Pt	(M+Na)+	1.48

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Fig. S7 High-resolution mass spectrum of **3**.

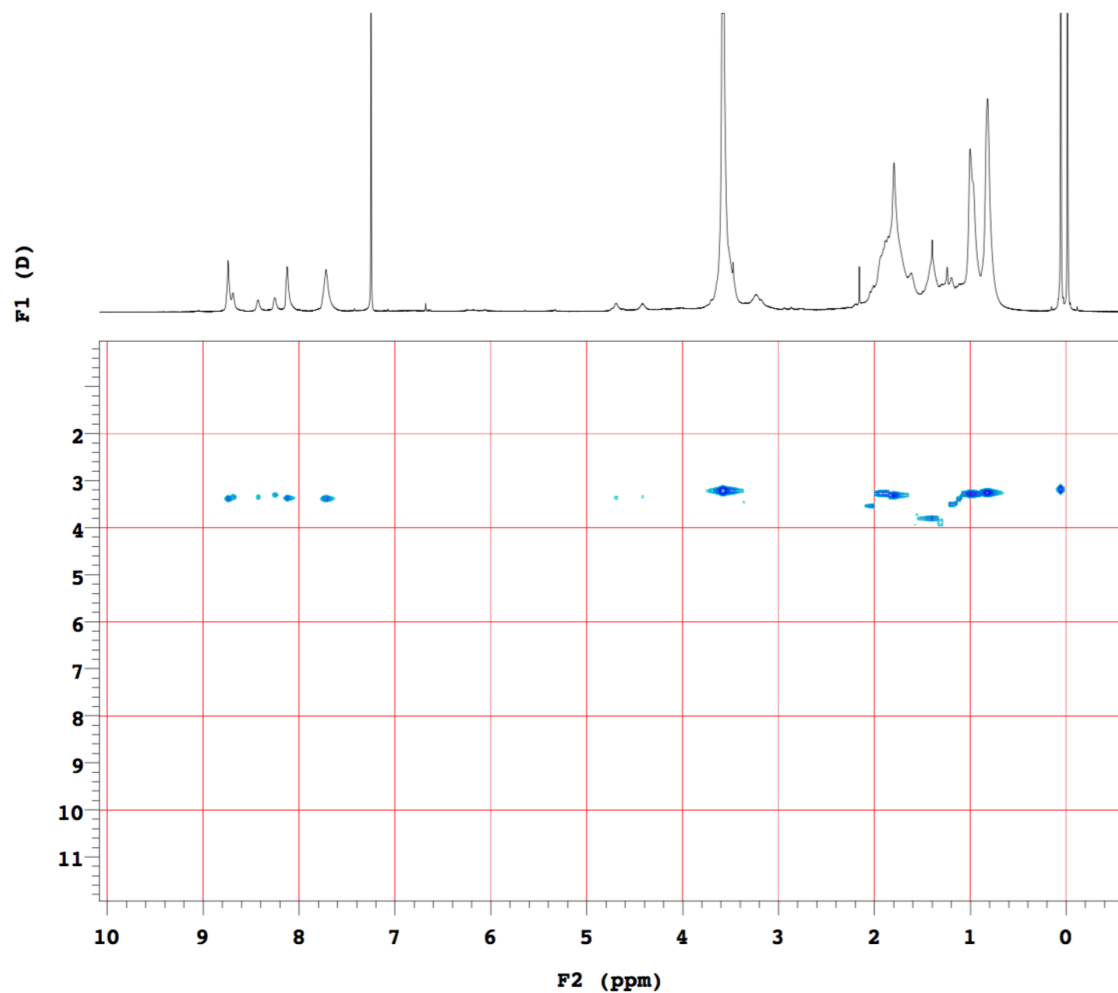## 4. Concentration-dependent DOSY NMR spectra of a mixture of 1 and 2
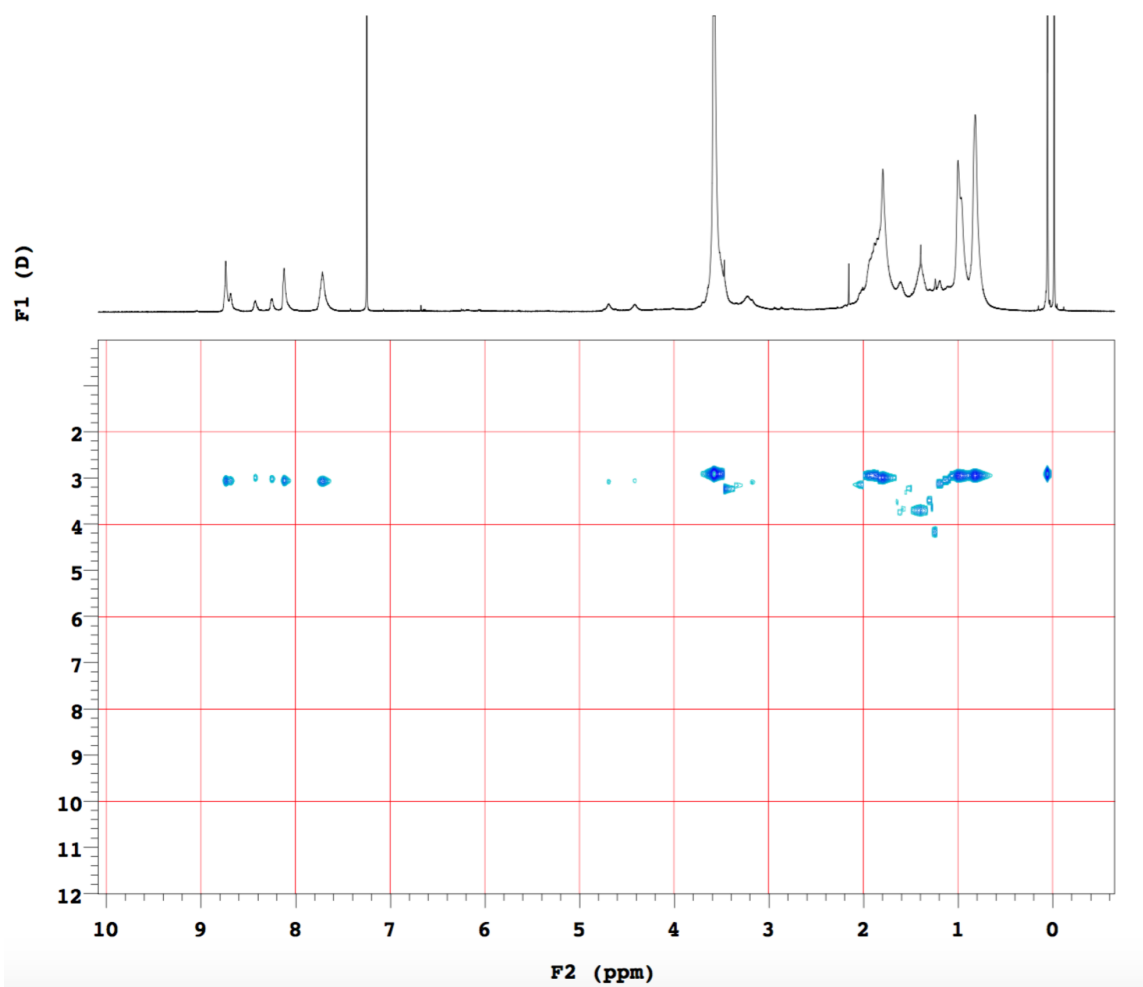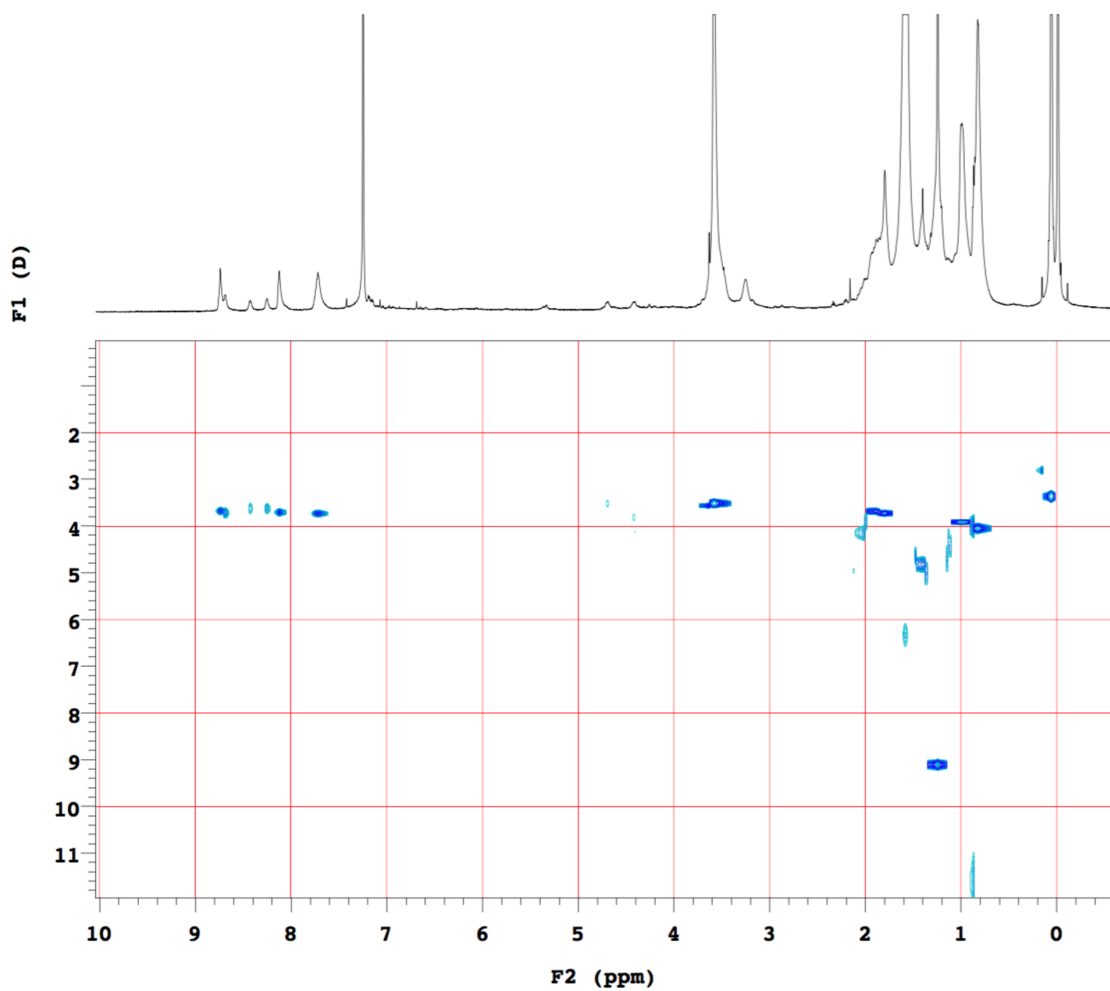

Fig. S8 DOSY NMR (500 MHz, CDCl₃, 298 K) spectral study of a mixture consisting of **1** (10 mg/mL, 0.387 mM) and **2** (1.94 mM).
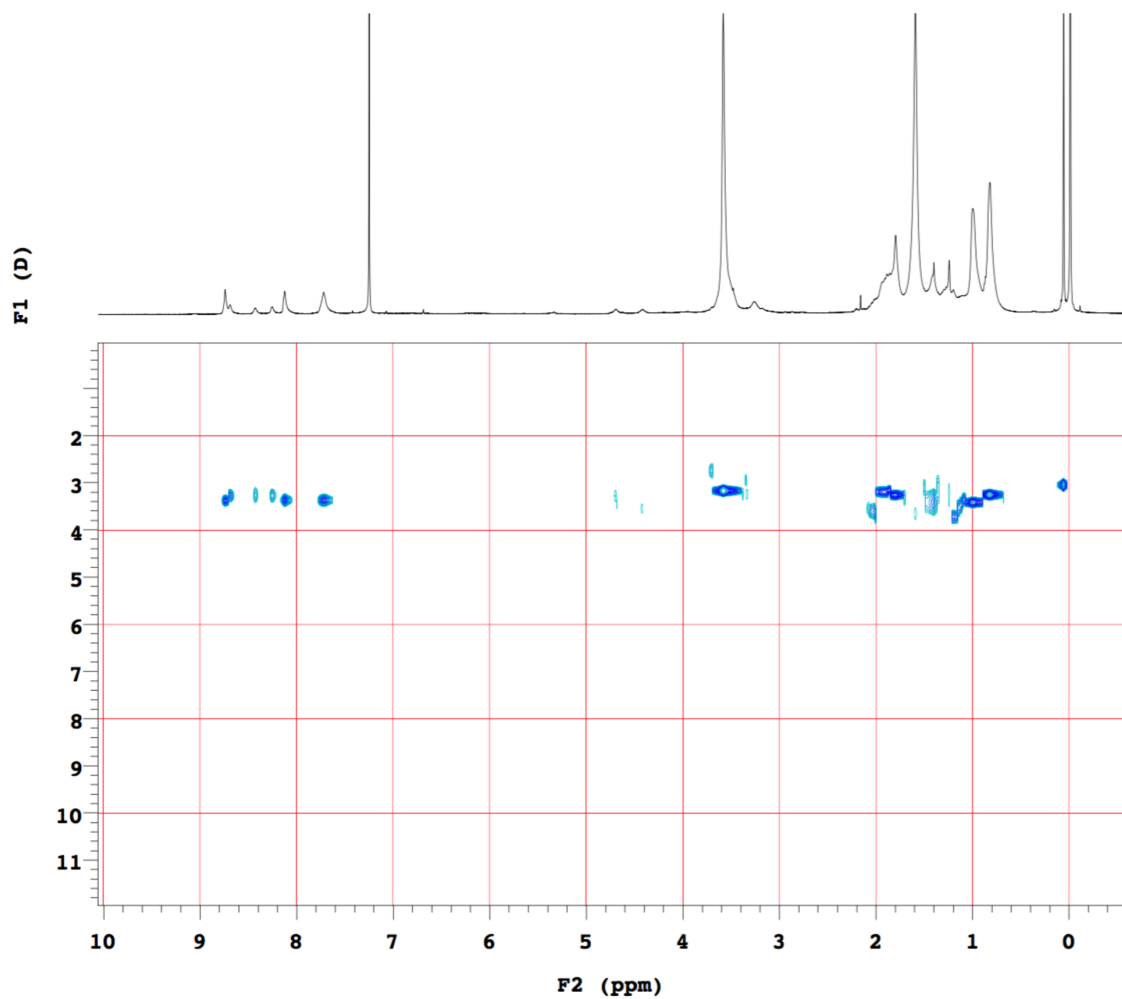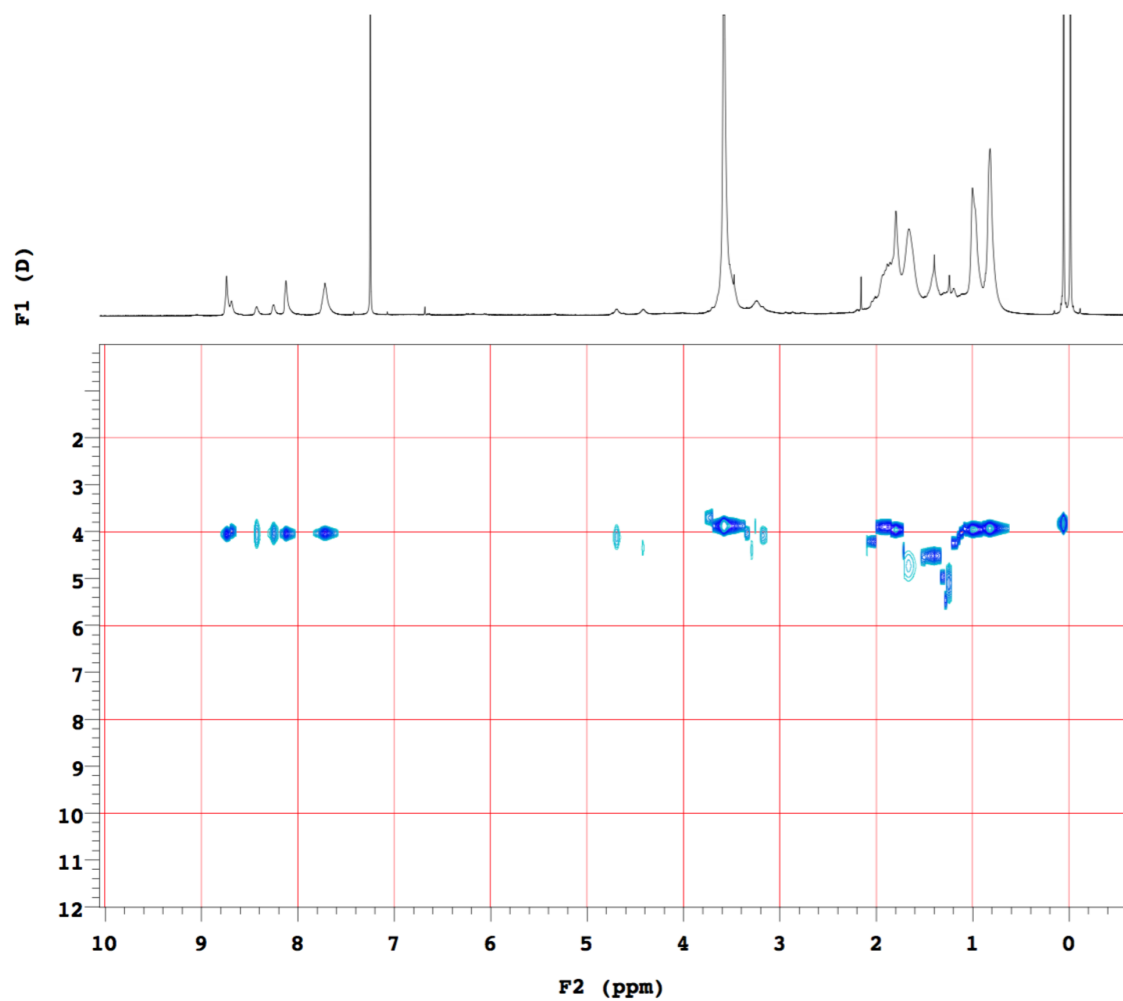
Fig. S9 DOSY NMR (500 MHz, CDCl₃, 298 K) spectral study of a mixture of **1** (8 mg/mL, 0.310 mM) and **2** (1.55 mM).
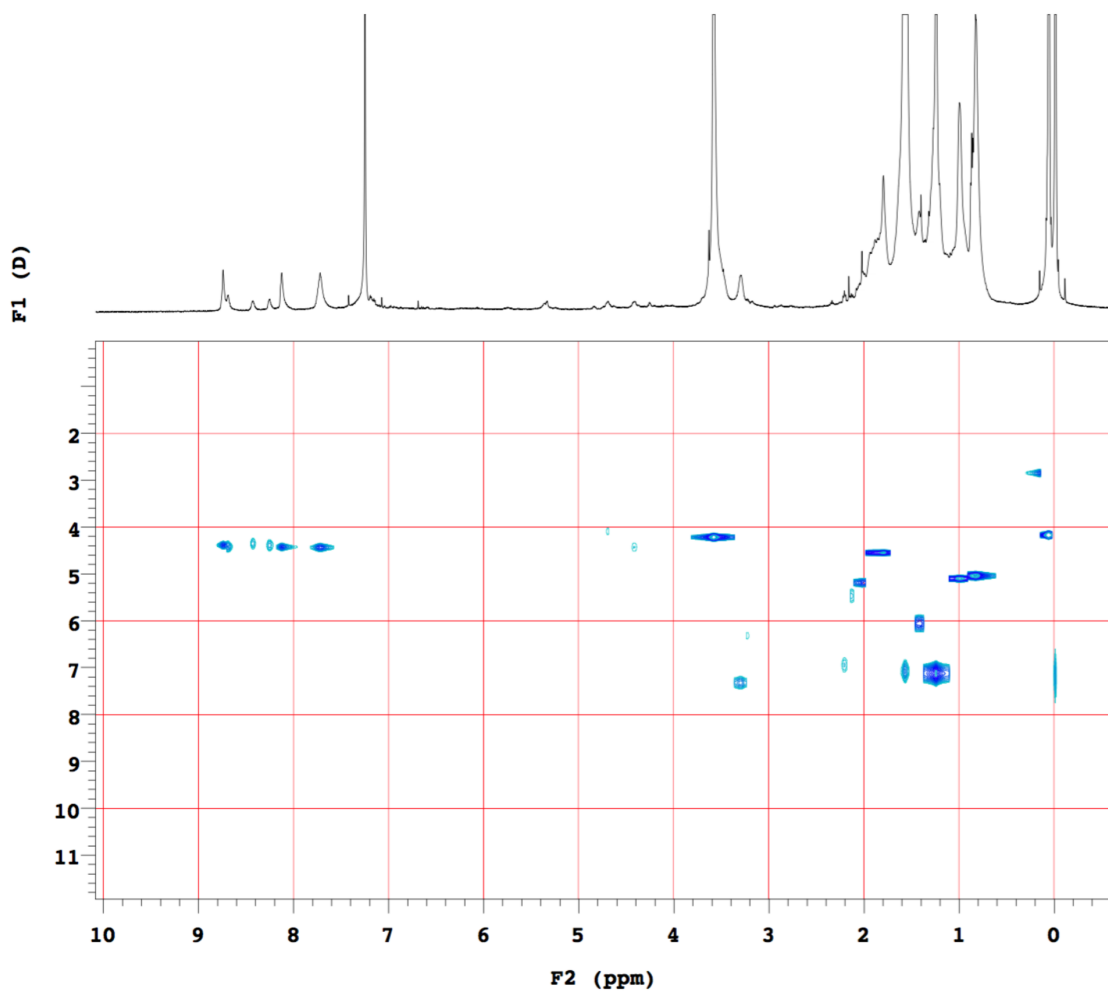
Fig. S10 DOSY NMR (500 MHz, CDCl₃, 298 K) spectral study of a mixture of **1** (5 mg/mL, 0.194 mM) and **2** (0.968 mM).
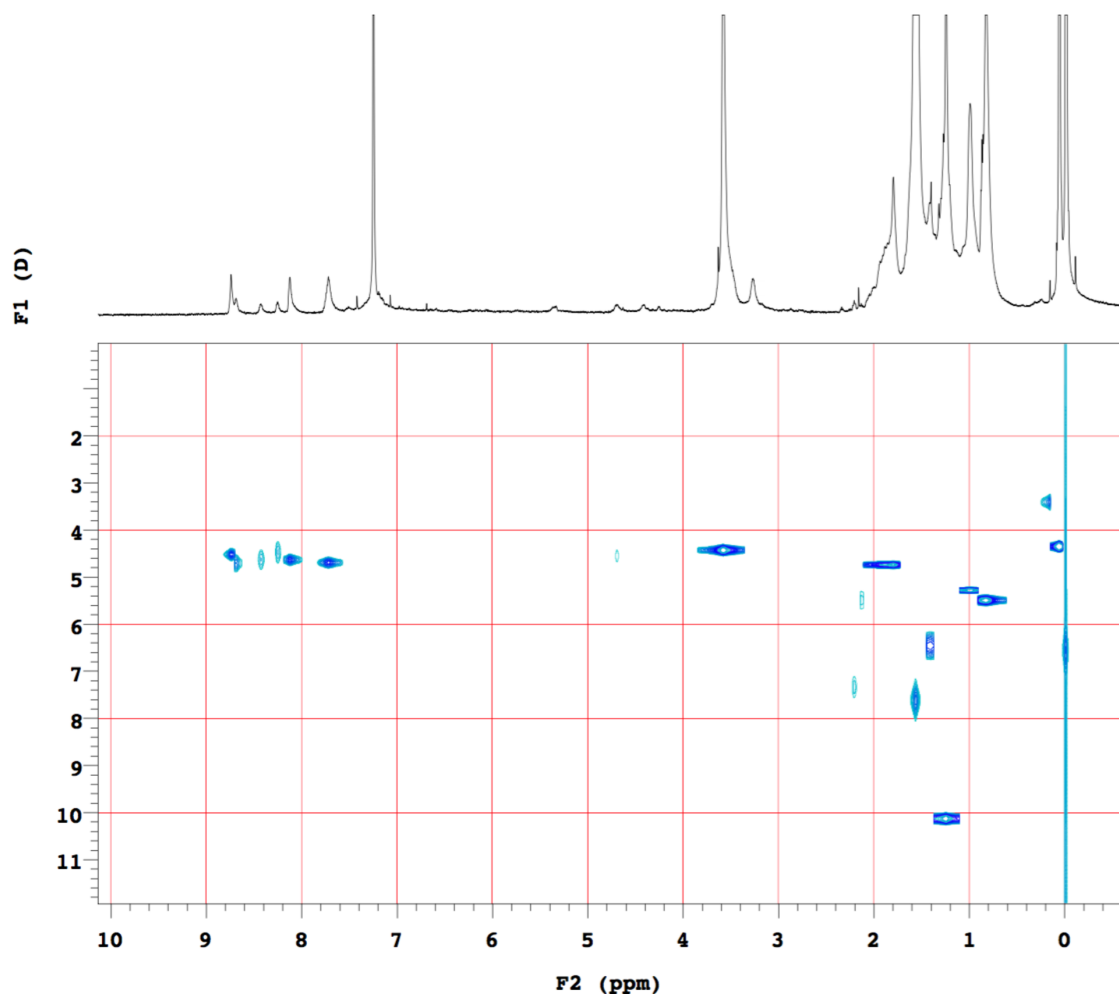
Fig. S11 DOSY NMR (500 MHz, CDCl₃, 298 K) spectral study of a mixture of **1** (2 mg/mL, 0.0774 mM) and **2** (0.387 mM).

Fig. S12 DOSY NMR (500 MHz, CDCl$_3$, 298 K) spectral study of a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM).
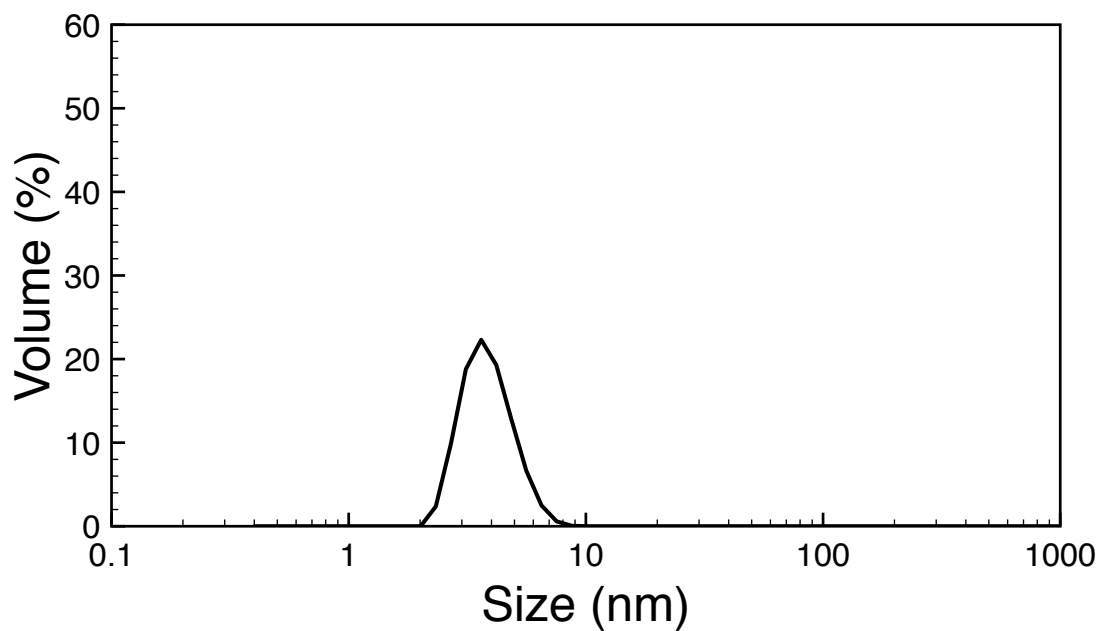
Fig. S13 DOSY NMR (500 MHz, CDCl₃, 298 K) spectral study of a mixture of **1** (0.5 mg/mL, 0.0194 mM) and **2** (0.0968 mM).
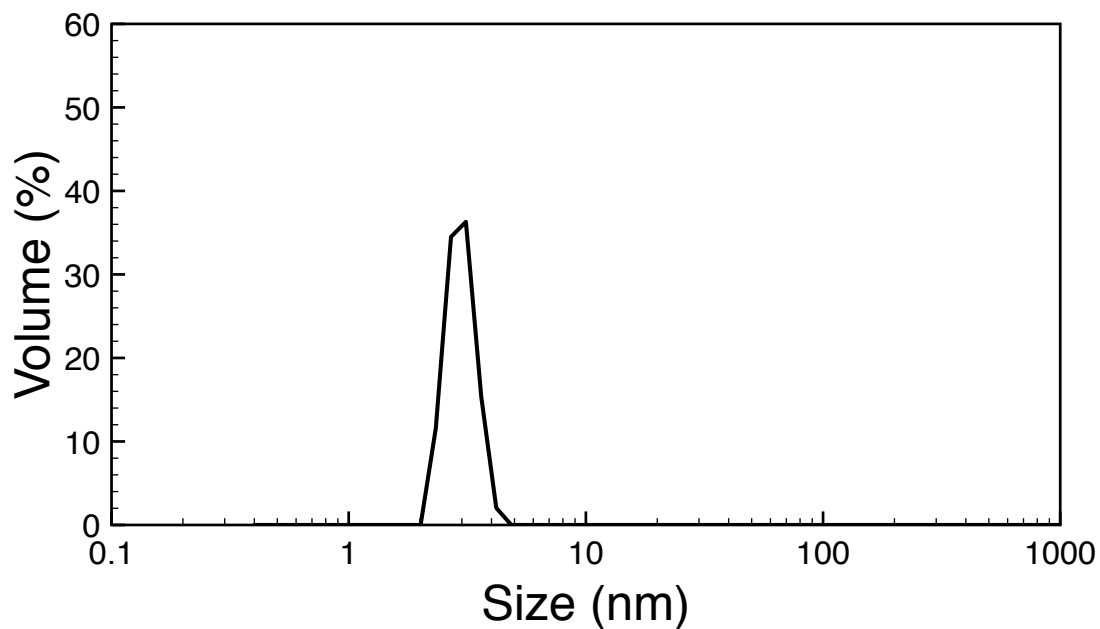
Fig. S14 DOSY NMR (500 MHz, CDCl₃, 298 K) spectral study of a mixture of **1** (0.2 mg/mL, 0.00774 mM) and **2** (0.0387 mM).
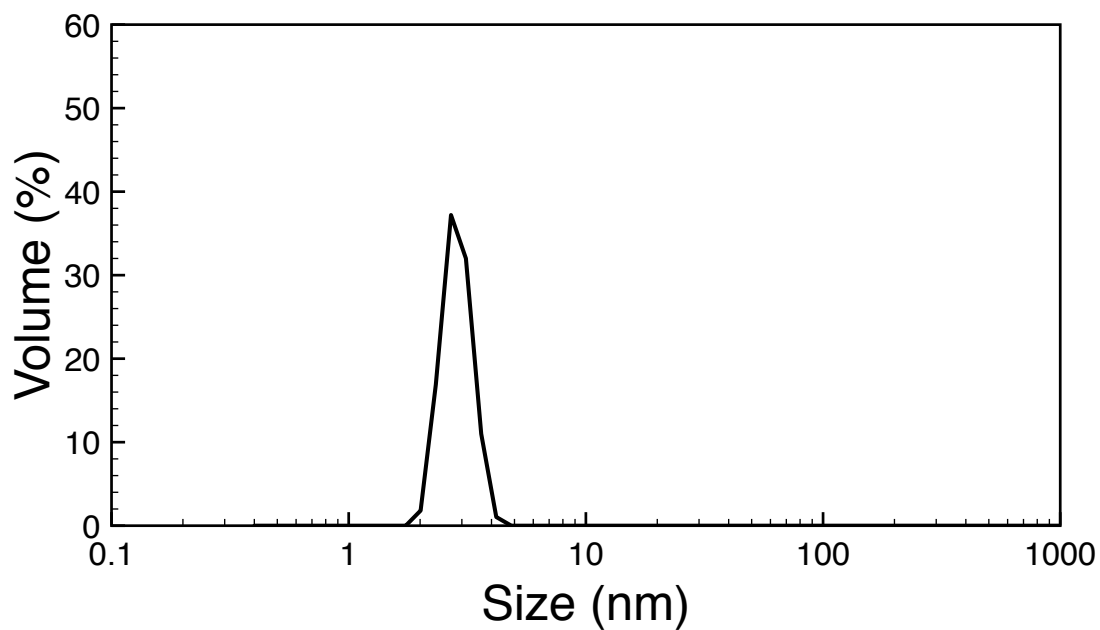
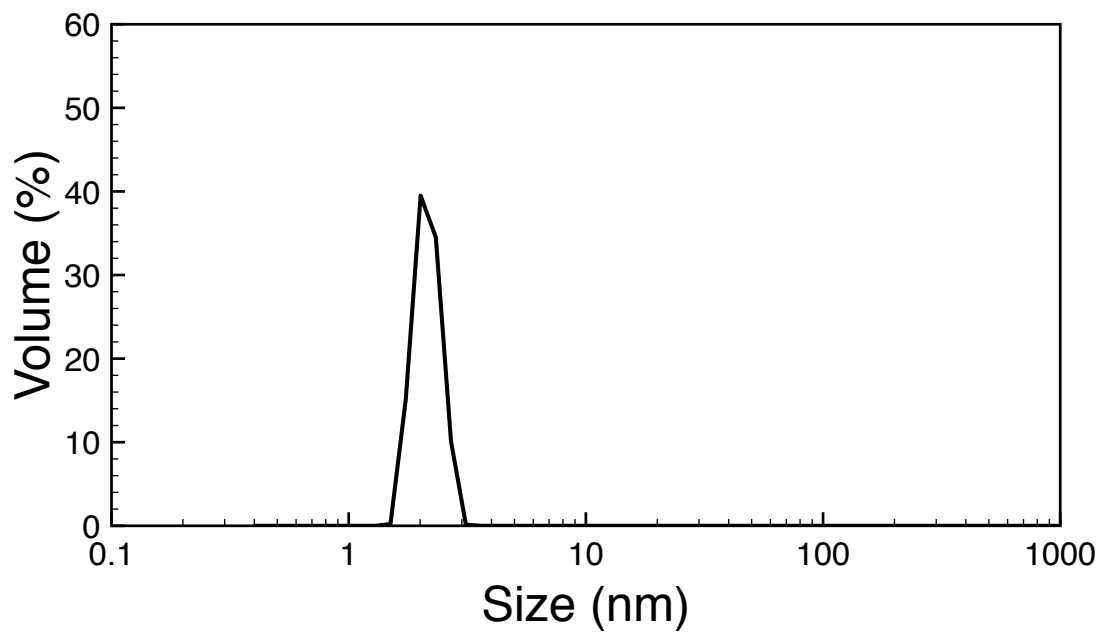*5. Concentration-dependent DLS studies of a mixture of **1** and **2***

Fig. S15 DLS study of a mixture of **1** (10 mg/mL, 0.387 mM) and **2** (1.94 mM).
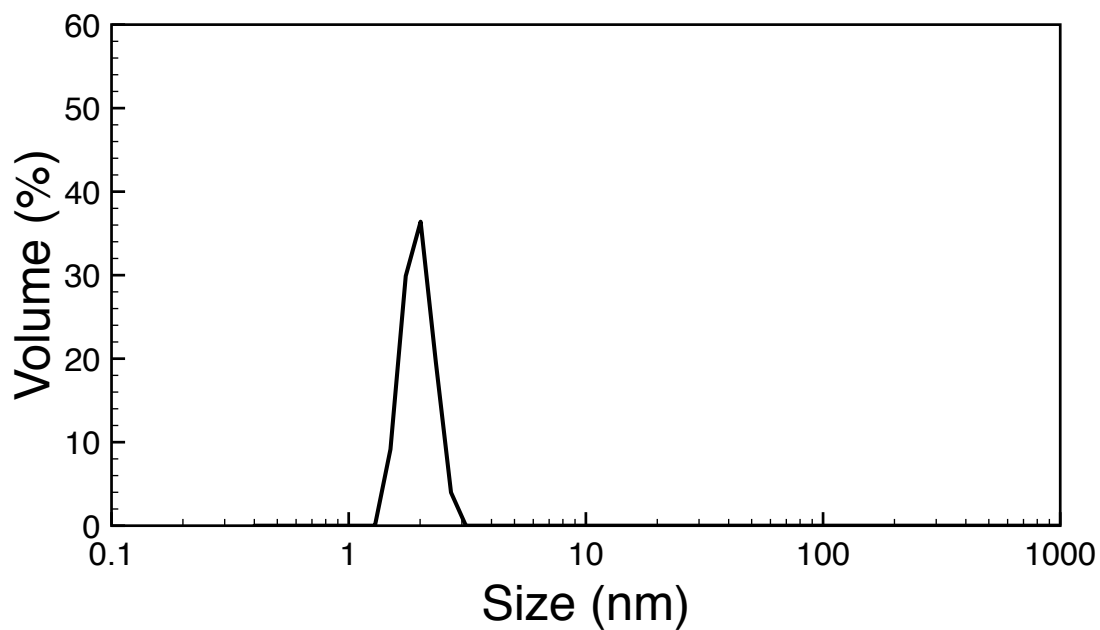

Fig. S16 DLS study of a mixture of **1** (8 mg/mL, 0.310 mM) and **2** (1.55 mM).
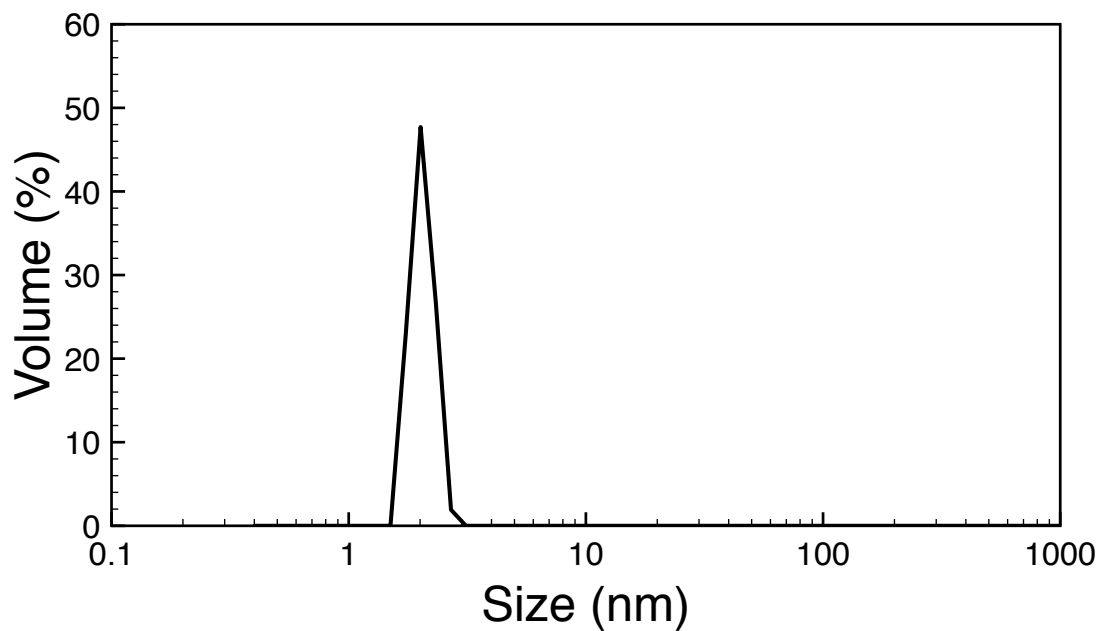
Fig. S17 DLS study of a mixture of **1** (5 mg/mL, 0.194 mM) and **2** (0.968 mM).
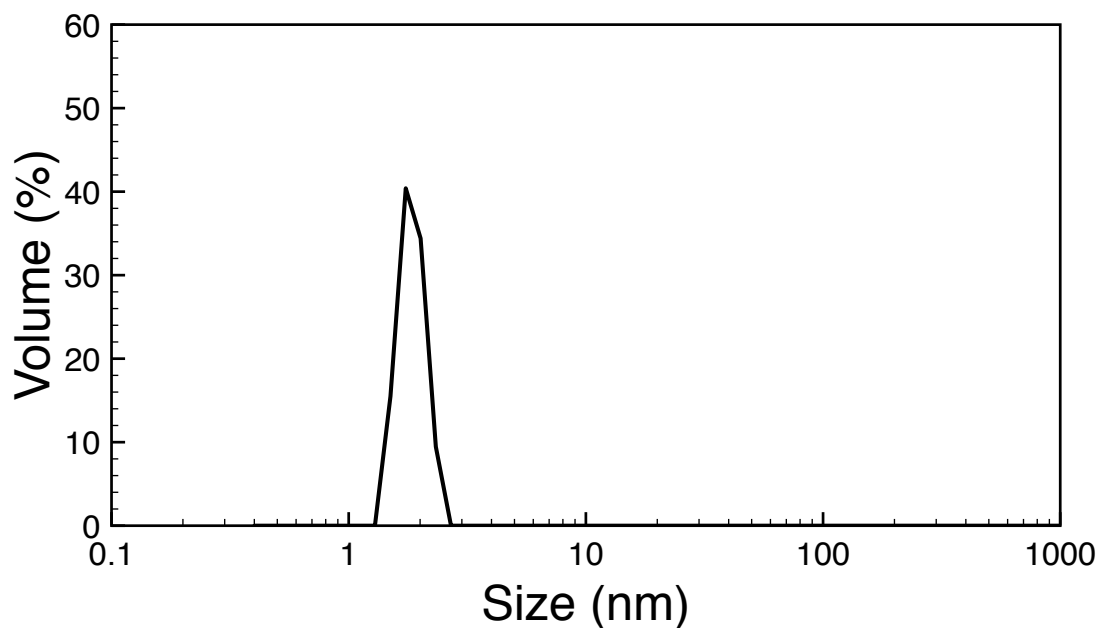

Fig. S18 DLS study of a mixture of **1** (2 mg/mL, 0.0774 mM) and **2** (0.387 mM).

Fig. S19 DLS study of a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM).
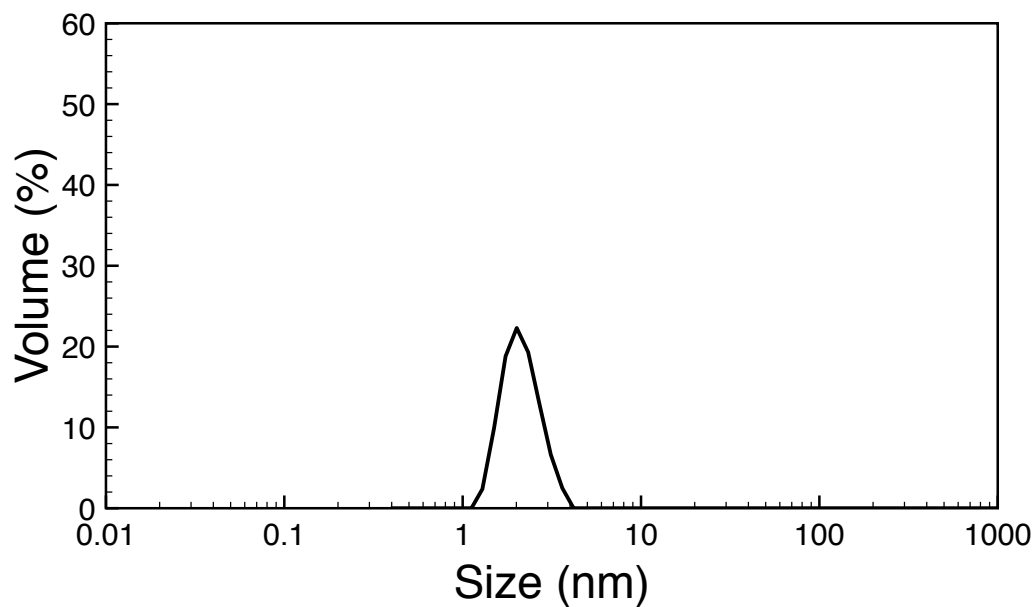

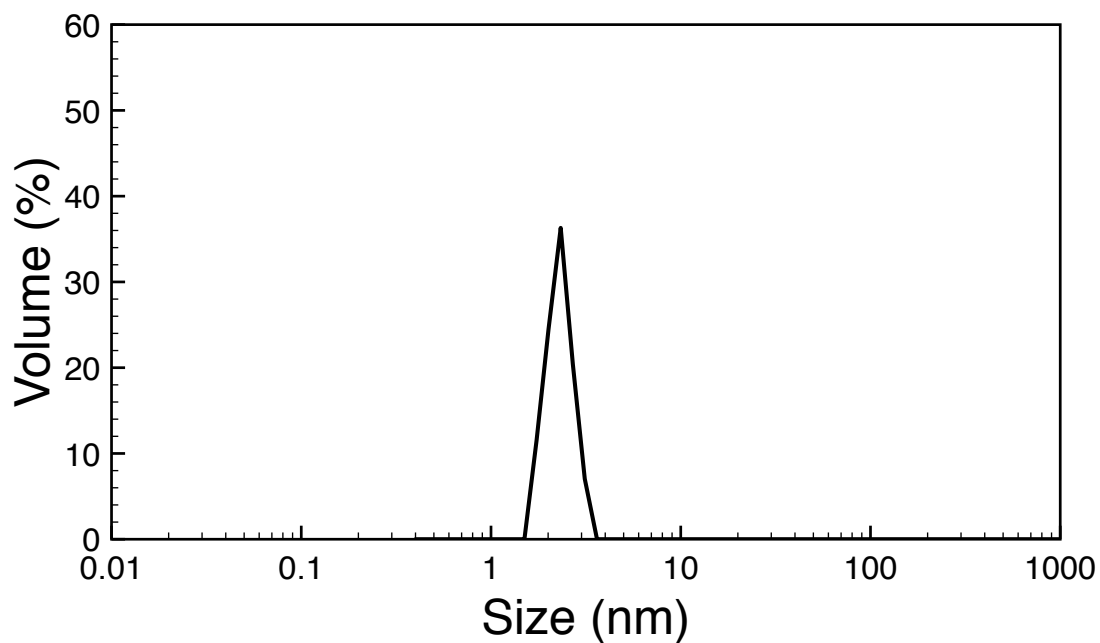***Fig. S20*** DLS study of a mixture of **1** (0.5 mg/mL, 0.0194 mM) and **2** (0.0968 mM).

Fig. S21 DLS study of a mixture of **1** (0.2 mg/mL, 0.00774 mM) and **2** (0.0387 mM).

6. DLS studies of a mixture of 1 and 2 as a function of increasing quantities of TBAHSO$_4$

Fig. S22 DLS study of a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM) in the presence of 0.2 molar equivalents of TBAHSO$_4$ (0.0774 mM).

Fig. S23 DLS study of a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM) in the presence of 0.5 molar equivalents of TBAHSO$_4$ (0.194 mM).
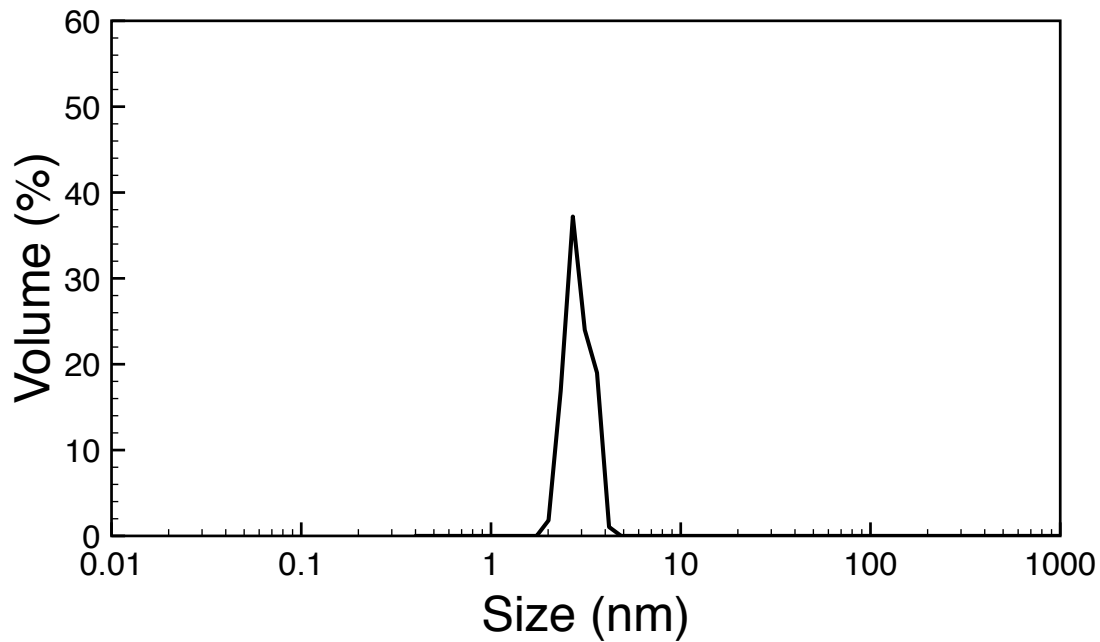
Fig. S24 DLS study of a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM) in the presence of 1.0 molar equivalents of TBAHSO$_4$ (0.387 mM).

Fig. S25 DLS study of a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM) in the presence of 2.0 molar equivalents of TBAHSO$_4$ (0.774 mM).

Fig. S26 DLS study of a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM) in the presence of 3.0 molar equivalents of TBAHSO$_4$ (1.16 mM).
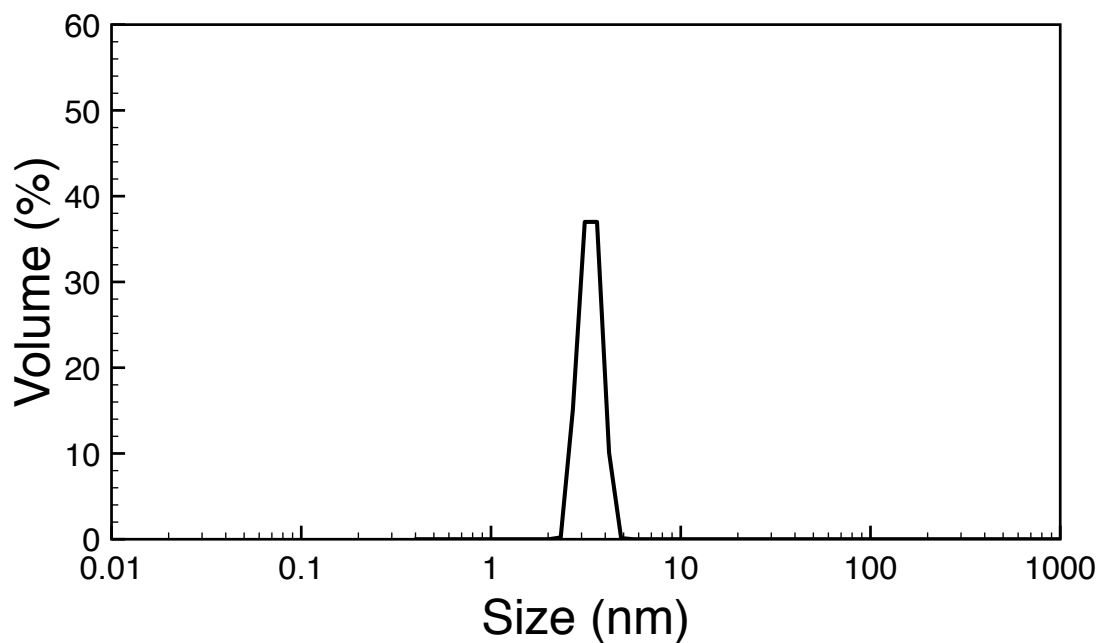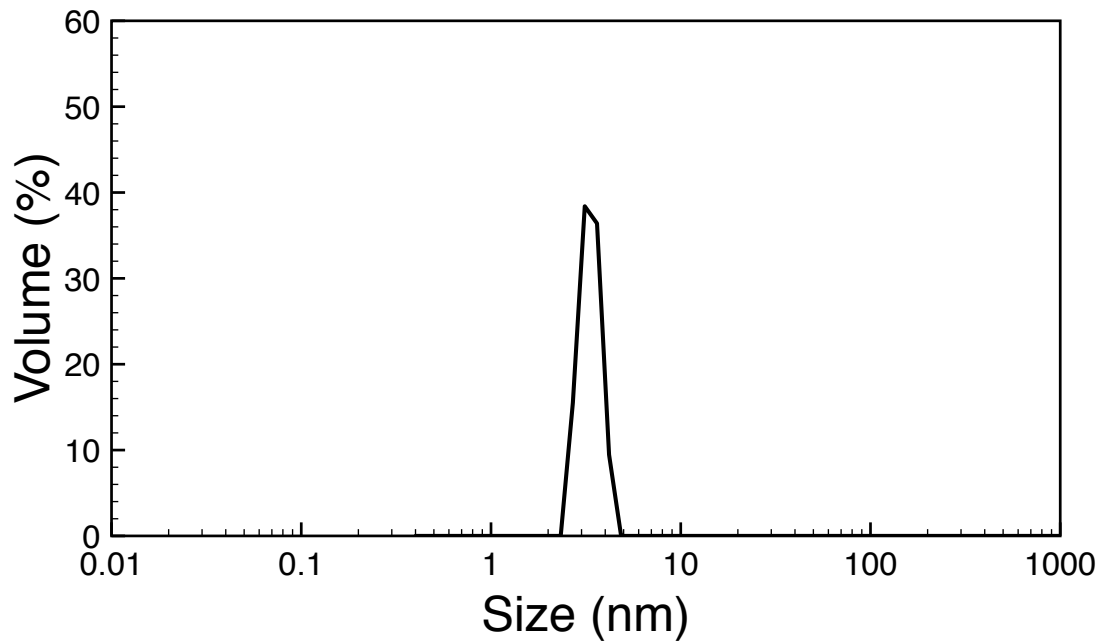
*7. Viscosity studies of mixtures of **1** and **2** upon treatment with competitive anions*

Fig. S27 Viscosity studies of a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM) alone and in the presence of 1.0 molar equivalent (0.387 mM) of other anion salts (TBAF, TBACl, TBABr, TBANO$_3$, TBAH$_2$PO$_4$, respectively).
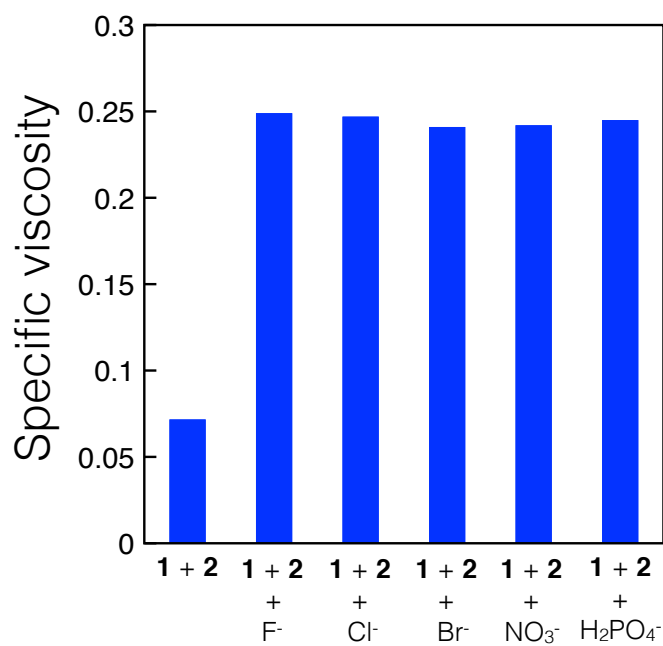
8. Phosphorescence features of SCPNs and constituent single chain polymer
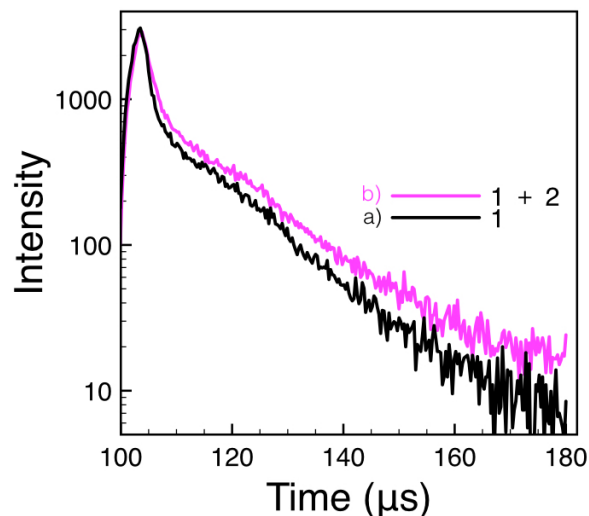
Fig. S28 Phosphorescence decays of a) **1** (1.0 mg/mL, 0.0387 mM); b) a mixture of **1** (1.0 mg/mL, 0.0387 mM) and **2** (0.194 mM).

The phosphorescence lifetimes of the single chain polymer and resulting SCPNs were calculated from the phosphorescence decay curves and found to be 370 ns and 1090 ns, respectively.

9. Influence of monomer ratio on the folding/unfolding process

For polymer **1**, the feed ratio of all monomers were: Pt(II) porphyrin (50.0 mg, 0.0519 mmol), unsubstituted methyl methacrylate (0.110 mL, 1.04 mmol), and calix[4]pyrrole repeat unit (54.6 mg, 0.104 mmol). We increased the relative percentage of the calix[4]pyrrole repeat unit by increasing the amount of this starting material to a) 65.6 mg (0.125 mmol), b) 86.6 mg (0.165 mmol), and c) 105 mg (0.200 mmol), respectively, while keeping the concentrations of the other constituents the same. This produced polymers **1-1**, **1-2**, and **1-3**.

|	Feed amount of C4P monomer	M_n (KDa)	C4P amount on polymer chain
polymer 1	54.6 mg, 0.104 mmol	25.8	10
polymer 1-1	65.6 mg, 0.125 mmol	26.9	12
polymer 1-2	86.6 mg, 0.165 mmol	28.4	15
polymer 1-3	105 mg, 0.200 mmol	29.8	18

Table. S1 Key data for polymers **1**, **1-1**, **1-2**, and **1-3**.
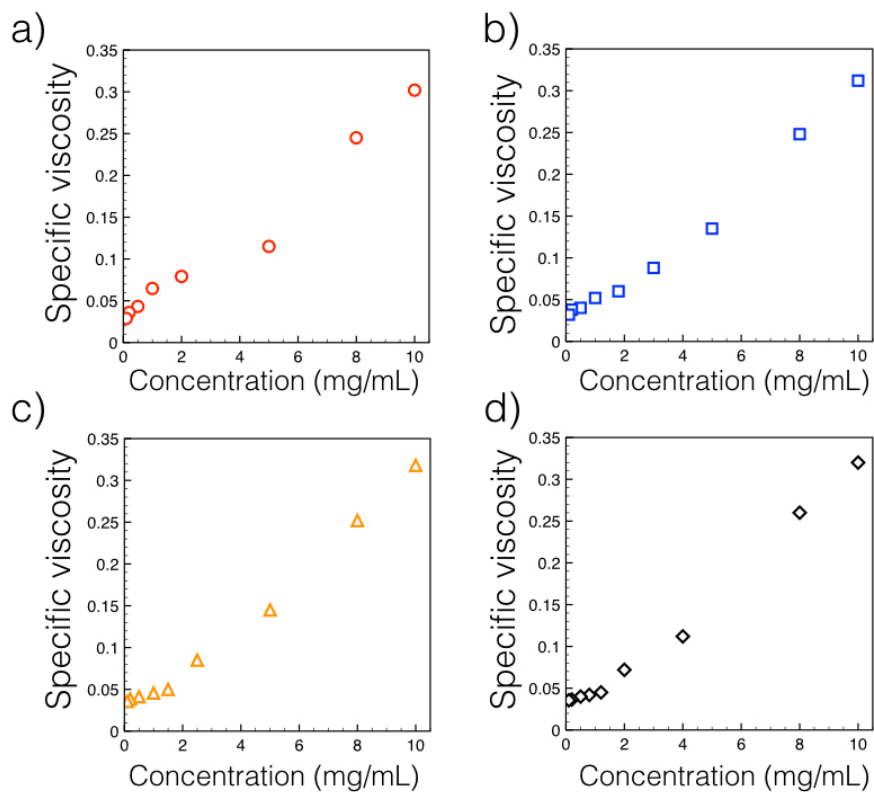
Fig. S29 Viscosity studies of mixtures of **2** with: a) polymer **1**; b) polymer **1-1**; c) polymer **1-2**; d) polymer **1-3** (1:1 molar ratio of recognition groups) versus polymer concentration.

From the above figure, it can be seen that the SCPNs were transformed into a more network-like structure at ca. 2.0, 1.8, 1.5, and 1.2 mg/mL for polymers **1**, **1-1**, **1-2**, and **1-3**, respectively. The results are taken as an indication that the SCPNs underwent conversion at lower concentrations when the amount of calix[4]pyrrole repeat unit was increased.

10. *Viscosity studies of **1** with different organic anions*
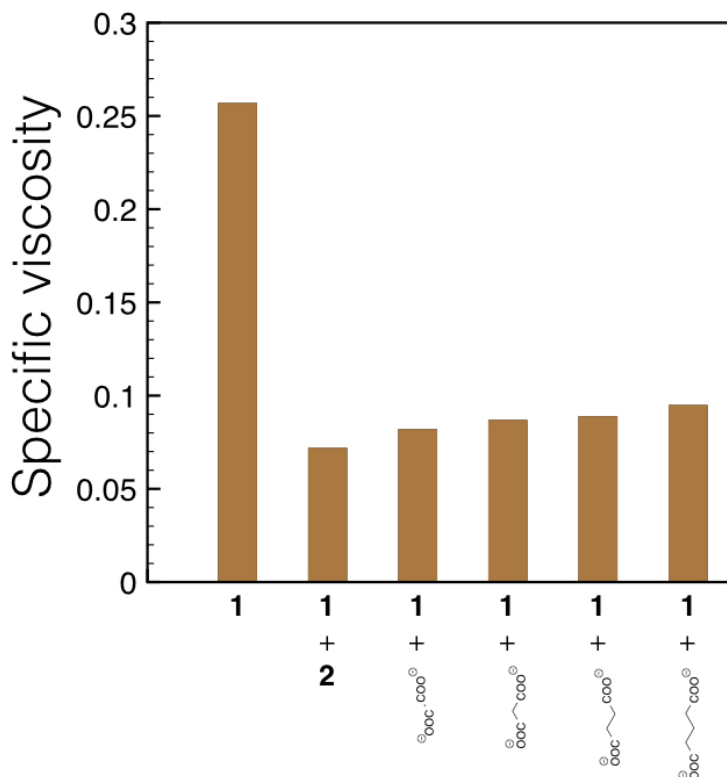
Fig. S30 Viscosity studies of **1** (1.0 mg/mL, 0.0387 mM) alone and in the presence of various organic anions[S3] (each at 0.194 mM).

As shown in the above figure (Fig. S30), the specific viscosity of **1** decreased upon the addition of various test organic anions. On this basis, we infer that these organic anions can replace **2** and be used to induce SCPN production.

References:

S1. K. K. Wang, K. H. Choi, H. W. Shin, B. J. Kim, J. E. Im, S. L. Oh, N. S. Park, M. Jung, J. B. Oh, M. J. Lee, H. K. Kim and Y. R. Kim, *Chem. Phys. Lett.,* 2009, **482**, 81.

S2. E. S. Silver, B. M. Rambo, C. W. Bielawski and J. L. Sessler, *J. Am. Chem. Soc.,* 2014, **136**, 2252.

S3. G. Cafeo, F. H. Kohnke, G. Mezzatesta, A. Profumo, C. Rosano, A. Villari and A. J. P. White, *Chem. Eur. J.*, 2015, **21**, 5323.