Electronic Supplementary Material (ESI) for ChemComm.

Charge Neutral Halogen Bonding Tetradentate-Iodotriazole Macrocycles Capable of Anion Recognition and Sensing in Highly Competitive Aqueous Media

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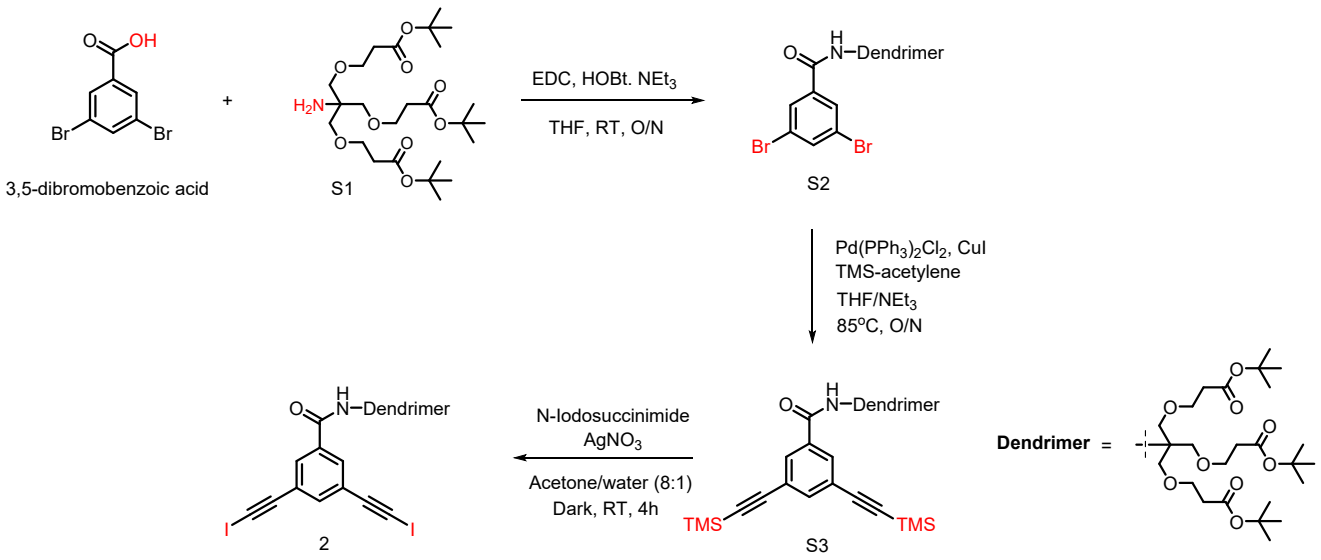
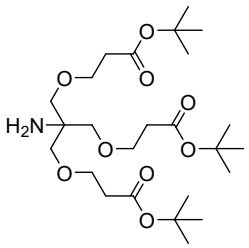
1. Synthesis and Characterisation

1.1 Synthesis of bis-Iodoalkyne 2



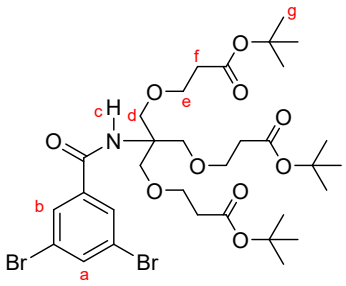
Scheme 1 A synthetic route to prepare bis-iodoalkyne **2**

Triester amine S1



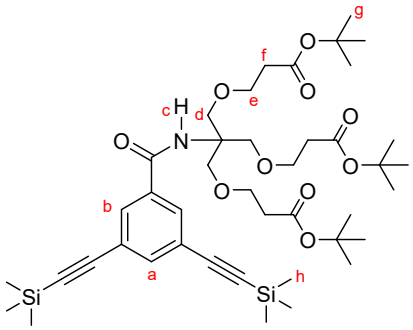
The compound **S1** was synthesised followed the method reported by Gawley and co-workers without any modification.[1]

Precursor S2



To a solution of triester amine **S1** (3.97g, 7.86 mmol, 2.2 equiv.) in DCM (50 ml), a mixture of 3,5-dibromobenzoic acid (1 g, 3.57 mmol, 1 equiv), EDC·HCl (1.64g, 8.57mmol, 2.4 equiv), and DMAP (0.436g, 3.57mmol, 1 equiv) was added in one portion. The mixture was stirred at room temperature for 48 hours and monitored by TLC. The mixture was washed with a 10% (w/v) citric acid solution, followed by a 10% (w/v) $NaHCO_3$ solution, water, and brine. The organic layer was collected, dried over $MgSO_4$ then concentrated by removing solvent *in vacuo*. The crude mixture was purified by silica gel column chromatography to afford **S2** (77%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (H_b, d, *J* = 1.8 Hz, 2H), 7.76 (H_a, t, *J* = 1.8 Hz, 1H), 6.68 (H_c, s, 1H), 3.82 (H_d, s, 6H), 3.68 (H_e, t, *J* = 6.2 Hz, 6H), 2.46 (H_f, t, *J* = 6.2 Hz, 6H), 1.42 (H_g, s, 27H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.03, 165.00, 138.87, 136.57, 129.46, 123.05, 80.67, 69.12, 67.21, 60.68, 36.25, 28.22. **HRMS** (ESI+ve) m/z: 766.17871 ($[M+H]^+$, $C_{32}H_{50}O_{10}N^{79}Br_2$ requires 766.17960)

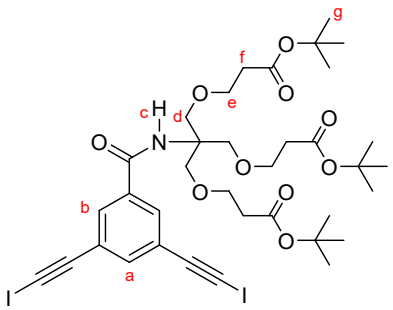
Precursor S3



S2 (1.426 g, 1.86 mmol, 1 equiv.), CuI (18 mg, 0.093 mmol, 0.05 equiv.), and $Pd(PPh_3)_2Cl_2$ (0.130 g, 0.186 mmol, 0.1 equiv.) were added to round bottom flask in one portion. Triethylamine (10 ml)

and THF (10 ml) were added to the mixture, and then deoxygenated by bubbling N_2 to the reaction. TMS-acetylene (0.475 g or 2.2 ml, 4.836 mmol, 2.6 equiv.) was added through a septum. The reaction container was sealed and heated to 75°C for 18 hours. After that, the mixture was allowed to cool to room temperature, and removed solvent to dryness *in vacuo*. The mixture was re-dissolved in DCM (50 ml), then the black solid was filtered off through a silica plug and collected a yellow organic solution. The combined organic phase was purified via a flash column chromatography using DCM as an eluent to afford a yellow waxy liquid of **S3** (80%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (H_b, d, *J* = 1.5 Hz, 2H), 7.63 (H_a, t, *J* = 1.5 Hz, 1H), 6.56 (H_c, s, 1H), 3.81 (H_d, s, 6H), 3.68 (H_e, t, *J* = 6.3 Hz, 6H), 2.45 (H_f, t, *J* = 6.3 Hz, 6H), 1.41 (H_g, s, 27H), 0.23 (H_h, s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.94, 166.28, 137.63, 135.98, 130.54, 123.81, 103.50, 95.89, 80.59, 69.16, 67.22, 60.52, 36.29, 28.23, -0.02. **HRMS** (ESI+ve) m/z: 802.43707 ($[M+H]^+$, $C_{42}H_{68}O_{10}N^{29}Si_2$ requires 802.43763)

Precursor 2



A solution of **S3** (1 g, 1.09 mmol, 1 equiv.) in acetone (10 ml) was added *N*-iodosuccinimide (0.613 g, 2.73 mmol, 2.5 equiv.). An aqueous solution of $AgNO_3$ (27.8 mg or 0.164 mmol in water 1 ml) was added dropwise, then the reaction was covered with foil to exclude light and stirred at room temperature for 4 hours. The reaction was diluted with DCM (50 ml) and an organic phase was washed thoroughly with a sufficient amount of water. After solvent removed, the crude product was purified by flash silica gel column chromatography using DCM as an eluent, to afford a yellow-waxy solid **2** (90%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.78 (H_b, d, *J* = 1.5 Hz, 2H), 7.55 (H_a, d, *J* = 1.3 Hz, 1H), 6.64 (H_c, s, 1H), 3.81 (H_d, s, 6H), 3.67 (H_e, t, *J* = 6.2 Hz, 6H), 2.45 (H_f, t, *J* = 6.2 Hz, 6H), 1.41 (H_g, s, 27H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.87, 165.92, 138.18, 136.02, 131.24, 123.86, 92.50, 80.49, 69.01, 67.05, 60.43, 36.11, 14.21, 8.87. **HRMS** (ESI+ve) m/z: 910.15106 ($[M+H]^+$, $C_{36}H_{50}O_{10}N^{127}I_2$ requires 910.15186).

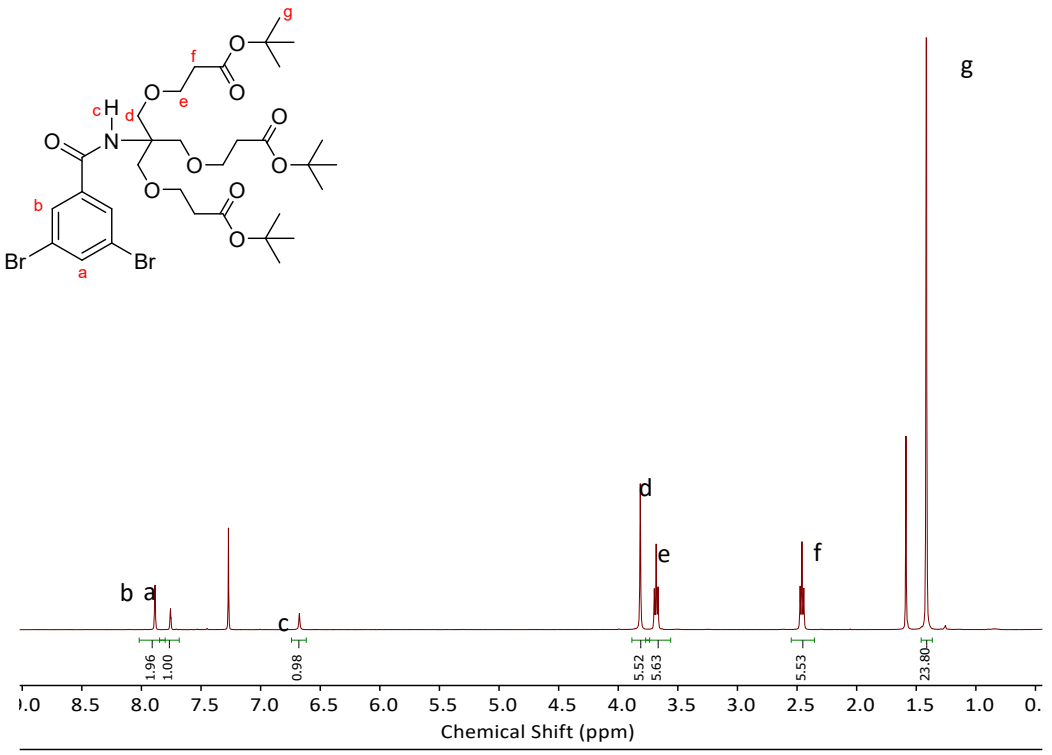


Figure S1 ^{1}H-NMR spectrum of **S2** in $CDCl_3$ (298K, 400 MHz)

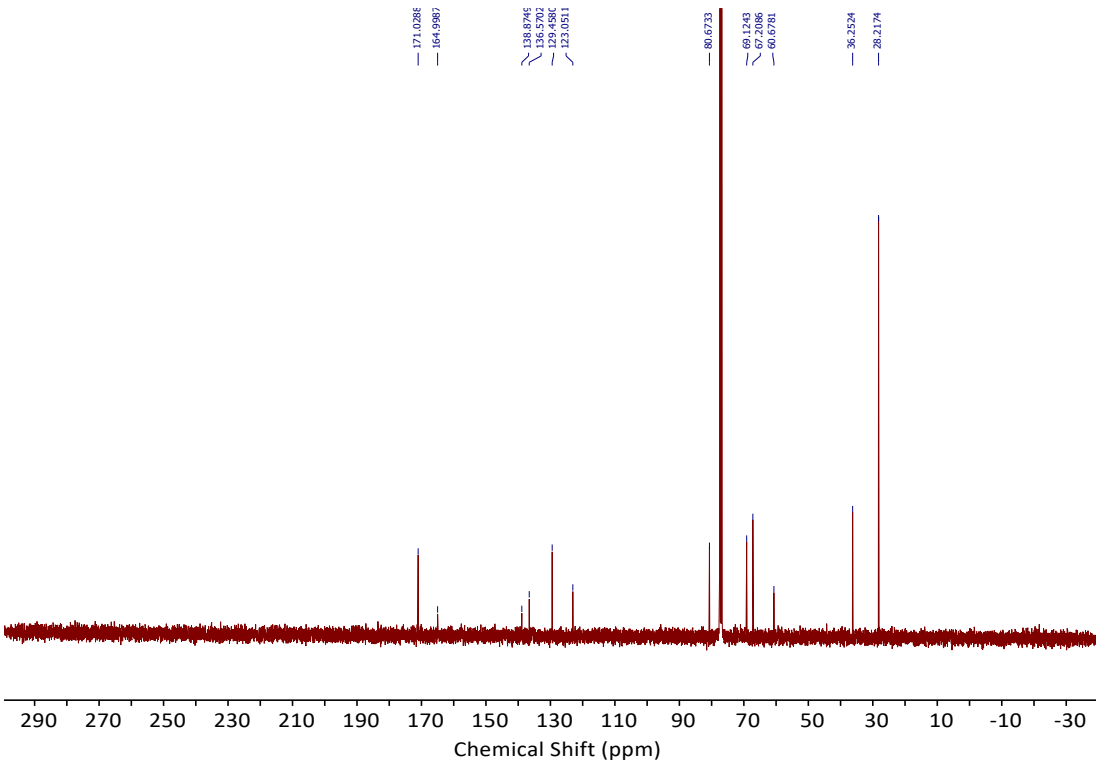


Figure S2 ^{13}C-NMR spectrum of **S2** in $CDCl_3$ (298K, 101 MHz)

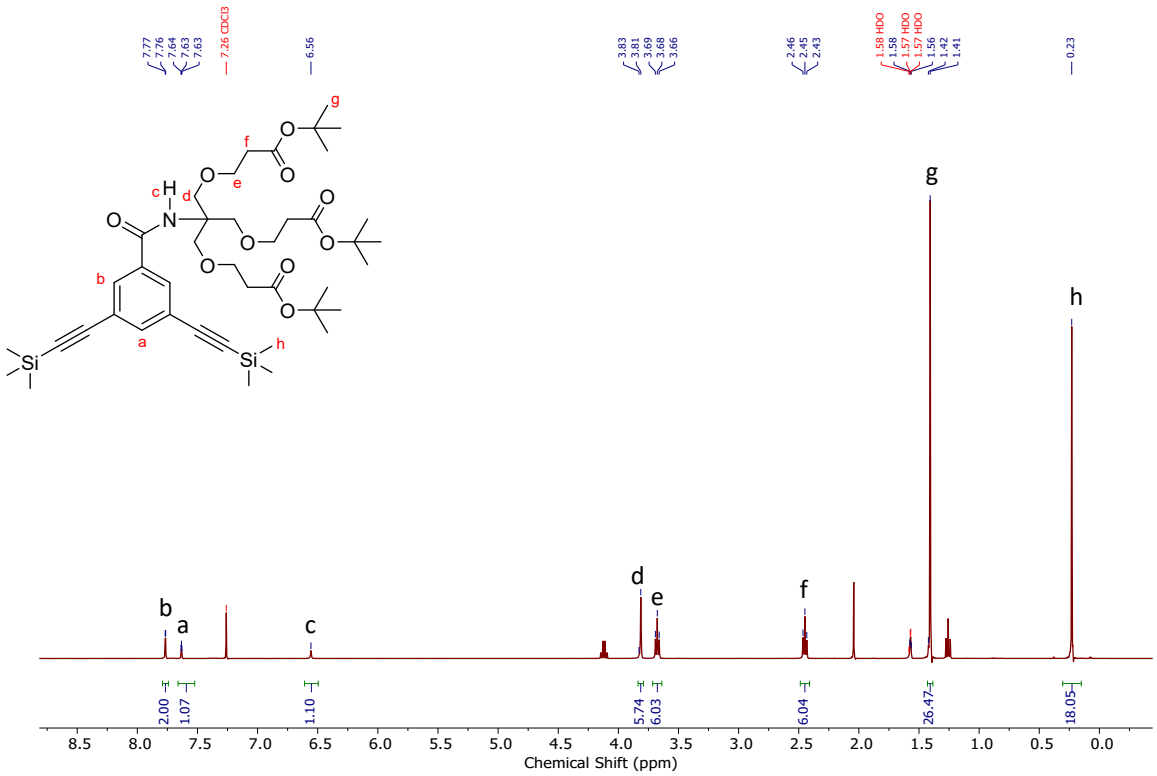


Figure S3 ^{1}H-NMR spectrum of **S3** in $CDCl_3$ (298K, 400 MHz)

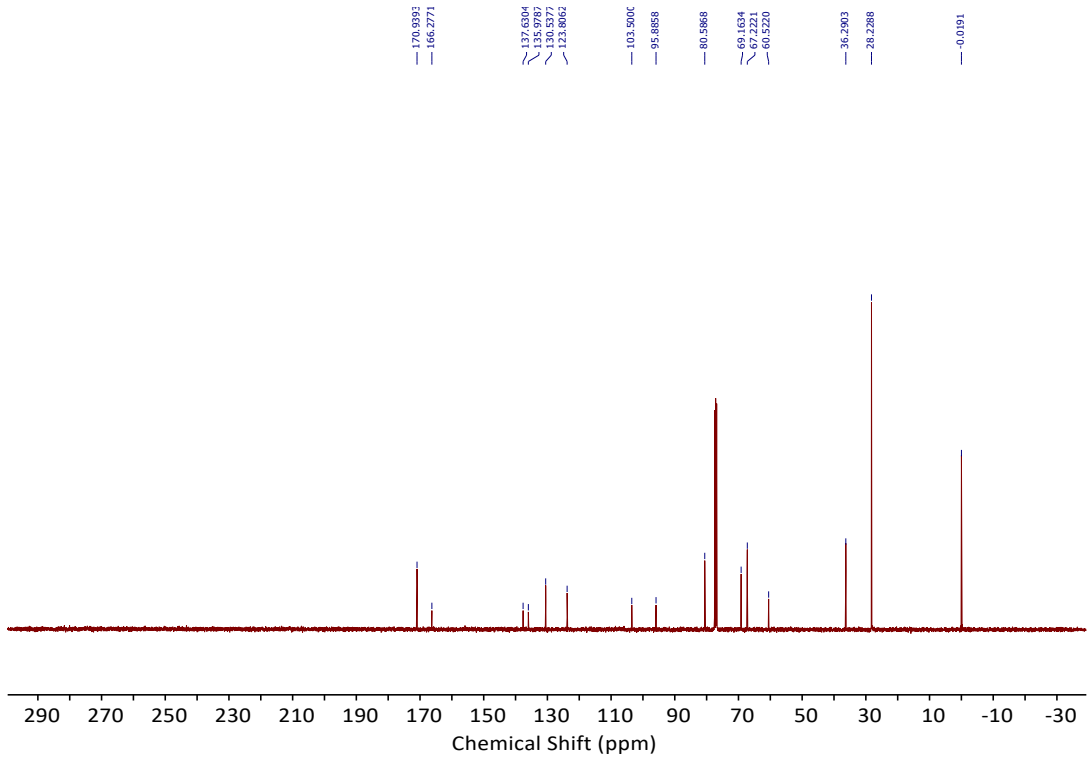


Figure S4 ^{13}C-NMR spectrum of **S3** in $CDCl_3$ (298K, 101 MHz)

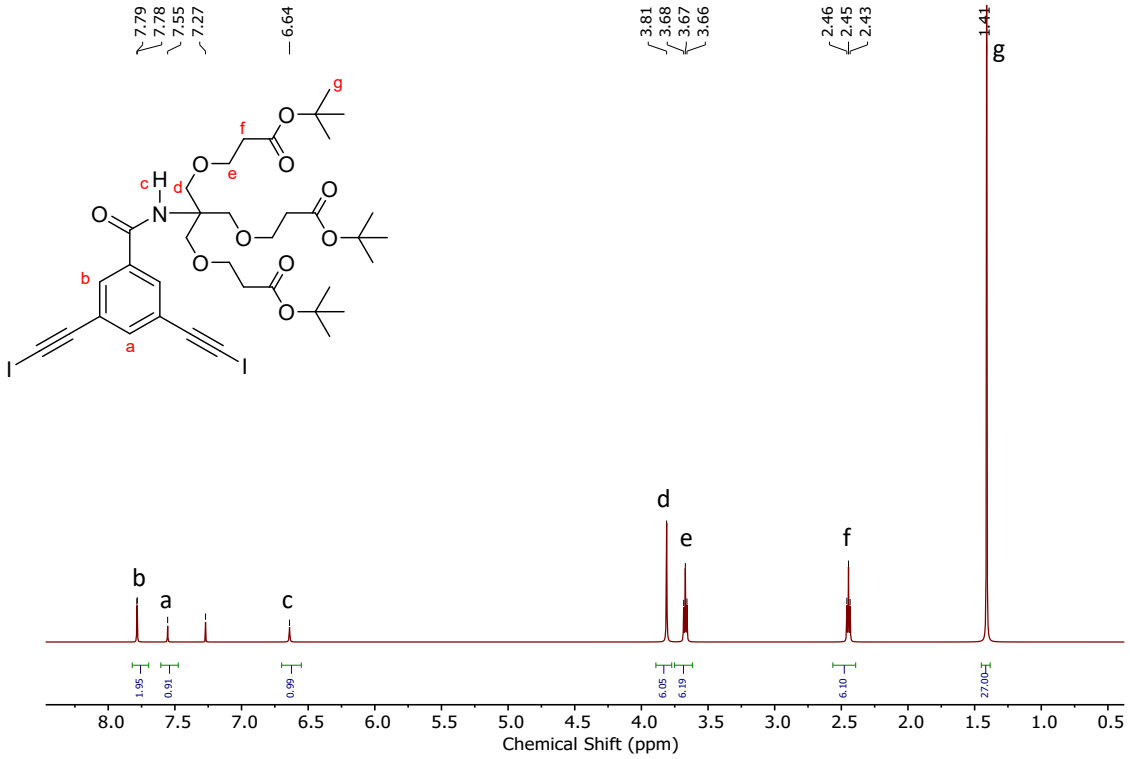


Figure S5 ^{1}H-NMR spectrum of **2** in $CDCl_3$ (298K, 400 MHz)

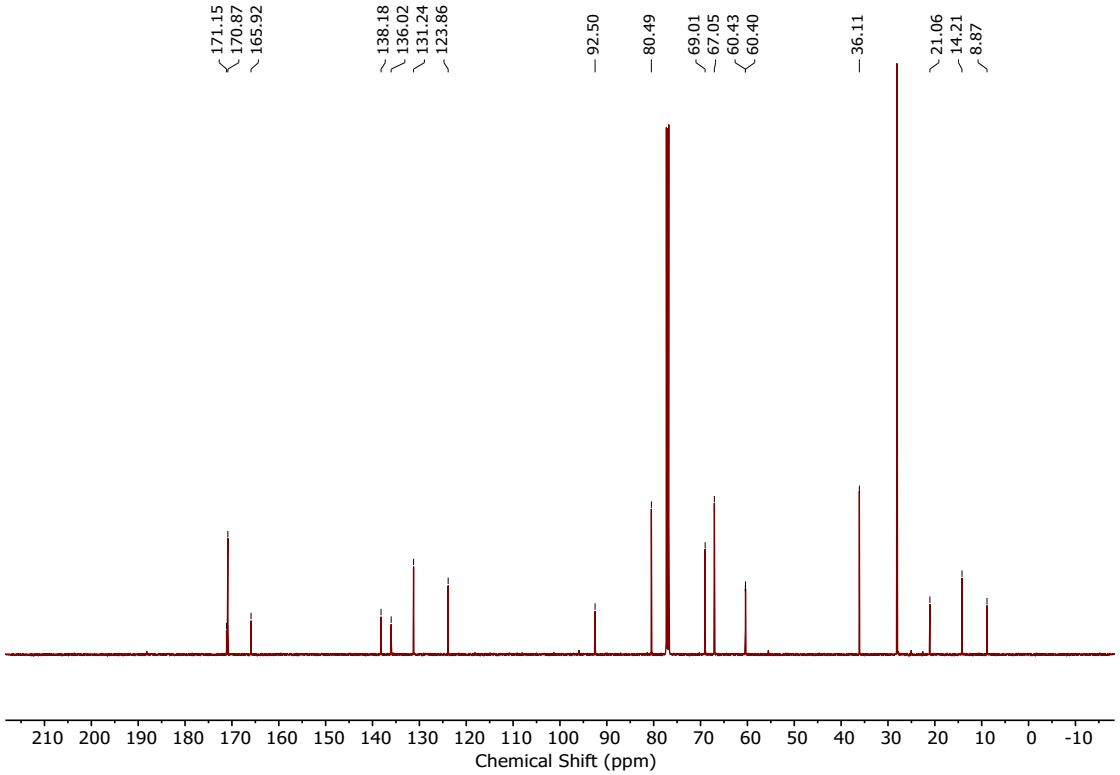
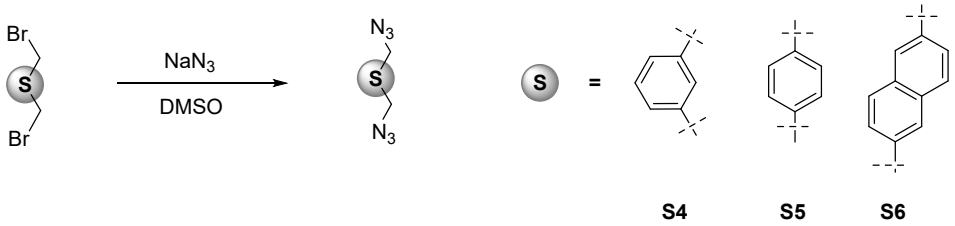


Figure S6 ^{13}C-NMR spectrum of **2** in $CDCl_3$ (298K, 101 MHz)

1.2 A typical procedure to prepare bis-azide precursors

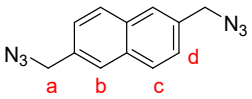
A typical procedure to prepare the bis-azide **S4-S6**



Scheme 2 General scheme for azide synthesis

To a solution of the bis-bromomethyl derivatives (1 equiv.) in DMSO (20 ml), NaN_3 (6 equiv.) was added in one portion and stirred at room temperature overnight. The mixture was diluted with water and extracted the product from an aqueous phase with Et_2O (3×20 ml). The ether layer was washed with water and brine, then dried over Na_2SO_4. Solvent was removed in vacuo to afford the product in almost quantitative yield. **S4** and **S5** were synthesised following a literature procedure reported by Sierra and co-workers.[2]

Precursor S6



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (H_c, d, *J* = 8.3 Hz, 2H), 7.80 (H_b, d, *J* = 1.7 Hz, 2H), 7.47 (H_d, dd, *J* = 8.4, 1.6 Hz, 2H), 4.53 (H_a, s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.55, 133.03, 128.94, 127.12, 126.61, 55.04.

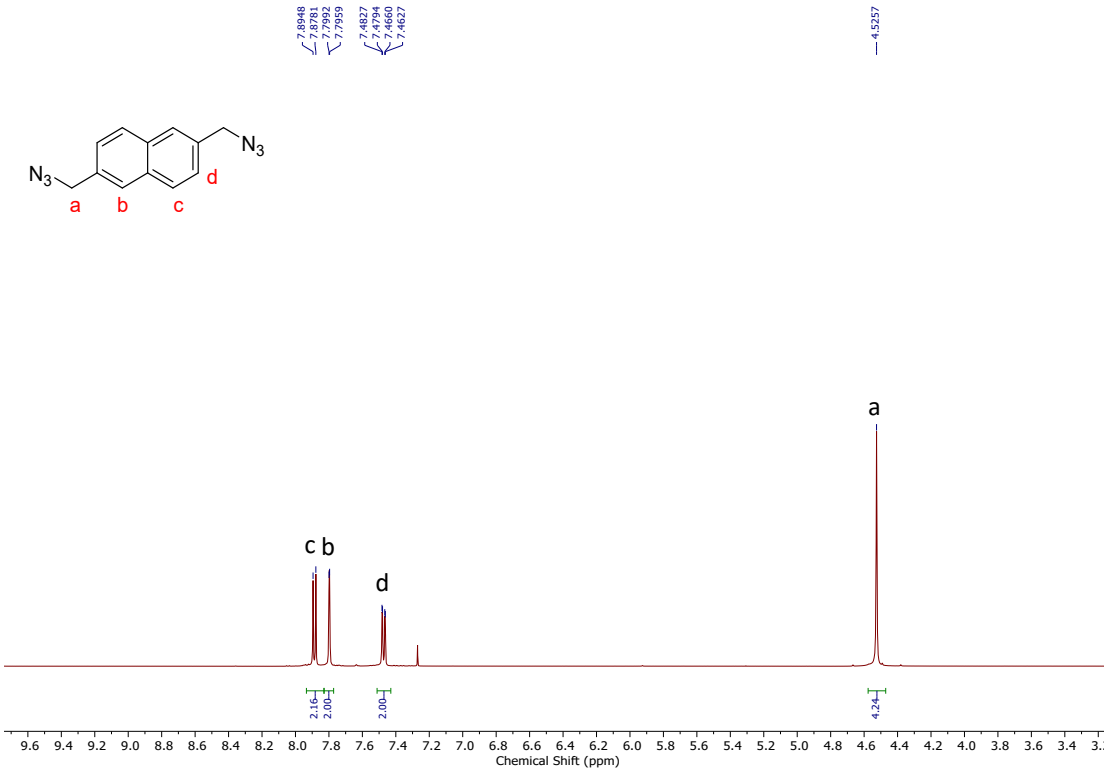


Figure S7 ^{1}H-NMR spectrum of **S6** in $CDCl_3$ (298K, 400 MHz)

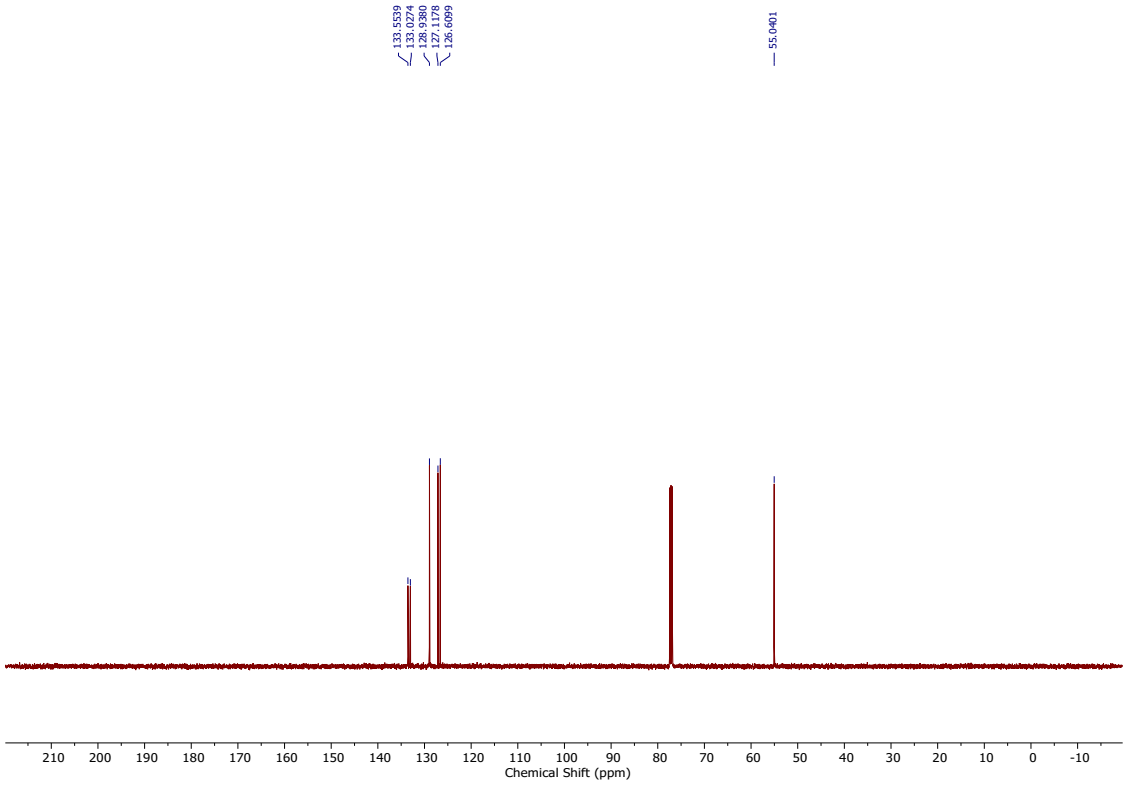
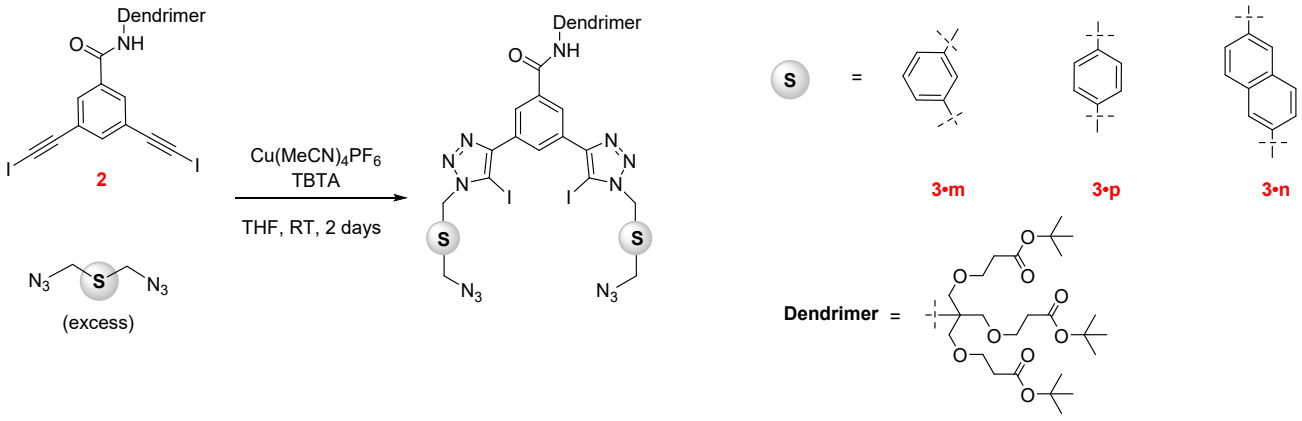


Figure S8 ^{13}C-NMR spectrum of **S6** in $CDCl_3$ (298K, 101 MHz)

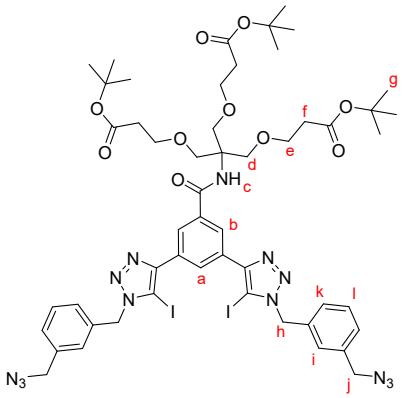
1.3 A typical procedure to prepare the XB macrocycle bis-azide precursors



Scheme 3 General scheme for preparation of the XB macrocycle bis-azide precursors

Bis-iodoalkyne **2** (0.5 g, 0.55 mmol, 1 equiv.) and bis-azide (5.5 mmol, 10 equiv.) were dissolved in dry DCM (5 ml) under N_2 atmosphere. $[Cu(MeCN)_4]PF_6$ (62 mg, 0.17 mmol, 0.3 equiv) and TBTA (58 mg, 0.11 mmol, 0.2 equiv) were subsequently added into the solution, then stirred at room temperature for 48 hours and monitored by TLC. After reached completion, NH_4OH (conc., 10 ml) was added and stirred for 0.5 hours to remove copper residues. An organic phase was separated and washed with water, brine, followed by adding Na_2SO_4. The reaction mixture was purified by silica gel column chromatography using a gradient eluent from DCM to 1% MeOH/DCM to afford the corresponding product.

Bis-azide 3·m



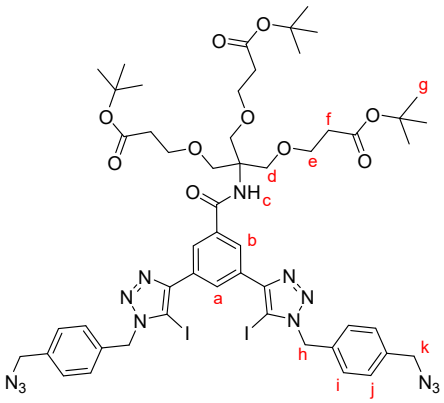
Yield = 80%

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.69 (H_a, t, *J* = 1.7 Hz, 1H), 8.40 (H_b, d, *J* = 1.7 Hz, 2H), 7.42 – 7.35 (H_i, m, 2H), 7.32 – 7.25 (H_k+ H_l, m, 6H), 6.69 (H_c, s, 1H), 5.69 (H_h, s, 4H), 4.34 (H_j, s, 4H), 3.85 (H_d, s, 6H), 3.68 (H_e, t, *J* = 6.4 Hz, 6H), 2.45 (H_f, t, *J* = 6.4 Hz, 6H), 1.36 (H_g, s, 27H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.96, 166.96, 149.38, 136.44, 136.38, 135.08, 131.10, 129.64, 129.02, 128.42, 127.84, 127.61, 126.06, 80.58, 69.26, 67.25, 60.43, 54.49, 54.28, 36.38, 28.15.

HRMS (ESI+ve) m/z: 1286.31079 ($[M+H]^+$, $C_{52}H_{66}O_{10}N_{13}I_2$ requires 1286.31395)

Bis-azide 3·p



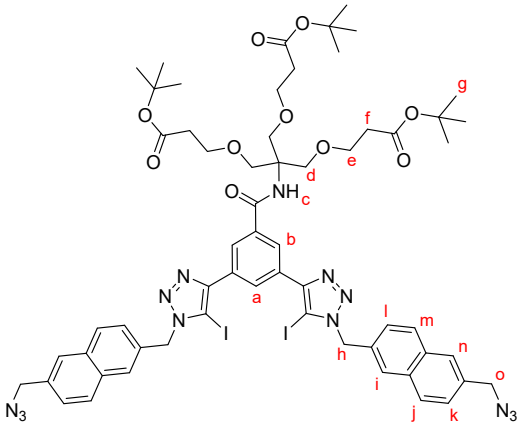
Yield = 75%

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.55 (H_a, t, *J* = 1.7 Hz, 1H), 8.27 (H_b, d, *J* = 1.7 Hz, 2H), 7.19 (H_i+ H_j, d, *J* = 1.6 Hz, 7H), 6.57 (H_c, s, 1H), 5.55 (H_h, s, 4H), 4.20 (H_k, s, 4H), 3.72 (H_d, s, 6H), 3.55 (H_e, t, *J* = 6.3 Hz, 6H), 2.31 (H_f, t, *J* = 6.4 Hz, 6H), 1.23 (H_g, s, 27H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.95, 166.95, 149.34, 136.37, 135.95, 134.45, 131.09, 128.79, 128.40, 126.04, 80.57, 69.26, 67.24, 60.42, 54.40, 54.13, 36.38.

HRMS (ESI+ve) m/z: 1286.31383 ([M+H]$^+$, $C_{52}H_{66}O_{10}N_{13}I_2$ requires 1286.31395)

Bis-azide 3·n



Yield =72%

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.72 (H_a, t, *J* = 1.7 Hz, 1H), 8.43 (H_b, d, *J* = 1.7 Hz, 2H), 7.84 (H_{j+m}, dd, *J* = 8.5, 3.2 Hz, 4H), 7.75 (H_{i+n}, dd, *J* = 9.2, 1.7 Hz, 4H), 7.45 (H_{k+l}, td, *J* = 8.3, 1.8 Hz, 4H), 6.72 (H_c, s, 1H), 5.84 (H_h, s, 4H), 4.50 (H_b, s, 4H), 3.85 (H_d,s, 6H), 3.68 (H_e, t, *J* = 6.3 Hz, 6H), 2.45 (H_f, t, *J* = 6.3 Hz, 6H), 1.35 (H_g, s, 27H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.00, 167.04, 149.39, 136.43, 133.79, 133.07, 132.94, 132.35, 131.13, 129.09, 129.00, 127.07, 126.70, 126.09, 125.86, 80.59, 69.28, 67.25, 60.45, 54.98, 54.61, 36.37, 28.13.

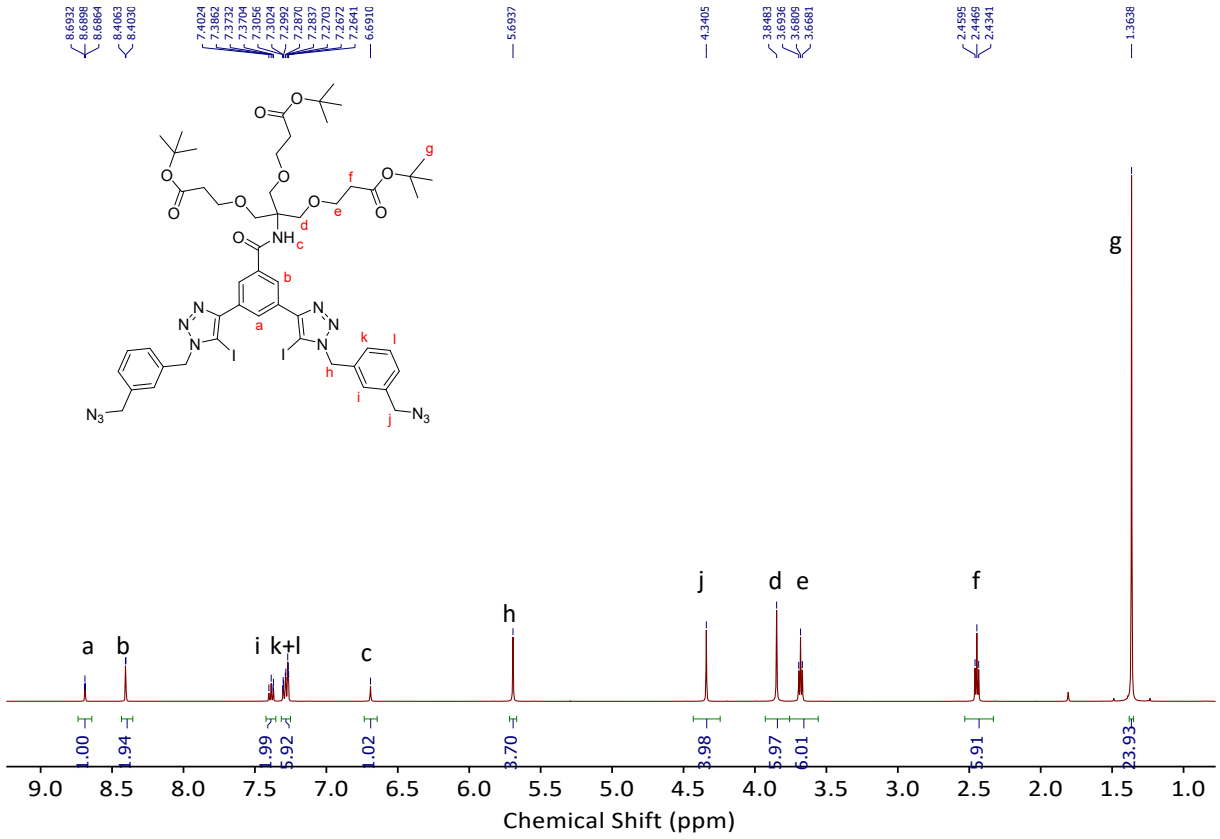


Figure S9 ^{1}H-NMR spectrum of **3·m** in $CDCl_3$ (298K, 500 MHz)

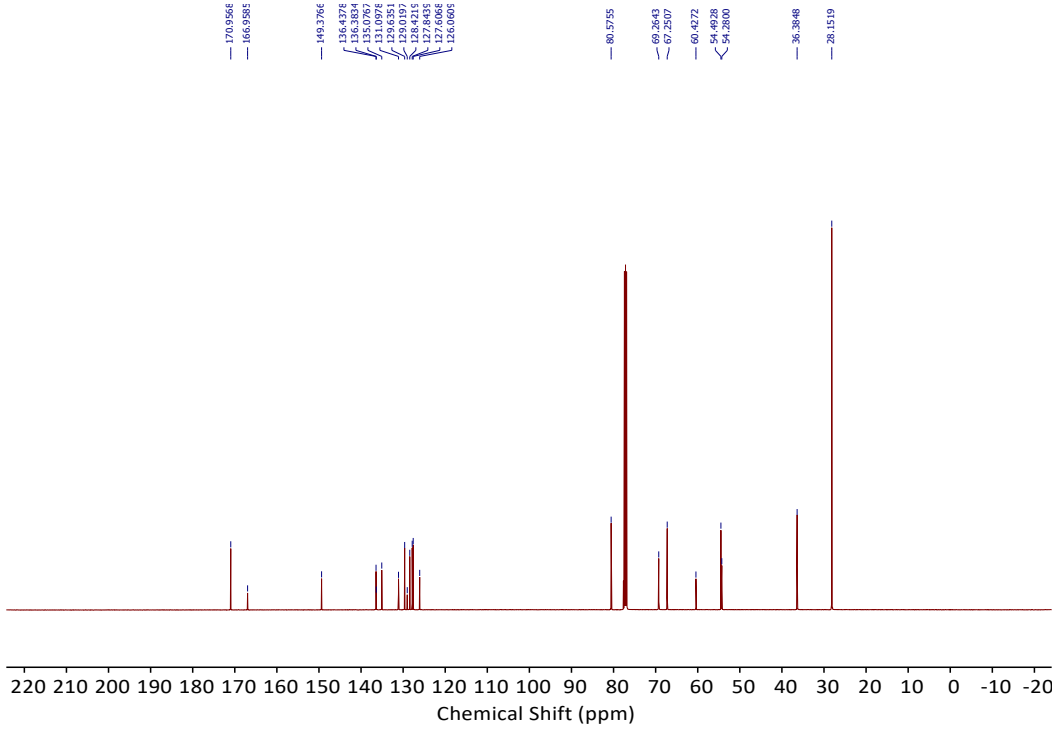


Figure S10 ^{13}C-NMR spectrum of **3·m** in $CDCl_3$ (298K, 126 MHz)

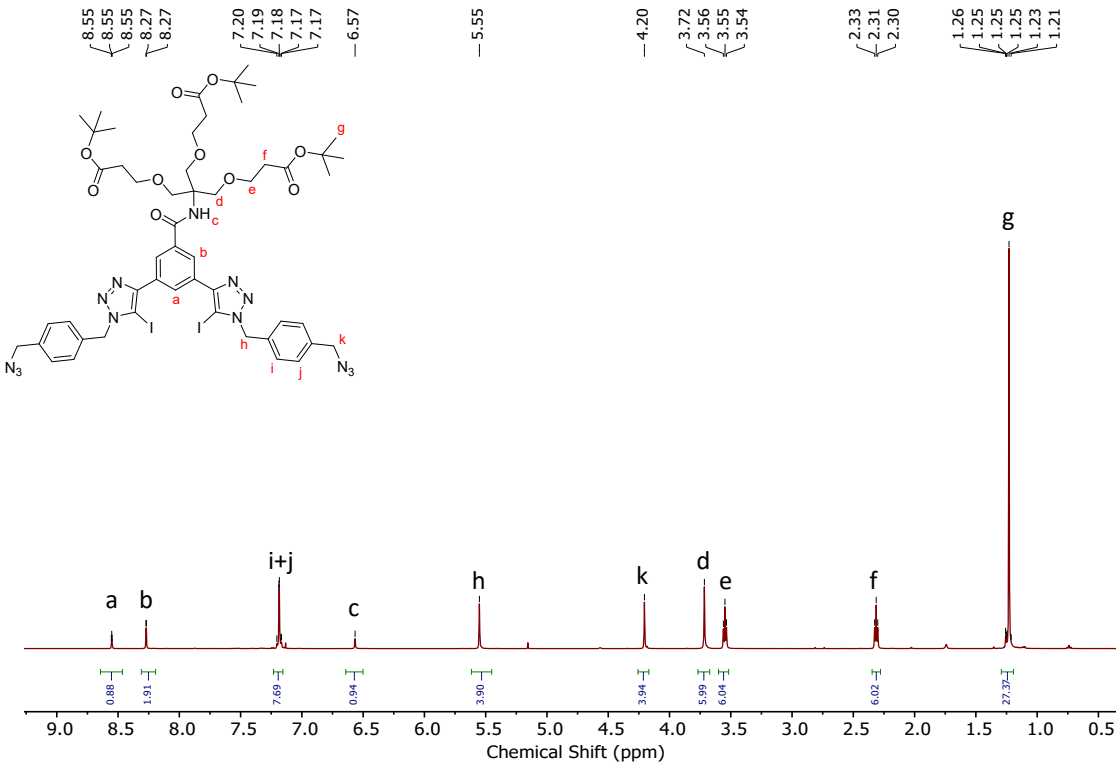


Figure S11 ^{1}H-NMR spectrum of **3·p** in $CDCl_3$ (298K, 500 MHz)

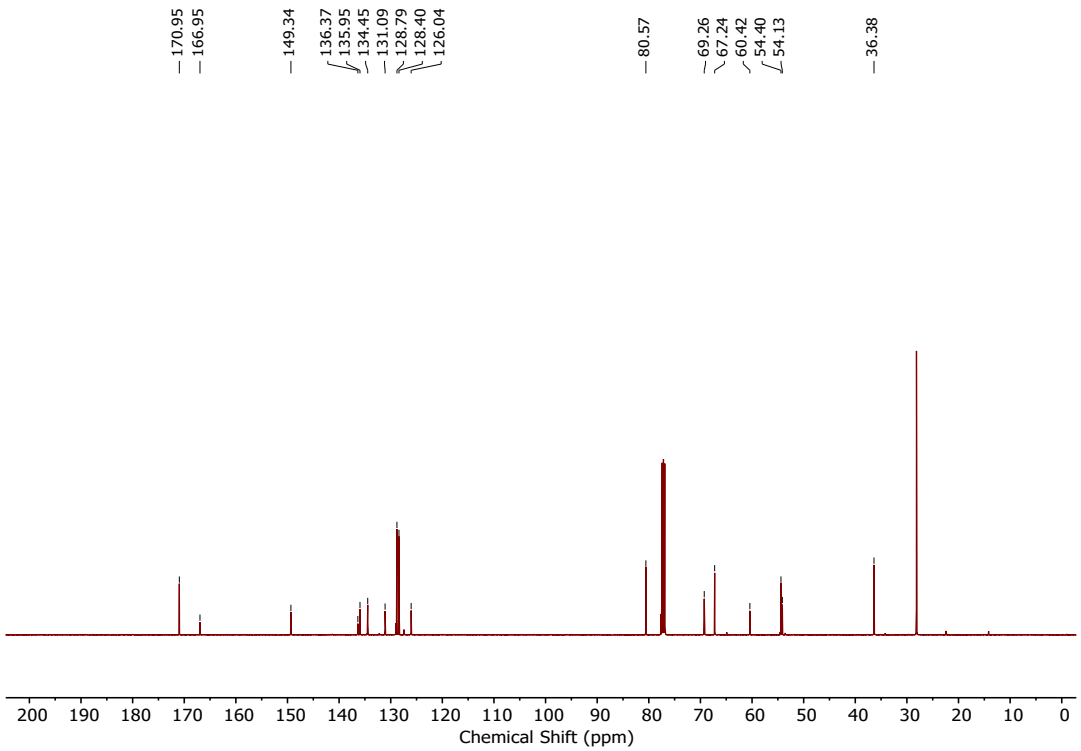


Figure S12 ^{13}C-NMR spectrum of **3·p** in $CDCl_3$ (298K, 126 MHz)

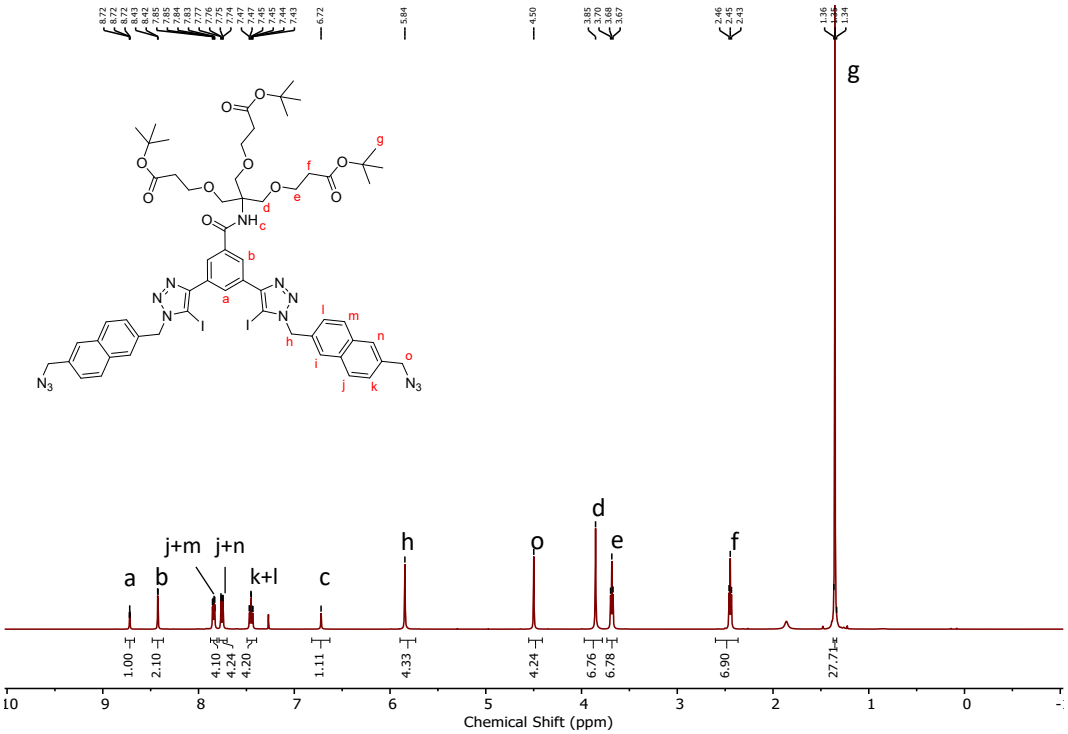


Figure S13 ^{1}H-NMR spectrum of **3·n** in $CDCl_3$ (298K, 500 MHz)

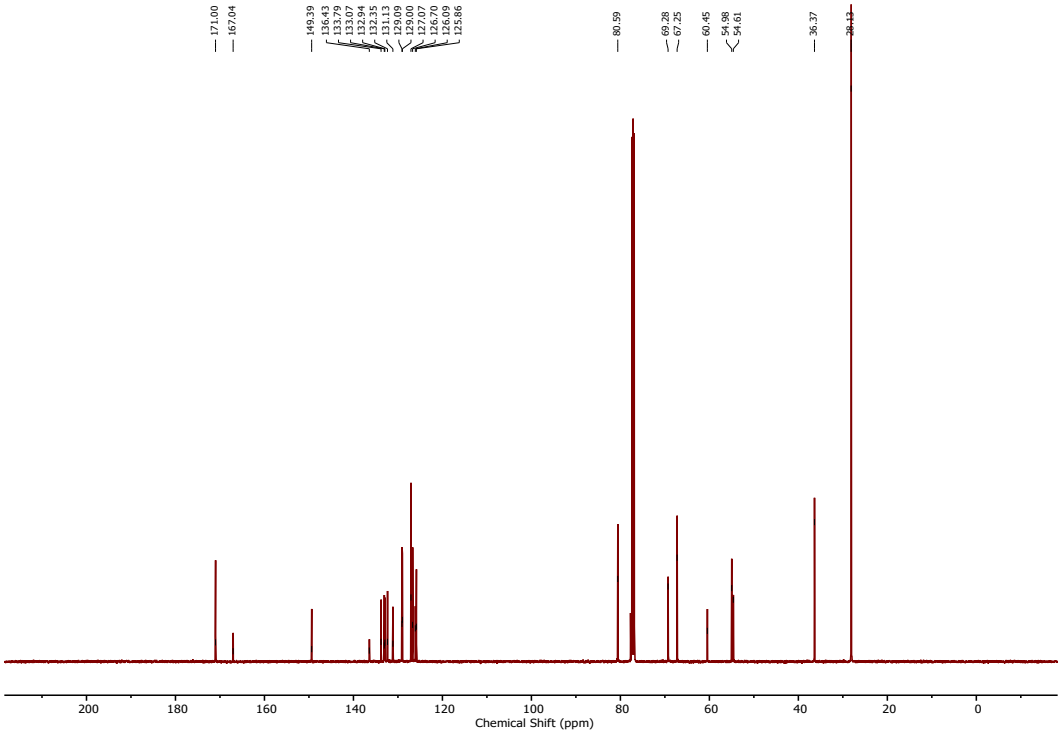
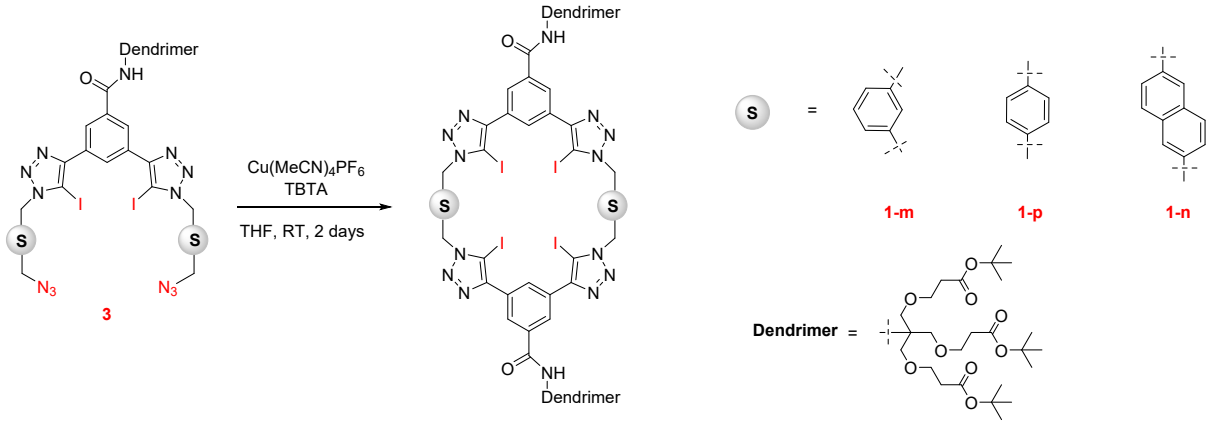


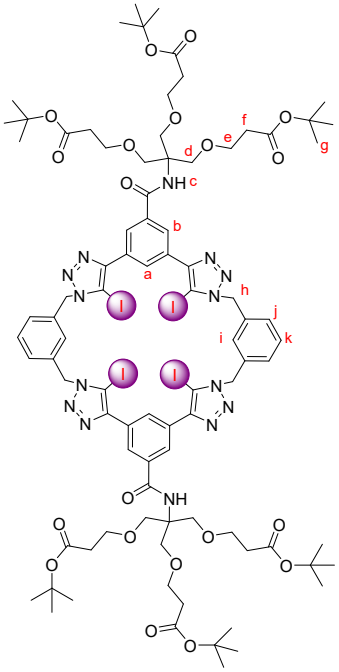
Figure S14 ^{13}C-NMR spectrum of **3·n** in $CDCl_3$ (298K, 126 MHz)

1.4 A typical procedure for high-dilution macrocyclization reaction to prepare macrocycles



Bis-iodoalkyne **2** (1 equiv.) and XB macrocycle bis-azide **3** (1 equiv.) were diluted to the concentration of 5 mM by adding dry DCM. The solution mixture was degassed by bubbling N_2 through the reaction for 5 minutes. $[Cu(MeCN)_4]PF_6$ (0.4 equiv) and TBTA (0.3 equiv.) were subsequently added into the solution, then stirred at room temperature for 48 hours. The reaction was monitored by either TLC or ESI-MS. If the reaction was not complete, another portion of $Cu(MeCN)_4PF_6$ (0.1 equiv.) could be added and the reaction was left stirring overnight. A solution of NH_4OH (10 ml) was added to remove copper residue. The organic layer was collected and washed thoroughly with water and brine, and dried over Na_2SO_4. The reaction mixture was purified by silica gel column chromatography using a 1-3% MeOH/DCM eluent to afford the corresponding product.

Macrocycle 3·m



Chemicals: Bis-iodoalkyne **2** (71 mg, 0.078 mmol), Bis-azide **3·m** (100 mg, 0.078 mmol), $[Cu(MeCN)_4]PF_6$ (12 mg, 0.031 mmol), TBTA (12 mg, 0.023 mmol), DCM (16 ml)

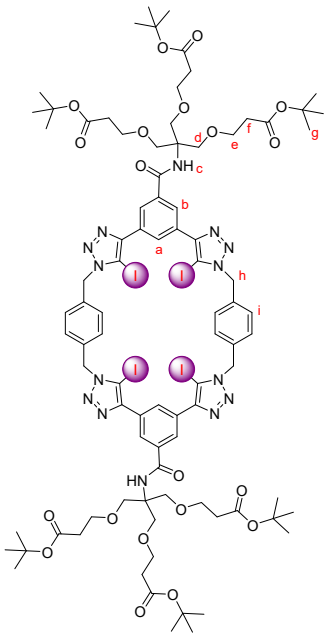
Yield = 70%

^{1}H-NMR (500 MHz, Chloroform-*d*) δ 8.58 (H_a, t, *J* = 1.7 Hz, 2H), 8.40 (H_b, d, *J* = 1.7 Hz, 4H), 7.41 (s, 6H), 6.82 (s, 2H), 5.64 (s, 8H), 3.87 (s, 12H), 3.69 (t, *J* = 6.4 Hz, 12H), 2.46 (t, *J* = 6.4 Hz, 12H), 1.38 (s, 54H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 171.02, 167.09, 149.28, 136.99, 135.43, 130.77, 129.75, 128.12, 127.66, 126.89, 126.35, 80.55, 69.32, 67.25, 60.49, 54.09, 36.37, 28.17.

HRMS (ESI+ve) m/z: 2195.45361 ($[M+H]^+$, $C_{88}H_{115}O_{20}N_{14}{}^{127}I_4$ requires 2195.45853)

Macrocycle 3·p



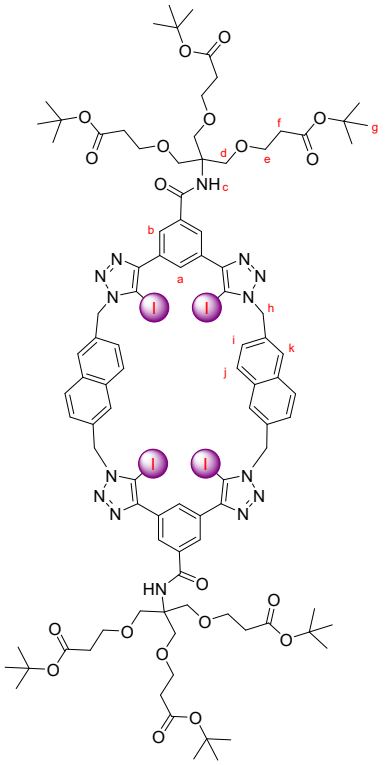
Chemicals: Bis-iodoalkyne **2** (71 mg, 0.078 mmol), Bis-azide **3·p** (100 mg, 0.078 mmol), $[Cu(MeCN)_4]PF_6$ (12 mg, 0.031 mmol), TBTA (12 mg, 0.023 mmol), DCM (16 ml)

Yield = 65%

^{1}H-NMR (500 MHz, Chloroform-*d*) δ 8.46 (H_a, t, *J* = 1.6 Hz, 2H), 8.34 (H_b, d, *J* = 1.6 Hz, 4H), 7.28 (H_i, d, *J* = 6.3 Hz, 8H), 6.69 (H_c, s, 2H), 5.66 (H_h, s, 8H), 3.86 (H_d, s, 12H), 3.69 (H_e, t, *J* = 6.4 Hz, 12H), 2.46 (H_f, t, *J* = 6.4 Hz, 12H), 1.39 (H_g, s, 54H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.98, 166.94, 149.63, 136.64, 134.87, 130.97, 128.88, 128.65, 126.58, 80.60, 69.30, 67.28, 60.46, 53.98, 36.41, 28.20.

HRMS (MALDI-TOF) m/z: 2217.5487 ($[M+Na]^+$, $C_{88}H_{114}O_{20}N_{14}{}^{127}I_4Na$ requires 2217.4405)



Chemicals: Bis-iodoalkyne **2** (66 mg, 0.072 mmol), Bis-azide **3·n** (100 mg, 0.072 mmol), $[Cu(MeCN)_4]PF_6$ (11 mg, 0.029 mmol), TBTA (38 mg, 0.022 mmol), DCM (15 ml)

Yield = 58%

^{1}H-NMR (500 MHz, Chloroform-*d*) δ 8.45 (H_a, t, *J* = 1.6 Hz, 2H), 8.39 (H_b, d, *J* = 1.6 Hz, 4H), 7.76 (H_i, d, *J* = 8.5 Hz, 4H), 7.71 (H_k, s, 4H), 7.43 – 7.38 (H_j, m, 4H), 6.73 (H_c, s, 2H), 5.82 (H_h, s, 8H), 3.87 (H_d, s, 12H), 3.71 (H_e, t, *J* = 6.4 Hz, 12H), 2.48 (H_f, t, *J* = 6.4 Hz, 12H), 1.40 (H_g, s, 54H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 171.03, 167.00, 149.65, 136.71, 132.93, 132.60, 130.97, 129.16, 128.48, 127.28, 126.65, 126.07, 80.63, 69.30, 67.28, 60.48, 54.61, 36.41, 28.21.

HRMS (MALDI-TOF) m/z: 2317.8826 ($[M+Na]^+$, $C_{96}H_{118}O_{20}N_{14}{}^{127}I_4Na$ requires 2317.4718)

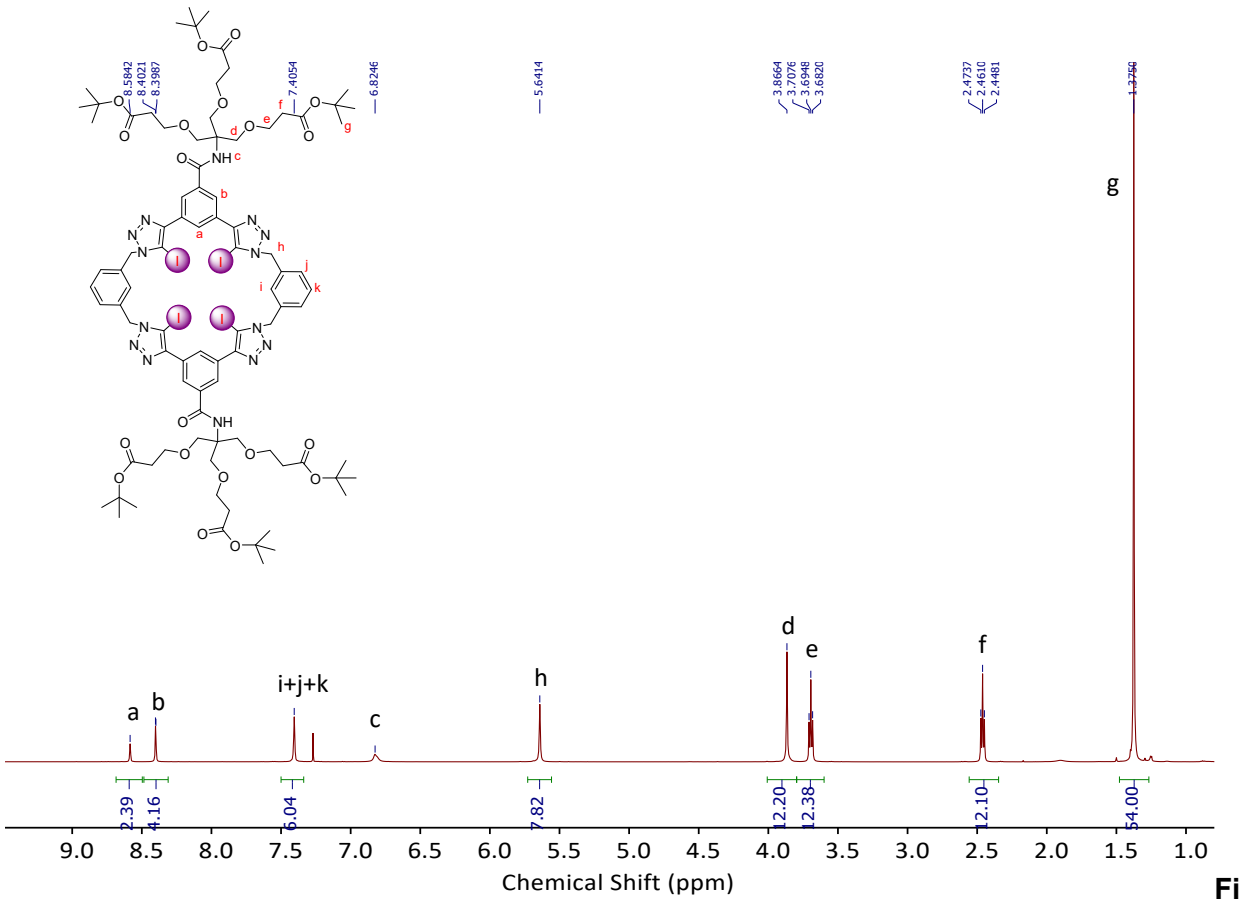


Figure S15 ^{1}H-NMR spectrum of **3·m** in $CDCl_3$ (298K, 500 MHz)

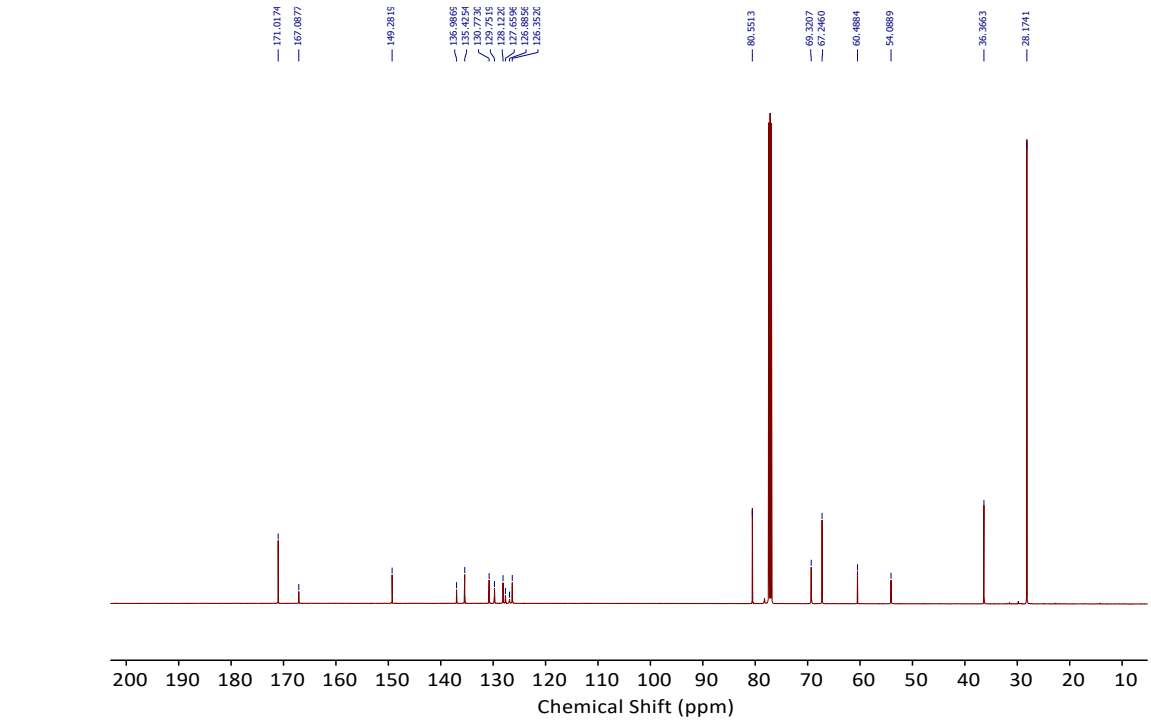


Figure S16 ^{13}C-NMR spectrum of **3·m** in $CDCl_3$ (298K, 126 MHz)

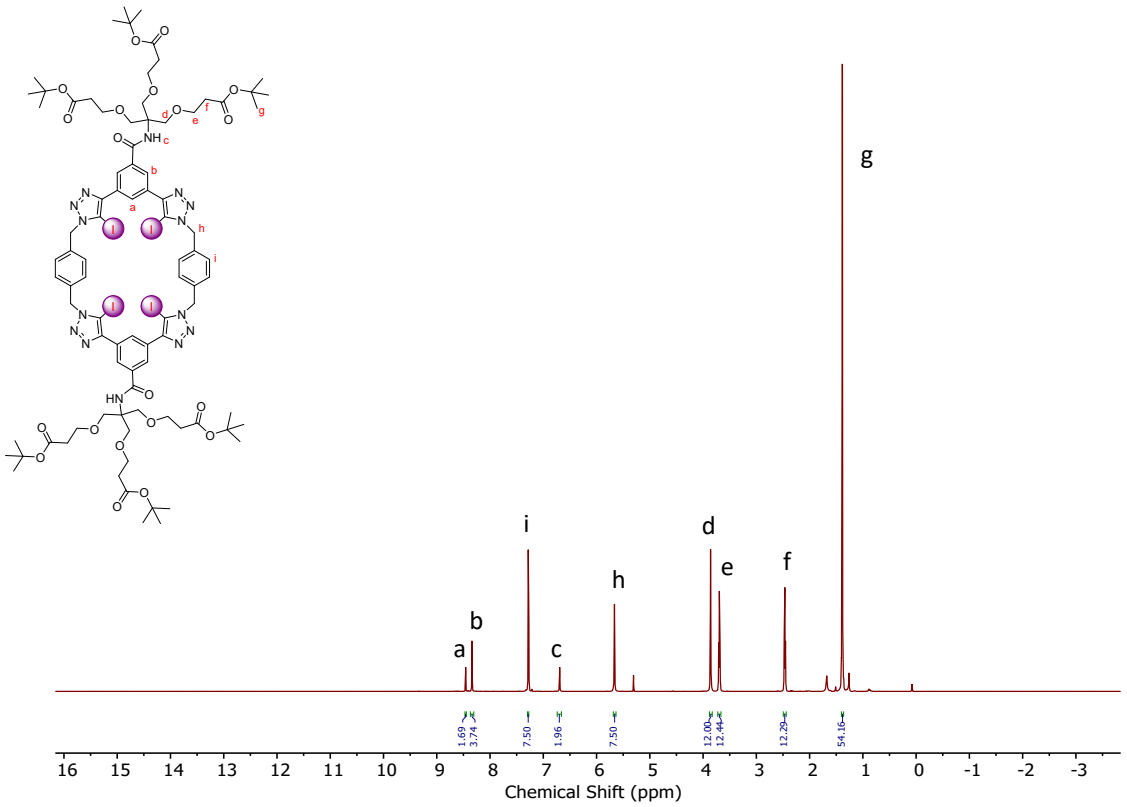


Figure S17 ^{1}H-NMR spectrum of **3·p** in $CDCl_3$ (298K, 500 MHz)

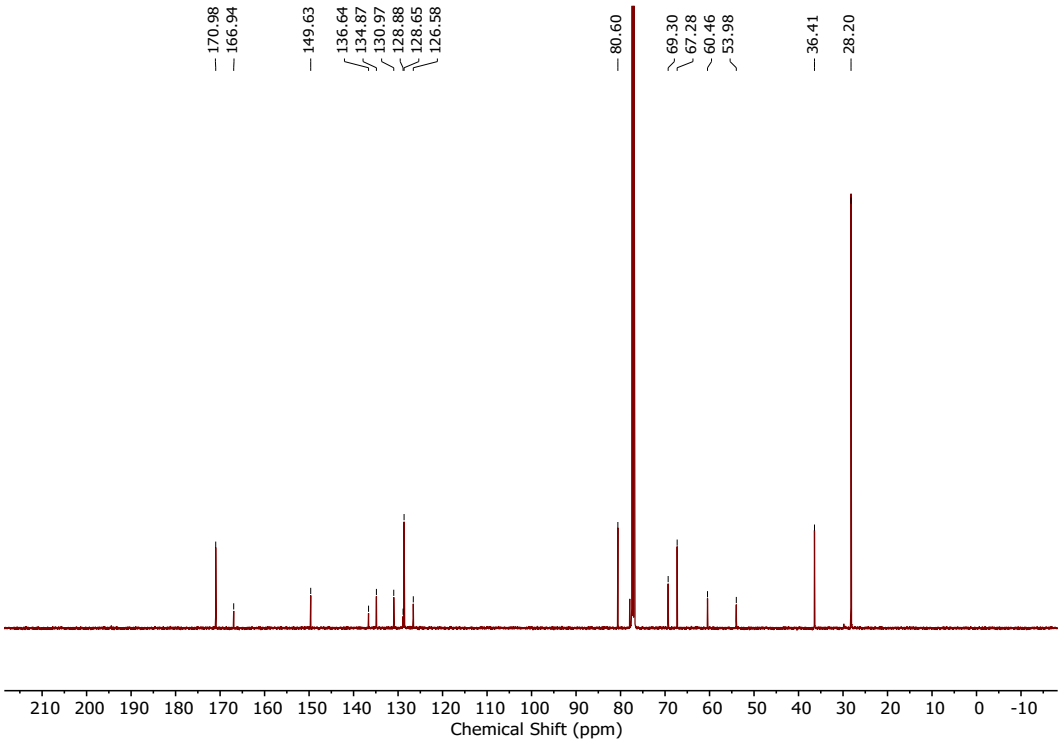


Figure S18 ^{13}C-NMR spectrum of **3·p** in $CDCl_3$ (298K, 126 MHz)

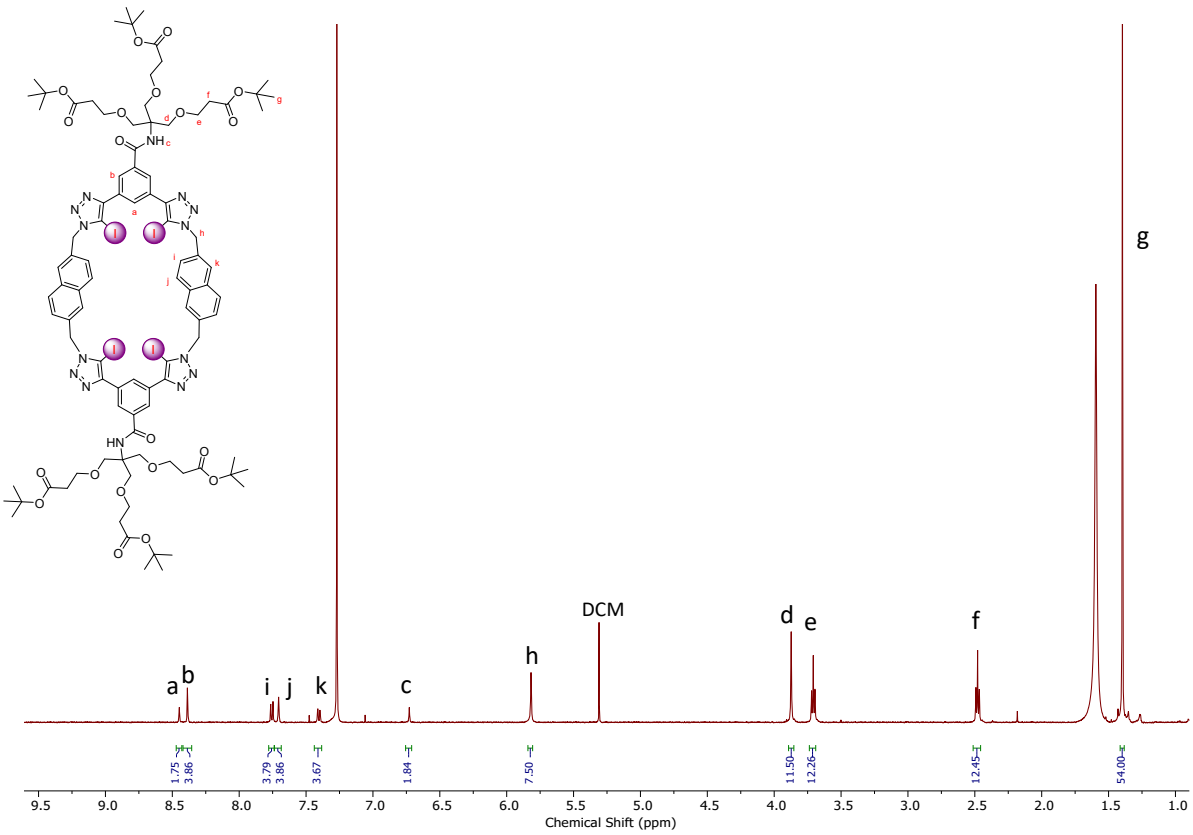


Figure S19 ^{1}H-NMR spectrum of **3·n** in $CDCl_3$ (298K, 500 MHz)

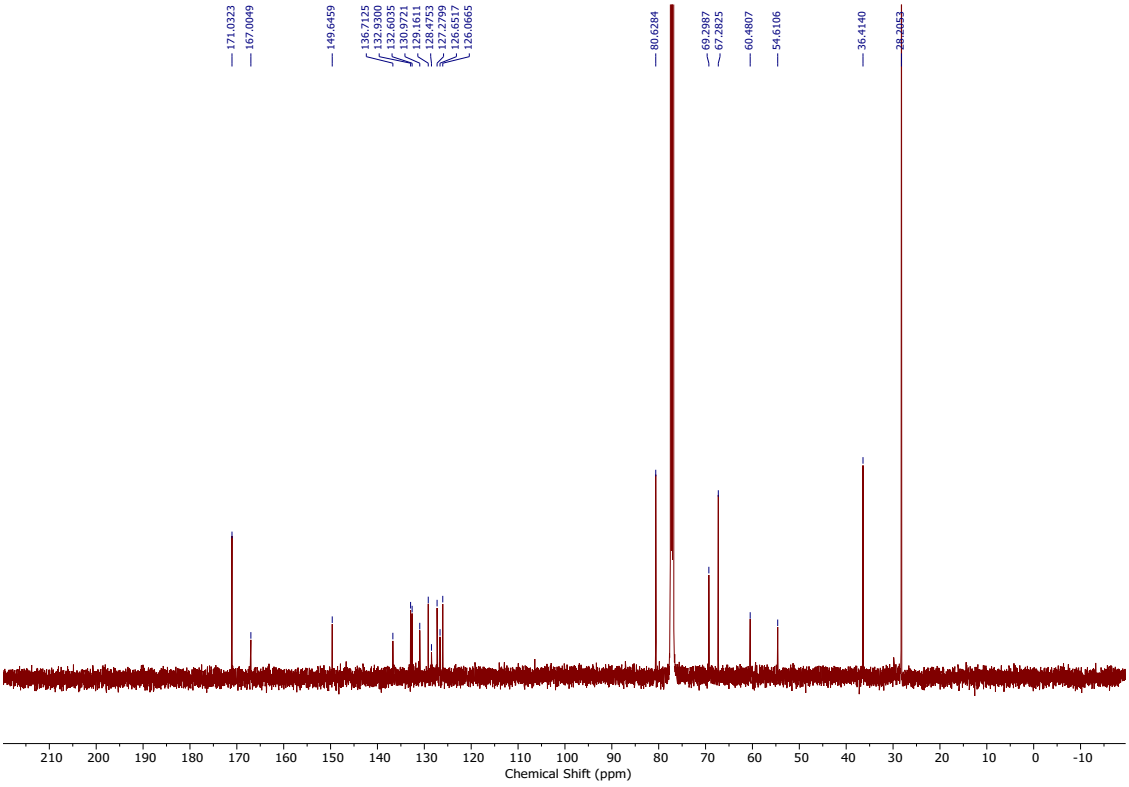


Figure S20 ^{13}C-NMR spectrum of **3·n** in $CDCl_3$ (298K, 126 MHz

2. ^{1}H-NMR Titration Protocol

^{1}H-NMR spectroscopic titration experiments were carried out at 298 K on a Varian Unity Plus 500 spectrometers with ^{1}H operating at 500 MHz. Initial sample volumes were 0.5 mL and concentrations were 1.0 mM of host in all experiments. Anion solution as tetrabutylammonium salts (50 mM) was added in aliquots, the samples were shaken and spectra recorded. Spectra were recorded at 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10 equivalents of anion. Some anions required addition up to 20-30 equivalents to reach a binding equilibrium. In all cases where association constants were calculated, bound and unbound species were found to be in fast exchange on the NMR timescale. Stability constants were obtained by analysis of the resulting data using the online program called Bindfit.[3]

Summary of anion binding data for 1·m

Table S1 Summary of Bindfit output data for **1·m** with TBACl from ^{1}H-NMR titration (40% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		18.37036133	2.091827874			0.002021479
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	5.442582092	-255.345076	4.209551335	-14.49754949	0.000782598
	Non-Cooperative					
	Additive	28.09632447	4.078263917	5.548558701	51.43050888	0.001964805
	Statistical	38.40469867	9.601174667	2.134383665		0.002035948

Table S2 Summary of Bindfit output data for **1·m** with TBABr from ^{1}H-NMR titration (40% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		452.9245079	2.662495296			0.001294209
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	288.0896825	-92.54566841	0.967790121	-0.967790121	0.000404624
	Non-Cooperative	1033.770192	258.4425479	2.98064542		0.000952744
	Additive	1602.45027	305.7020393	9.616775909	8.900688781	0.001001545
	Statistical	1592.705081	398.1762704	3.604584855		0.001222635

Table S3 Summary of Bindfit output data for **1·m** with TBAI from ^{1}H-NMR titration (40% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		17727.68402	20.35610554			0.003858322
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	16599.20375	97.1055468	27.59624731	285.2261235	0.003762384
	Non-Cooperative	14185.0183	3546.254575	45.29948993		0.006703052
	Additive	15849.30233	-2.34111684	20.0653306	-177.5215192	0.003774507
	Statistical	268905.2521	67226.31302	728.8001217		0.217625206

Table S4 Summary of Bindfit output data for **1·m** with TBA_2(oxalate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		2219	17			0.018167158
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	Too high	9234	198346707	15	0.000348065
	Non-Cooperative	816	204	11		0.010286946
	Additive	1093	-24	11	-20	0.011623441
	Statistical	65808	16452	50		0.004507658

Table S5 Summary of Bindfit output data for **1·m** with TBA_2(malonate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		2037.621441	15.55835744			0.016662775
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	2569	12506	8	30	0.000353
	Non-Cooperative	771	193	9		0.007740441
	Additive	1008	-24	9	-17	0.009464886
	Statistical	46738	11684	37		0.003501196

Table S6 Summary of Bindfit output data for **1·m** with TBA_2(succinate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		1679	9			0.006006055
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	2008	2195	5	23	0.000323958
	Non-Cooperative	889	222	4		0.001761192
	Additive	985	-19	5	-12	0.002598388
	Statistical	18076	4519	26		0.005816542

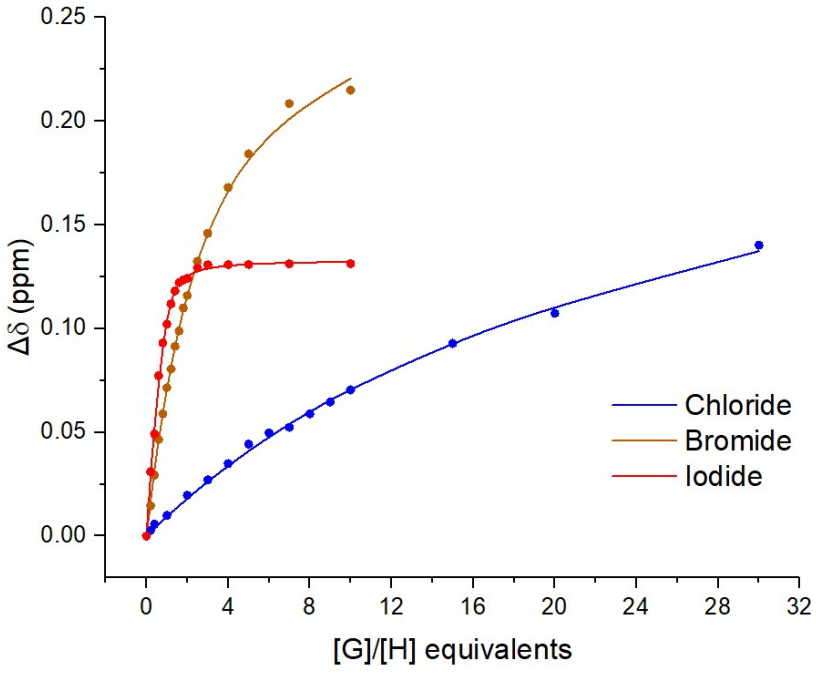


Figure S21 Halide binding isotherms derived from ^{1}H-NMR titrations of **1·m** with halides as a tetrabutylammonium salts (40% v/v D_2O in d_6-Acetone, 1 mM), where circles-represent experimental data and solid lines represent the fitted binding isotherm.

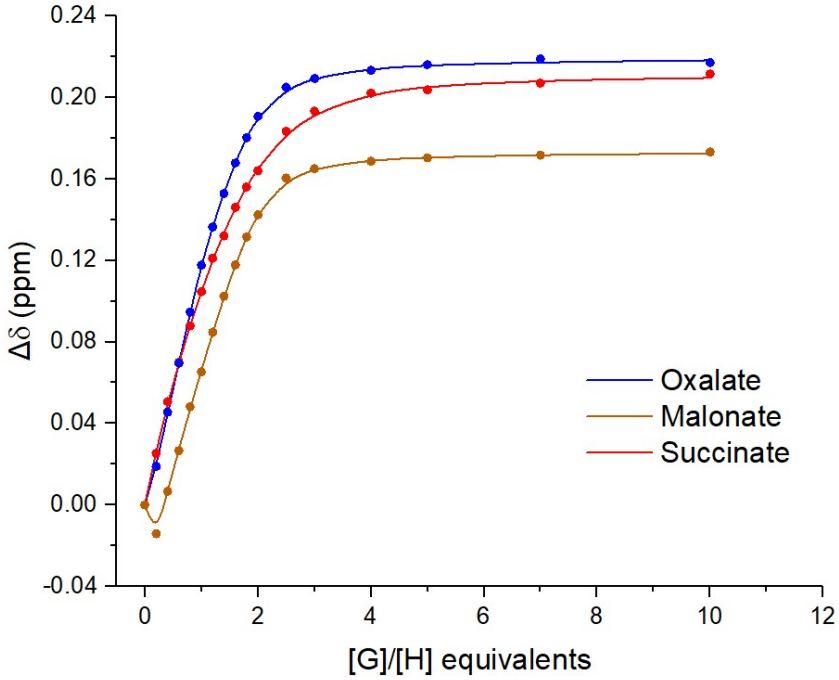


Figure S22 Dicarboxylate binding isotherms derived from ^{1}H-NMR titrations of **1·m** with dicarboxylate anions as a tetrabutylammonium salts (5% v/v D_2O in d_6-Acetone, 1 mM), where circles-represent experimental data and solid lines represent the fitted binding isotherm.

Summary of anion binding data for 1·p

Table S7 Summary of Bindfit output data for **1·p** with TBACl from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		334.152558	2.029189611			0.000780021
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	242.2700231	-70.69601114	1.249758168	-1.249758168	0.000603157
	Non-Cooperative	465.8244163	116.4561041	2.336391913		0.000754131
	Additive	967.9043753	169.2812524	6.817763665	7.429026996	0.00083659
	Statistical	975.3179536	243.8294884	3.254048338		0.001171832

Table S8 Summary of Bindfit output data for **1·p** with TBABr from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		334.5991122	4.63416487			0.003968354
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	126.0941968	151.6891353	1.244459729	3.976450293	0.000232513
	Non-Cooperative	1691.185987	422.7964968	3.298621923		0.00094109
	Additive	919.271155	452.4428787	9.634703077	9.078592045	0.000729143
	Statistical	1022.668892	255.667223	4.126387435		0.001922045

Table S9 Summary of Bindfit output data for **1·p** with TBAI from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		2729.068795	20.5693072			0.02365515
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	266.6248658	993.8267736	4.459639735	8.462018107	0.002216629
	Non-Cooperative	584.6672118	146.1668029	4.085548905		0.00241718
	Additive	924.6805872	-31.88958111	4.7396029	-5.897898907	0.003290126
	Statistical	75466.71143	18866.67786	108.3947566		0.018898807

Table S10 Summary of Bindfit output data for **1·p** with TBA_2(oxalate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		290.9258257	1.168517209			0.000292355
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	4345.537148	237.9300251	7.033947917	1.842303514	0.000110095
	Non-Cooperative	749.6928275	187.4232069	1.068257862		0.000158405
	Additive	856.872824	191.3563182	2.930510261	3.436061241	0.000149723
	Statistical	872.6263842	218.1565961	1.121743834		0.000181598

Table S11 Summary of Bindfit output data for **1·p** with TBA_2(malonate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		176.0459091	1.183123496			0.000370974
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	474.1596686	57.7271972	3.069794852	4.708841798	0.000298066
	Non-Cooperative	296.5629696	74.14074241	1.496396303		0.000455767
	Additive	307.8153038	34.06435442	2.379663185	7.321323459	0.000301633
	Statistical	459.4070997	114.8517749	1.727193748		0.000577484

Table S12 Summary of Bindfit output data for **1·p** with TBA_2(succinate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		92.55347788	1.78865438			0.000777271
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	38.61803107	-77.85458781	0.305006569	-0.305006569	0.000101436
	Non-Cooperative					
	Additive	220.3938734	76.40837885	4.119224559	5.215138409	0.000430538
	Statistical	210.1862488	52.54656221	1.725642463		0.000634435

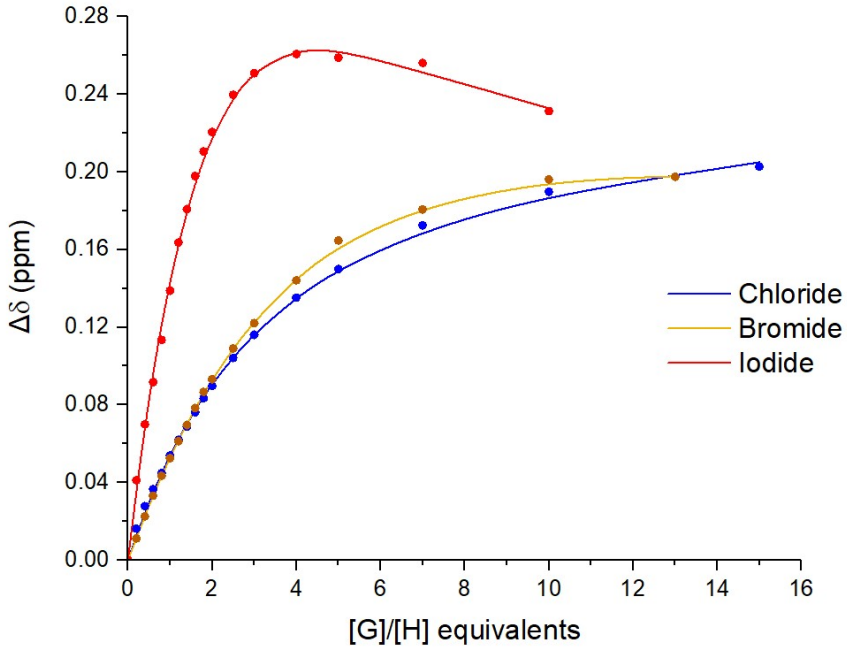


Figure S23 Halide binding isotherms derived from ^{1}H-NMR titrations of **1·p** with halides as a tetrabutylammonium salts (5% v/v D_2O in d_6-Acetone, 1 mM), where circles-represent experimental data and solid lines represent the fitted binding isotherm.

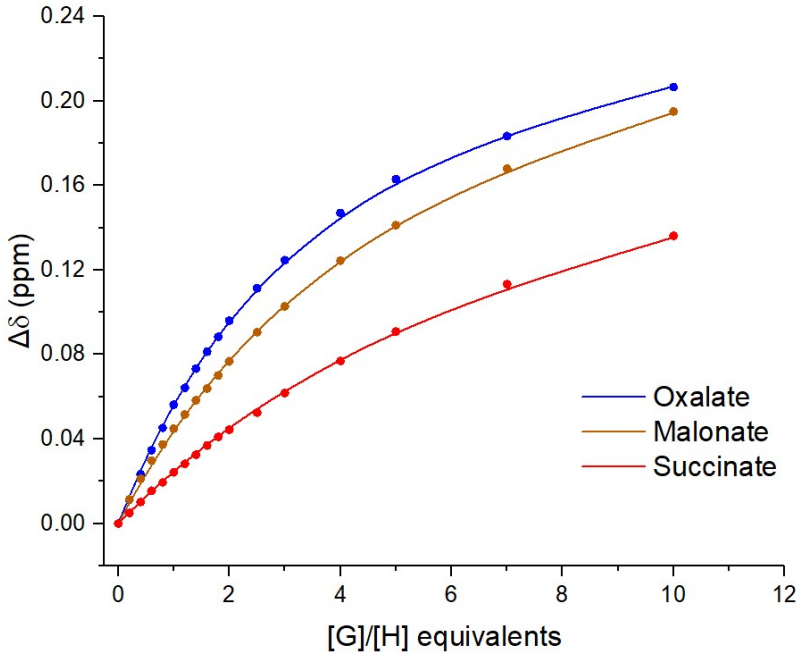


Figure S24 Dicarboxylate binding isotherms derived from ^{1}H-NMR titrations of **1·p** with dicarboxylate anions as a tetrabutylammonium salts (5% v/v D_2O in d_6-Acetone, 1 mM), where circles-represent experimental data and solid lines represent the fitted binding isotherm

Summary of anion binding data for 1·n

Table S13 Summary of Bindfit output data for **1·n** with TBACl from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		48.80793752	2.328371586			0.00140827
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	235.6243466	83.10876134	3.372140599	1.877995032	9.24802E-05
	Non-Cooperative					
	Additive	122.3605848	92.2221375	2.804717258	2.957468824	0.000103733
	Statistical	106.0009673	2.340219166			0.001305713

Table S14 Summary of Bindfit output data for **1·n** with TBABr from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		192.3690388	1.992966459			0.000766482
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	23309725.11	194.5238839	41230.45081	1.645524628	0.000168176
	Non-Cooperative	642.171061	160.5427653	1.758329683		0.000412302
	Additive	490.5072792	143.7200818	4.772382549	5.482080485	0.000442818
	Statistical	487.7897248	121.9474312	1.801150851		

Table S15 Summary of Bindfit output data for **1·n** with TBAI from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		1348.920562	7.569989179			0.005951516
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	4878.88484	93.44158409	13.71626758	12.09659375	0.002396721
	Non-Cooperative	1719.114004	429.778501	12.97556491		
	Additive	4932.080554	99.76222161	13.24742306	11.66429488	0.002398323
	Statistical	7280.249402	1820.06235	34.74587566		0.031458997

Table S16 Summary of Bindfit output data for **1·n** with TBA_2(oxalate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		55.35647631	2.259151223			0.001694882
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	-20.49182898	95.85220533	-0.89235146	0.89235146	0.000978373
	Non-Cooperative					
	Additive	141.748971	46.05762493	7.033520898	14.1537426	0.001617787
	Statistical	122.8371753	30.70929382	2.356853473		0.00167385

Table S17 Summary of Bindfit output data for **1·n** with TBA_2(malonate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		40.70114017	1.089687856			0.00040928
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	0.091402147	-7226.080417	1.695448536	-4.335948237	0.000288567
	Non-Cooperative					
	Additive	107.1209338	38.11747254	3.311860601	6.26161048	0.000331875
	Statistical	88.16917844	22.04229461	1.110549969		0.000396096

Table S18 Summary of Bindfit output data for **1·n** with TBA_2(succinate) from ^{1}H-NMR titration (5% v/v D_2O in d_6-Acetone, 1 mM)

Stoichiometry		**K**	**K error (%)**			**Covariance**
1:1		24.68149057	0.961937361			0.000400439
Stoichiometry	**Mode**	**K_{11}**	**K_{12}**	**K_{11} error (%)**	**K_{12} error (%)**	**Covariance**
1:2	Full	97794.54349	19.11057831	476.1538691	1.21343168	0.000279202
	Non-Cooperative					
	Additive	37.87430625	5.494491896	2.741418505	24.65673644	0.000389619
	Statistical	52.23056227	13.05764057	0.988859642		0.000404049

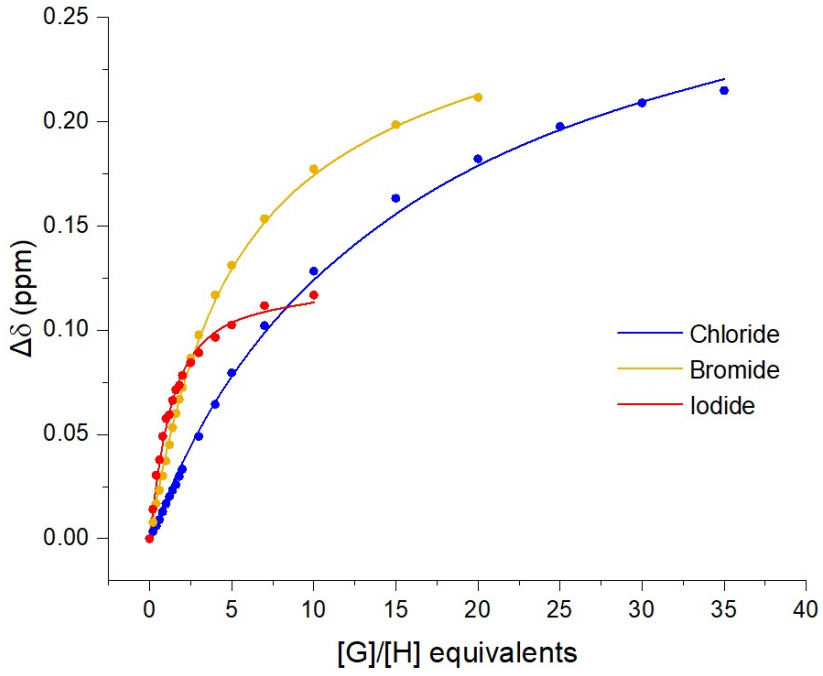


Figure S25 Halide binding isotherms derived from ^{1}H-NMR titrations of **1·n** with halides as a tetrabutylammonium salts (5% v/v D_2O in d_6-Acetone, 1 mM), where circles-represent experimental data and solid lines represent the fitted binding isotherm.

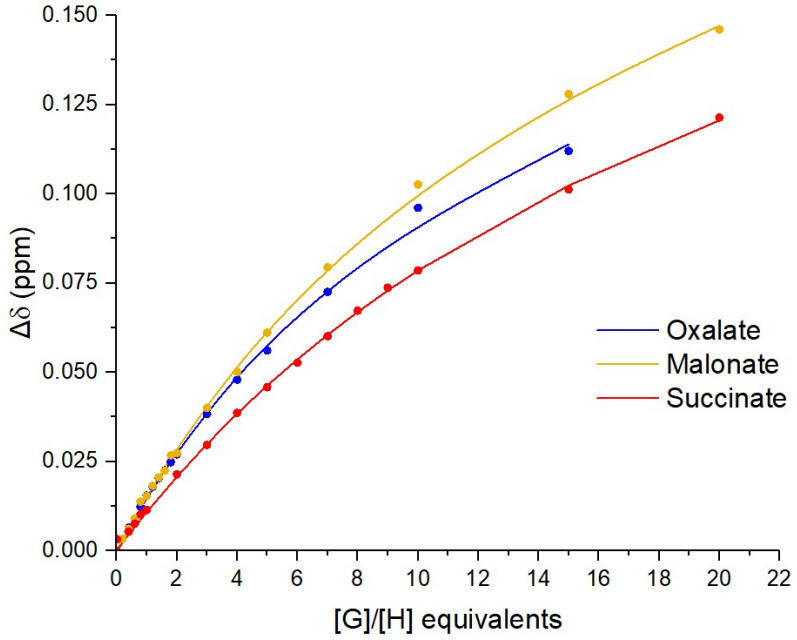


Figure S26 Dicarboxylate binding isotherms derived from ^{1}H-NMR titrations of **1·n** with dicarboxylate anions as a tetrabutylammonium salts (5% v/v D_2O in d_6-Acetone, 1 mM), where circles-represent experimental data and solid lines represent the fitted binding isotherm.

3. Fluorescence Anion Binding Titration Protocol

Fluorescence titration experiments were typically carried out by starting with 2.0 mL of a 1.0 × 10^{-4} M solution of the host **1·n** and adding aliquots of a solution containing the same concentration of the host together with a known concentration of the anion under study. Emission spectra of all samples were recorded from 350-650 nm with slit width of 5 nm, by applying an excitation wavelength at 330 nm with the slit width of 5 nm. Spectral changes were monitored at varying equivalent of anion from 0-100 equivalents or 0 – 10 mM of anion solutions.

3.1 Concentration-Independent Excimer Formation

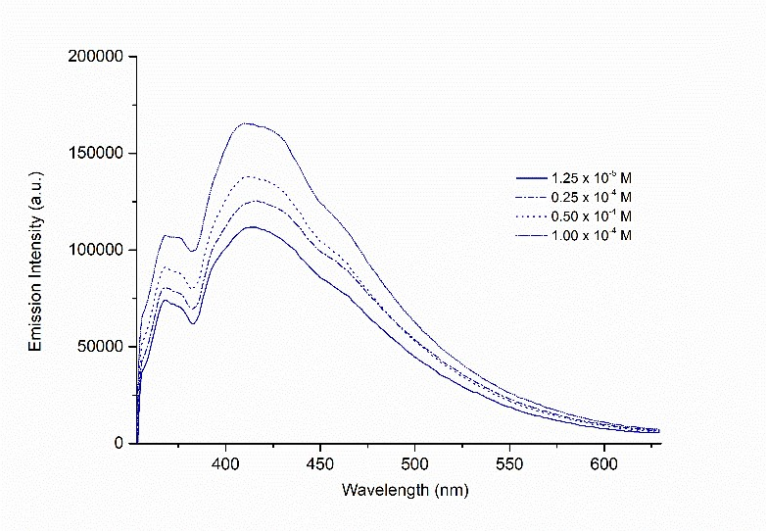


Figure S27 Fluorescence spectra of **1·n** in 5%H_2O/acetone at concentration of a) 1.00 x 10^{-4} M, b) 0.50 x 10^{-4} M, c) 0.25 x 10^{-4} M, and d) 1.25 x 10^{-5} M (Excitation wavelength 330 nm, slit width 5 nm)

3.2 Fluorescence Anion Titration Spectra

3.2.1 Halides

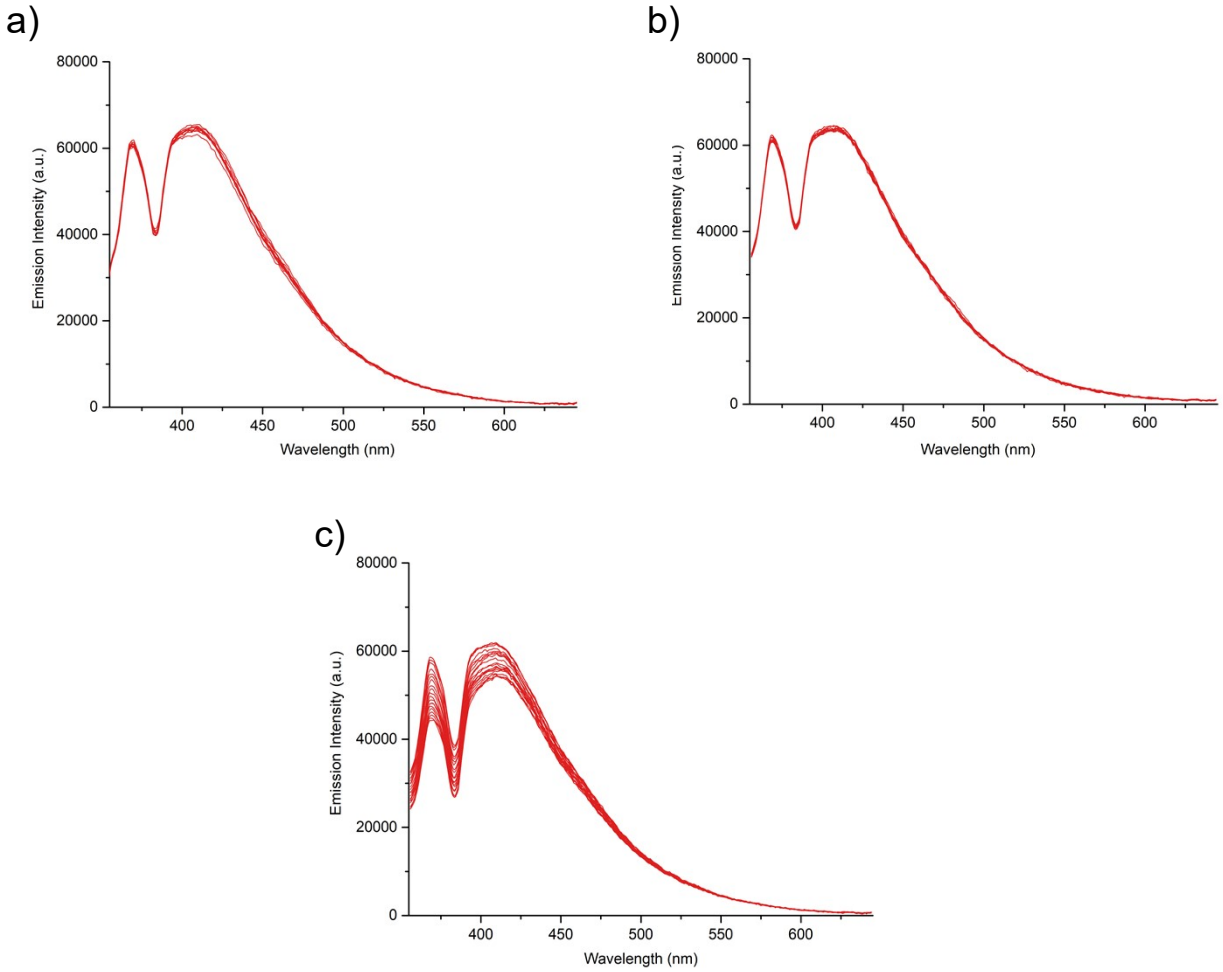


Figure S28 Fluorescence spectra of **1·n** in 5%H_2O/acetone at concentration of 1.00 x 10^{-4} M in the presence of 0-100 equivalents of a) TBACl b) TBABr and c) TBAI

3.2.2 Dicarboxylate anions

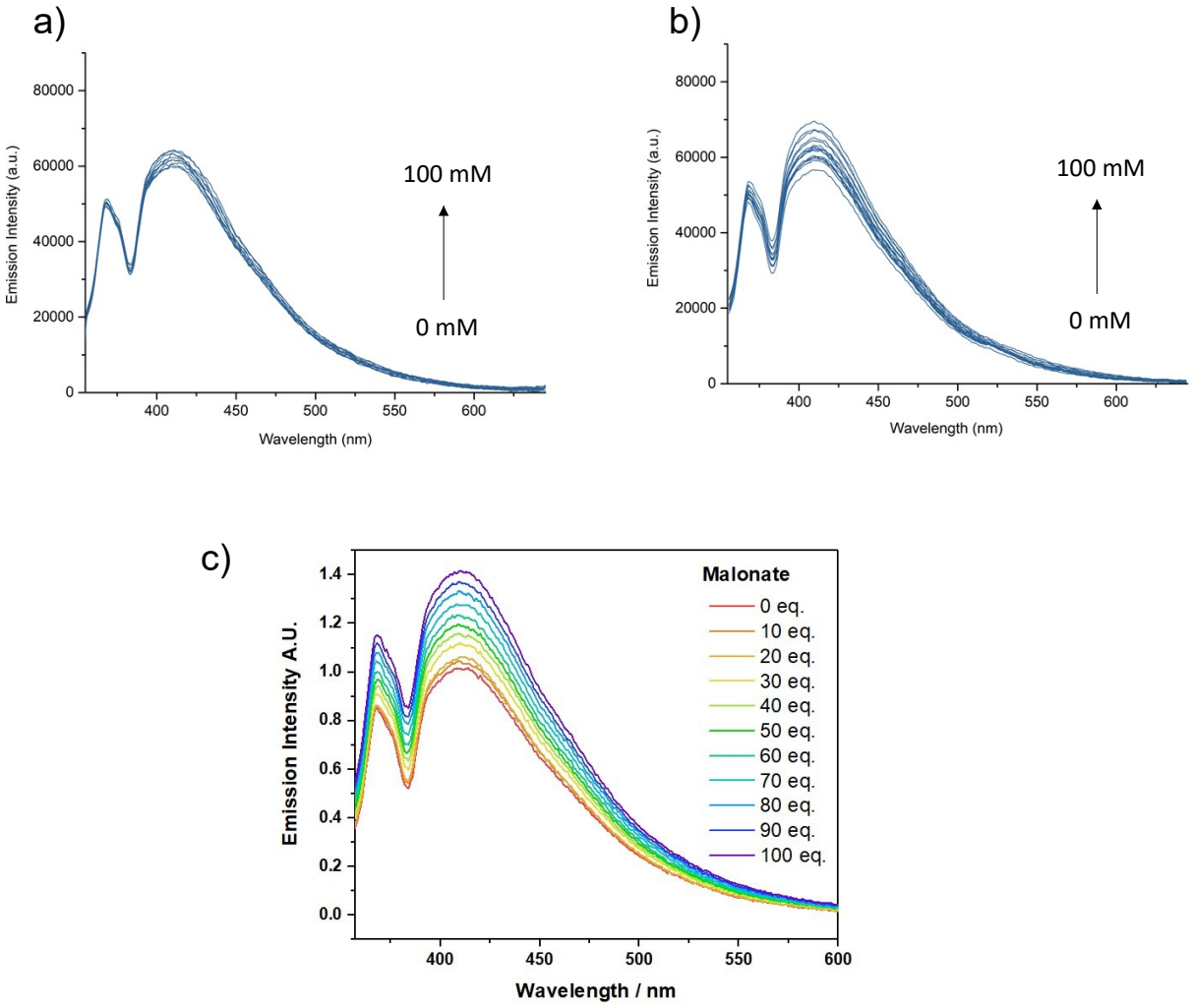


Figure S29 Fluorescence spectra of **1·n** in 5%H_2O/acetone at concentration of 1.00 x 10^{-4} M in the presence of 0-100 equivalents of a) TBA_2Oxalate b) TBA_2Succinate c) TBA_2Malonate.

3.2.3 Other Anions

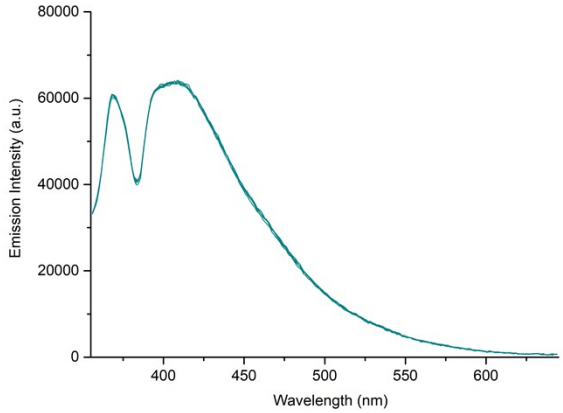


Figure S30 Fluorescence spectra of **1·n** in 5%H_2O/acetone at concentration of 1.00 x 10^{-4} M in the presence of 0-100 equivalents of $TBANO_3$

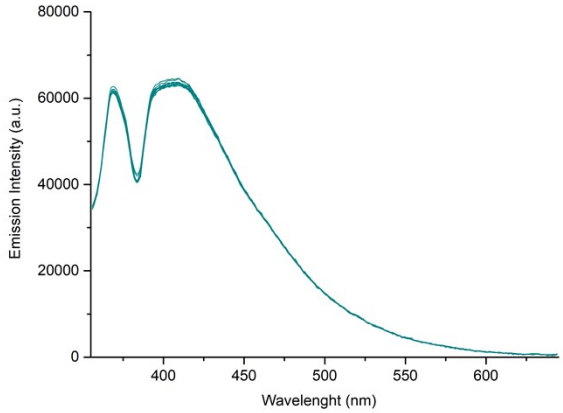


Figure S31 Fluorescence spectra of **1·n** in 5%H_2O/acetone at concentration of 1.00 x 10^{-4} M in the presence of 0-100 equivalents of TBASCN

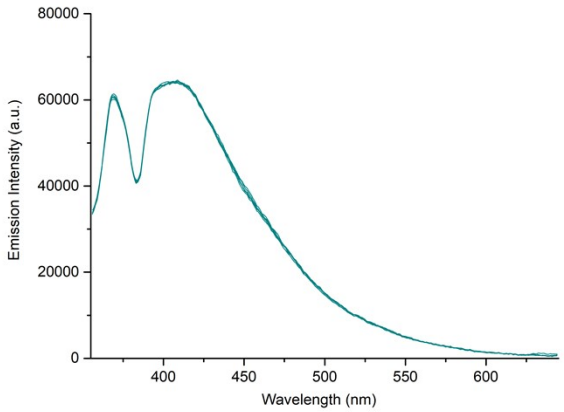


Figure S32 Fluorescence spectra of **1·n** in 5%H_2O/acetone at concentration of 1.00 x 10^{-4} M in the presence of 0-100 equivalents of $TBACIO_4$

4. Computational details

All calculations were performed by Gaussian 09[4] program. All gas-phase geometry optimizations and frequency calculations were carried out by M06-2X functional[5] and basis set 1 (BS1). In BS1, def2-TZVP[6] basis set was used for halogens, 6-31++G(d,p)[7-9] basis set for N and O and 6-31G(d)[7-9] basis set for all other C and H atoms. Single point energy calculation for solvent correction was performed on all structures using the same functional and basis set in solvent using an SMD[10] continuum solvation model with water solvent parameter ε = 78.3553. The molecular electrostatic potential (MEP) was plotted over electron density surface with an isovalue of 0.004 au. The color scale is ranged from 0.05 (red) to 0.10 (blue) au. The surface maxima on the MEP surfaces, between the most negative and most positive values, were calculated using multiwfn[11] program. The NBO analysis was performed using NBO 6.0.[12]

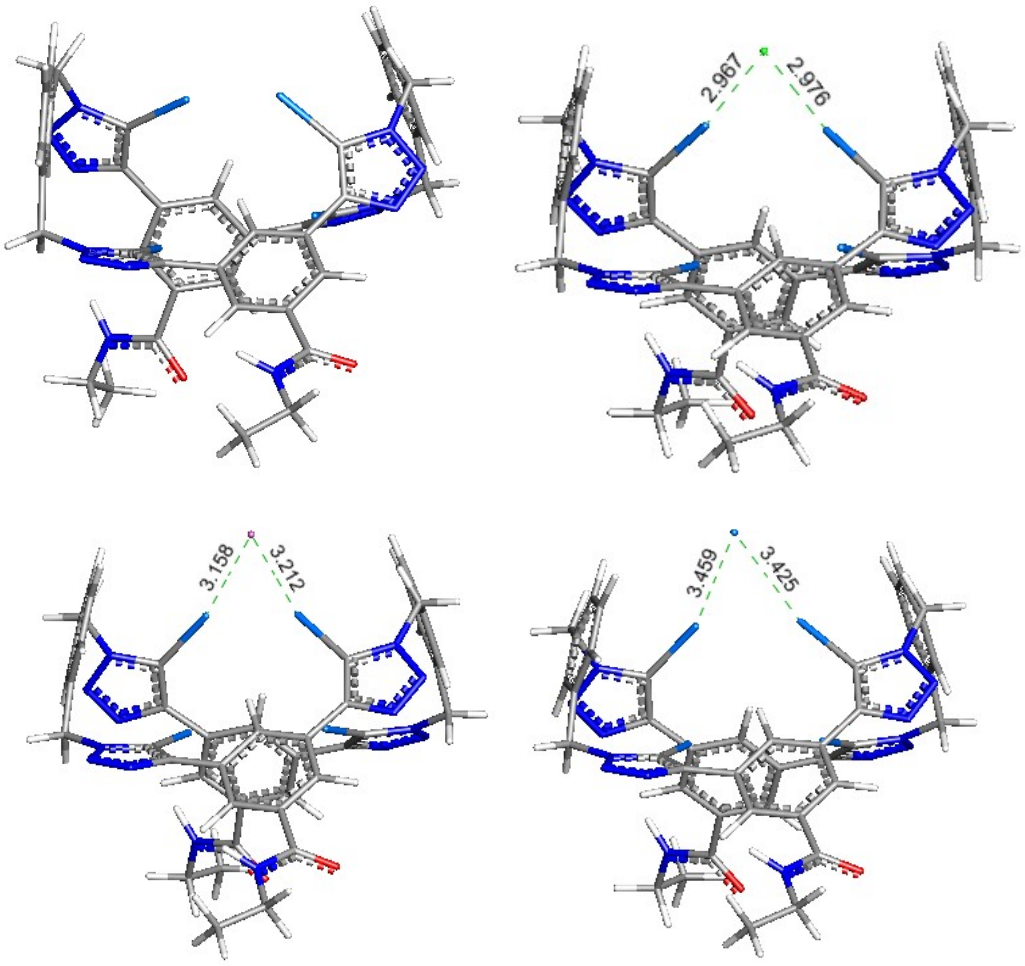


Figure S33. Optimized geometry of **1·m** and **1·m**–**X**$^-$ (X = Cl, Br, and I). The I···X distances are shown in Å

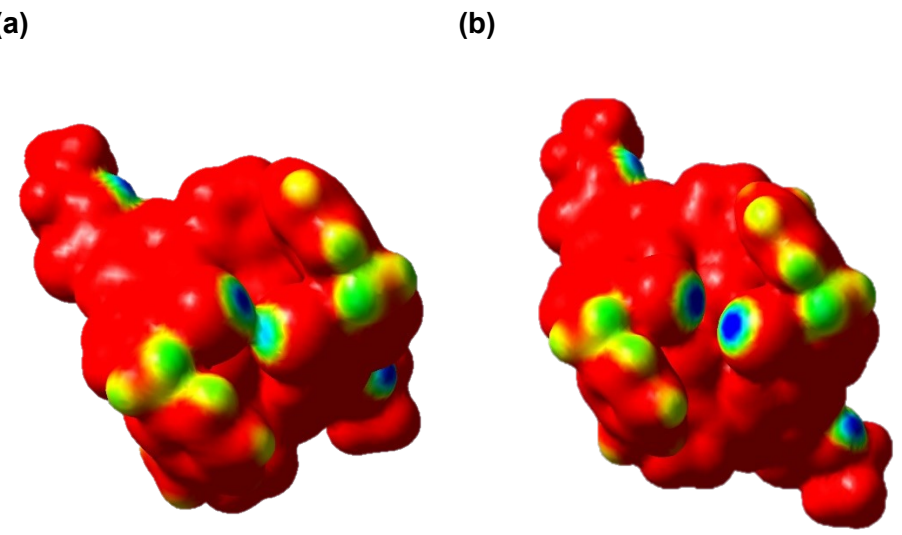


Figure S34. Electrostatic potential plots (ESPs) were mapped over electron density surfaces with isodensity of 0.004 au with the color scale from 0.05 (red) to 0.10 (blue) au for **1·m** and **1·m–Cl**$^-$ (The Cl atom is omitted for clarity).

Table S19 Maximum electrostatic potential at the binding sites of **1·m–Cl**$^-$**, 1·m–Br**$^-$**,** and **1·m–I**$^-$ in gas phase. Electrostatic potential plots (ESPs) were mapped over electron density surfaces with isodensity of 0.004 au.

Complex	Maximum electrostatic potential (in au)			
	I^1	I^3	I^2	I^4
1·m	0.1041	0.0921	0.0651	0.0735
1·m–Cl$^-$	0.1119	0.1133	0.0710	0.0824
1·m–Br$^-$	0.1100	0.1131	0.0845	0.0818
1·m–I$^-$	0.1096	0.1107	0.0854	0.0823

Table S20 Second-order perturbative energy, E(2), (in kcal/mol) for the orbital interaction from the lone pair of halide, LP (X^-), to σ*(C-I) of **1·m–X**$^-$ (X = Cl, Br, and I) in gas phase[a] and aqueous phase[b]

Donor	Acceptor	**1·m–X**$^-$		
		Cl	Br	I
[a]LP (X^-)	σ*(C-I^1)	18.81	15.00	13.38
[a]LP (X^-)	σ*(C-I^3)	20.60	17.38	11.65
[b]LP (X^-)	σ*(C-I^1)	16.98	14.23	10.68
[b]LP (X^-)	σ*(C-I^3)	18.24	16.14	9.16

Table S21 Optimized geometry parameters of **1·m** and **1·m–X⁻** (X = Cl, Br, and I)

Bond Distance (Å)	**1·m**	**1·m–X⁻**		
		Cl	Br	I
$I^1 \cdots X^-$	-	2.976	3.212	3.425
$I^3 \cdots X^-$	-	2.967	3.158	3.459
$I^2 \cdots X^-$	-	5.406	5.639	5.867
$I^4 \cdots X^-$	-	5.160	5.647	6.190
$C - I^1$	2.053	2.102	2.092	2.095
$C - I^3$	2.054	2.103	2.101	2.088
$C - I^2$	2.055	2.053	2.054	2.054
$C - I^4$	2.056	2.053	2.054	2.055

Table S22 Gas phase hydration energies (in kcal/mol) for the $[X(H_2O)_4]^-$ cluster formation (X = Cl, Br, and I).

Reaction	ΔE (kcal/mol)
$Cl^- + (H_2O)_4 \rightarrow [Cl(H_2O)_4]^-$	-39.49
$Br^- + (H_2O)_4 \rightarrow [Br(H_2O)_4]^-$	-33.26
$I^- + (H_2O)_4 \rightarrow [I(H_2O)_4]^-$	-26.98

Table S23 Solvent corrected binding energies for the binding of an anion to the sigma hole type receptors.

Reaction [a]	ΔE (kcal/mol)
1·m + $[Cl(H_2O)_4]^- \rightarrow$ **1·m**-Cl^- + $(H_2O)_4$	3.90
1·m + $[Br(H_2O)_4]^- \rightarrow$ **1·m**-Br^- + $(H_2O)_4$	3.10
1·m + $[I(H_2O)_4]^- \rightarrow$ **1·m**-I^- + $(H_2O)_4$	2.92

[a]Optimizations were performed in gas phase and single-point calculations were performed in water with 4 explicit water molecules on halide.

Table S24 Calculated gas phase binding energies for the binding of an anion to the sigma hole type receptors.

Reaction [a]	ΔE (kcal/mol)
1·m + Cl^- → **1·m**-Cl^-	-52.60
1·m + Br^- → **1·m**-Br^-	-46.11
1·m + I^- → **1·m**-I^-	-40.102

Cartesian coordinates of the optimized structures

1·m

96

scf done: -3727.40069561

C	-2.868777596	-0.934572208	0.347176151
C	-2.950202765	-2.256689424	0.794185069
C	-3.962910412	-2.626799544	1.679668833
C	-3.809501434	0.012732749	0.766336542
C	-4.802845462	-0.366541414	1.675704752
C	-4.884483159	-1.681048265	2.124946032
C	-5.994775030	-2.017349118	3.083331210
O	-6.510553903	-1.163942772	3.790525443
N	-6.383691602	-3.321050520	3.117888701
C	3.202781852	-1.962189819	-4.332768828
C	-7.486093925	-3.738485187	3.972418051
C	-7.551122635	-5.255692406	4.047879188
C	8.132131146	-1.259083362	5.150273759
N	-0.464047171	-4.537543674	-0.517593447
N	-1.603906716	-5.227539088	-0.619211741
N	-2.558622554	-4.497823961	-0.141172900
C	-2.055567609	-3.297934656	0.266954915
C	-0.693401817	-3.317019075	0.031596931
I	0.796061107	-1.993160501	0.531420621
C	0.728274941	-5.037600021	-1.192901142
N	-3.775953041	3.283699916	-0.816900023
N	-4.432223661	3.487528705	0.328849467
N	-4.474104067	2.370403810	0.973196043
C	-3.831912180	1.397640168	0.264243373
C	-3.368354223	1.990530592	-0.901058317
I	-2.405778837	1.265838809	-2.562121996
C	-3.441001103	4.432205510	-1.651469076
C	1.044209898	-3.079726239	-5.007904095

C	-0.029413262	-3.929008000	-4.746089673
C	-0.125567160	-4.579239440	-3.520838719
C	2.039072659	-2.893141064	-4.051524609
C	1.946246023	-3.559206740	-2.827521613
C	0.865432936	-4.391017214	-2.554456063
C	0.528987582	5.743157187	-0.631835883
C	-0.406966313	5.471215614	0.369727492
C	-1.697224159	5.097725350	0.018971633
C	0.169379291	5.619051951	-1.968862730
C	-1.117140061	5.202124585	-2.314737591
C	-2.055310598	4.942112392	-1.320495644
C	5.294144788	-0.843360974	3.769287808
O	4.919210537	-0.664193194	4.919456954
N	6.355214947	-1.638116617	3.458780397
C	7.157540309	-2.244315398	4.513439387
C	3.250205859	1.078828477	0.528830382
C	3.923420780	-0.116961911	0.275979928
C	4.587035715	-0.756104084	1.332727173
C	3.238819341	1.635286610	1.811488396
C	3.909794689	0.997958955	2.851696504
C	4.591336601	-0.195907946	2.607329550
N	3.762397584	-1.446785169	-3.093878416
N	4.825508843	-2.059401809	-2.562710790
N	4.976901938	-1.621088151	-1.357467156
C	3.994769005	-0.720100754	-1.063116561
C	3.198435240	-0.602881402	-2.191276437
I	1.489288777	0.462977293	-2.600684500
N	1.121711918	4.546832297	2.030667921
N	2.305544468	5.026201083	2.430018202
N	3.157635715	4.050850348	2.431329788
C	2.538643249	2.914042063	2.013530016
C	1.218008071	3.222647808	1.754721901
I	-0.346224022	1.999687883	1.222590866
C	0.003193547	5.460458927	1.825245945

H	-2.080136551	-0.665296157	-0.351139741
H	-3.996132605	-3.655743368	2.025506826
H	-5.526366071	0.359648229	2.031492934
H	-6.093467916	-3.940855415	2.373924567
H	4.027000139	-2.481216558	-4.828923448
H	2.891737433	-1.121829538	-4.959618620
H	7.685594130	-3.095994712	4.075375421
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H	8.834716909	-0.869528893	4.406971186
H	8.706530766	-1.747672528	5.942806197
H	7.581927986	-0.421906156	5.586754586
H	-7.318058849	-3.300864243	4.959430641
H	-8.429317584	-3.323308021	3.596261534
H	-6.624066550	-5.664878309	4.459983445
H	-8.379489643	-5.567466931	4.688530223
H	-7.713091014	-5.696118697	3.057834726
H	0.590151822	-6.118752364	-1.264070061
H	1.598958096	-4.830798756	-0.565745988
H	-3.519572314	4.139452966	-2.701271840
H	-4.212492458	5.176072566	-1.437219242
H	1.101642129	-2.552868685	-5.957209125
H	-0.801254455	-4.069964089	-5.495617236
H	-0.976548813	-5.219296760	-3.300532925
H	2.710045483	-3.415874313	-2.066129987
H	1.544320491	6.022289006	-0.358666704
H	-2.420631756	4.866364372	0.798404567
H	0.898922559	5.820785707	-2.746482167
H	-1.383081773	5.064972210	-3.359955470
H	6.750896307	-1.573482197	2.531141069
H	2.763271101	1.620389214	-0.275190558
H	5.083233997	-1.701193161	1.133711440
H	3.908848467	1.415318315	3.853884699
H	-0.831503996	5.150163124	2.460837910
H	0.366464182	6.431402624	2.170247203

1·m-Cl$^-$

97

scf done: -4187.74039612

C	3.724023780	0.410900189	0.546973286
C	4.056166047	1.644989573	1.111745038
C	5.127552004	1.732231985	2.001448640
C	4.438802622	-0.744468842	0.879972571
C	5.496975051	-0.645998824	1.791540243
C	5.850398346	0.586640674	2.333576435
C	7.027270743	0.631657772	3.264216683
O	7.391587676	-0.339086391	3.914008822
N	7.675044987	1.831288918	3.342340501
C	-2.985007647	3.789106460	-3.218837543
C	8.878109687	1.969477867	4.144527493
C	9.250720729	3.436956624	4.291254469
C	-9.723911278	0.666532426	4.366257255
N	1.896999049	4.425748556	0.275424086
N	3.101118404	4.998669094	0.373577329
N	3.957322377	4.075709750	0.676884652
C	3.322638850	2.872585702	0.770193755
C	1.980520780	3.093467616	0.513699804
I	0.346672103	1.851139856	0.542754661
C	0.747860993	5.209372685	-0.157876384
N	3.551890709	-3.779772132	-0.872155653
N	4.361342545	-4.210827858	0.105895068
N	4.715384813	-3.181687968	0.798695593
C	4.137138246	-2.056717818	0.284434614
C	3.365596232	-2.434160907	-0.810671488
I	2.100006147	-1.504322304	-2.207506031
C	2.990361214	-4.743926705	-1.806507311
C	-0.589659449	3.846109787	-4.007159907
C	0.764647514	4.083585158	-3.785411714

C	1.197767517	4.546663283	-2.548323219
C	-1.517712175	4.085539054	-2.997222729
C	-1.080494612	4.552676295	-1.758064914
C	0.273279509	4.775905702	-1.527417726
C	-1.235702983	-5.289350206	-1.201909258
C	-0.372330519	-5.246577385	-0.105835733
C	0.995861710	-5.096176132	-0.309160519
C	-0.728347523	-5.157832132	-2.489739240
C	0.639251325	-4.984680951	-2.687104152
C	1.507762621	-4.960433960	-1.598751145
C	-6.616622300	0.402680331	3.679642504
O	-6.594646373	-0.230098339	4.728380029
N	-7.533439762	1.388114489	3.455105940
C	-8.573767083	1.667327605	4.430467153
C	-3.825337235	-0.441876741	0.540545055
C	-4.431955966	0.816031966	0.573343287
C	-5.336325698	1.099076308	1.605088061
C	-4.099551841	-1.393730147	1.528997303
C	-5.013123093	-1.102670658	2.541499603
C	-5.638909689	0.142470020	2.570710581
N	-3.593221497	3.140255272	-2.067218605
N	-4.454472506	3.829335543	-1.307301303
N	-4.806306915	3.062802518	-0.330546860
C	-4.170495003	1.857895520	-0.434003901
C	-3.365979229	1.894710083	-1.569489589
I	-2.011740212	0.630636191	-2.568519391
N	-2.054990420	-4.372755146	1.455703780
N	-3.255654175	-4.850432530	1.804189870
N	-4.083234409	-3.855713821	1.852603141
C	-3.432962661	-2.704718116	1.523662204
C	-2.113190243	-3.031532888	1.267424377
I	-0.490373899	-1.878825941	0.764766325
C	-0.925031459	-5.280493196	1.300913825
CL	0.070451335	-0.684291998	-4.223426123

H	2.913982393	0.356014445	-0.172392286
H	5.355776710	2.697235796	2.444650444
H	6.058557157	-1.531062697	2.070945694
H	7.488550471	2.527320004	2.633124241
H	-3.563774606	4.705317697	-3.365627528
H	-3.115779507	3.147479067	-4.095114035
H	-8.929081392	2.687196917	4.254947662
H	-8.105517141	1.637777489	5.417231517
H	-10.206441326	0.691558397	3.383926955
H	-10.478025440	0.894054061	5.126297051
H	-9.343130855	-0.342312305	4.543817972
H	8.678129413	1.516034488	5.118553498
H	9.702258308	1.401136604	3.693803831
H	8.445757473	3.993927228	4.779664425
H	10.157686979	3.540962950	4.892564338
H	9.443304220	3.896637613	3.315440572
H	1.095392982	6.245764580	-0.148046042
H	-0.051482681	5.101465976	0.581521030
H	3.185040543	-4.398105032	-2.825852954
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1·m-Br⁻

97

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C	-4.356336917	0.524549591	0.985841400
C	-5.289239872	0.365072987	2.018327831
C	-5.566140284	-0.898595855	2.532649091
C	-6.599260002	-1.003243327	3.616504417
O	-6.872846046	-0.068413110	4.357076373
N	-7.218792599	-2.214089226	3.733104431
C	3.089118247	-3.362262116	-3.397837071
C	-8.274197284	-2.409874371	4.711995387
C	-8.622188525	-3.886028948	4.827017104
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C	-1.924999450	-3.243610451	0.155676922
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C	-0.739924555	-5.288811356	-0.789717534
N	-3.623933210	3.673117005	-0.640081275
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N	-4.750449547	2.946523895	1.004713285
C	-4.131022627	1.871147895	0.434864432
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C	-1.115350909	-4.199195658	-3.035376491
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C	-0.224635152	-4.637906357	-2.053303266
C	1.134935247	5.158295389	-0.590465836
C	0.194336264	5.122248915	0.441234441
C	-1.158102018	5.016151853	0.137210504
C	0.718862083	5.063012895	-1.913234533
C	-0.636024239	4.935743673	-2.212986543
C	-1.579251655	4.919831119	-1.188836443
C	6.392552777	-0.696924495	3.973432097
O	6.312385160	-0.211101259	5.095031448
N	7.377450130	-1.580438107	3.641200880
C	8.422419550	-1.917580748	4.593391358
C	3.614693811	0.372826350	0.894375854
C	4.268844157	-0.857690584	0.804392771
C	5.167788401	-1.216956221	1.816314098
C	3.843137474	1.227954387	1.977836101
C	4.749465902	0.863007189	2.972213433
C	5.417549129	-0.357591705	2.883744045
N	3.613199997	-2.861051300	-2.134487088
N	4.389731134	-3.653919083	-1.386315822
N	4.668123724	-3.012251557	-0.300868871
C	4.066979626	-1.785932316	-0.320651263
C	3.366861643	-1.673901016	-1.517598778
I	2.152215184	-0.260425431	-2.489554901
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N	2.955067325	4.649562656	2.460252862
N	3.789142645	3.658940830	2.470029227
C	3.152680083	2.523314219	2.068833579
C	1.834297332	2.854311987	1.810858638
I	0.222972165	1.711157479	1.249658899
C	0.646000517	5.099808085	1.884319889
BR	0.148290734	1.283481845	-4.380504642

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H	-7.134046967	-2.877832397	2.975424166
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H	8.859406350	-2.871008220	4.281833706
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H	10.253329054	-1.115788056	5.436308559
H	9.031166779	0.105157630	5.022022786
H	-7.914511867	-2.015884277	5.665925445
H	-9.158759926	-1.820179969	4.439216528
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H	-8.987084536	-4.282982856	3.873255287
H	-1.135773638	-6.292708243	-0.964374006
H	0.055142397	-5.353154955	-0.040080262
H	-3.195067267	4.435443528	-2.533778874
H	-3.637512040	5.606903212	-1.270908367
H	1.076856716	-2.625099160	-5.094540620
H	-1.336029174	-3.115301105	-4.878848350
H	-2.182731885	-4.367287287	-2.908154948
H	1.830780824	-4.696501216	-1.416002234
H	2.194995890	5.211624656	-0.351333279
H	-1.892664957	4.940206847	0.938502977
H	1.449417549	5.039139466	-2.714887035
H	-0.948474582	4.784779857	-3.243143875
H	7.515315873	-1.805668253	2.666648847
H	2.937272055	0.684626168	0.106226267
H	5.640193578	-2.192219653	1.753096450
H	4.939594520	1.519342527	3.815550038
H	-0.176356469	4.793789334	2.538755402
H	1.020801457	6.068660045	2.224499672

1·m-I⁻

97

scf done: -4025.1868276

C	3.614379231	-0.665081248	-0.683677470
C	3.879414410	-1.978065335	-1.079813069
C	4.838663210	-2.223074741	-2.062334619
C	4.288939801	0.410078333	-1.269769832
C	5.232144204	0.152244212	-2.272160231
C	5.516244343	-1.156436862	-2.653233718
C	6.568333470	-1.370322246	-3.702798474
O	6.840552120	-0.524820167	-4.544259359
N	7.206523366	-2.576264389	-3.662216086
C	-3.059334006	-3.049024532	3.586375724
C	8.287449358	-2.873569442	-4.586088605
C	8.633312037	-4.354001071	-4.535488102
C	-9.659216638	-1.247980657	-4.478941687
N	1.855747913	-4.525515915	0.499089661
N	3.059131914	-5.103252138	0.420593636
N	3.867341019	-4.268085365	-0.150298778
C	3.200782235	-3.116385140	-0.444314672
C	1.889682357	-3.277659869	-0.032185128
I	0.250510225	-2.051820200	-0.199767351
C	0.764542467	-5.213475945	1.179759920
N	3.587569018	3.685165424	0.095006884
N	4.361024970	3.950132089	-0.965435313
N	4.653154132	2.824875480	-1.526030298
C	4.063277482	1.800512354	-0.842837496
C	3.355310582	2.351807106	0.220363188
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C	3.023488472	4.788820769	0.860185447
C	-0.676184641	-2.713530098	4.362176364
C	0.691813735	-2.944143868	4.226896254

C	1.160374087	-3.791078904	3.229126284
C	-1.578022086	-3.346111237	3.510616157
C	-1.103979493	-4.194691616	2.510365321
C	0.260664497	-4.407923546	2.355930977
C	-1.158792959	5.186410473	-0.062165640
C	-0.222399629	5.030146315	-1.087190733
C	1.128759418	4.936687290	-0.776027990
C	-0.738710396	5.223189291	1.262218455
C	0.615642151	5.107109352	1.571593808
C	1.553910009	4.973640842	0.551905628
C	-6.521956927	-1.056411053	-3.916640599
O	-6.491652653	-0.660846049	-5.075423524
N	-7.490290828	-1.909038381	-3.473233094
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C	-3.602328940	0.248342992	-1.065285944
C	-4.275233890	-0.952330605	-0.830036519
C	-5.219013962	-1.390377642	-1.767035406
C	-3.863846298	1.000808197	-2.215451682
C	-4.816853571	0.560253692	-3.132916899
C	-5.498473733	-0.634226308	-2.902523838
N	-3.595169948	-2.668840418	2.283219237
N	-4.360747131	-3.535201615	1.610287484
N	-4.643849311	-3.000905918	0.468903816
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I	-0.212212587	1.542096963	-1.640205564
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H	5.016871275	-3.249504075	-2.369942843
H	5.758589417	0.972097704	-2.749205301
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H	8.962644496	-4.650275229	-3.533325434
H	1.186990092	-6.177204938	1.476294290
H	-0.043624676	-5.391987816	0.463280359
H	3.176387895	4.595933911	1.925335244
H	3.612090382	5.663564892	0.571611614
H	-1.029136709	-1.988449794	5.091433415
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H	2.229927113	-3.935225909	3.090497452
H	-1.807707045	-4.635414870	1.804742886
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H	1.859828201	4.775889006	-1.567447034
H	-1.467318935	5.303271821	2.062075401
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H	-7.588857347	-2.054079500	-2.478915723
H	-2.885210828	0.621622095	-0.341492488
H	-5.702010448	-2.345872296	-1.589385062
H	-5.034629116	1.137835602	-4.025573732
H	0.144059366	4.515704476	-3.149136635
H	-1.062198926	5.803997778	-2.943913396

$(H_2O)_4$

12

scf done: -305.5912421

O	-1.358631620	1.358631620	0.047267730
O	-1.358631620	-1.358631620	-0.047267730
O	1.358631620	-1.358631620	0.047267730
O	1.358631620	1.358631620	-0.047267730
H	-0.383904359	1.508219533	-0.001895863
H	-1.670494280	1.823580413	0.834390297
H	-1.508219533	-0.383904359	0.001895863
H	-1.823580413	-1.670494280	-0.834390297
H	0.383904359	-1.508219533	-0.001895863
H	1.670494280	-1.823580413	0.834390297
H	1.508219533	0.383904359	0.001895863
H	1.823580413	1.670494280	-0.834390297

$[Cl(H_2O)_4]^-$

13

scf done: -765.910047624

O	-0.671779681	-2.042565556	-0.230041284
O	-0.590282444	0.112234143	-2.071569562
O	-0.927858026	1.954115679	0.056774636
O	-1.010372008	-0.201121129	1.899072830
CL	1.730106429	0.095674280	0.186651205
H	-1.076550794	-1.581536578	0.532946598
H	0.258248380	-1.744414952	-0.162759448
H	0.319497668	0.198585567	-1.720192038
H	-0.889576346	-0.707589227	-1.628019528

H -1.105334958 1.460867918 -0.770199671

H 0.021954368 1.761702185 0.194524798

H -0.042175795 -0.180679776 1.756310607

H -1.295534598 0.585297009 1.390425220

$[Br(H_2O)_4]^-$

13

scf done: -2879.91521472

O -1.332413467 -0.216873166 1.984617398

O -1.331954072 -1.985032199 -0.216727881

O -1.332363713 0.216806656 -1.984692552

O -1.332150624 1.984962210 0.216808192

BR 1.441331735 0.000044702 0.000020148

H -1.585125187 0.602360576 1.508345462

H -0.369183420 -0.250447023 1.823169290

H -0.368625165 -1.823449198 -0.250878412

H -1.584694421 -1.508410947 0.602260466

H -1.584977462 -0.602414578 -1.508455128

H -0.369161667 0.250299136 -1.823187716

H -0.368842199 1.823132449 0.250199038

H -1.584946119 1.508456986 -0.602199441

$[I(H_2O)_4]^-$

13

scf done: -603.356461692

O -1.770624718 1.985902674 0.098684363

O -1.770235836 -0.098800403 1.985027717

O -1.770625411 -1.985904680 -0.098797819

O -1.769906799 0.098815568 -1.985145115

I 1.279028170 -0.000002381 0.000037292

H -1.986223609 1.446027573 -0.692780002

H	-0.798240485	1.913566142	0.138928043
H	-0.797895118	-0.138790974	1.911670074
H	-1.986499586	0.692815346	1.445672188
H	-1.986374727	-1.446051941	0.692638214
H	-0.798235929	-1.913536592	-0.138874081
H	-0.797575633	0.138759891	-1.911584326
H	-1.986305796	-0.692768556	-1.445799757

5. ^{1}H NMR concentration dependence

To confirm that any peak width changes observed during the ^{1}H NMR anion titration experiments for **1·m** are due to a perturbation of macrocycle dynamism and not de-aggregation effects, ^{1}H NMR spectra were measured in the range 0.05 - 1.00 mM, wherein in this concentration range, no chemical shift changes were observed suggesting the aggregation effect do not operate under these conditions.

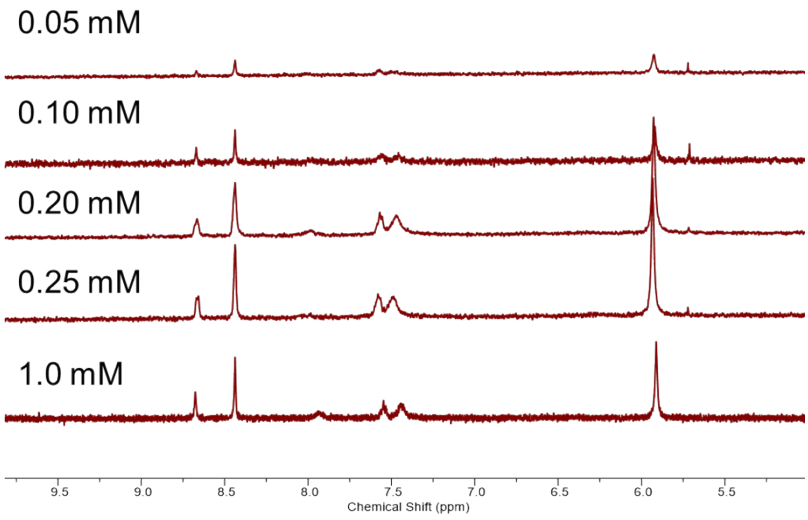

Figure S35. ^{1}H NMR spectra of **1·m** of various concentration ranges in 5%D_2O/d_6-acetone.

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