Supporting Information

Stimuli-Induced Folding Cascade of a Linear Oligomeric Guest Chain Programmed through Cucurbit[*n*]uril Self-Sorting (*n* = 6, 7, 8)

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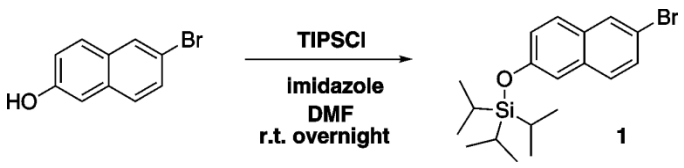
1. Experimental Details.

1.1. General Methods.

All reagents were commercially available and used without further purification unless otherwise stated. Thin-layer chromatography (TLC) was performed on aluminum sheets coated with silica gel 60/F254 (Merck KGaA). Column chromatography was performed on silica gel60 (Merck 40 - 60 nm, 230 - 400 mesh). Melting points were determined on a Reichert Thermovar apparatus and are uncorrected. ^{1}H NMR, ^{13}C NMR and ^{1}H,^{1}H COSY spectra were recorded on Bruker ECX 400 MHz, Jeol Eclipse 500 MHz or Bruker AVANCE III 700 MHz NMR spectrometers with triple inverse cryoprobe on the latter instrument. All chemical shifts are reported in ppm with the residual undeuterated solvents as the internal standards. Coupling constants (*J*) are given in Hz. UV/Vis spectra were recorded on Varian Cary 50 Bio. Electrospray-ionization time-of-flight-resolution mass spectrometric (ESI-TOF-HRMS) experiments were conducted on an Agilent 6210 ESI-TOF mass spectrometer. Electrospray-ionization Fourier-transforn ion-cyclotron-resonance mass spectrometry (ESI-FTICR-MS) and tandem mass spectrometric (MS/MS) experiments were done on a Varian/IonSpec QFT-7 instrument. In both cases, aqueous solutions of the complexes were sprayed into the ion sources. For MS/MS experiments, the ion of interest was mass-selected in the FTICR analyzer cell and fragmented in infrared multiphoton dissociation (IRMPD) experiments by irradiation with a CO_2 laser (0 - 25W, 10.6 μm).

1.2. Synthetic procedures.

((6-Bromonaphthalene-2-yl)oxy)triisopropylsilane (1):



This compound was prepared according to a modified literature procedure.[1] To a solution of 6-bromo-2-naphthol (1.99 g, 8.95 mmol) and imidazole (0.671 g, 9.85 mmol) in dimethylformamide (DMF, 10 mL), triisopropylsilyl chloride (TIPSCl) (2.77 g, 14.39 mmol) was added dropwise at 0°C and the reaction was warmed up to room temperature. After 4 h, the DMF was removed in *vacuo* and the solid obtained was dissolved in CH_2Cl_2 (DCM, 100 mL) and washed with sat. aqueous NH_4Cl solution (100 × 3 mL). The organic layer was dried ($MgSO_4$), filtered, and the solvent removed in *vacuo* to give a yellow viscous liquid. The crude product was purified by flash chromatography (SiO_2, 1:6 DCM/hexane) to afford compound **1** (3.33 g, 98 %) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$), δ = 7.92 (s, 1H, H_b), 7.63 (d, J_d = 8.5, 1H, H_d), 7.56 (d, J_d = 8.7, 1H, H_a), 7.48 (d, J_d = 8.5, 1H, H_c), 7.19 (s, 1H, H_e), 7.14 (d, J_d = 8.7, 1H, H_f), 1.32 (m, 3H, H_g), 1.15 (d, J_d = 7.4, 18H, H_h); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.3, 133.2, 130.1, 129.5, 128.5, 128.4, 123.1, 117.3, 114.6, 18.0, 12.8; ESI-TOF-HRMS: *m/z* calcd for $[M-H]^+$ $C_{19}H_{28}BrOSi$, 379.1093; found, 379.1102.

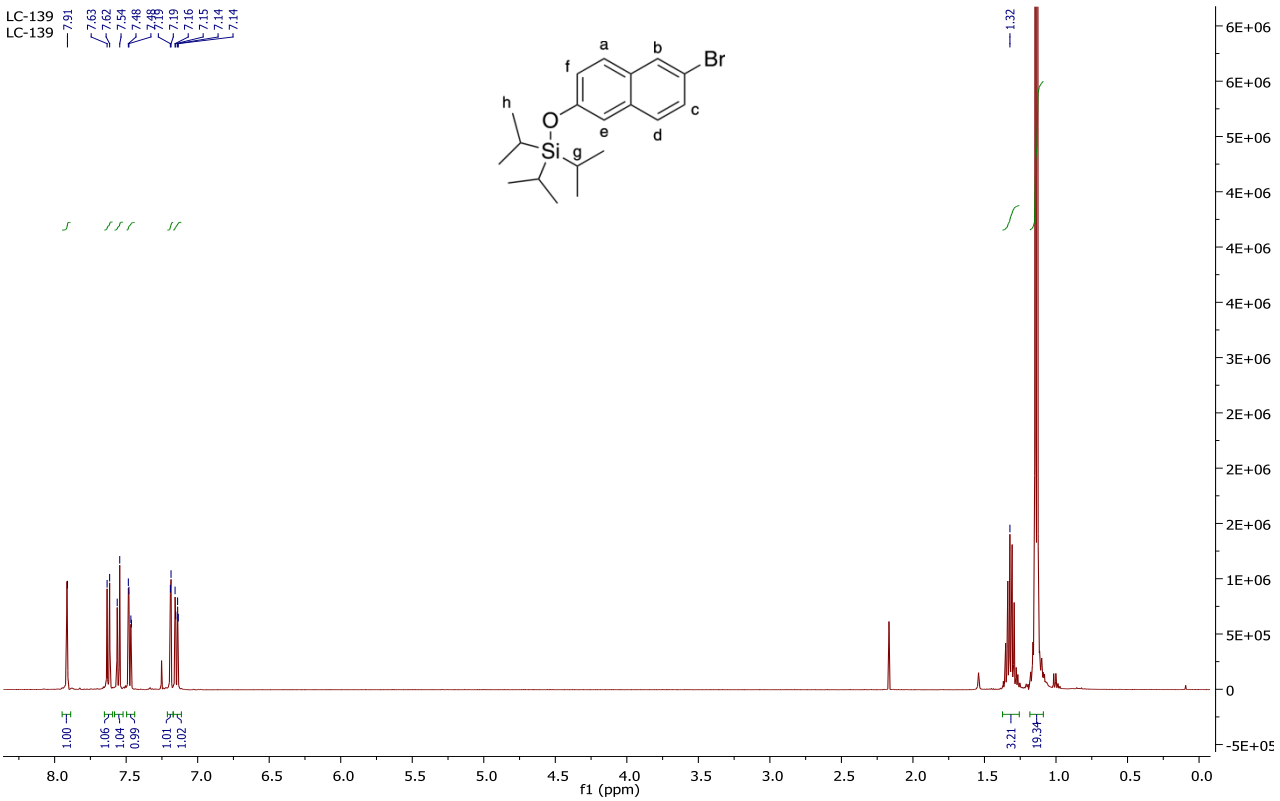


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1**.

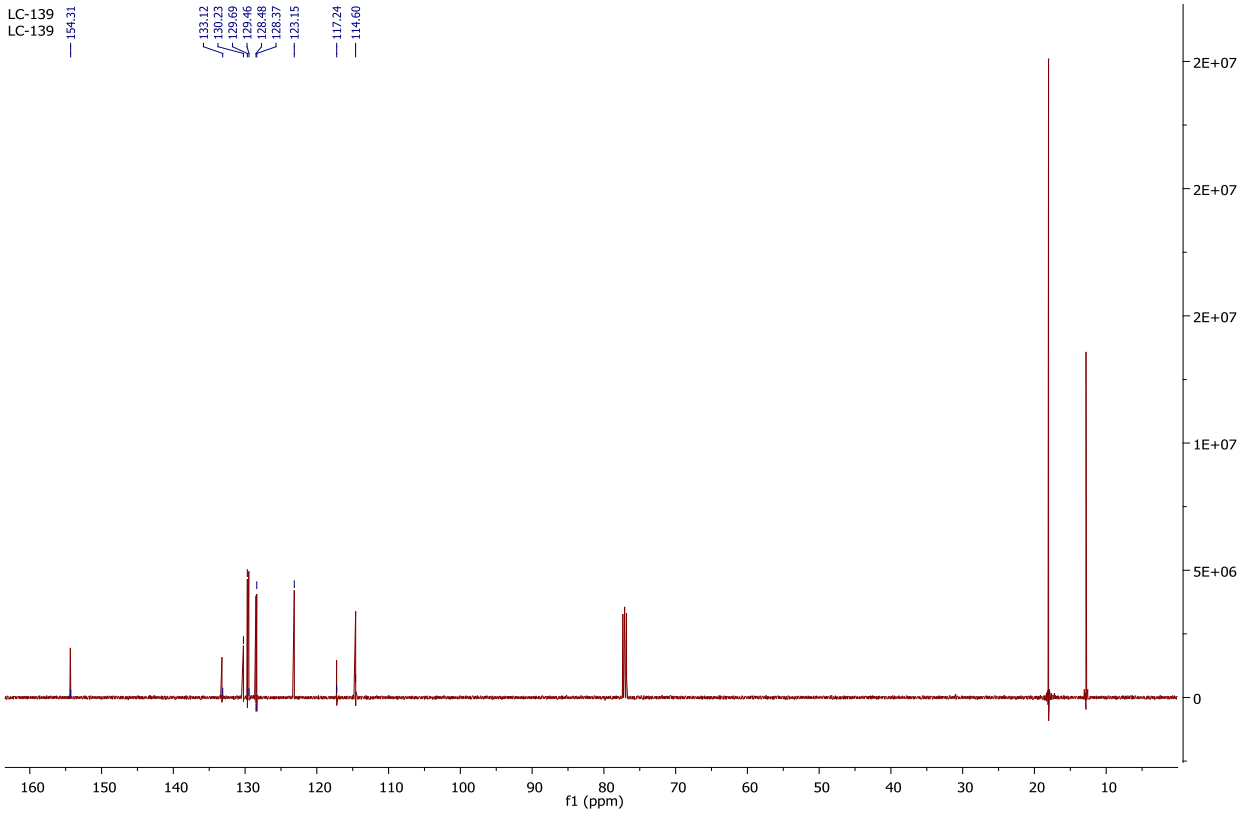
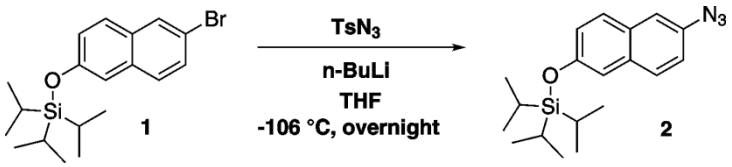


Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1**.

((6-Azidonaphthalene-2-yl)oxy)triisopropylsilane (2):



This compound was prepared according to a modified literature procedure.[2] Under N_2 atmosphere, a solution of **1** (2.50 g, 6.61 mmol) in anhydrous tetrahydrofuran (THF) (40 ml) was cooled to -106 °C and 3.00 mL of *n*-BuLi (2.5M, in hexane, 7.50 mmol) was added dropwise over a period of 10 min. After 1 h of stirring at -106 °C, a solution of tosyl azide (1.58 g, 9.03 mmol) in anhydrous THF (10 mL) was added and the reaction was allowed to warm to room temperature and stirred for other 20 h. The solvent was removed in *vacuo* and the orange solid obtained was dissolved in ethylacetate (EtOAc. 100 mL) and washed with brine (100 × 2 mL). The organic layer was dried ($MgSO_4$), filtered, and the solvent removed in *vacuo* to give an orange oil. The crude product was purified by flash chromatography (SiO_2, 1:4 DCM/hexane) to afford azide **2** (1.69 g, 77%) as an orange viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$), δ = 7.66 (d, J_d = 8.8, 1H, H_d), 7.63 (d, J_d = 8.8, 1H, H_a), 7.37 (s, 1H, H_b), 7.19 (s, 1H, H_e), 7.14 (d, J_d = 8.8, 1H, H_f),7.10 (d, J_d = 8.8, 1H, H_c), 1.30 (m, 3H, H_g), 1.13 (d, J_d = 7.4, 18H, H_h); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 135.4, 132.4, 129.5, 128.6, 128.3, 123.2, 119.0, 115.8, 18.0, 12.8; ESI-TOF-HRMS: *m/z* calcd for $[M+H]^+$ $C_{19}H_{28}N_3OSi$, 342.2002; found, 342.2056.

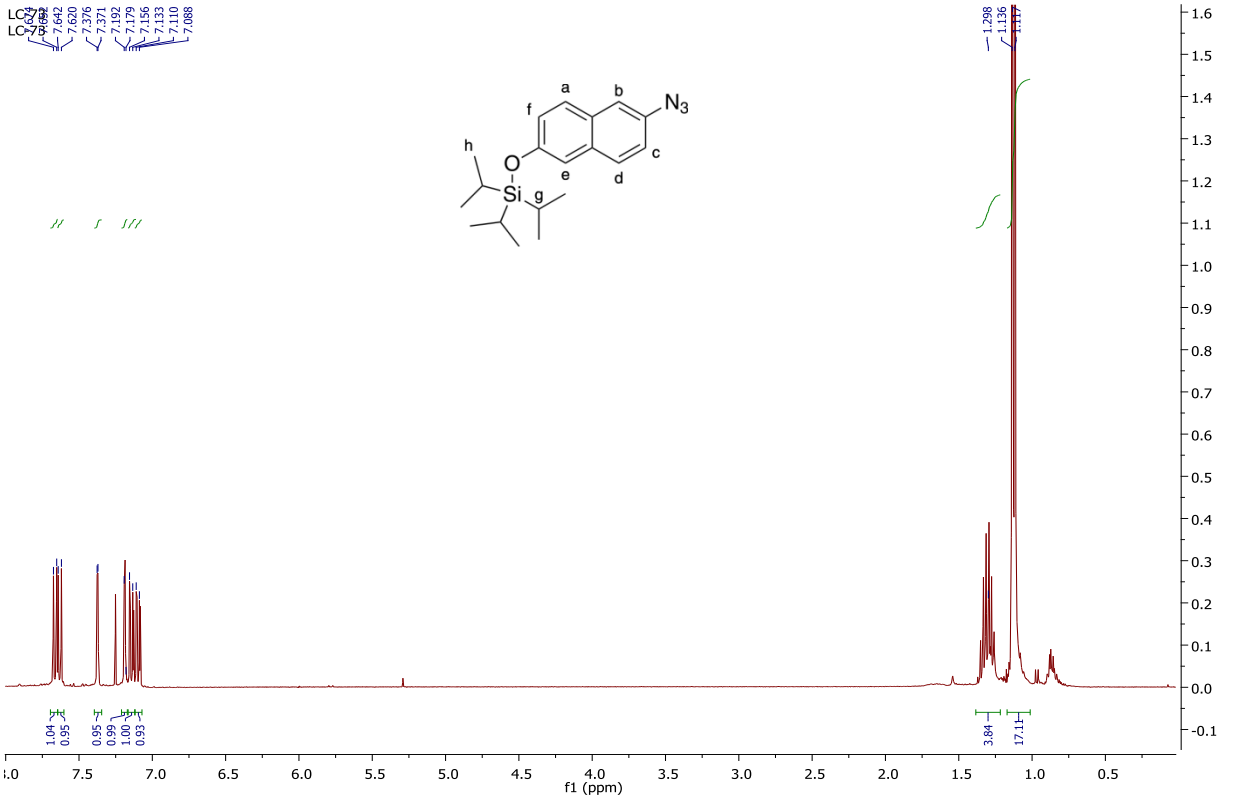


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2**.

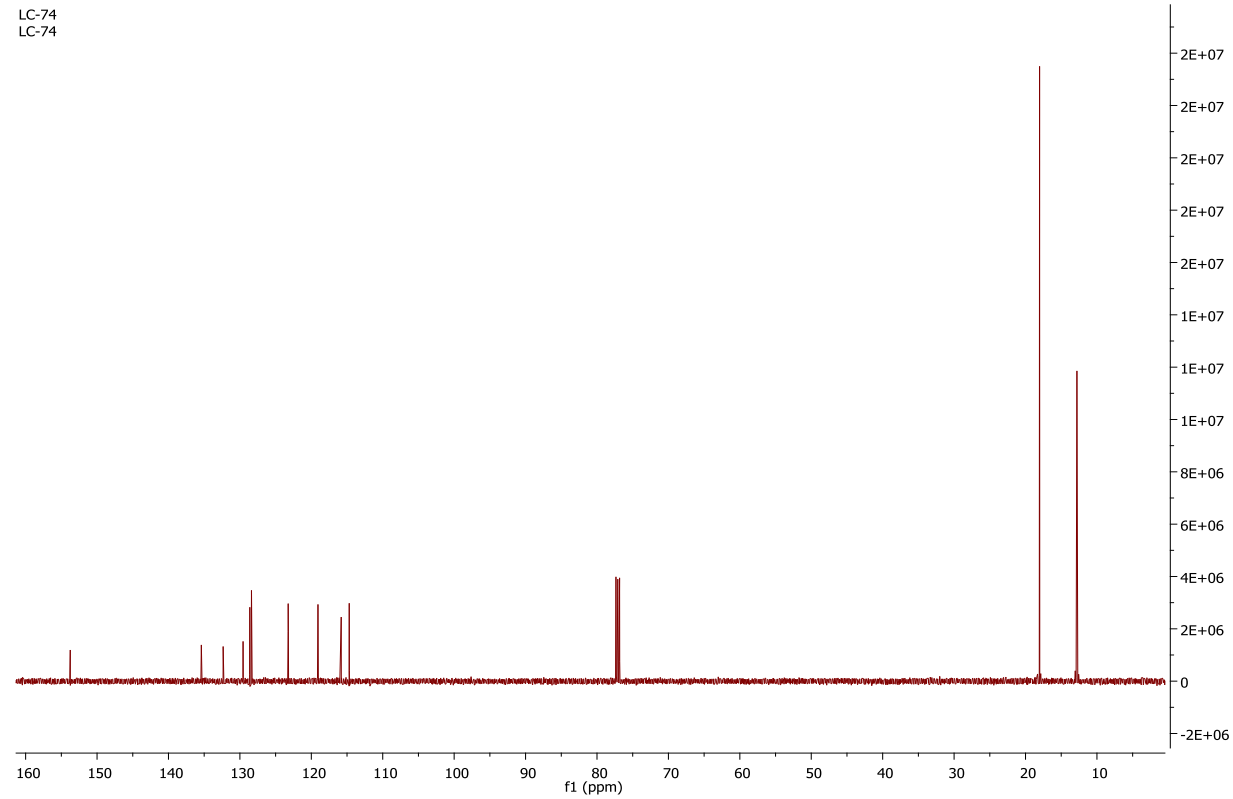
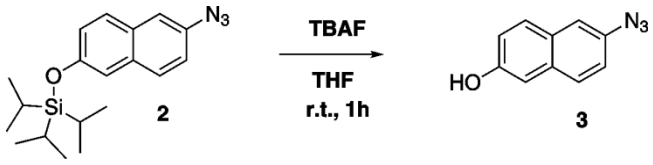


Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **2**.

6-Azido-2-naphthol (3):



This compound was prepared according to a modified literature procedure.[2] To a solution of **2** (168 mg, 0.49 mmol) in THF (12 mL), a solution of tetrabutylammonium fluoride (TBAF) (156 mg, 0.59 mmol) in THF (0.7 mL) was added dropwise at 0° C and the reaction was warmed to room temperature and stirred for 1 h. The reaction was diluted with sat. aqueous NH_4Cl solution (50 mL), extracted with EtOAc (50 × 3 mL) and the combined organic layer were dried ($MgSO_4$), filtered and the solvent removed in *vacuo* to give a green oil. The crude product was purified by flash chromatography (SiO_2, 1:5 EtOAc/hexane) to afford **3** (11mg, 12 %) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$), δ = 7,55 (d, J_d = 8.4, 1H, $H_{d,}$), 7.43 (d, J_d = 9.4, 1H, $H_{,a}$), 7.27 (s, 1H, H_b), 7.08-7.05 (m, 2H, $H_{c,e}$), 7.00 (d, J_d = 9.2, 1H, H_f).

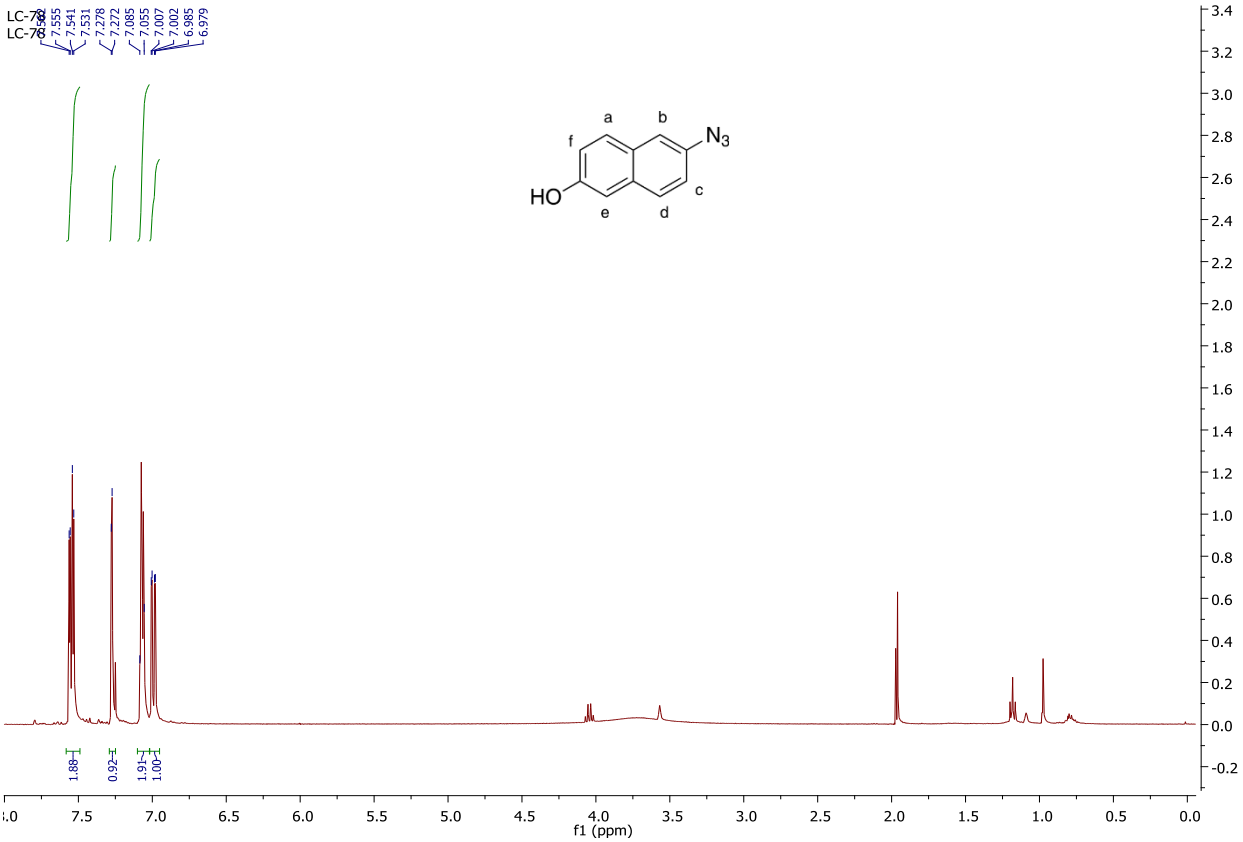
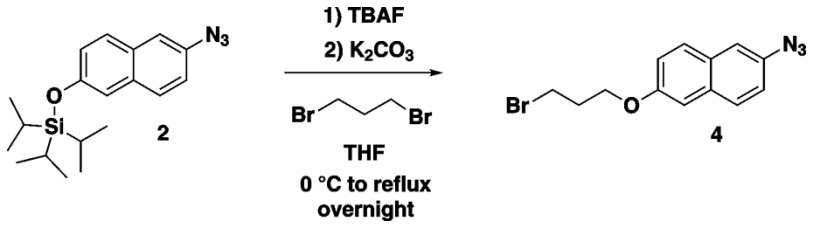


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **3**.

2-Azido-6-(3-bromopropoxy)naphthalene (4):



This compound was prepared according to a modified literature procedure.[1,3] To a solution of **2** (496 mg, 1.45 mmol) in THF (5 mL), a solution of TBAF (416 mg, 1.59 mmol) in THF (2 mL) was added dropwise at 0° C and then the reaction was warmed to room temperature and stirred for 15 min. K_2CO_3 (501 mg, 3.62 mmol) was added to the red solution and dibromopropene (7.3 mmol 0.75 mL) was added dropwise to the suspension. After refluxing the reaction mixture for 20 h, it was diluted with H_2O (50 mL) and extracted with DCM (50 × 3 mL) and the combined organic layer were dried ($MgSO_4$), filtered and the solvent removed in *vacuo* to give a red oil. The crude product was purified by flash chromatography (SiO_2, 1:4 DCM/hexane) to afford **4** (237 mg, 53 %) as a yellow viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$), δ = 7.70 (d, J_d = 8.8, 1H, H_a), 7.65 (d, J_d = 8.9, 1H, H_d), 7.37 (s, 1H, H_e), 7.15 (d, J_d = 8.8, 1H, H_f), 7.13-7.10 (m, 2H, $H_{b,c}$), 4.20 (t, J_t = 6.0, 2H, H_i), 3.64 (d, J_t = 6.0, 1H, H_g), 2.38 (p, J_p = 6.1, 6.2, 2H, H_h); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 135.5, 132.2, 129.6, 128.7, 128.6, 119.9, 119.3, 115.9, 107.0, 65.5, 30.1; ESI-TOF-HRMS: *m/z* calcd for $[M+H]^+$ $C_{13}H_{13}BrN_3O$, 306.0242; found, 306.0250.

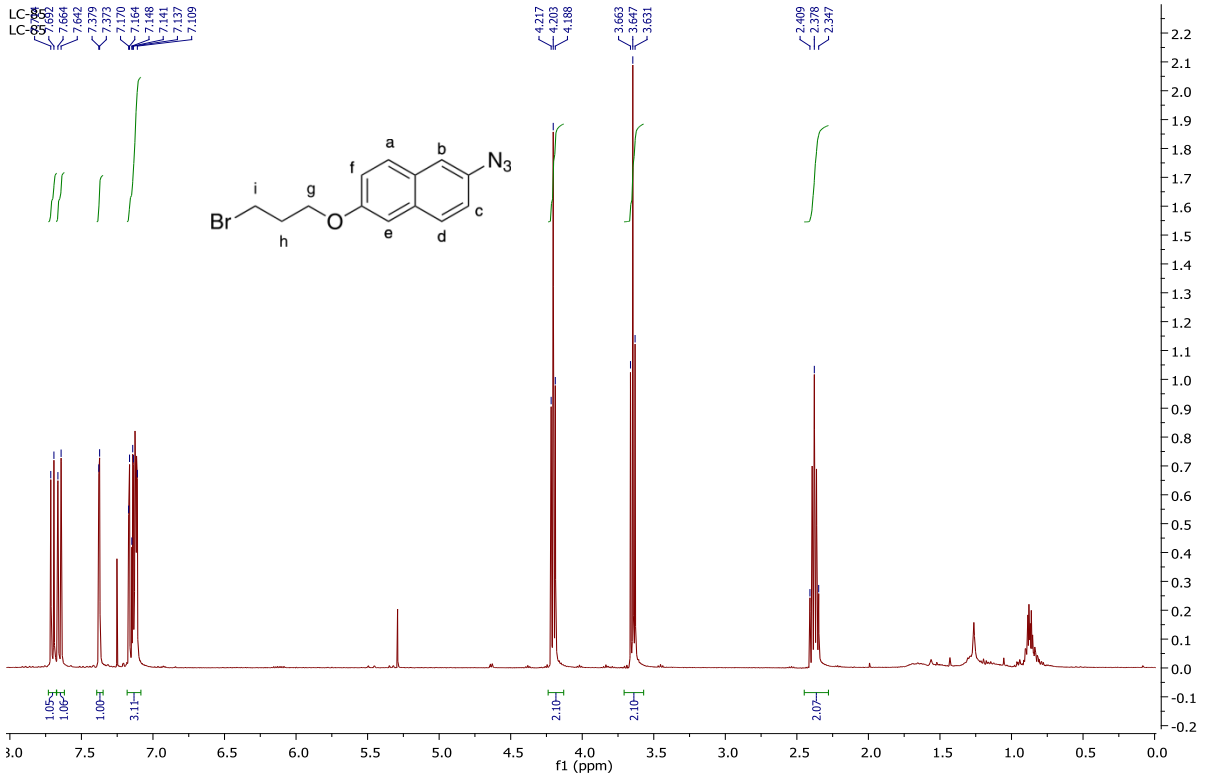


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **4**.

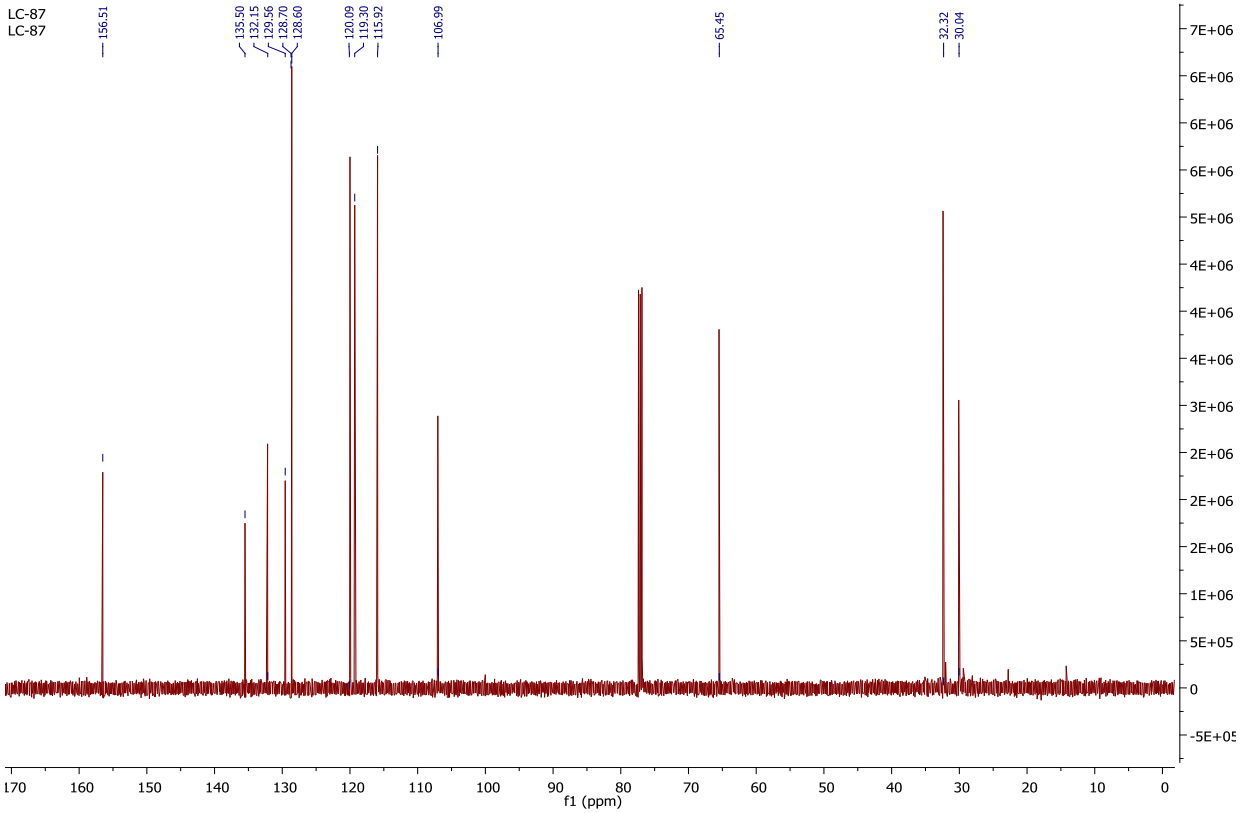
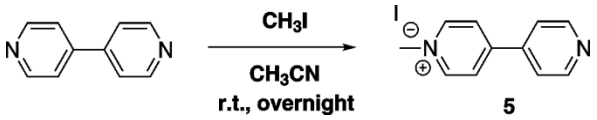


Figure S7. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **4**.

1-Methyl-[4,4'-bipyridin]-1-ium iodide (5):



This compound was prepared according to the literature procedure.[4] A solution of methyl iodide (1.25 g, 8.83 mmol) and 4,4-bipyridine (1.50 g, 9.57 mmol) in MeCN (18 mL) was stirred at room temperature for 24 h. The precipitate formed was filtered and recrystallized from EtOH (150 mL) to obtain **5** as yellow solid (2.05 g, 72%). ^{1}H NMR (400 MHz, DMSO-*d6*), δ = 9.14 (d, J_d = 7.2, 1H, H_d), 8.87 (d, J_d = 6.0, 1H, H_a), 8.62 (d, J_d = 6.4, 1H, H_c), 8.04 (d, J_d = 6.8, 1H, H_b), 4.39 (s, 3H, H_e).

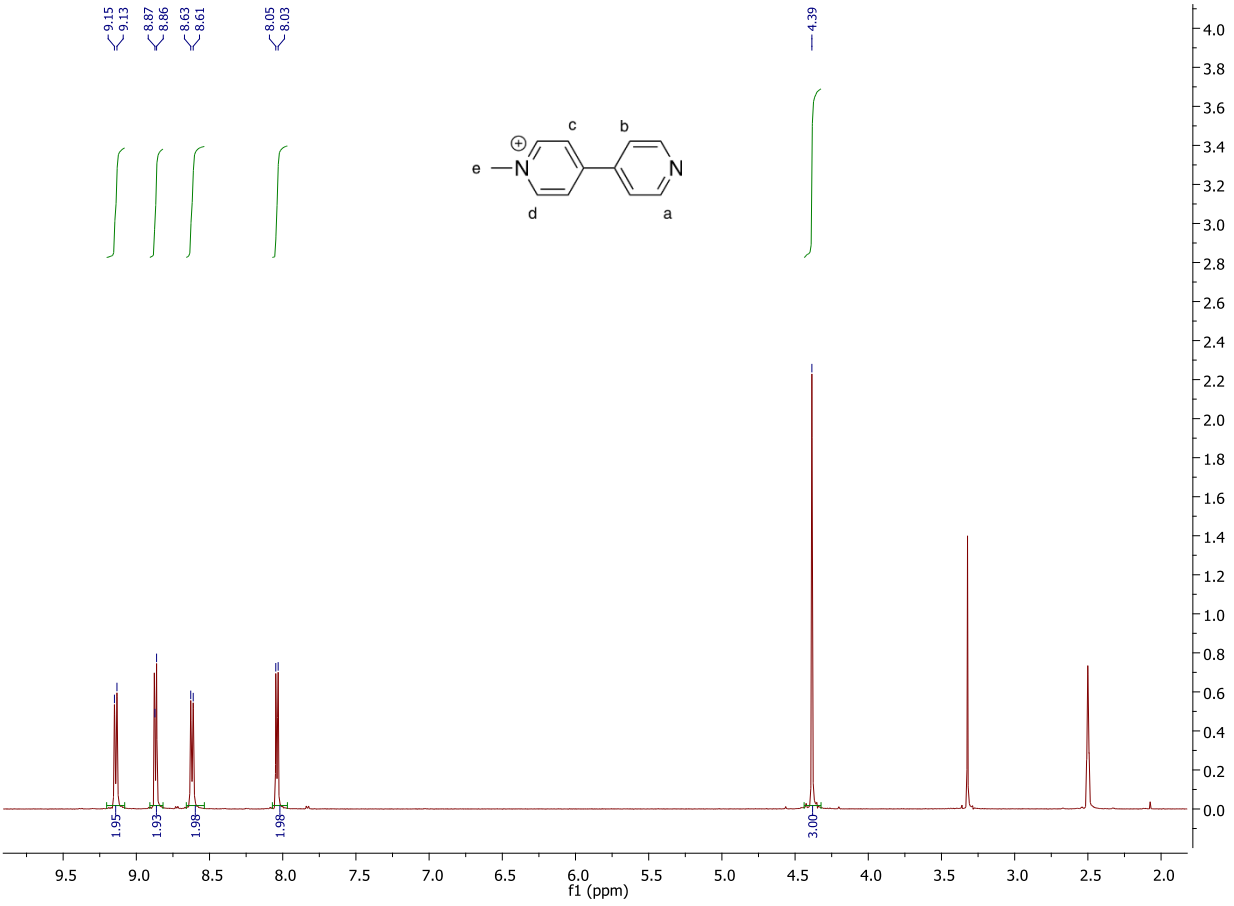
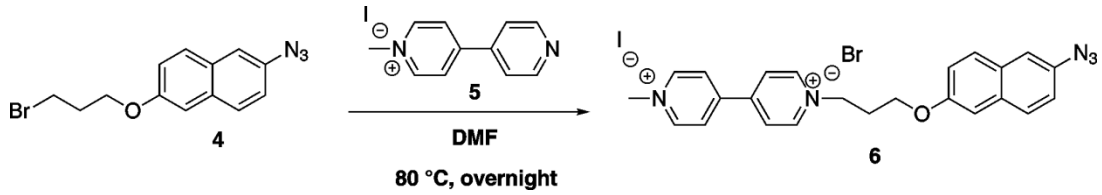


Figure S8. ^{1}H NMR spectrum (500 MHz, DMSO-*d6*, 298 K) of **5**.

1-(3-((6-Azidonaphthalene-2-yl)oxy)propyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium bromide iodide (6):



This compound was prepared according to a modified literature procedure.[5] A solution of **5** (738 mg, 2.41 mmol) and **4** (683 mg, 2.28 mmol) in DMF (8 mL) was stirred for 48 h at 80 °C. DMF was removed in *vacuo*, the solid was suspended in acetonitrile (MeCN) and the desired product **6** was obtained as an orange solid by filtration (1.15 g, 83%): IR (cm^{-1}) 2105.9, 1636.3, 1590.4; m.p. > 250 °C; ^{1}H NMR (500 MHz, DMSO-*d6*), δ = 9.52 (d, J_d = 4.5, 2H, H_j), 9.33 (d, J_d = 5.5, 2H, H_m), 8.83 (d, J_d = 5.5, 2H, H_k), 8.80 (d, J_d = 5.2, 2H, H_l), 7.84 (d, J_d = 9.1, 1H, H_a), 7.77 (d, J_d = 9.0, 1H, H_d), 7.38 (s,1H, H_e), 7.32 (s,1H, H_b),7.21 (d, J_d = 9.1, 1H, H_f), 6.97 (d, J_d = 9.5, 1H, H_c), 4.97 (t, J_t = 6.0, 2H, H_i), 4.47 (s, 3H, H_n), 4.26 (m, 2H, H_g), 2.58 (m, 2H, H_h); ^{13}C NMR (125 MHz, DMSO-*d6*): δ = 156.2, 149.2, 148.7, 147.2, 146.7, 135.3, 132.3, 129.6, 129.3, 129.0, 126.9, 126.6, 119.9, 119.8, 116.3, 107.6, 65.5, 59.3, 48.62, 30.50; ESI-FTICR-HRMS: *m/z* calcd for $[M-I-Br+CB[8]]^{2+}$ $C_{72}H_{70}N_{37}O_{17}$, 862.7909; found, 862.7937.

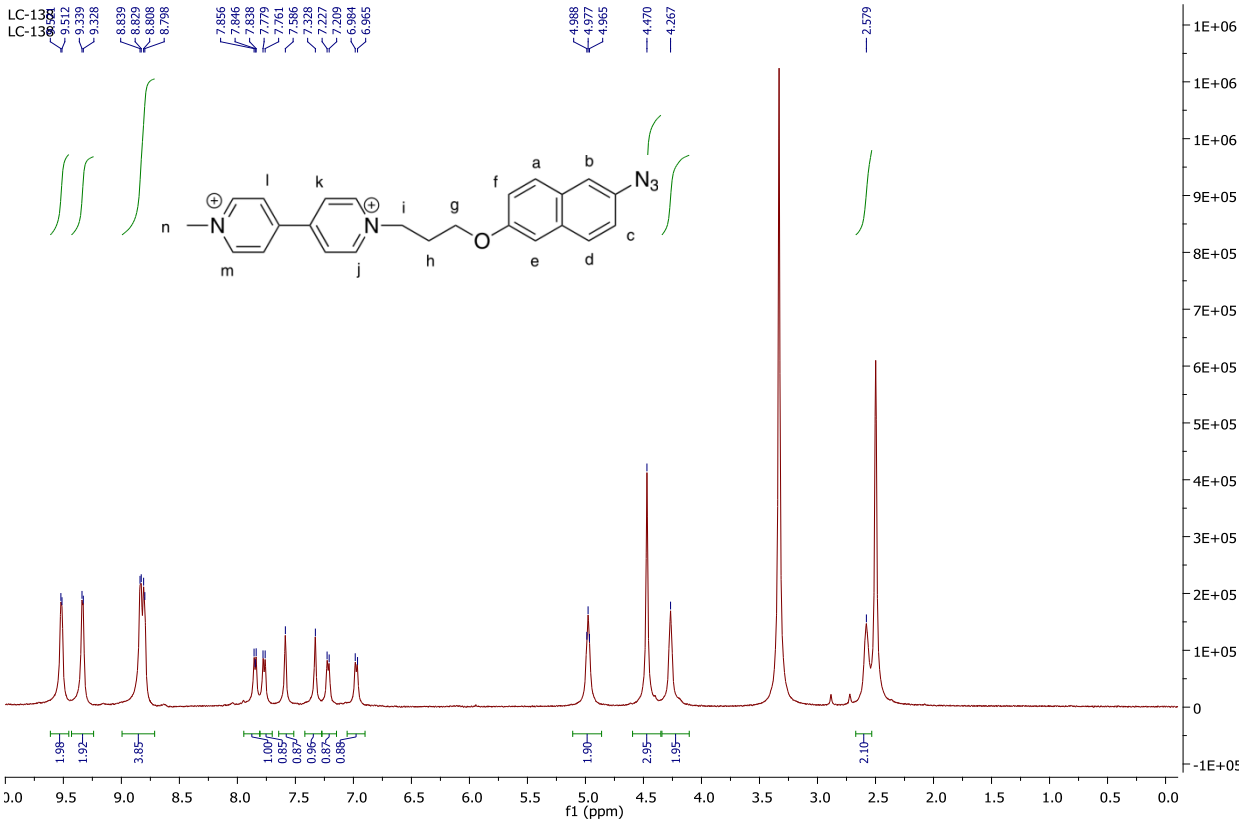


Figure S9. ^{1}H NMR spectrum (500 MHz, DMSO-*d6*, 298 K) of **6**.

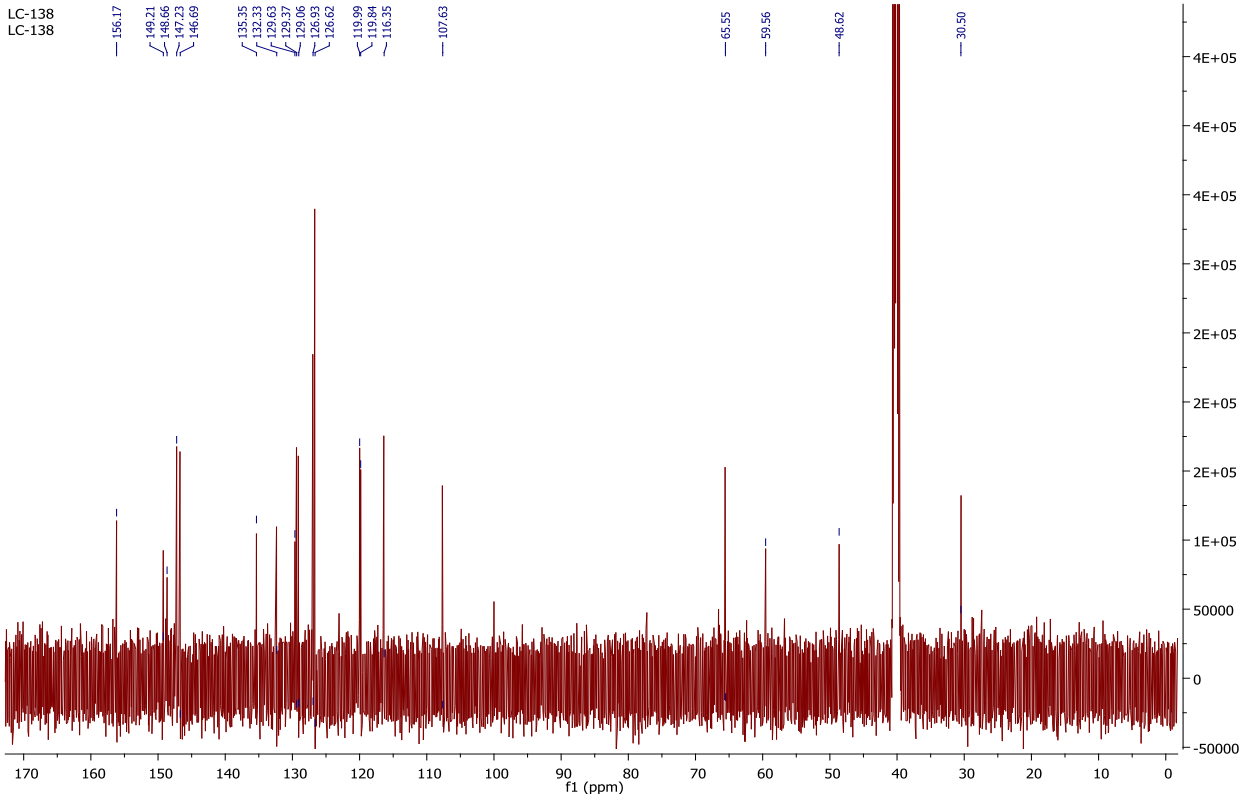
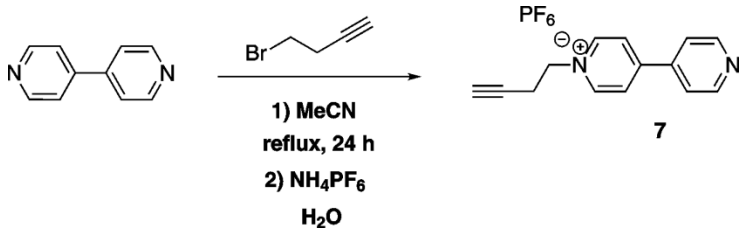


Figure S10. ^{13}C NMR spectrum (125 MHz, DMSO-*d6*, 298 K) of **6**.

1-(But-3-yn-1-yl)-[4,4'-bipyridin]-1-ium hexafluorophosphate (7):



This compound was prepared according to a modified literature procedure.[6] A solution of 4-bromobut-1-yne (0.901 g, 6.77 mmol) and 4,4-bipyridine (1.05 g, 6.75 mmol) in MeCN (12 mL) was refluxed for 24 h. The precipitate formed was filtered, washed with MeCN (3 × 10 mL) and then dissolved in H_2O (8 mL). After the addition of a sat. aqueous solution of NH_4PF_6 (3 mL), the precipitate formed was collected by filtration and washed with cold H_2O to afford **7** (714 mg, 65%) as colorless solid: ^{1}H NMR (500 MHz, d6-DMSO), δ = 9.31 (d, J_d = 7.1, 2H, H_d), 8.86 (d, J_d = 6.2, 2H, H_a), 8.71 (d, J_d = 7.1, 2H, H_c), 8.07 (d, J_d = 6.0, 2H, H_b), 4.83 (t, J_t = 6.5, 2H, H_e), 3.09 (t, J_t = 2.5, 1H, H_g), 3.03 (dt, J_t, = 6.5, J_t, = 2.5, 2H, H_f); ^{13}C NMR (125 MHz, DMSO-*d6*): δ = 153.3, 151.6, 146.1, 141.5, 125.8, 122.5, 79.6, 75.6, 58.7, 20.8; ESI-FTICR-HRMS: *m/z* calcd for $[M\text{-}PF_6+H+CB[8]]^{2+}$ $C_{56}H_{56}N_{30}O_{14}$, 686.2291; found, 686.2298.

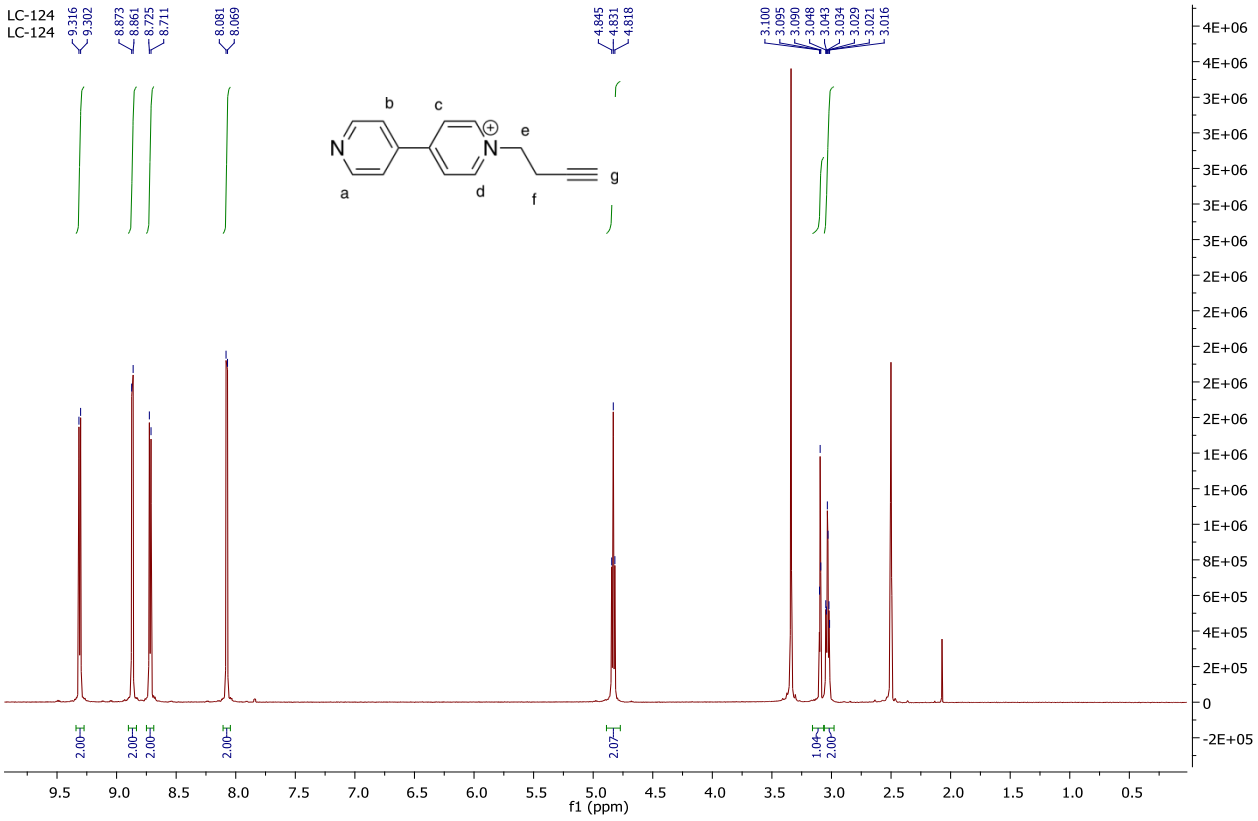


Figure S11. ^{1}H NMR spectrum (500 MHz, DMSO-*d6*, 298 K) of **7**.

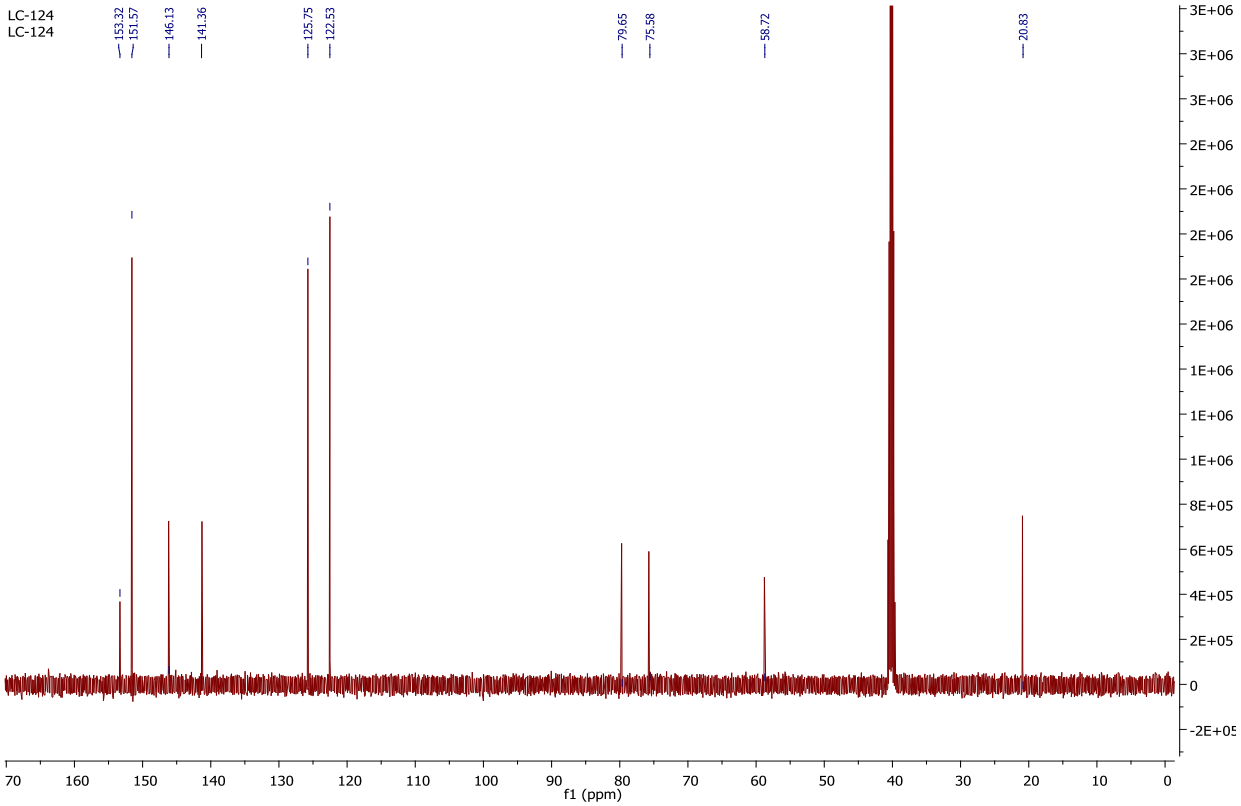
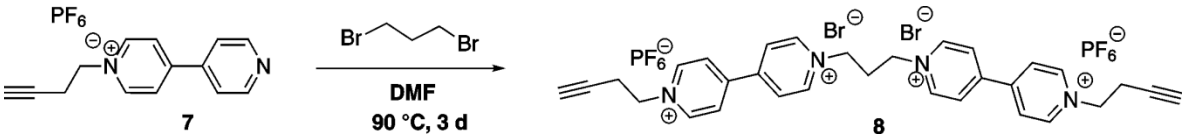


Figure S12. ^{13}C NMR spectrum (125 MHz, DMSO-*d6*, 298 K) of **7**.

1',1'''-(Propane-1,3-diyl)bis(1-(but-3-yn-1-yl)-[4,4'-bipyridin]-1,1'-diium) dibromide bis(hexafluorophosphate) (8):



This compound was prepared according to the modified literature procedure.[3] A solution of **7** (470 mg, 0.66 mmol) and 1,3-dibromopropane (109 mg, 0.54 mmol) in DMF was stirred at 70 °C for 3 days. The precipitate was collected by filtration and washed with MeCN (2 × 7 mL) to afford the desired product **8** (714 mg, 65%) as a pale yellow solid: m.p. > 250 °C; ^{1}H NMR (500 MHz, d6-DMSO), δ = 9.41 (s, 8H, $H_{d,a}$), 8.85 (bs, 8H, $H_{c,b}$), 4.86 (s, 8H, $H_{h,e}$), 3.09 (bs, 2H, H_g), 3.05 (bs, 4H, H_f), 2.77 (bs, 2H, H_i); ^{13}C NMR (125 MHz, DMSO-*d6*): δ = 149.1, 148.9, 146.2, 126.7, 126.4, 79.1, 75.3, 58.9, 57.7, 31.6, 20.4; ESI-FTICR-HRMS: *m/z* calcd for $[M\text{-}2PF_6\text{-}2Br+2CB[8]]^{4+}$ $C_{73}H_{74}N_{72}O_{14}$, 545.6817; found, 545.6832.

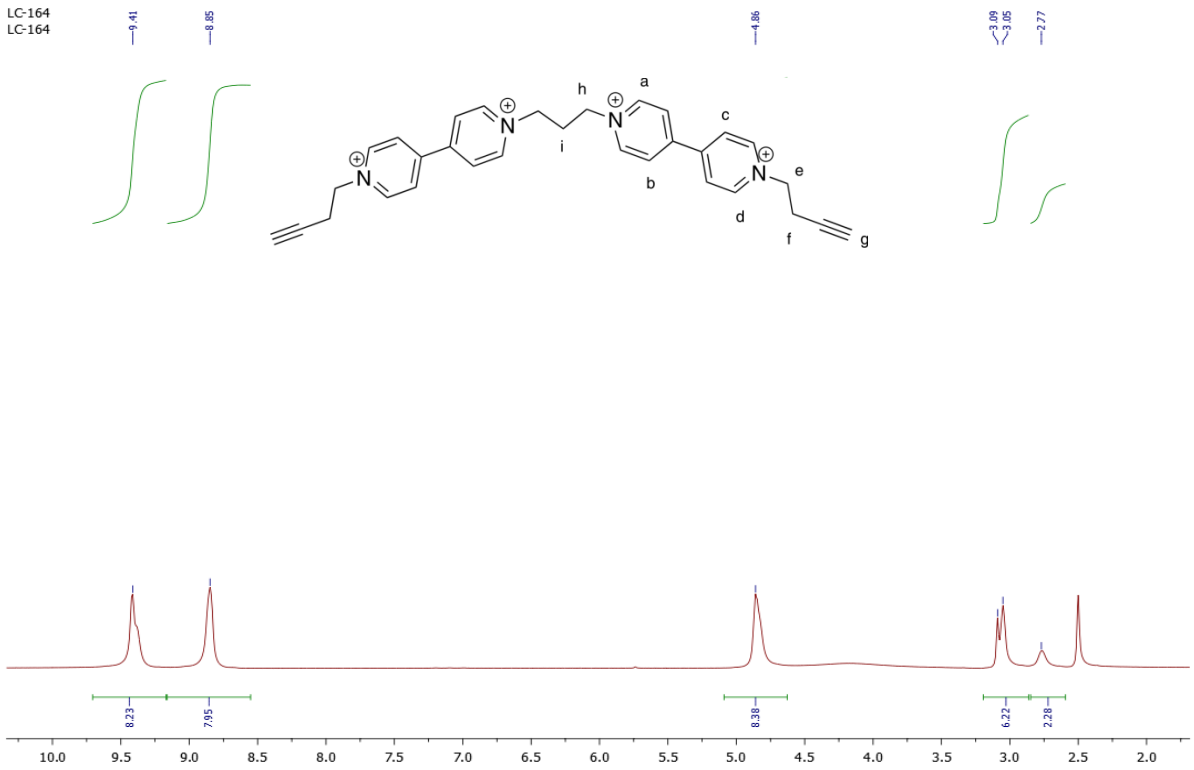


Figure S13. ^{1}H NMR spectrum (500 MHz, DMSO-*d6*, 298 K) of **8**.

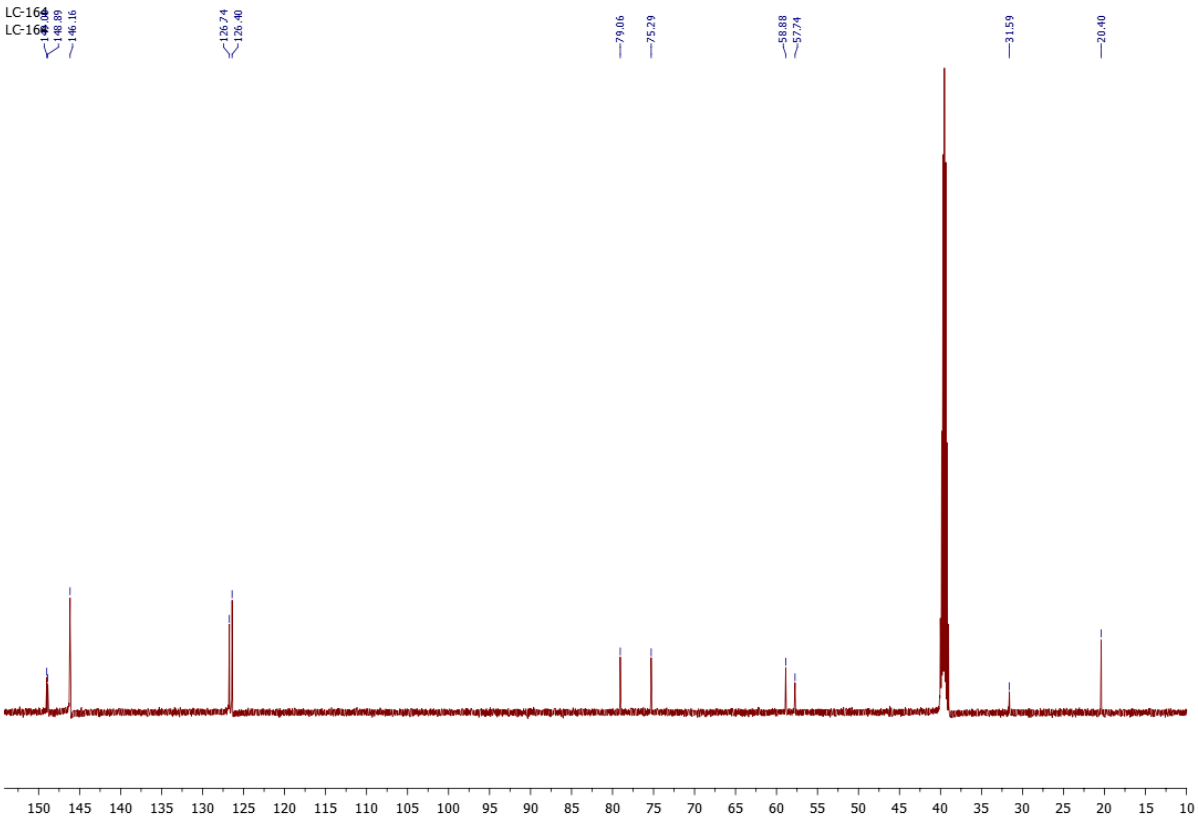
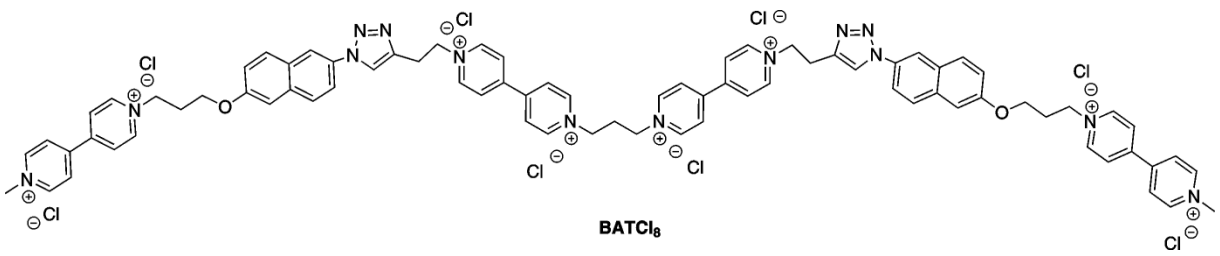


Figure S14. ^{13}C NMR spectrum (125 MHz, DMSO-*d6*, 298 K) of **8**.

BATCl$_8$:



A solution of **6** (210 mg, 3.62 × 10^{-1} mmol), tris-(benzyltriazolylmethyl) amine (TBTA) (40.1 mg, 7.25 × 10^{-2} mmol), CuI (13.8 mg, 7.24× 10^{-2} mmol) and **8** (159.1 mg, 1.74 × 10^{-1} mmol) in H_2O/DMF (1:5, 0.6 mL) was stirred at room temperature for 2 days. The solvent was removed in *vacuo* and the reddish solid obtained was washed with MeCN (3 × 3 mL) and precipitated in methanol using $HCl_{aq.}$ 37% to afford the desired product **BATCl$_8$** (166 g, 62%) as an orange solid: m.p. > 250 °C; ^{1}H NMR (700 MHz, D_2O), δ = 9.23 (d, J_d = 6.3, 2H, H_s), 9.19 (d, J_d = 6.3, 2H, H_d), 9.14 (d, J_d = 6.3, 2H, H_v), 9.02 (d, J_d = 5.6, 2H, H_a), 8.62 (d, J_d = 5.6, 2H, H_u), 8.58 (d, J_d = 5.6, 2H, H_t), 8.51 (s, 2H, $H_{triazole}$), 8.46 (d, J_d = 5.6, 2H, H_c), 8.42 (d, J_d = 5.6, 2H, H_b), 8.17 (s,1H,H_o), 7.98 (d, J_d = 8.4, 2H, H_n), 7.90 (d, J_d = 8.4, 2H, H_l), 7.81 (d, J_d = 9.1, 2H, H_m),7.35 (s, 2H, H_i), 7.11 (d, J_d = 9.1, 2H, H_h), 5.14 (t, J_t = 7.0, 4H, H_r), 5.02 (t, J_t = 7.7, 4H, H_e), 4.99 (t, J_t = 7.7, 4H, H_z), 4.48 (s, 6H, H_k), 4.41 (t, J_t = 4.9, 4H, H_g), 3.63 (t, J_t = 7.0, 4H, H_q), 2.96 (p, J_p = 7.0, 7.7, 2H, H_y), 2.71 (p, J_p = 5.6, 5.6, 4H, H_f); ^{13}C NMR (175 MHz, D_2O): δ = 156.5, 150.6, 150.4, 149.9, 149.4, 146.3, 145.8, 145.7, 142.8, 134.1, 132.3, 130.1, 128.8, 128.3, 127.4, 127.1, 126.7, 126.5, 123.2, 119.9, 119,7, 119.4, 107.2, 64.9, 61.2, 59.9, 58.3, 48.3, 31.7, 29.5, 26.9; ESI-FTICR-HRMS: *m/z* calcd for [M-8Br+4CB[7]]$^{8+}$ $C_{247}H_{246}N_{126}O_{58}$, 738.3775; found, 738.3790.

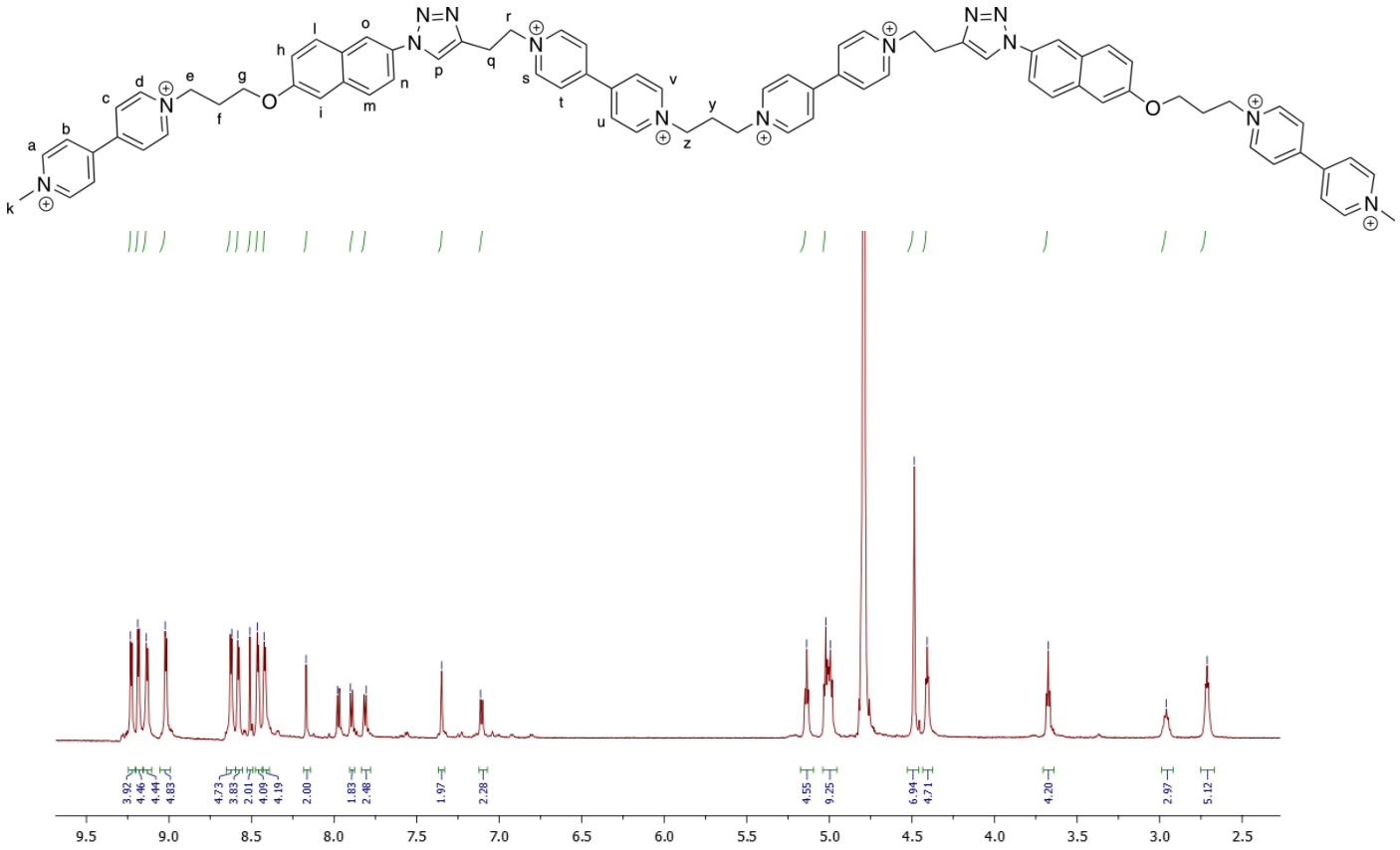


Figure S15. ^{1}H NMR spectrum (700 MHz, D_2O, 298 K) of **$BATCl_8$**.

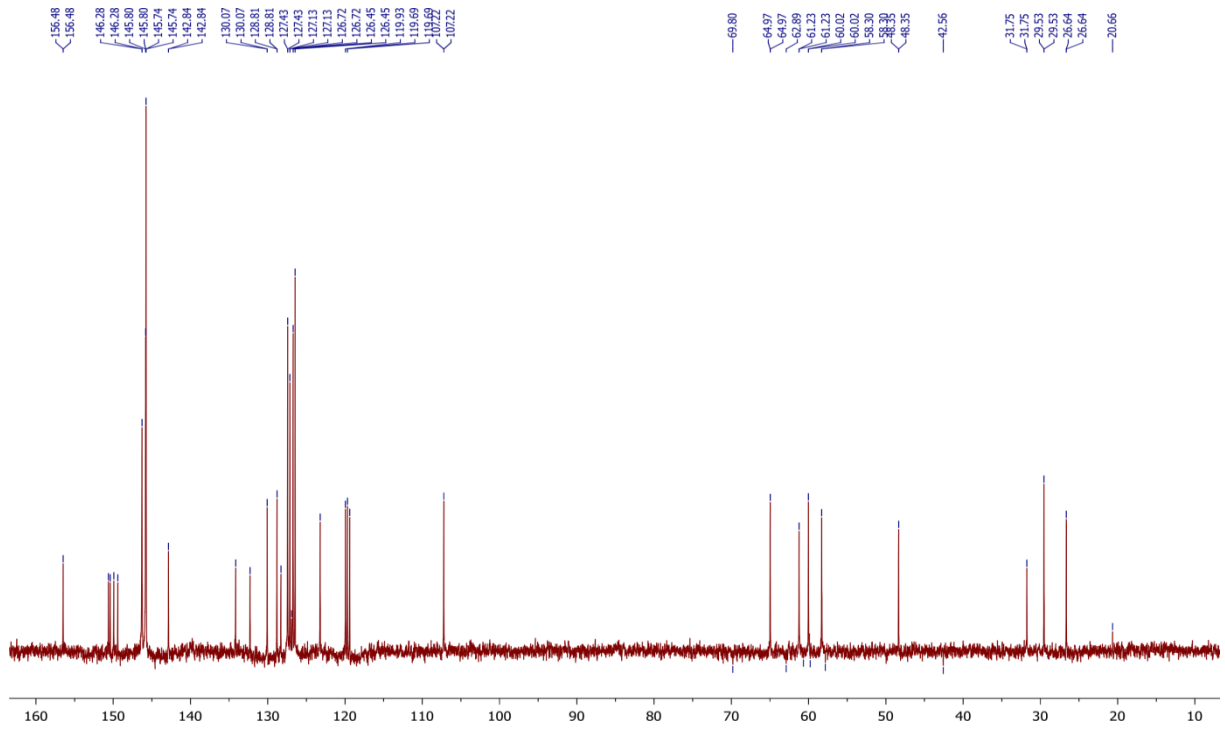


Figure S16. ^{13}C NMR spectrum (175 MHz, D_2O, 298 K) of **$BATCl_8$**.

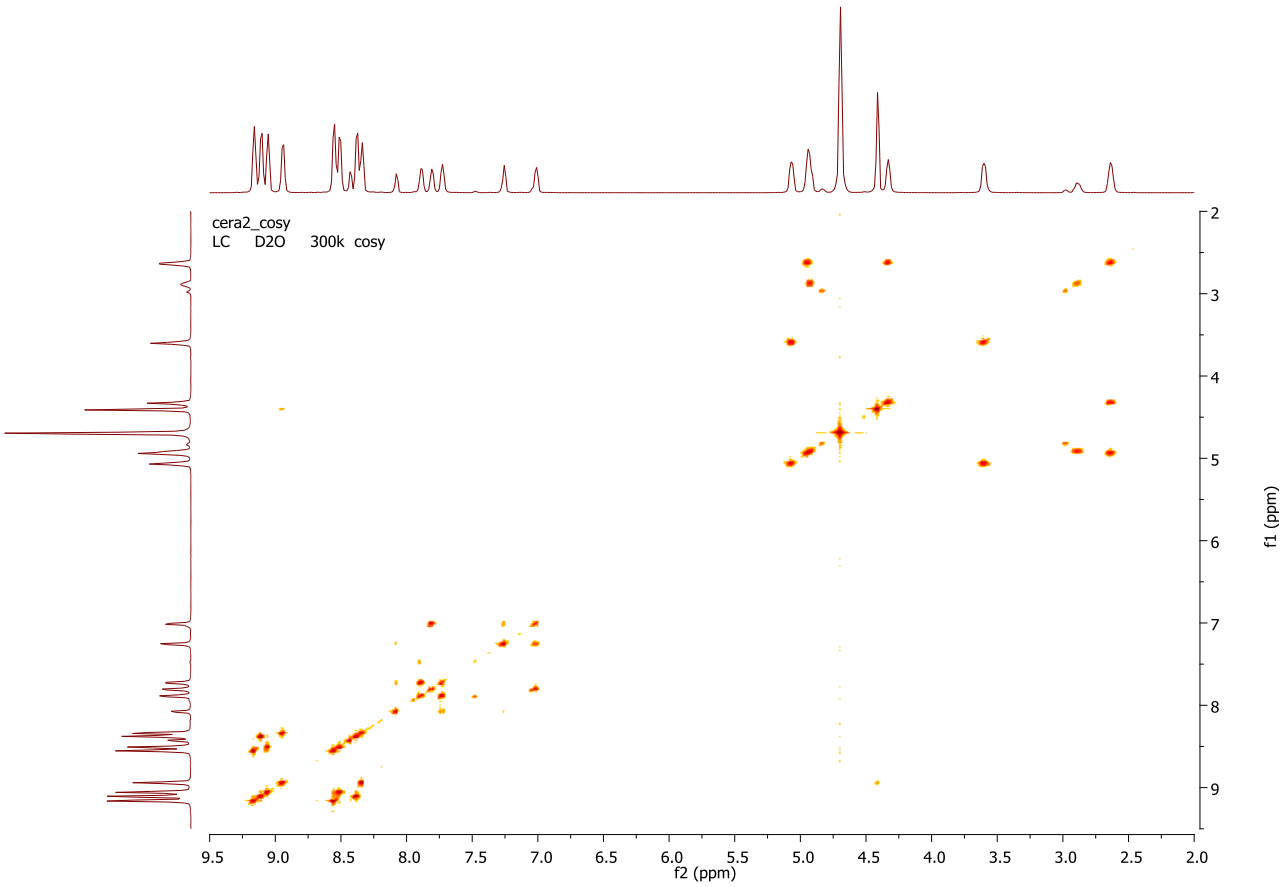


Figure S17. $^{1}H,^{1}H$ COSY NMR spectrum (700 MHz, 300 K, D_2O,) of **$BATCl_8$.**

2. NMR and MS Experiments Complementary to those in the Main Text.

2.1. *Step 1:* [**BAT@CB7$_4$**]$^{8+}$ structural information.

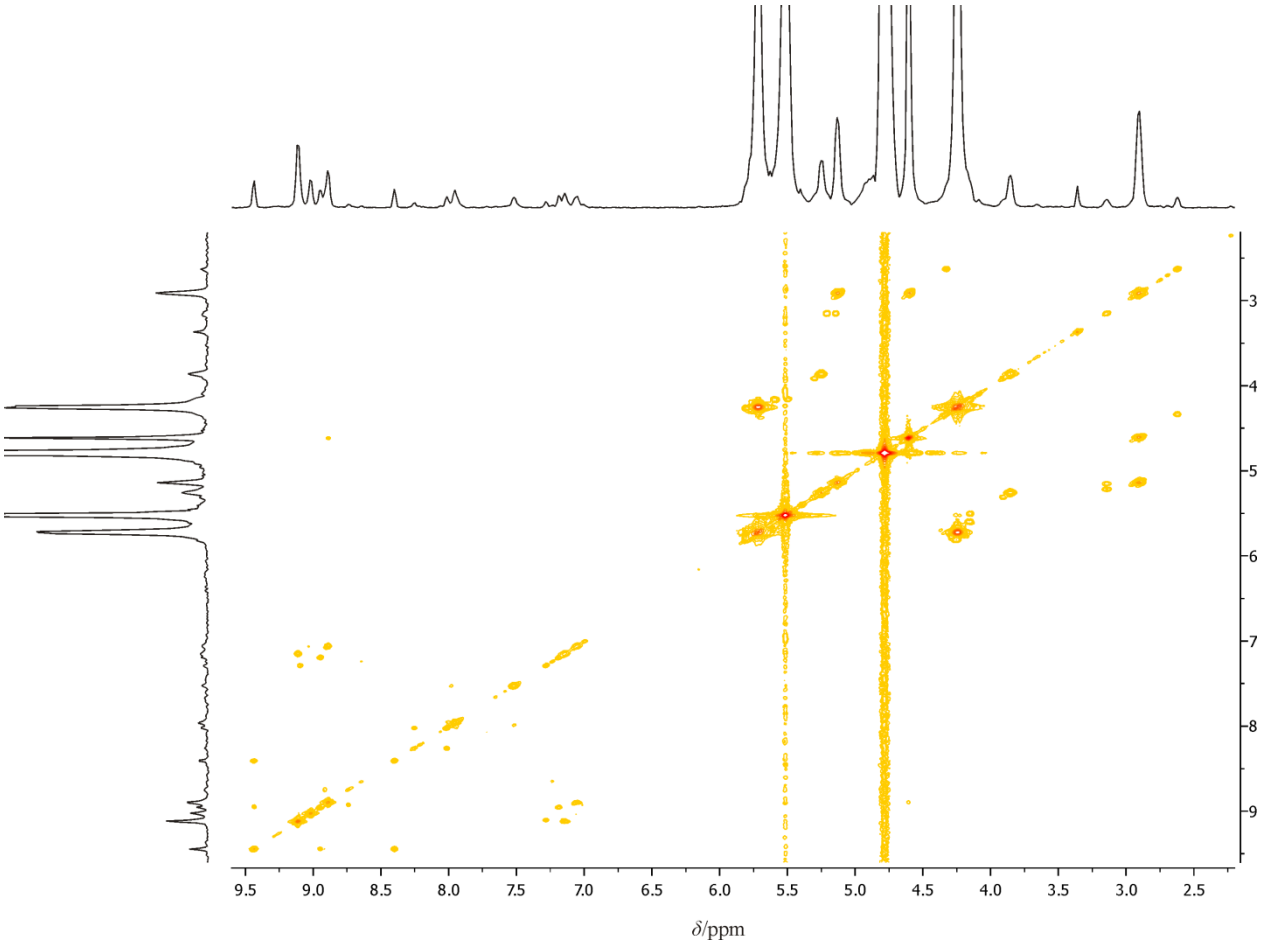


Figure S18. ^{1}H,^{1}H COSY NMR spectrum (700 MHz, 298 K, D_2O,) of a 8.57 × 10^{-1} mM water solution of **BATCl$_8$** in presence of 4 eq. of **CB7**.

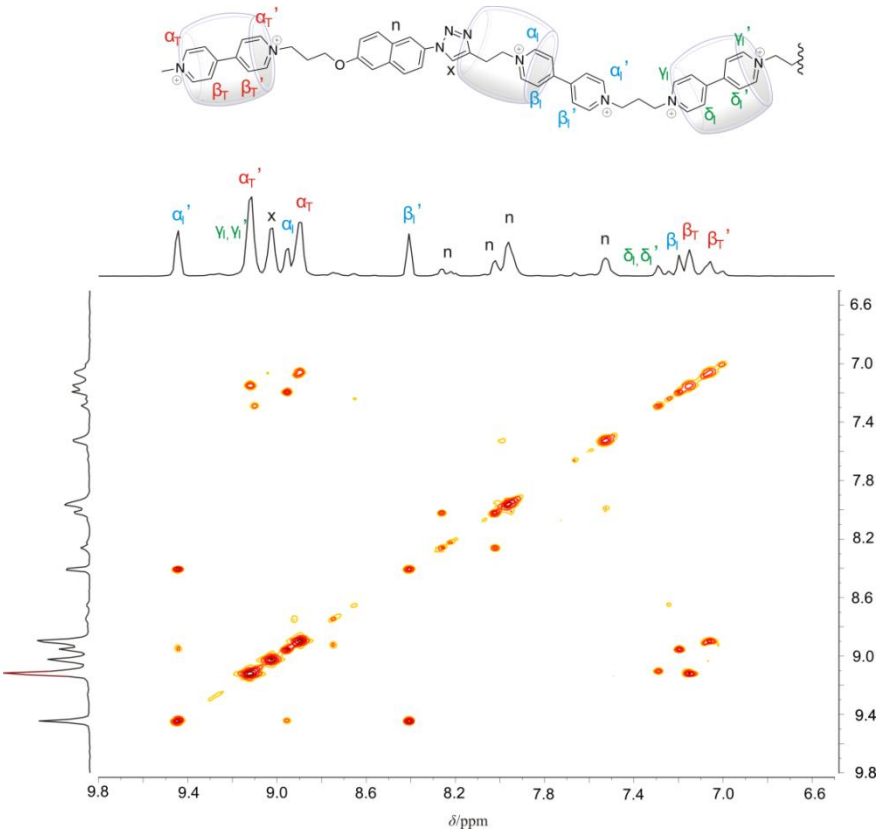


Figure S19. Zoomed in ^{1}H,^{1}H COSY NMR spectrum (700 MHz, 298 K, D_2O,) of a 8.57 × 10^{-1} mM water solution of **BATCl$_8$** in presence of 4 eq. of **CB7**. The high-field chemical shift of both protons **β_T'** and **β_T** (7.15 and 7.06 ppm) indicates that the terminal viologens are fully threaded inside the cavity of **CB7**. For the inner-viologen, instead, there are two set of signals indicating the presence of an equilibrium between two different host-guest complexes in slow exchange. In the first set of signals (protons **α_I**, **α_I'**, **β_I**, and **β_I'**,) only proton **β_I** is high field shifted (7.19 ppm) while proton **β_I'** appears at higher ppm (8.41 ppm) compared to **β_T'** and this has been already observed for a host-guest complex where the I-viologen unit is only half threated inside the cavity of **CB7**.[3] The second set of signals (protons **δ**, **δ'**, **γ** and **γ'**), instead, shows the same chemical shift trend of a fully threaded viologen since **γ** and **γ'** are at 7.28 ppm. The 0.51 ppm low-field chemical shift of the triazole proton **x** supports the hypothesis that **CB7** can form a hydrogen bond with the latter, shuttling over the aliphatic ethylene spacer and leaving the viologen unit partially unshielded.

2.2. *Step 1:* Fragmentation of [**BAT@CB7$_5$**]$^{8+}$.

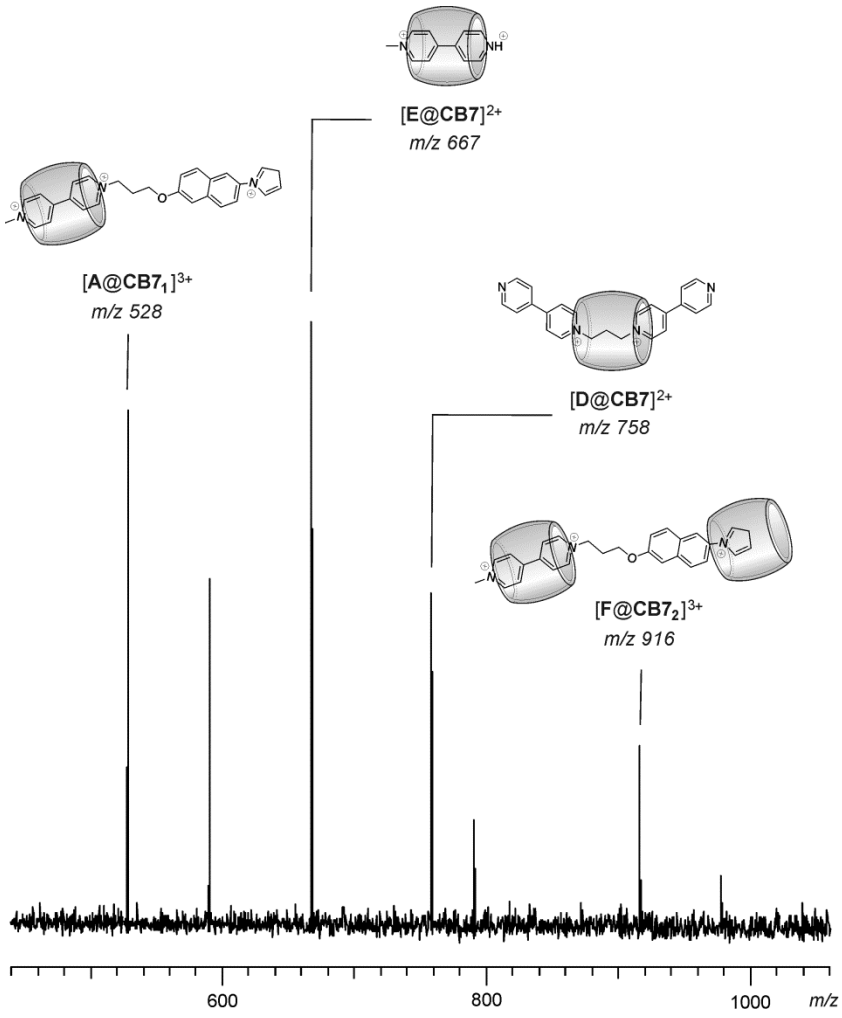


Figure S20. ESI-FTICR IRMPD mass spectrum of the isolated [**BAT@CB7$_5$**]$^{8+}$ parent ion (884 *m/z*). The dissociation experiment only leads to the formation of the same fragments also observed for [**BAT@CB7$_4$**]$^{8+}$: No fragments specific for a complex [**BAT@CB7$_5$**]$^{8+}$ are detected. Therefore, we conclude that [**BAT@CB7$_5$**]$^{8+}$ is an unspecific complex between [**BAT@CB7$_4$**]$^{8+}$ and a very weakly bound **CB7**, which dissociates from the parent ion before any other fragmentation reaction begins to compete. The pyrrolium ion structure in [**A@CB7**]$^{3+}$ and [**F@CB7**]$^{3+}$ was assigned based on exact mass differences (Δm = 28.012 corresponding to an N_2 rather an C_2H_4 loss). For such a reaction of triazoles, literature precedents exist.[7]

2.3. *Step 2:* **[BAT@CB7$_2$·CB8$_2$]$^{8+}$** structural information.

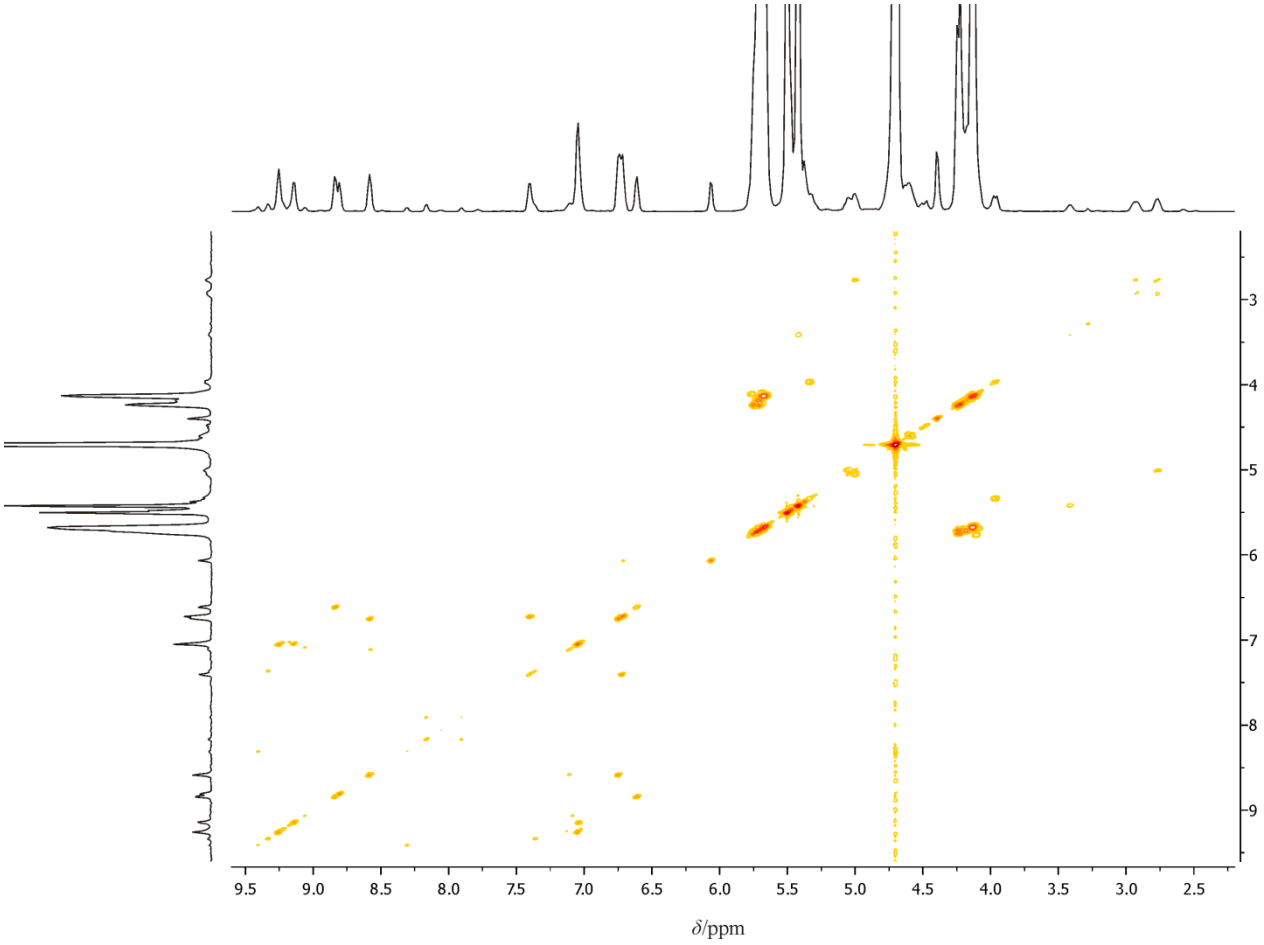


Figure S21. ^{1}H,^{1}H COSY NMR spectrum (700 MHz, 298 K, D_2O,) of a 8.57 × 10^{-1} mM water solution of **BATCl$_8$** in presence of 4 eq. of **CB7** and 2 eq. of **CB8**.

2.4. *Step 3:* using Zn as reducing agent.

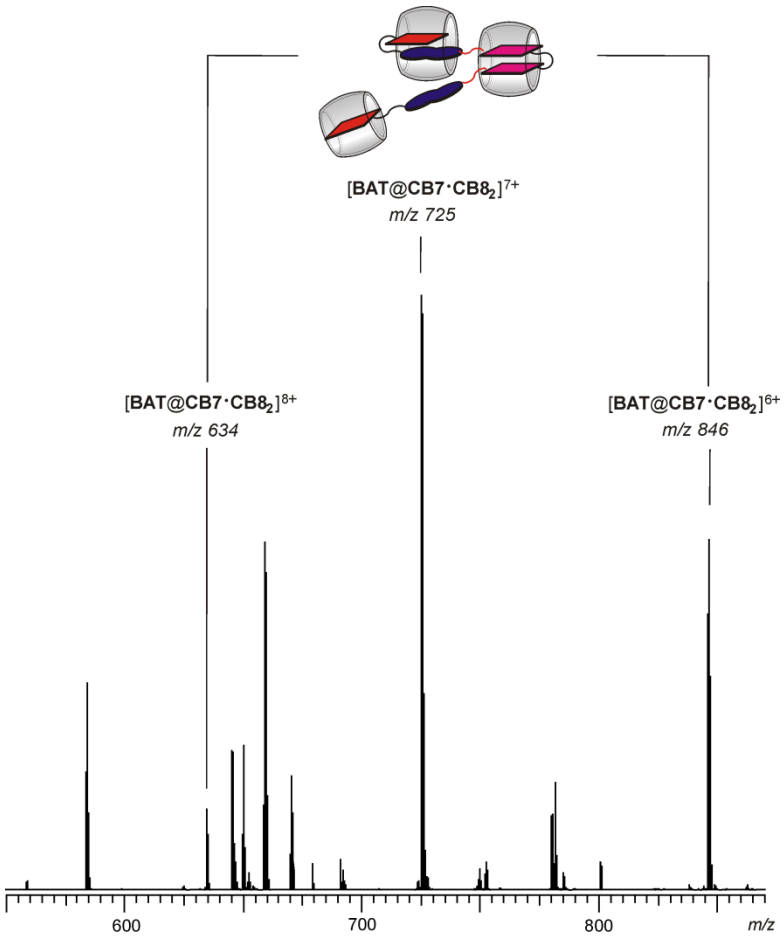


Figure S22. ESI-FTICR mass spectrum of a 8.57 × 10^{-1} mM water solution of **BATCl$_8$** in presence of 4 eq. of **CB7**, 2 eq. of **CB8** and Zn as the reducing agent. The mass spectrum shows only the partial reduction of [**BAT@CB7$_2$·CB8$_2$**]$^{8+}$ to give [**BAT@CB7·CB8$_2$**]$^{6+}$. Its oxidized derivatives [**BAT@CB7·CB8$_2$**]$^{7+}$ and [**BAT@CB7·CB8$_2$**]$^{8+}$ are very likely formed by reoxidation during the electrospray process as a sample solution of **BAT^{8+}**, 4 eq. of **CB7** and 2 eq. of **CB8** only generates [**BAT@CB7$_2$·CB8$_2$**]$^{8+}$, but none of these complexes. Therefore, the reduction with Zn leads only to a double, but not a fourfold reduction of the guest chain.

2.5. *Step 3:* using $Na_2S_2O_4$ as the reducing agent.

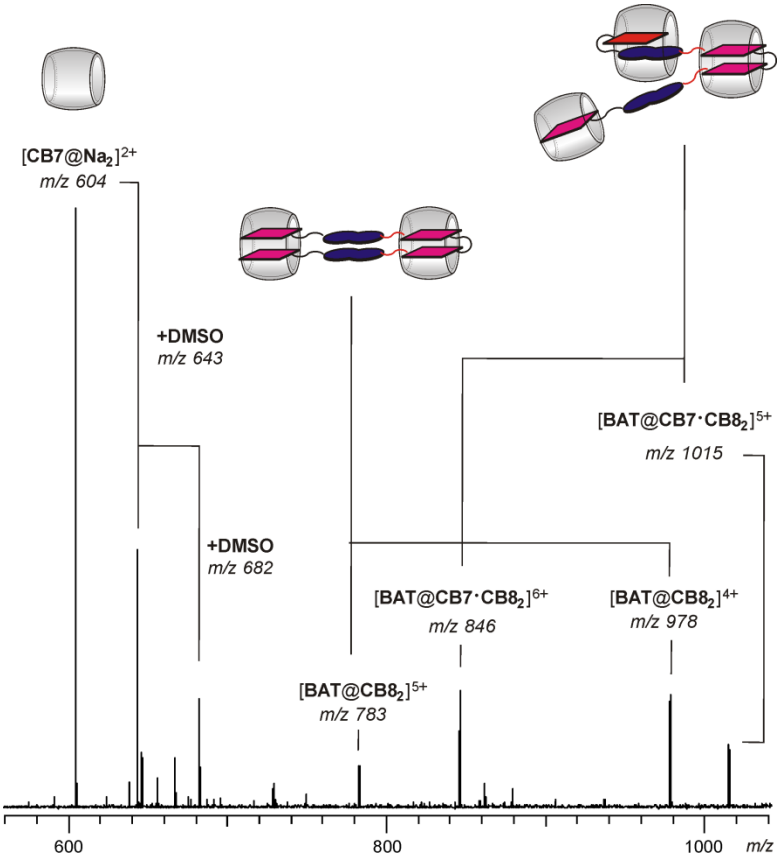


Figure S23. ESI-FTICR mass spectrum of a 8.57 × 10^{-1} mM water solution of **BATCl$_8$** in presence of 4 eq. of **CB7**, 2 eq. of **CB8** and $Na_2S_2O_4$ as the reducing agent. Under these experimental conditions [**BAT@CB7$_2$·CB8$_2$**]$^{8+}$ is reduced to the desired tetraradical species [**BAT@CB8$_2$**]$^{4+}$ which is, however, still in equilibrium with the (4)pseudorotaxane [**BAT@CB7·CB8$_2$**]$^{5+}$. Also in this case, [**BAT@CB7·CB8$_2$**]$^{6+}$ and [**BAT@ CB8$_2$**]$^{5+}$ are generated through the oxidation of [**BAT@CB7·CB8$_2$**]$^{5+}$ and [**BAT@CB8$_2$**]$^{4+}$, respectively, as described for experiment 2.2. The mass spectrum clearly shows that **CB7** and **CB8** compete for complex formation with the viologen cation-radicals.

2.6. *Step 3:* Control experiment for the formation of the viologen radical dimer in absence of host.

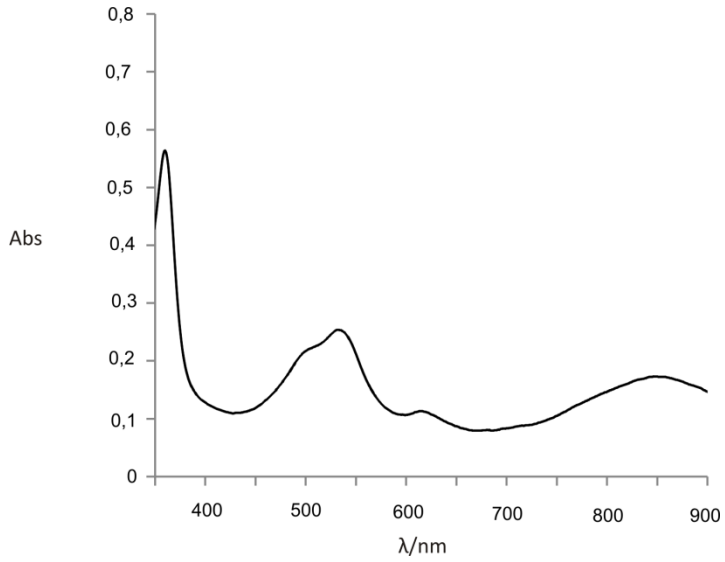


Figure S24. UV/Vis spectrum of the guest chain **$BATCl_8$** in a 1.76×10^{-2} mM $Na_2S_2O_4$ aqueous solution. The spectrum recorded immediately after the addition of the reducing agent shows only the formation of the typical absorption bands of the viologen cation-radical dimer at 365, 508, 539 and 850 nm and no traces of the viologen cation-radical monomer. Therefore we deduce that, in absence of **CB8**, the monomer is not stabilized in a charge transfer complex and, as the result, the kinetics of the folding process of **$BATCl_8$** is much faster as compared to that of **$BATCl_8@CB8_2$**.[8]

2.7. *Step 4*: Complexes structural information.

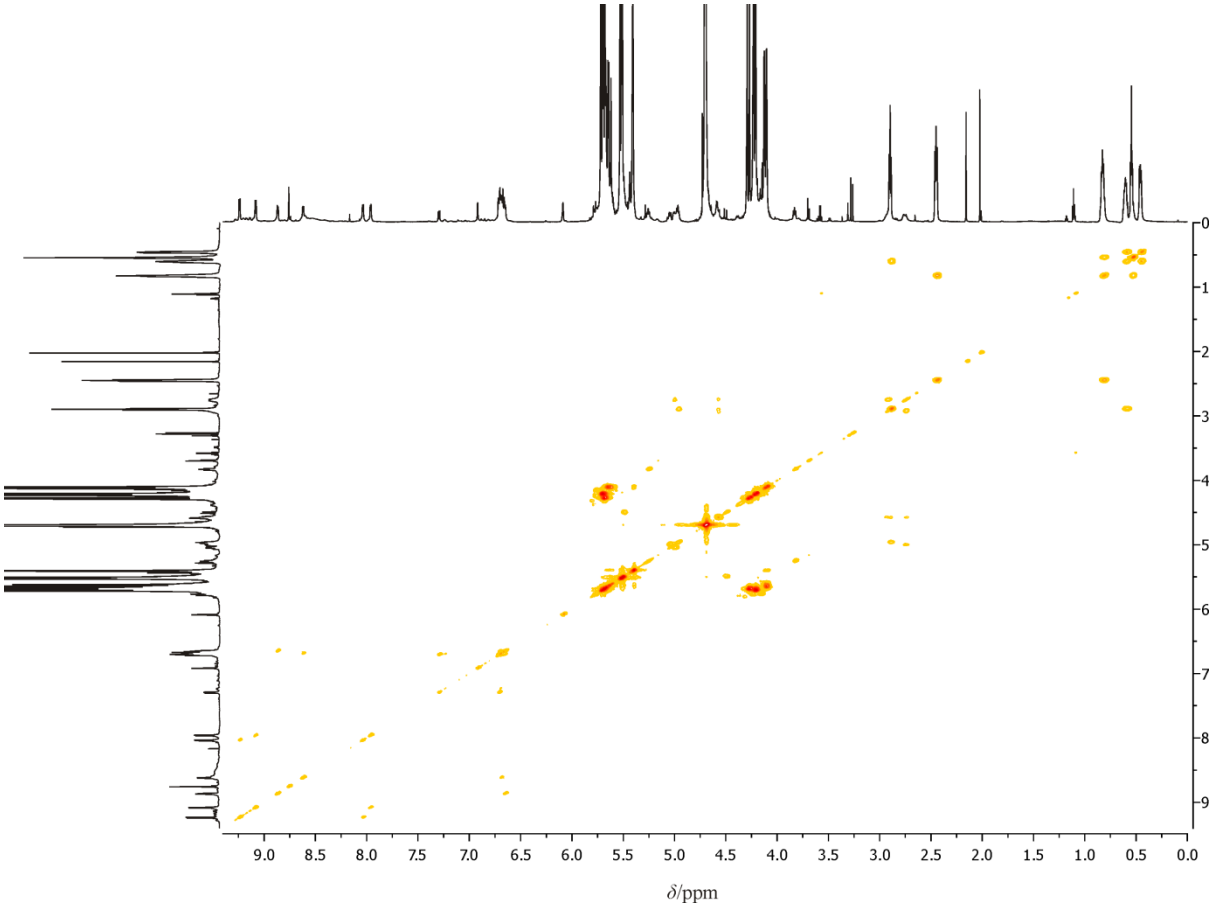


Figure S25. ^{1}H,^{1}H COSY NMR spectrum (700 MHz, 298 K, D_2O,) of a 8.57 × 10^{-1} mM water solution of **BATCl$_8$** in presence of 4 eq. of **CB7**, 2 eq. of **CB8**, 2 eq. of **CB6** and 4 eq. of **DAHCl$_2$**. As for the second step of the transformation cascade, the formation of a charge transfer complex inside the cavity of **CB8** is indicated by a high-field shift of both the viologen and naphthalene proton signals between 6.0 and 6.80 ppm.

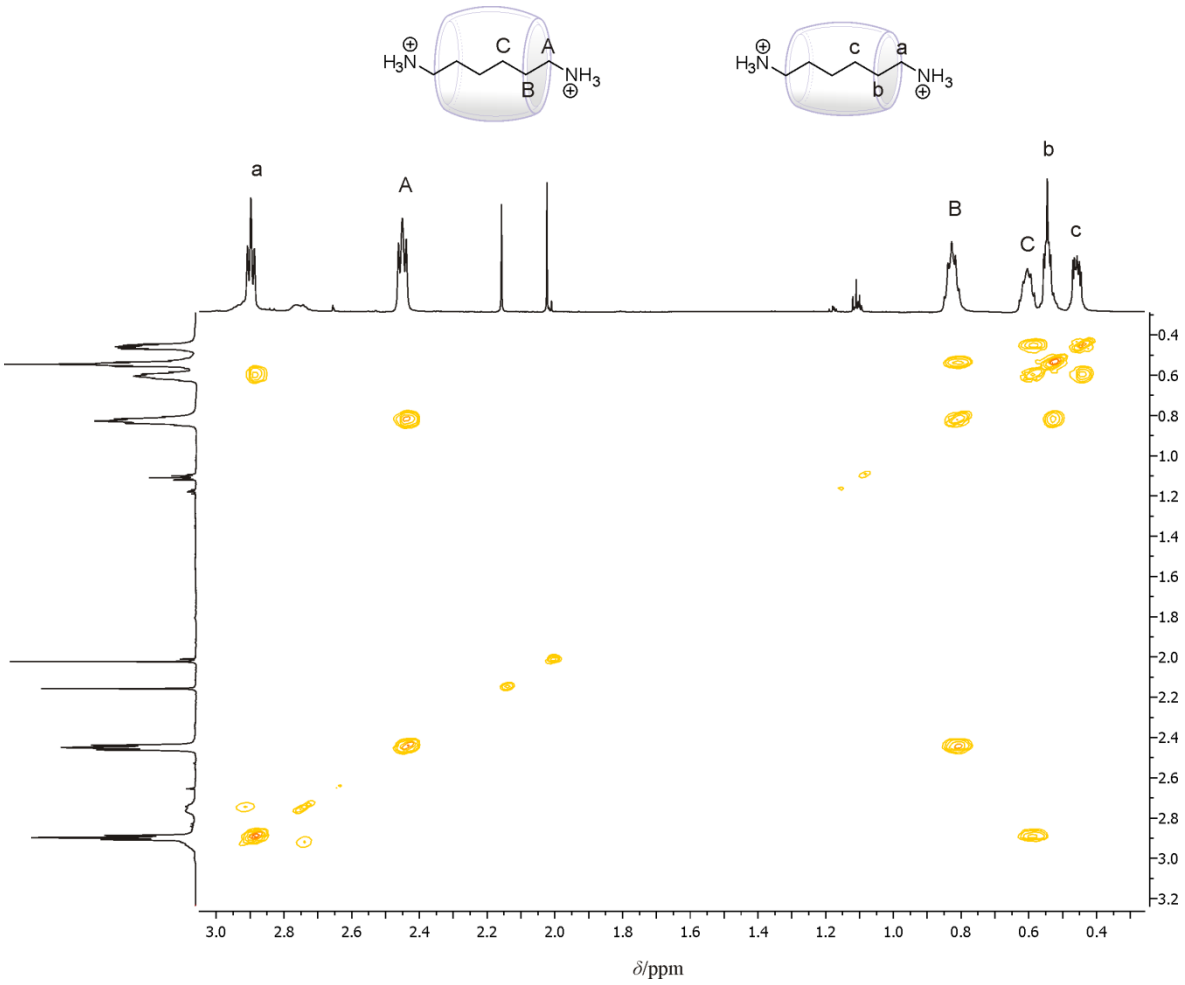


Figure S26. Zoomed-in ^{1}H,^{1}H COSY NMR spectrum (700 MHz, 298 K, D_2O,) of a 8.57×10^{-1} mM water solution of **$BATCl_8$** in presence of 4 eq. of **CB7**, 2 eq. of **CB8**, 2 eq. of **CB6** and 4 eq. of **$DAHCl_2$**. The two sets of signals A, B and C and a, b, and c show the formation of complex **$DAHCl_2$@CB7** and complex **$DAHCl_2$@CB6**, respectively, which are formed in a 1:1 ratio as expected.[9]

2.8. *Step 4*: Control experiment for the reconversion of the viologen radical dimer into the charge transfer complex.

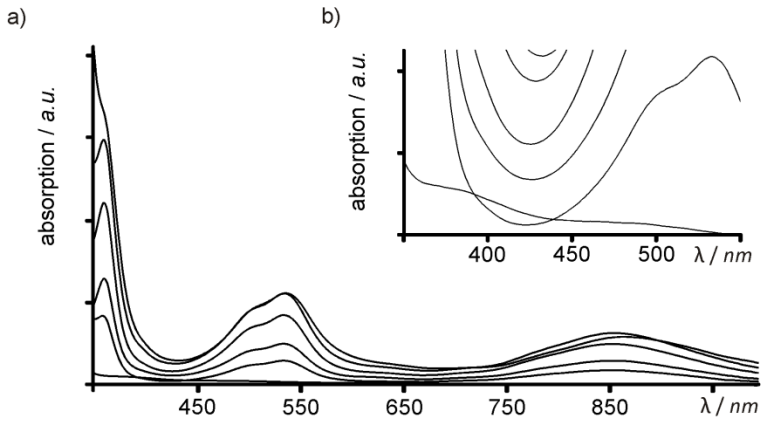


Figure S27. a) Time-dependent UV/Vis spectrum of a 8.90 × 10^{-3} mM **$BATCl_4$@$CB8_2$** water solution during its oxidation upon air flux (10 minutes): the spectrum shows the expected gradual decrease of the viologen cation-radical dimer bands; b) The inset zooms in on the absorption bands of the regenerated viologen-naphthalene CT complex inside the **CB8** cavity (384 and 487 nm), which is obtained only after complete oxidation of the viologen cation-radical dimers. The intensity of the CT complex bands is much lower than those of the bands of the cation-radical dimers. Nevertheless, the inset suggests that the reoxidation is likely faster than the rearrangement of the complex into the CT foldamer.

2.9. *Step 5*: Complexes structural information.

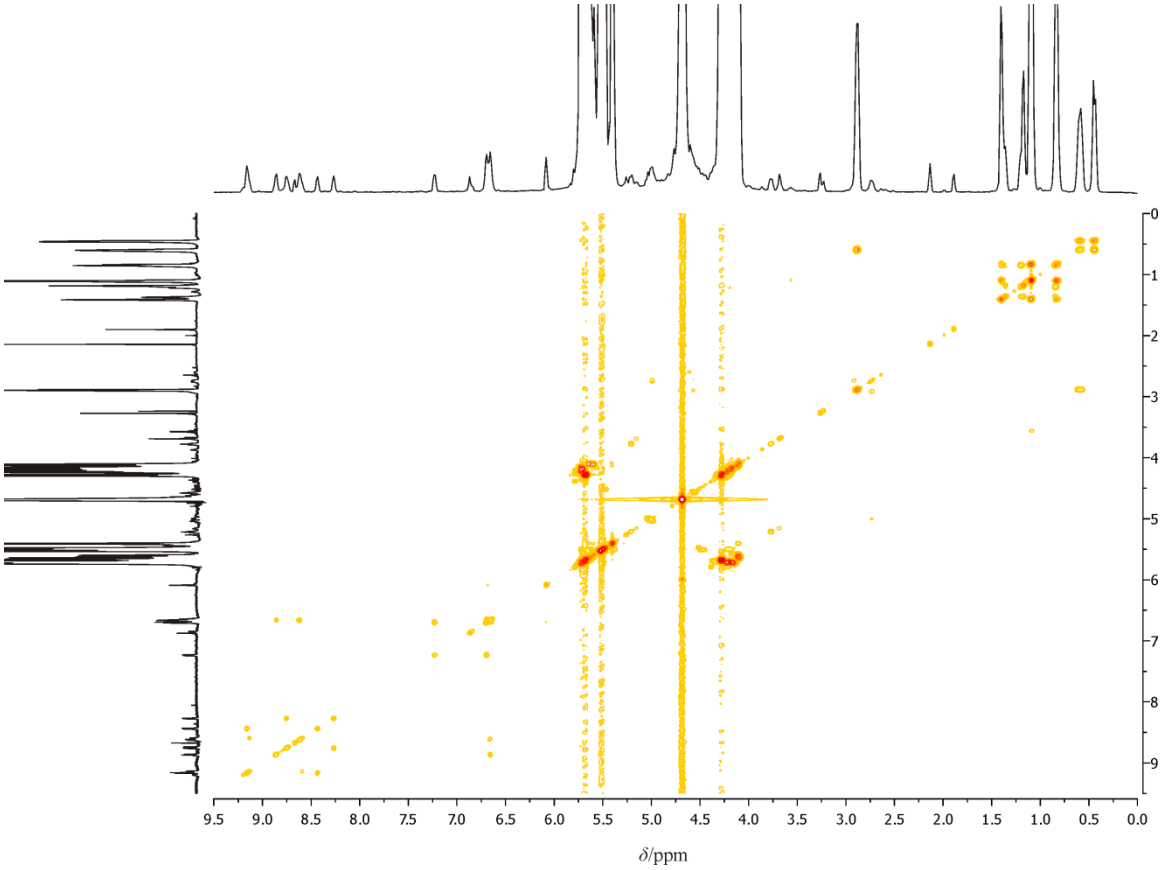


Figure S28. ^{1}H,^{1}H COSY NMR spectrum (700 MHz, 298 K, D_2O,) of a 8.57 × 10^{-1} mM water solution of **BATCl$_8$** in presence of 4 eq. of **CB7**, 4 eq. of **CB8**, 4 eq. of **CB6,** 4 eq. of **DAHCl$_2$** and 4 eq. of **ADACl**. Also in this case, the high-field shifts of both the naphthalene and viologen proton signals indicate the formation of the charge-transfer complex inside the **CB8** cavity (6.0 - 6.8 ppm range).

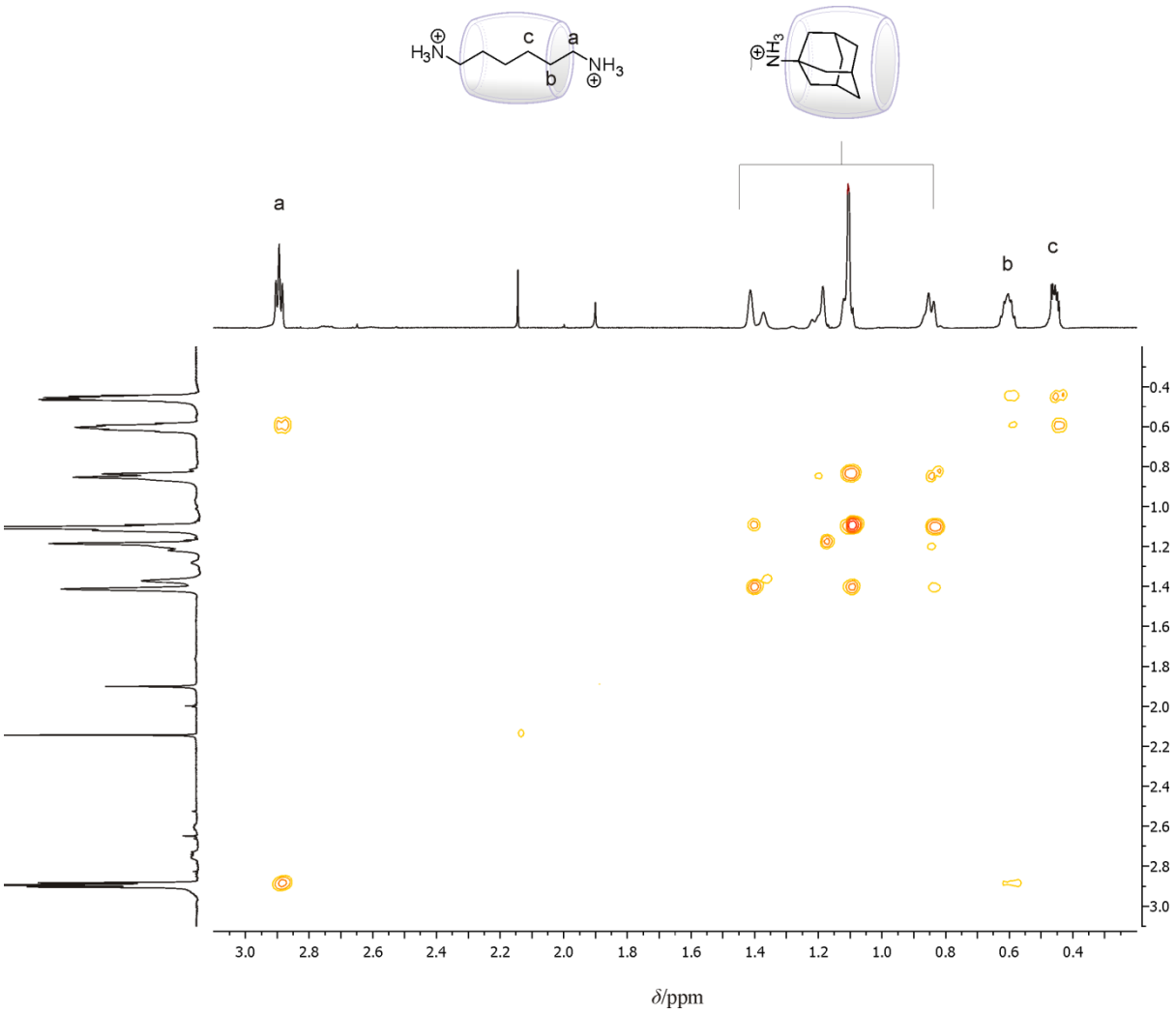


Figure S29. Zoomed-in ^{1}H,^{1}H COSY NMR spectrum (700 MHz, 298 K, D_2O,) of a 8.57 × 10^{-1} mM water solution of **$BATCl_8$** in presence of 4 eq. of of **CB7**, 4 eq. of **CB8**, 4 eq. of **CB6,** 4 eq. of **$DAHCl_2$** and 4 eq. of **ADACl**. The disappearance of the proton signals A B and C for **$DAHCl_2$@CB7** (see *Figure S26*) and the presence of proton signals between 1.43 and 0.83 ppm indicate the full conversion of complex **$DAHCl_2$@CB7** into complex **$DAHCl_2$@CB6** and the subsequent formation of complex **ADACl@CB7.**[9]

3. References

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