Electronic Supporting Information (ESI)

Light-driven control of the composition of a supramolecular network

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**General methods and materials**

The DTE derivative **1** was prepared by a modified published procedure (see below). All chemicals for the synthesis were used as received without further purification, unless stated otherwise. CH_2Cl_2 was distilled over CaH_2. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 or 125 MHz) spectra for the characterization of **1** and its precursor were recorded on Varian Unity 400 or 500 spectrometers at 25 °C. In the ^{1}H and ^{13}C NMR spectra, chemical shifts (δ/ppm) are referenced to the residual solvent peak: $CDCl_3$, 7.26 ppm (^{1}H NMR) and 77.20 ppm (^{13}C NMR); D_2O, 4.80 (^{1}H NMR); MeOH-d_4, 49.00 ppm (^{13}C NMR). Thin-layer chromatography to monitor the reactions was performed on silica gel plates (Merck Kieselgel 60, F_{254}).

All measurements (at room temperature) were done in water (miliQ quality) or in deuterium oxide (D_2O, >99 atom% D) at pH or pD 5.0, respectively. The pH/pD was adjusted by additions of HCl/DCl or NaOH/NaOD. The pD values were obtained after correction for isotope effects (pD = pH* + 0.4).[1] Cucurbit[7]uril (CB7) was prepared by following a published procedure.[2] The water content was taken as 20 weight-%, determined by ^{1}H NMR spectroscopy using malonic acid as internal standard. Cucurbit[8]uril (CB8; 20 weight-% water) and geranylamine (**2**) are commercial products and were used in the highest quality available.

^{1}H NMR experiments to characterize the network were done with a Varian Mercury 500 MHz NMR spectrometer. For the irradiation two light sources were used: 365-nm light was generated by a UVP handheld UV lamp (Model VL-4.LC, 4 W) and light at λ > 590 nm by a 150 W Xenon lamp (Oriel GmbH & Co.KG), using a long-pass optical filter.

Note: For the four-component mixture (**1**, **2**, CB7, and CB8; all at 500 μM) a small amount of precipitate was observed on prolonged standing of the solution. This can be re-dissolved by heating gently with a hairdryer.

Experimental procedure for the synthesis of 1
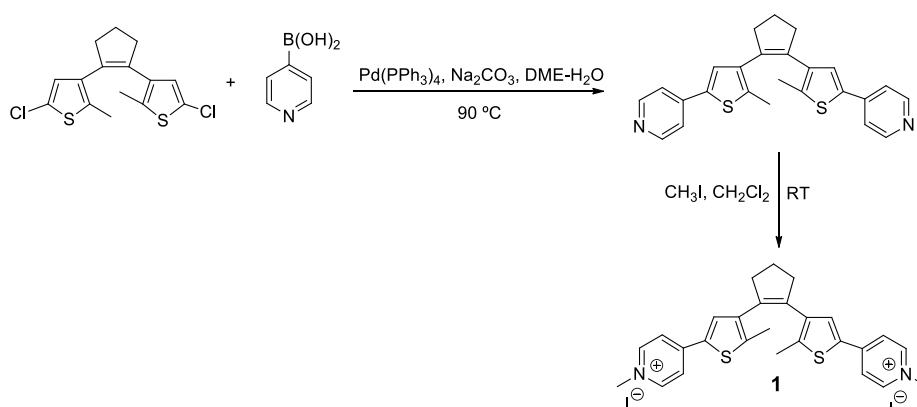
Scheme S1. Synthesis of **1**.

Synthesis of 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene

A published method[3] was modified to synthesize 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene. 1,2-Bis(5-chloro-2-methyl-3-thienyl)cyclopentene[4] (493 mg, 1.5 mmol), 4-pyridinylboronic acid (406 mg, 3.3 mmol), Na_2CO_3 (720 mg, 3 mmol) and $Pd(PPh_3)_4$ (174 mg, 0.15 mmol) were placed in a flask under Ar. Dimethoxyethane (DME, 20 mL, degassed) and water (5 mL, degassed) were subsequently added and the reaction mixture was refluxed (90 °C) for 48 h under argon. After cooling to room temperature, the reaction was quenched with water (40 mL) and Et_2O (100 mL). The organic layer was separated, and the water phase was extracted with Et_2O (2 × 100 mL). The combined organic phases were dried (Na_2SO_4), filtered, and the solvent was evaporated in *vacuo*. The crude product was purified by column chromatography (SiO_2, MeOH/CH_2Cl_2 = 2:98) to afford the product (173 mg, 28% yield). The ^{1}H and ^{13}C NMR data are in agreement with the published data.[5]

^{1}H NMR (400 MHz, CDCl$_3$): 8.53 (m, 4H, pyridine-H). 7.35 (m, 4H, pyridine-H), 7.22 (s, 2H, thiophene-H), 2.86 (t, J = 7.4 Hz, 4H, CH_2), 2.18-2.06 (m, 2H, CH_2), 2.03 (s, 6H, CH_3).

^{13}C NMR (101 MHz, CDCl$_3$): 150.4, 141.5, 137.5, 137.3, 136.9, 135.0, 126.5, 119.5, 38.7, 23.2, 14.8.

Synthesis of 1

2-Bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene (69 mg, 0.093 mmol) was dissolved in dry CH_2Cl_2 (3 mL) under argon and CH_3I (0.3 mL) was injected. The solution was stirred at room temperature for 3 h. The greenish precipitate was collected by filtration, washed repeatedly with dry CH_2Cl_2 afforded the NMR-pure **1** (55 mg, 55% yield). The ^{1}H NMR data are in agreement with the published data.[6]
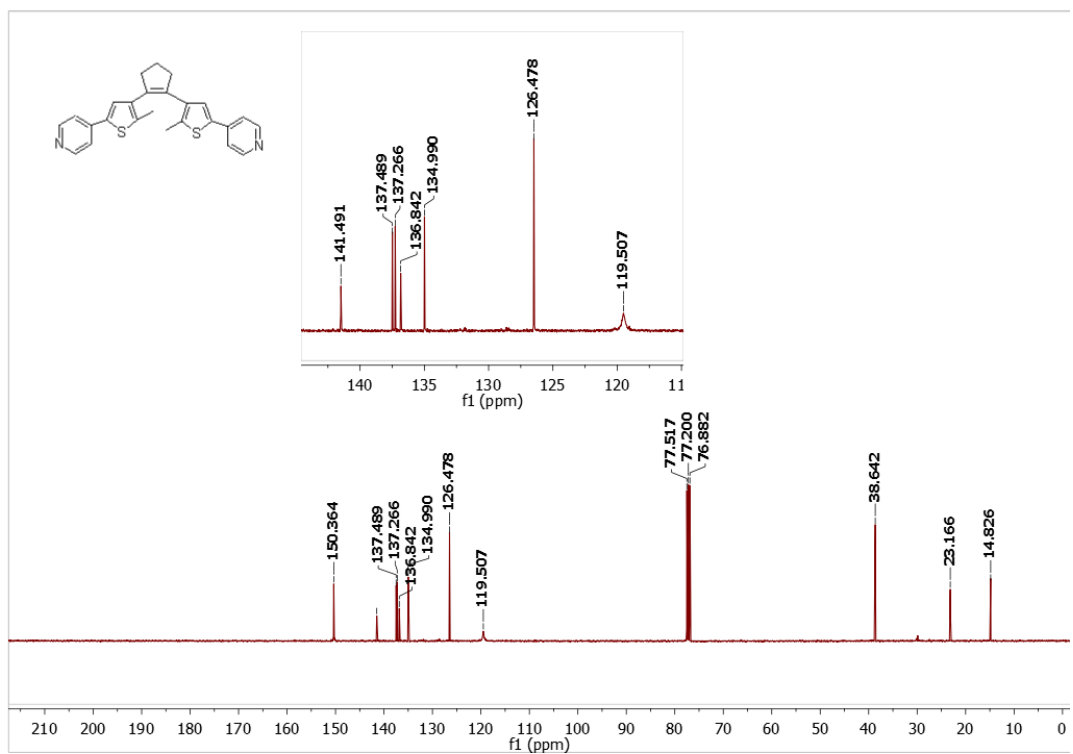
^{1}H NMR (400 MHz, D_2O) 8.50 (d, J = 6.8 Hz, 4H, pyridine-H), 7.97 (d, J = 7.2 Hz, 4H, pyridine-H), 7.84 (s, 2H, thiophene-H), 4.22 (s, 6H, CH_3), 2.88 (t, J = 7.4 Hz, 4H, CH_2), 2.18-2.06 (m, 2H, CH_2), 2.05 (s, 6H, CH_3).

^{13}C NMR (125 MHz, MeOH-d_4): 150.1, 146.4, 145.9, 140.4, 136.8, 134.6, 134.3, 122.8, 47.8, 39.5, 24.0, 15.2.

¹H and ¹³C NMR spectra
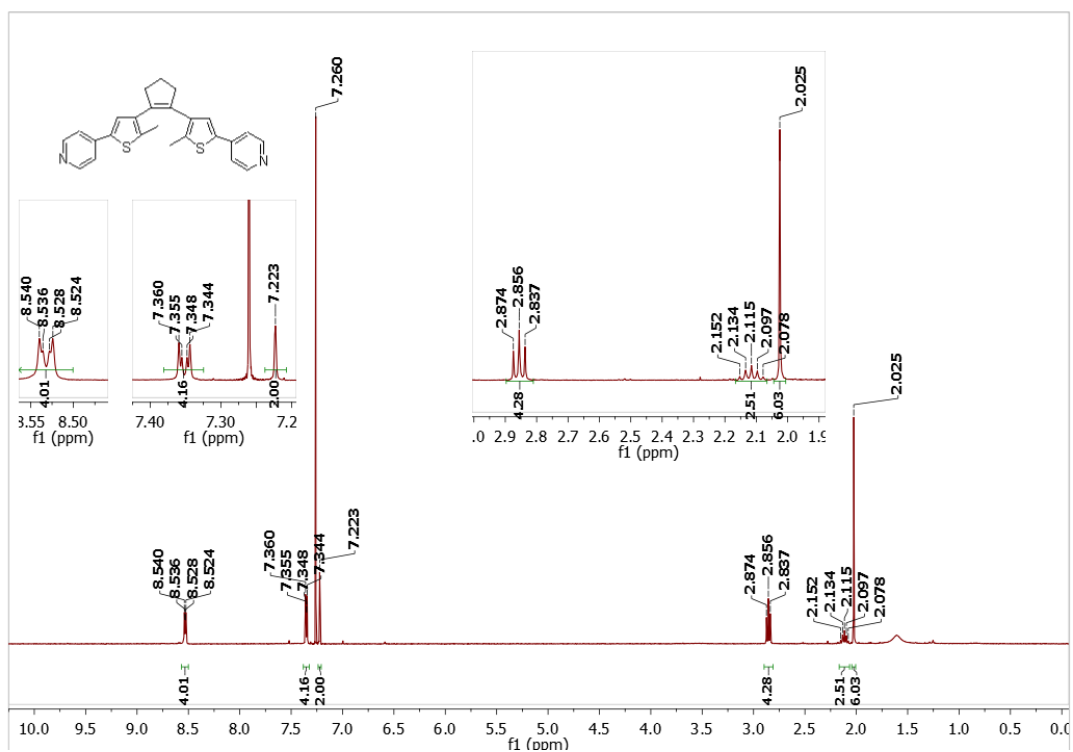
Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene.

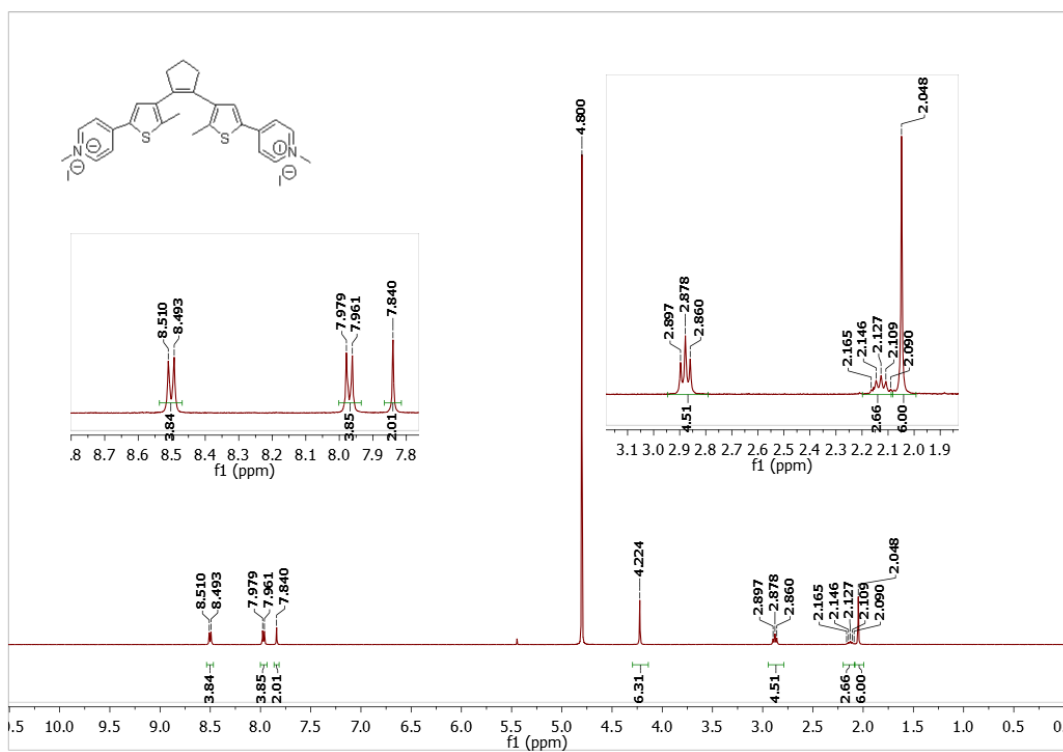**Figure S2**. ¹³C NMR spectrum (101 MHz, CDCl₃) of 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene.

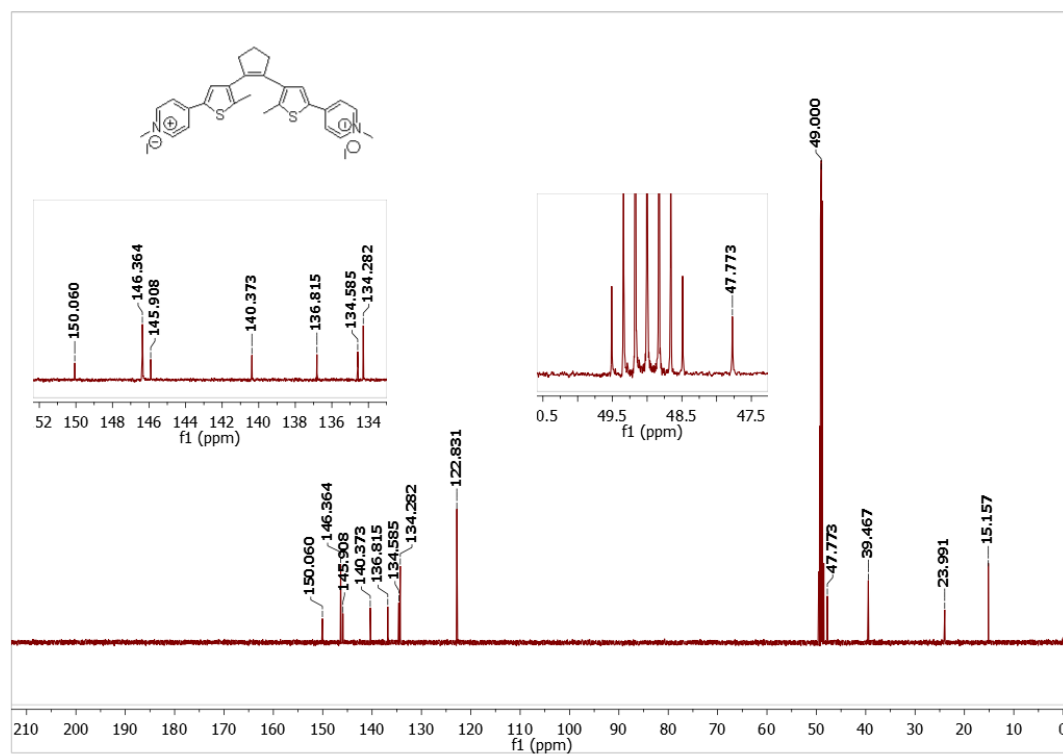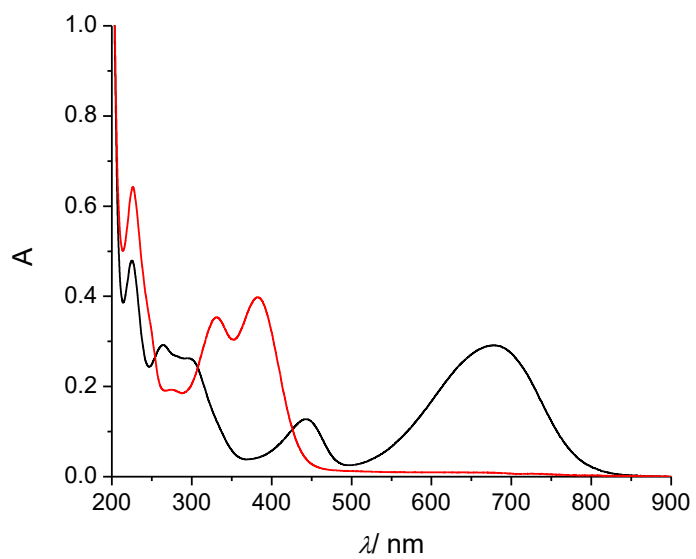**Figure S3**. ^{1}H NMR spectrum (400 MHz, D$_2$O) of **1**.

Figure S4. ^{13}C NMR spectrum (125 MHz, MeOH-d_4) of **1**.

UV/vis absorption spectra of the four-component mixture on irradition with light


Figure S5. UV/vis absorption spectra of the four-component mixture (**1**, **2**, CB7, and CB8; all at 15 μM) at pH 5 before (red) and after (black) irradiation at 365 nm.

**NMR spectra for the different binding and switching state situations**

Note: The protons *b*, *c*, and *d* (Figure 1 in main text) were assigned to aid fast identification of the binding situation. These protons define the structural frame of the symmetric DTE. They are color-coded: **1**$_o$ – black; **1**$_o$-CB7 – blue; **1**$_o$-CB8 – red; **1**$_c$ – gray; **1**$_c$-CB7 – green; **1**$_c$-CB8 – magenta.
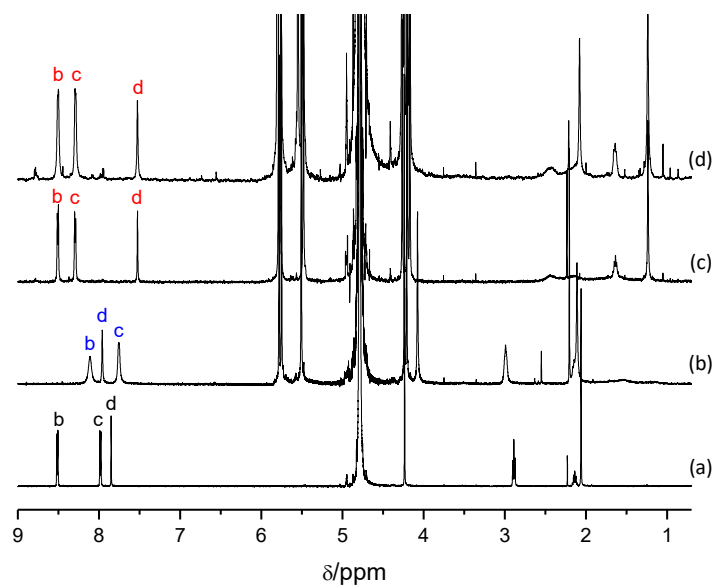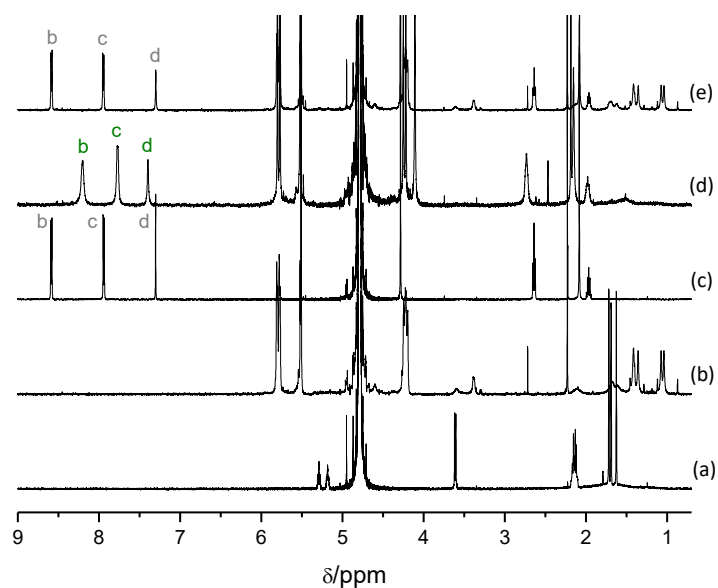

Figure S6. ^{1}H NMR spectra (all at pD 5.0) of (a) **1**$_o$ (500 µM); (b) **1**$_o$ in the presence of CB7 (both at 500 µM); (c) **1**$_o$ in the presence of CB8 (both at 500 µM); (d) **1**$_o$ in the presence of CB8 and CB7 (all at 500 µM). **1**$_o$ binds preferably to CB8.
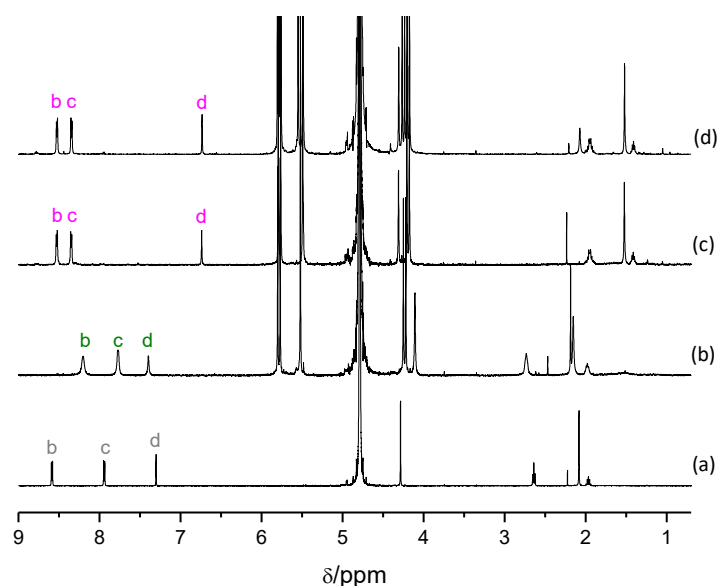
Figure S7. ^{1}H NMR spectra (all at pD 5.0) of (a) **1**$_c$ (500 µM); (b) **1**$_c$ in the presence of CB7 (both at 500 µM); (c) **1**$_c$ in the presence of CB8 (both at 500 µM); (d) **1**$_c$ in the presence of CB8 and CB7 (all at 500 µM). **1**$_c$ binds preferably to CB8.
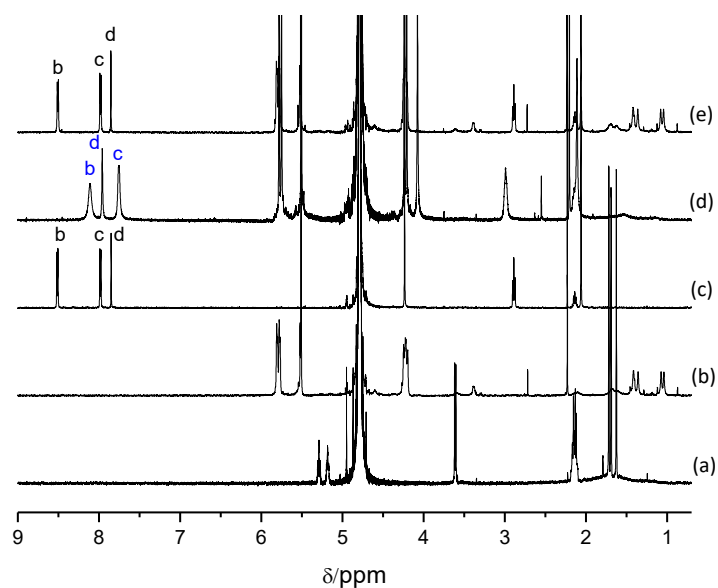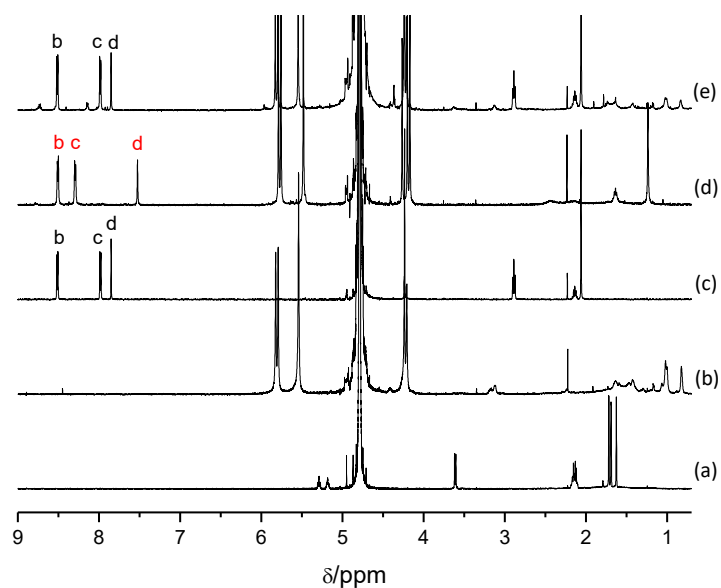
Figure S8. ^1H NMR spectra (all at pD 5.0) of (a) **2** (1 mM); (b) **2** in the presence of CB7 (both at 500 μM); (c) **1**$_o$ (500 μM); (d) **1**$_o$ in the presence of CB7 (both at 500 μM); (e) mixture **1**$_o$ and **2** in the presence of CB7 (all at 500 μM). **2** displaces **1**$_o$ completely from CB7.

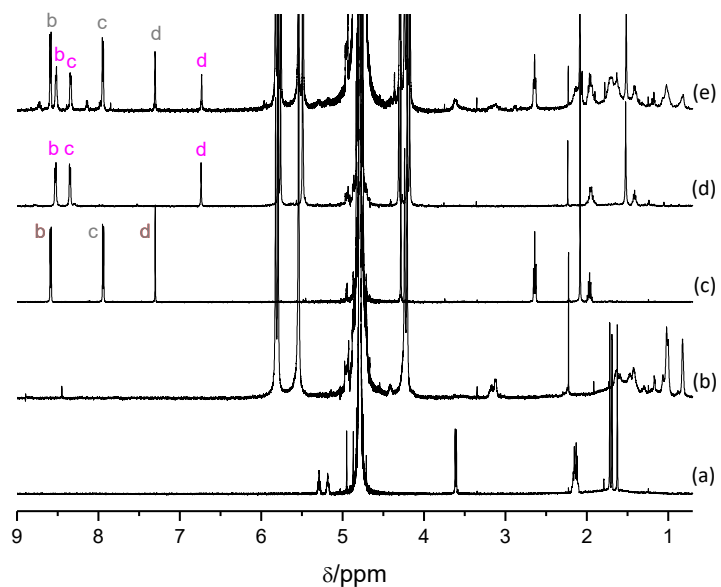
Figure S9. ^1H NMR spectra (all at pD 5.0) of (a) **2** (1 mM); (b) **2** in the presence of CB7 (both at 500 μM); (c) **1**$_c$ (500 μM); (d) **1**$_c$ in the presence of CB7 (both at 500 μM); (e) mixture of **1**$_c$ and **2** in the presence of CB7 (all at 500 μM). **2** displaces **1**$_c$ completely from CB7.

Figure S10. ^{1}H NMR spectra (all at pD 5.0) of (a) **2** (1 mM); (b) **2** in the presence of CB8 (both at 500 μM); (c) **1**$_o$ (500 μM); (d) **1**$_o$ in the presence of CB8 (both at 500 μM); (e) mixture **1**$_o$ and **2** in the presence of CB8 (all at 500 μM). **2** displaces **1**$_o$ completely from CB8.

Figure S11. ^{1}H NMR spectra (all at pD 5.0) of (a) **2** (1 mM); (b) **2** in the presence of CB8 (both at 500 μM); (c) **1**$_c$ (500 μM); (d) **1**$_c$ in the presence of CB8 (both at 500 μM); (e) mixture of **1**$_c$ and **2** in the presence of CB8 (all at 500 μM). **2** displaces **1**$_c$ partially from CB8.

References

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