One-pot, highly efficient, cavity controllable synthesis, and binding properties of carbazole-based macrocycles with sulfonamide linkages

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Electronic Supporting Information (ESI)

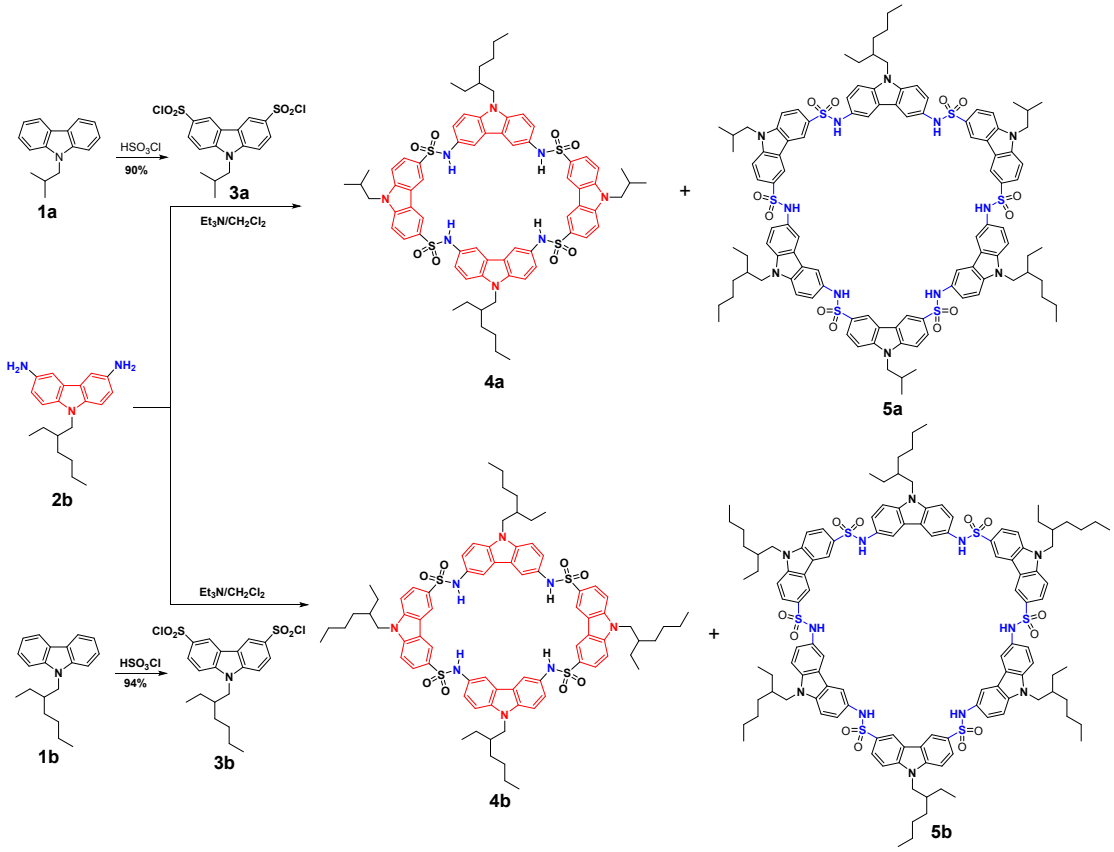
1. General Information

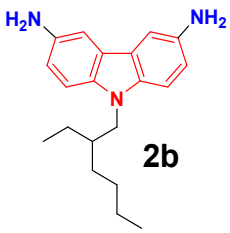
All solvents for reactions and column chromatography were used directly as received.

Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 MHz or 100 MHz instruments. Chemical shifts were expressed in parts per million (δ) using residual solvent protons as internal standards. Coupling constants (*J* values) are given in hertz (Hz). Chloroform (δ = 7.26 ppm) was used as an internal standard for chloroform-*d*. DMSO (δ = 2.50 ppm) was used as an internal standard for DMSO-d_6. Alcohol free chloroform was used as solvent for spectroscopic measurements, which was freshly distilled from P_2O_5. Dimethyl sulfoxide (DMSO) were commercially available and used directly. UV-vis data were recorded on UV-2600 PC SHIMADZU at room temperature. The fluorescence data were recorded on a LS-45 spectrofluorophotometer (Shimadzu Corporation, Japan). HRMS analysis was performed using a MALDI-TOF or ESI mass spectrometer. The melting points were collected on a SHPSIC WRX-4 automatic melting point apparatus.

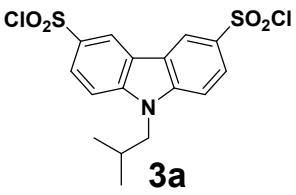
Compounds **2b**[S1], **1a**[S2], **1b**[S2] were synthesized according to similar literature procedures. All NMR experiments were performed on a Bruker AV 400 MHz instruments at 298 K if not specifically indicated.

2. One-Pot Synthesis of the Macrocycles





This compound was synthesized according to similar literature procedures.[S1]



A solution of chlorosulphonic acid (6.4 mL, 96 mmol) in CH_2Cl_2 (20 mL) was added dropwise into a stirred solution of *N*-(2-methylpropyl)carbazole **1a** (3.353 g, 15 mmol) in CH_2Cl_2 (40 mL) at -5 °C over a period of 1.5 hours. The mixture was allowed to reach room temperature and stirred for another 3 hours. The reaction mixture was poured into ice water and extracted three times with CH_2Cl_2. The combined organic phase was washed with brine and water, and then dried

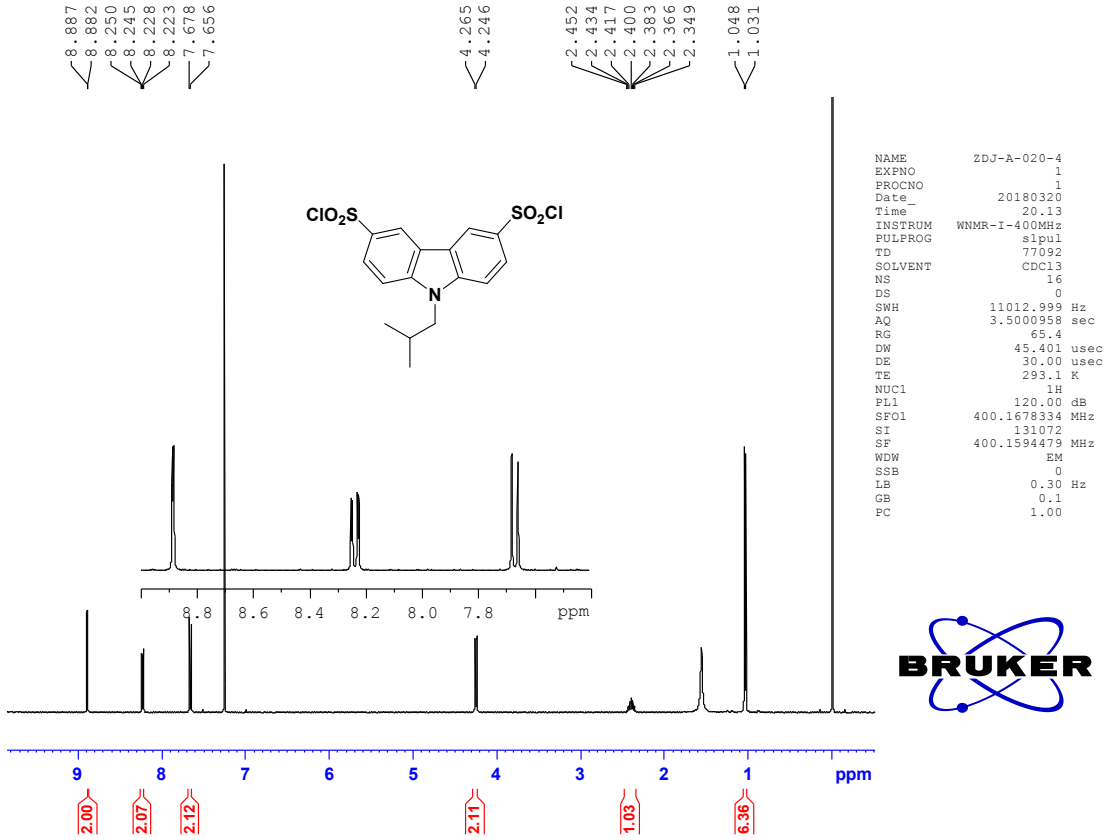
over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was triturated with petroleum ether to give the product as an orange solid (5.7 g, 90%).

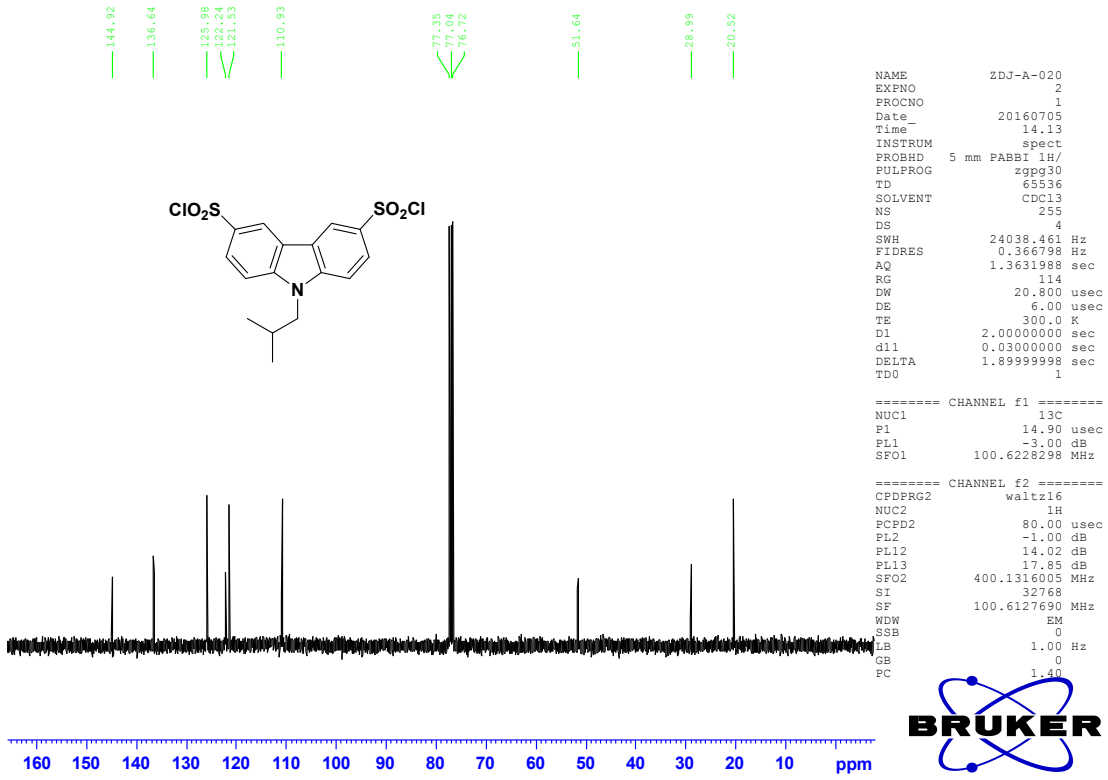
M.p: 195.3-196.1 ºC.

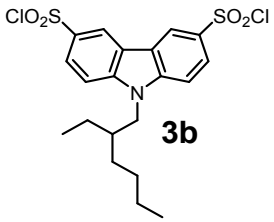
^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.88 (s, 2H, Ar*H*), 8.23 (dd, *J* = 2.0 Hz, *J* = 8.8 Hz, 2H, Ar*H*), 7.66 (d, *J* = 8.9 Hz, 2H, Ar*H*), 4.25 (d, *J* = 7.5 Hz, 2H, NCH_2), 2.46-2.34 (m, 1H, C*H*), 1.03 (d, *J* = 6.6 Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 144.9, 136.6, 126.0, 122.2, 121.5, 110.9, 51.6, 29.0, 20.5.

HRMS (ESI$^+$) calcd. for $[C_{16}H_{15}Cl_2NO_4S_2+NH_4]^+$ 437.0158, found: 437.0156.







A solution of chlorosulphonic acid (8 mL, 120 mmol) in CH_2Cl_2 (30 mL) was added dropwise into a stirred solution of *N*-(2-ethylhexyl)carbazole **1b** (4.188 g, 15 mmol) in CH_2Cl_2 (50 mL) at -5 °C over a period of 1.5 hours. The mixture was allowed to reach room temperature and stirred for another 3 hours. The reaction mixture was poured into ice water and extracted three times with CH_2Cl_2. The combined organic phase was washed with brine and water, and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was triturated with petroleum ether to give the product as an orange solid (6.676 g, 94%).

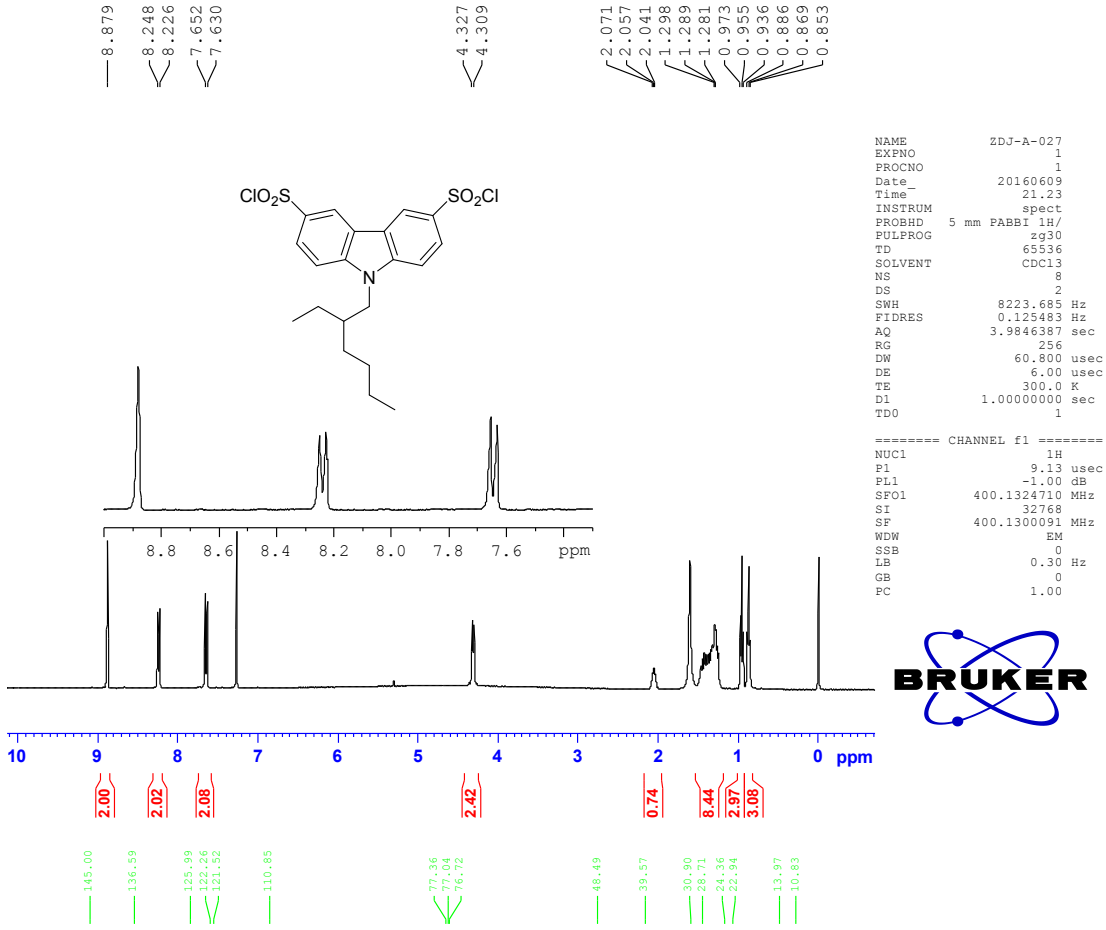
M.p: 167.4-168.1 ºC.

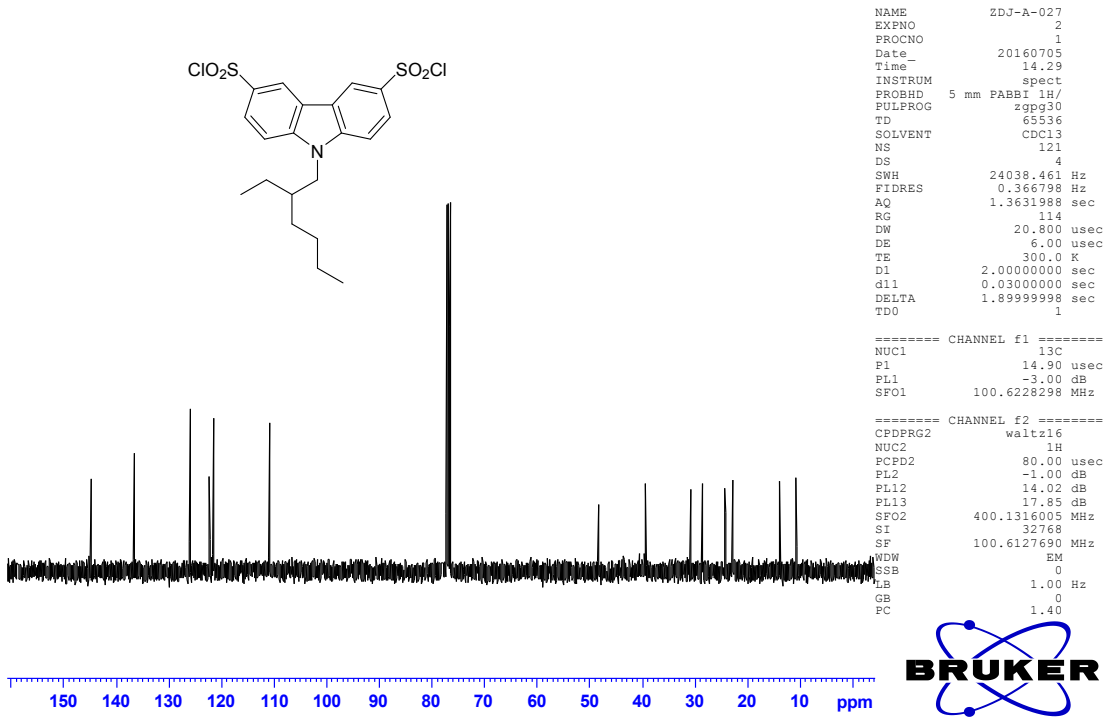
^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.88 (s, 2H, Ar*H*), 8.24 (d, *J* = 8.9 Hz, 2H, Ar*H*), 7.64 (d, *J* = 8.9 Hz, 2H, Ar*H*), 4.32 (d, *J* = 7.3 Hz, 2H, NCH_2), 2.17-1.95 (m, 1H, C*H*), 1.53-1.18 (m, 8H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3), 0.87 (t, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 145.0, 136.6, 126.0, 122.3, 121.5, 110.8, 48.5,

39.6, 30.9, 28.7, 24.4, 22.9, 14.0, 10.8.

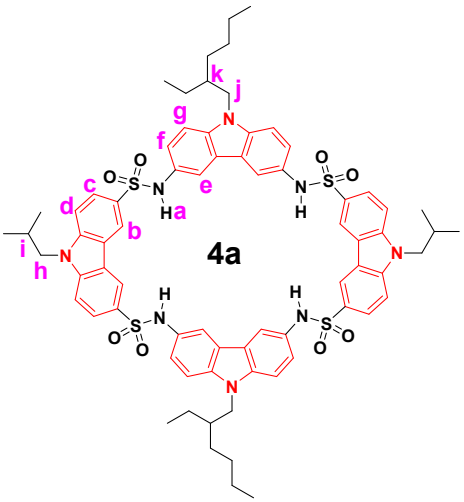
HRMS (ESI$^+$) calcd. for $[C_{20}H_{23}Cl_2NO_4S_2+NH_4]^+$ 493.0784, found: 493.0786.





Condition 1: A solution of triethylamine (0.14 mL, 1 mmol) in CH_2Cl_2 (50 mL) was stirred at -12 °C. A solution of 3, 6-di(chlorosulfonyl)-9-isobutylcarbazole **3a** (238.2 mg, 0.5 mmol) in dry CH_2Cl_2 (15 mL) and 3, 6-diamino-9-(2-ethylhexyl)carbazole **2b** (154.7 mg, 0.5 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise into the above solution simultaneously and seperately in 2 hours. And then the mixture was allowed to reach room temperature over a period of 4-6 hours. The mixture was heated under reflux for another 24 hours. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, CH_2Cl_2: CH_3OH = 150:1 as eluent for to give the "2+2" product **4a** and CH_2Cl_2: CH_3OH =100:1 for the "3+3" product **5a**). Further purification was achieved *via* trituration with hot methanol, "2+2" product: 20 mg, 6% and "3+3" product: 73 mg, 21%.

Condition 2: A solution of triethylamine (0.70 mL, 5 mmol) in CH_2Cl_2 (250 mL) was stirred at -12 °C. 3, 6-di(chlorosulfonyl)-9-isobutylcarbazole **3a** (1191.1 mg, 2.5 mmol) and 3, 6-diamino-9-(2-ethylhexyl)carbazole **2b** (773.6 mg, 2.5 mmol) was added into above solution simultaneously and seperately. The mixture was stirred for 4 hours and then allowed to reach room temperature over a period of 6-8 hours. The mixture was then heated to reflux for 20 hours. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel). Eluting with CH_2Cl_2: CH_3OH = 150:1 gave the "2+2" product **4a**. Further purification was achieved *via* trituration with hot methanol to afford **4a** (251 mg, 15%). Eluting with CH_2Cl_2: CH_3OH = 100:1 gave the "3+3" product **5a**. Further purification via trituration with hot methanol was also successful to afford **5a** (673 mg, 41%).

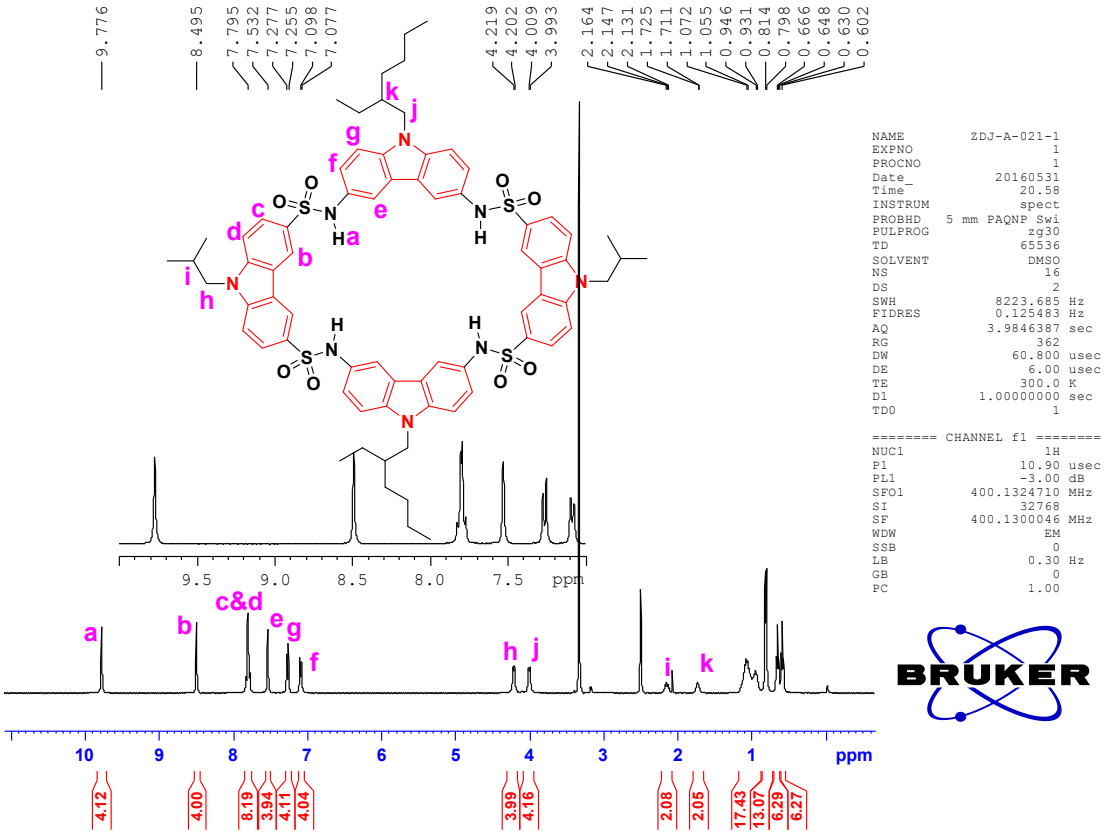


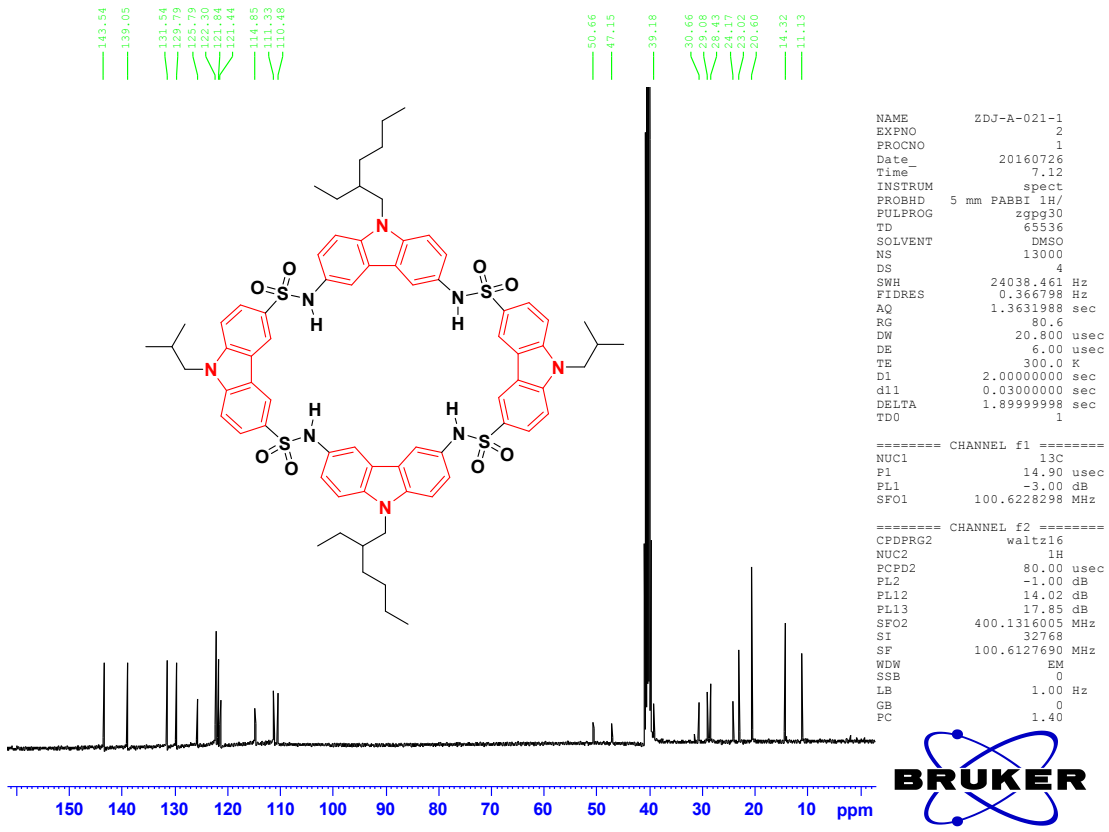
M.p: >265 ºC.

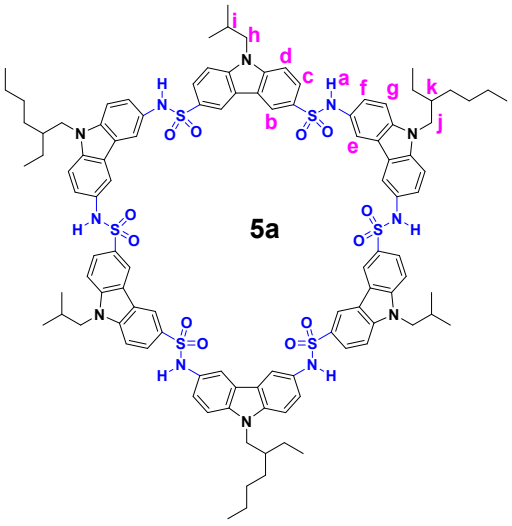
^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.78 (s, 4H, NH^{a}), 8.49 (s, 4H, ArH^{b}), 7.85-7.75 (m, 8H, Ar$H^{c\&d}$), 7.53 (s, 4H, ArH^{e}), 7.27 (d, J = 8.8 Hz, 4H, ArH^{g}), 7.09 (d, J = 8.0 Hz, 4H, ArH^{f}), 4.21 (d, J = 7.1 Hz, 4H, NCH_2^{h}), 4.00 (d, J = 6.6 Hz, 4H, NCH_2^{j}), 2.22-2.08 (m, 2H, NCH$_2$CH^{i}), 1.79-1.65 (m, 2H, NCH$_2$CH^{k}), 1.18-0.88 (m, 16H, CH_2), 0.81 (d, J = 6.5 Hz, 12H, CH(CH_3)$_2$), 0.65 (t, J = 7.3 Hz, 6H, CH_3), 0.58 (t, J = 7.0 Hz, 6H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 143.5, 139.0, 131.5, 129.8, 125.8, 122.3, 121.8, 121.4, 114.9, 111.3, 110.5, 50.7, 47.2, 39.2, 30.7, 29.1, 28.4, 24.2, 23.0, 20.6, 14.3, 11.1.

HRMS (ESI^{+}) calcd. for [$C_{72}H_{80}N_8O_8S_4$+H]$^{+}$ 1313.5055, found: 1313.5037.







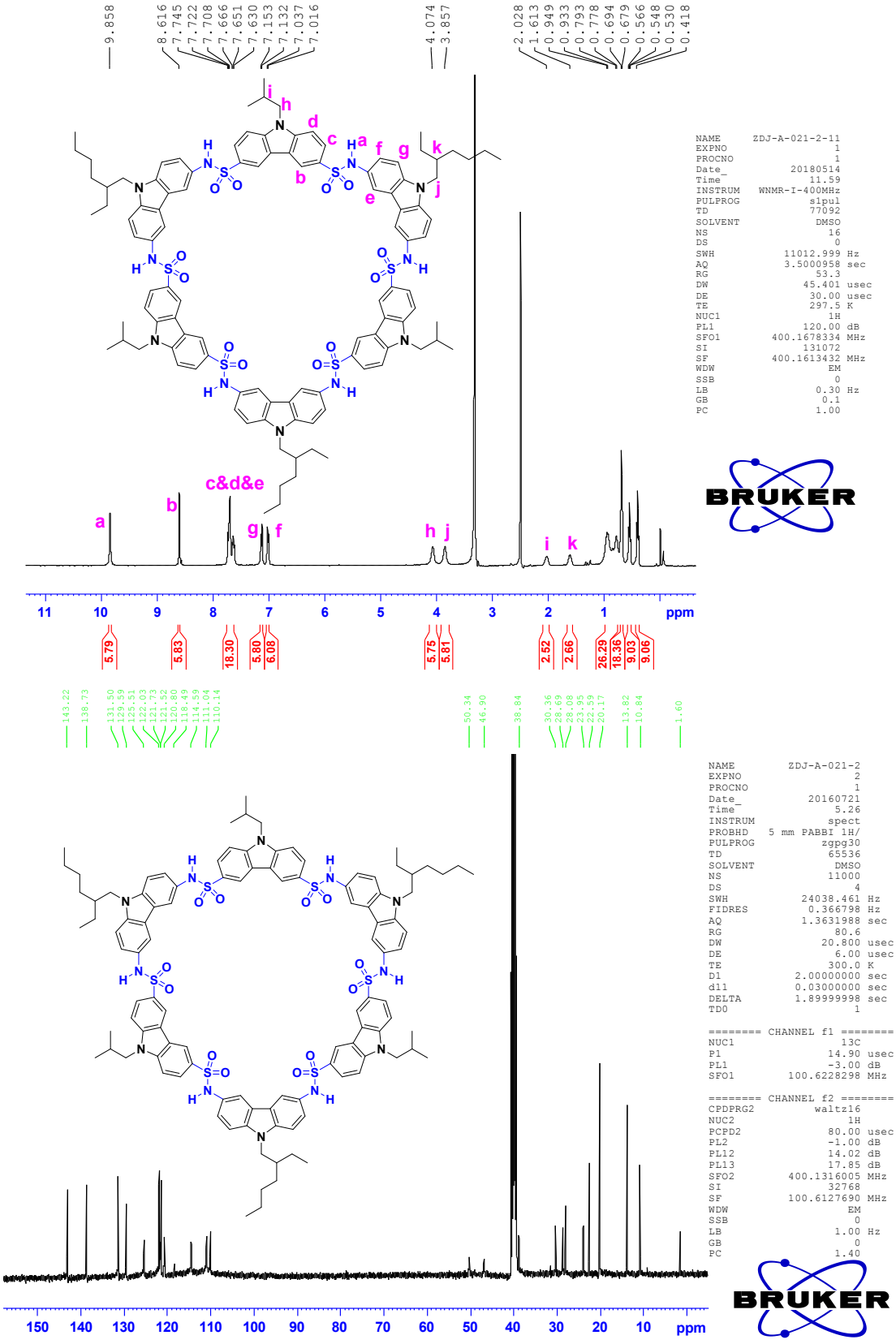
M.p: >250 ºC.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.86 (s, 6H, NH^{a}), 8.62 (s, 6H, ArH^{b}), 7.76-7.62 (m, 18H, Ar$H^{c\&d\&e}$), 7.14 (d, J = 8.5 Hz, 6H, ArH^{g}), 7.03 (d, J = 8.1 Hz, 6H, ArH^{f}), 4.07 (s, 6H, NCH_2^{h}), 3.86 (s, 6H, NCH_2^{j}), 2.07-1.96 (m, 3H, NCH$_2$CH^{i}), 1.66-1.53 (m, 3H, NCH$_2$CH^{k}), 1.08-0.74 (m, 26H, CH_2), 0.72-0.64 (m, 18H, CHCH_3), 0.55 (t, J = 7.2 Hz, 9H, CH_3), 0.40 (t, J = 6.8 Hz, 9H, CH_3).

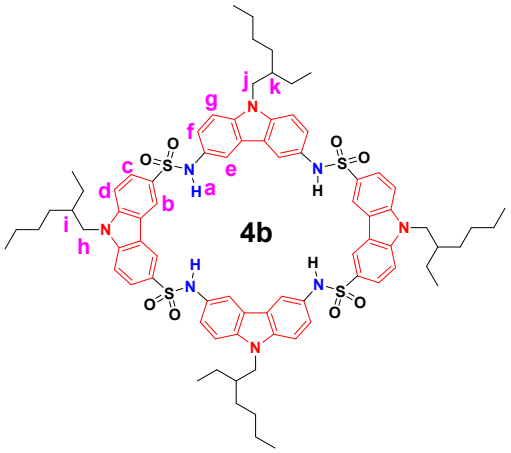
^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 143.2, 138.7, 131.5, 129.6, 125.5, 122.0, 121.7, 121.5, 120.8, 118.5, 114.6, 111.0, 110.1, 50.3, 46.9, 38.8, 30.4, 28.7, 28.1, 23.9, 22.6, 20.2,

13.8, 10.8.

HRMS (ESI$^+$) calcd. for $[C_{108}H_{120}N_{12}O_{12}S_6+H]^+$ 1969.7546, found: 1969.7552; calcd. for $[C_{108}H_{120}N_{12}O_{12}S_6+Na]^+$ 1991.7365, found: 1991.7563.



A solution of triethylamine (1.10 mL, 8 mmol) in CH_2Cl_2 (400 mL) was stirred at -12 °C. 3, 6-di(chlorosulfonyl)-9-isooctylcarbazole **3b** (1.906 g, 4 mmol) and 3, 6-diamino-9-(2-ethylhexyl)carbazole **2b** (1.238 g, 4 mmol) in solid state were added into above solution in one portion. The mixture was stirred for 4 hours and then allowed to reach room temperature over a period of 6-8 hours. The mixture was then heated under reflux for additional 20 hours. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, CH_2Cl_2: CH_3OH = 160:1 for the "2+2" product **4b** (287 mg, 10%) and CH_2Cl_2: CH_3OH = 100:1 for the "3+3" product **5b** (1.589 g, 56%). Further purification could be achieved *via* trituration with hot methanol.

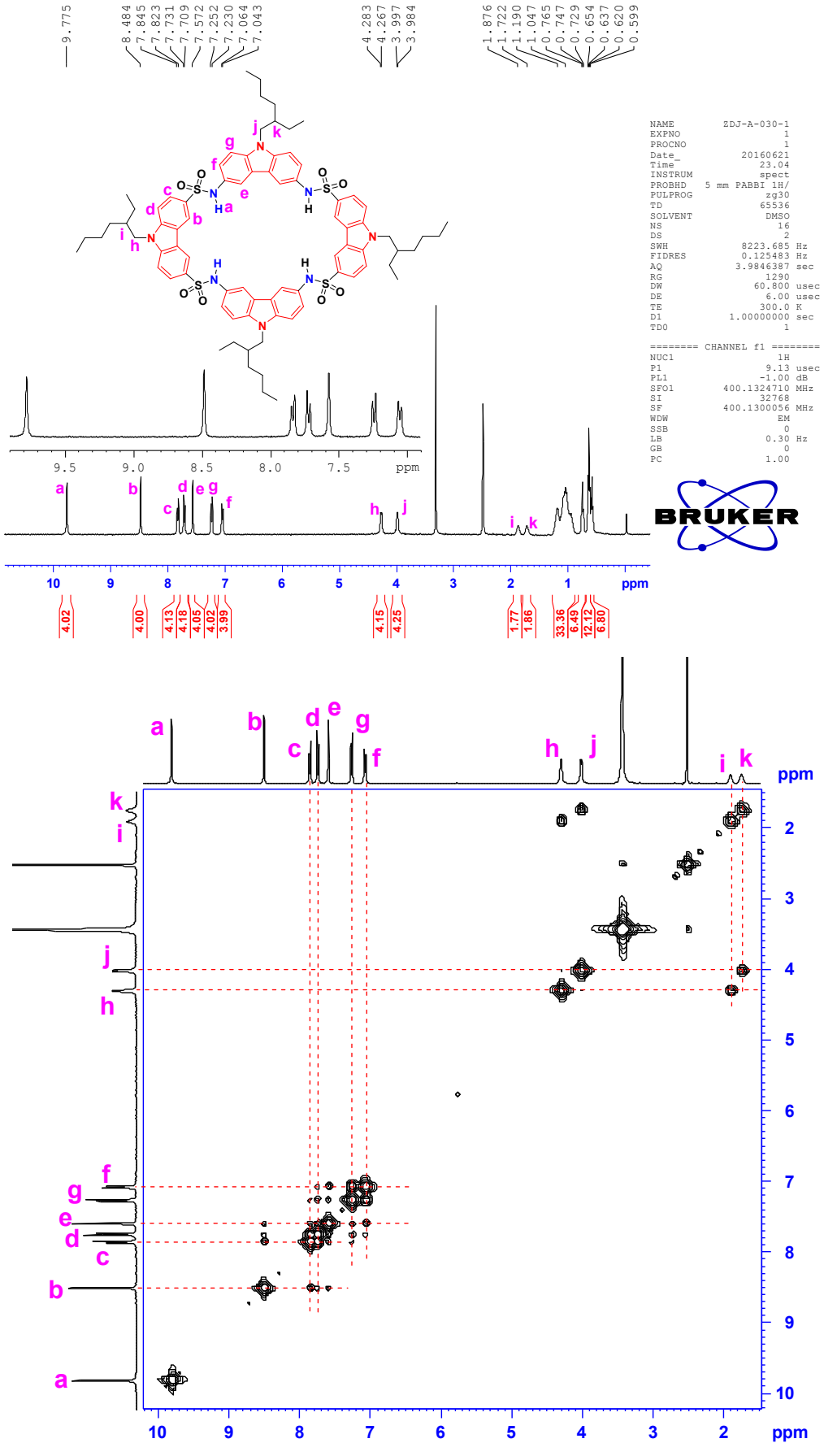


M. p: >220 ºC.

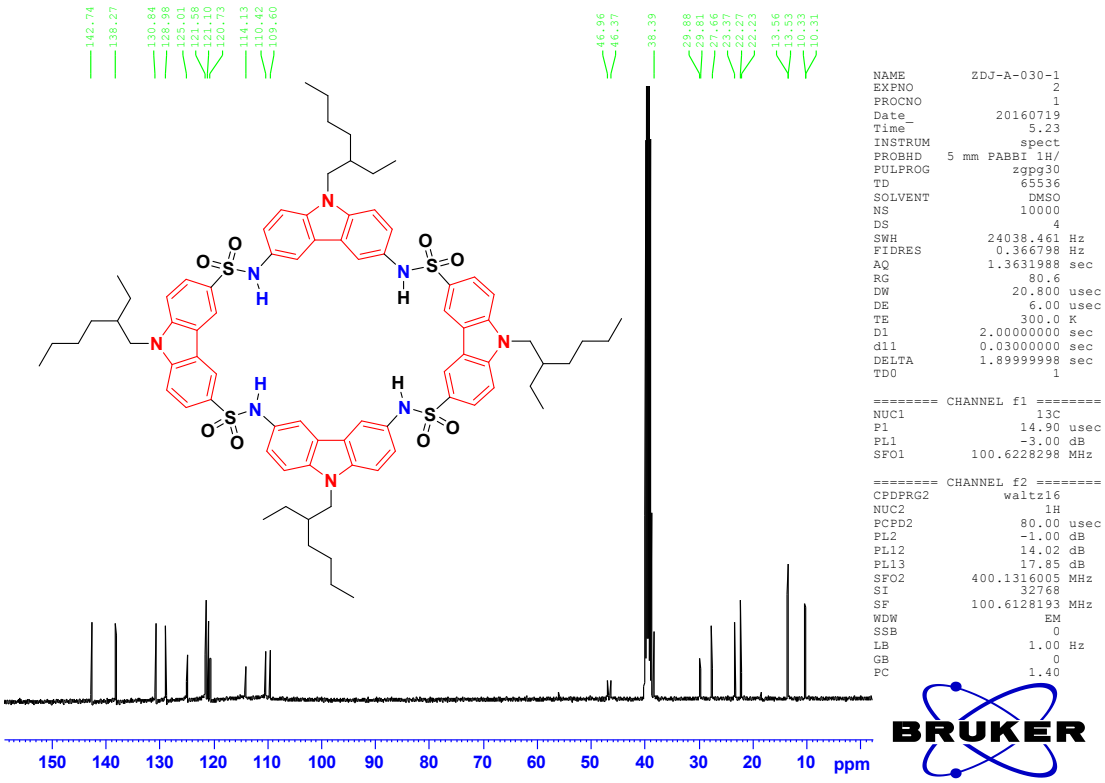
^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.78 (s, 4H, NH^a), 8.48 (s, 4H, ArH^b), 7.83 (d, J = 8.7 Hz, 4H, ArH^c), 7.72 (d, J = 8.8 Hz, 4H, ArH^d), 7.57 (s, 4H, ArH^e), 7.24 (d, J = 8.8 Hz, 4H, ArH^g), 7.05 (d, J = 8.6 Hz, 4H, ArH^f), 4.28 (d, J = 6.3 Hz, 4H, NCH_2^h), 3.99 (d, J = 5.3 Hz, 4H, NCH_2^j), 1.95-1.82 (m, 2H, NCH$_2$CH^i), 1.78-1.65 (m, 2H, NCH$_2$CH^k), 1.30-0.85 (m, 32H, CH_2), 0.75 (t, J = 7.2 Hz, 6H, CH_3), 0.64 (t, J = 6.9 Hz, 12H, CH_3), 0.58 (t, J = 6.9 Hz, 7H, CH_3).

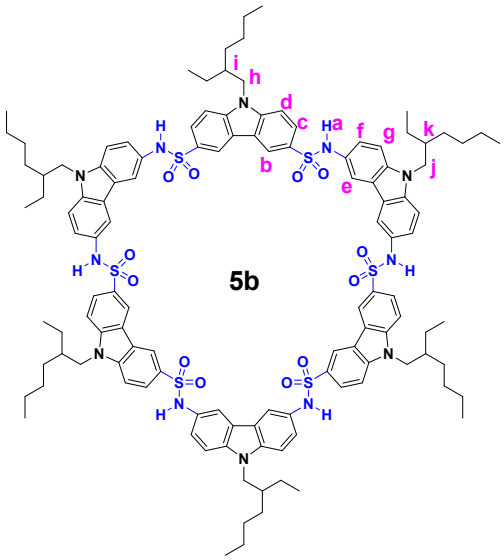
^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 142.7, 138.3, 130.8, 129.0, 125.0, 121.6, 121.1, 120.7, 114.1, 110.4, 109.6, 47.0, 46.4, 38.4, 29.9, 29.8, 27.7, 23.4, 22.3, 22.2, 13.6, 13.5, 10.33, 10.31.

HRMS (MALDI$^+$) calcd. for $[C_{80}H_{96}N_8O_8S_4+Na]^+$ 1447.6126, found: 1447.6122.



COSY spectrum for compound **4b,** DMSO-d_6, 400 MHz, 298 K.



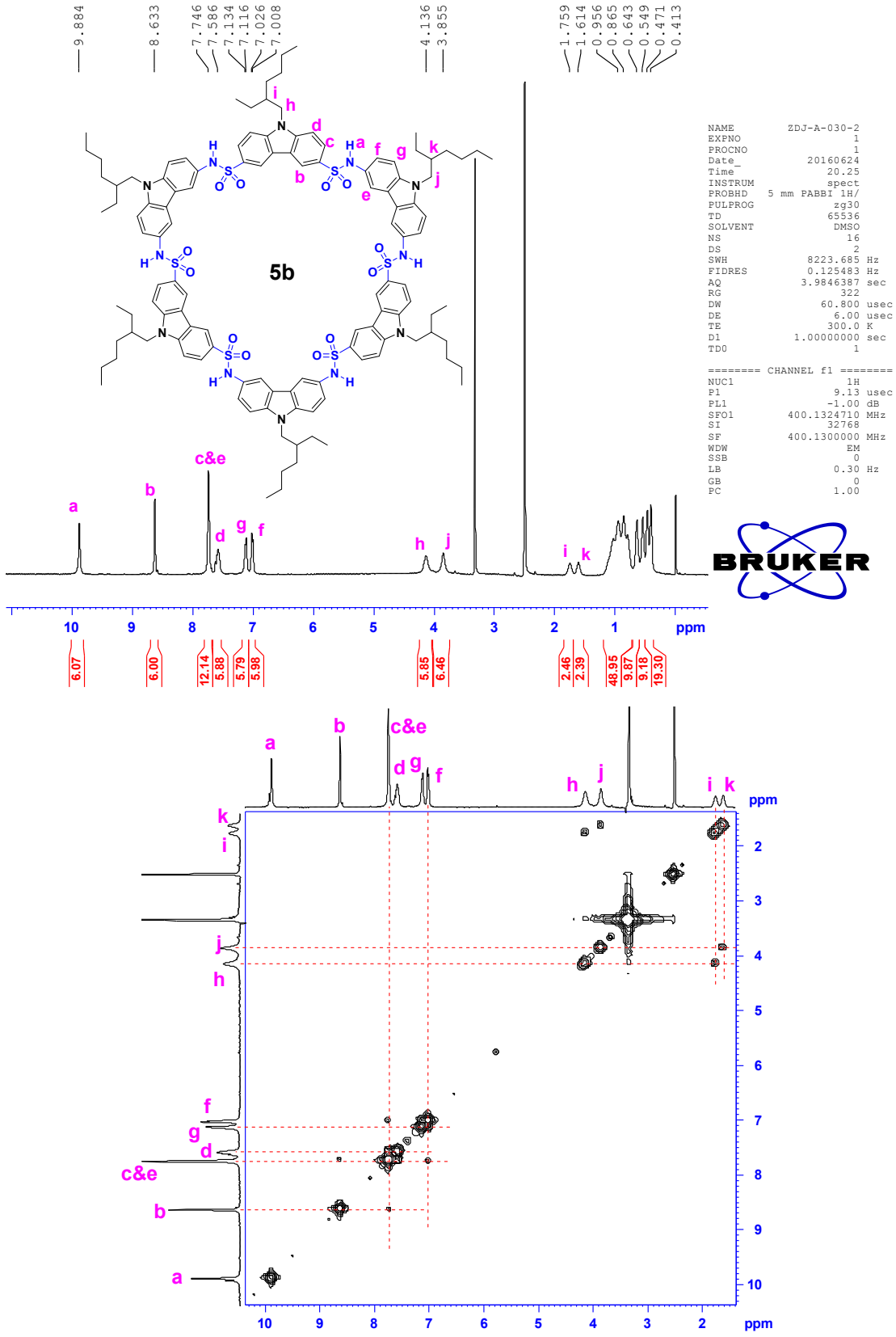


M.p: >210 ºC.

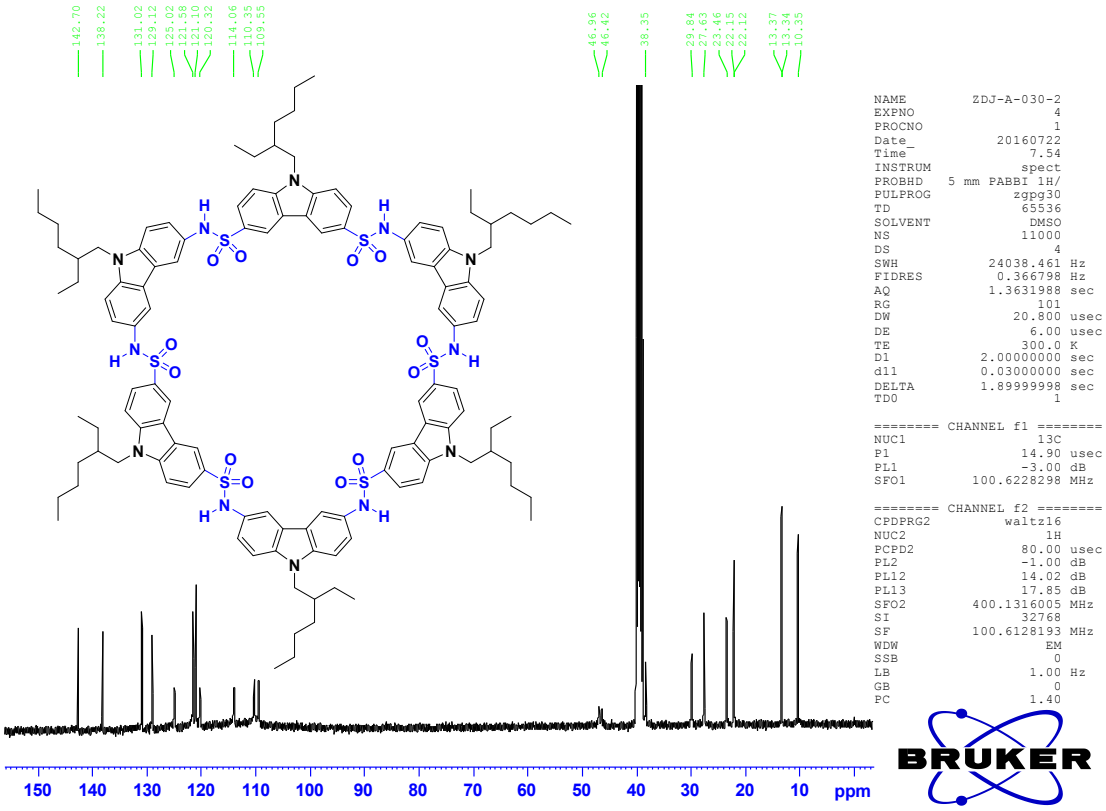
^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.88 (s, 6H, NH^{a}), 8.63 (s, 6H, ArH^{b}), 7.75 (s, 12H, Ar$H^{c\&e}$), 7.66-7.52 (m, 6H, ArH^{d}), 7.13 (d, J = 7.2 Hz, 6H, ArH^{g}), 7.02 (d, J = 7.4 Hz, 6H, ArH^{f}), 4.14 (s, 6H, NCH_2^{h}), 3.85 (s, 6H, NCH_2^{j}), 1.76 (s, 3H, NCH$_2$CH^{i}), 1.61 (s, 3H, NCH$_2$CH^{k}), 1.20-0.72 (m, 48H, CH_2), 0.64 (s, 9H, CH_3), 0.55 (s, 9H, CH_3), 0.51-0.36 (m, 18H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 142.7, 138.2, 131.0, 129.1, 125.0, 121.6, 121.1, 120.3, 114.1, 110.4, 109.5, 47.0, 46.4, 38.3, 29.8, 27.6, 23.5, 22.15, 22.12, 13.37, 13.34, 10.4.

HRMS (MALDI$^+$) calcd. for $[C_{120}H_{144}N_{12}O_{12}S_6+Na]^+$ 2159.9243, found: 2159.9247.



COSY spectrum for compound **5b,** DMSO-d_6, 400 MHz, 298 K.

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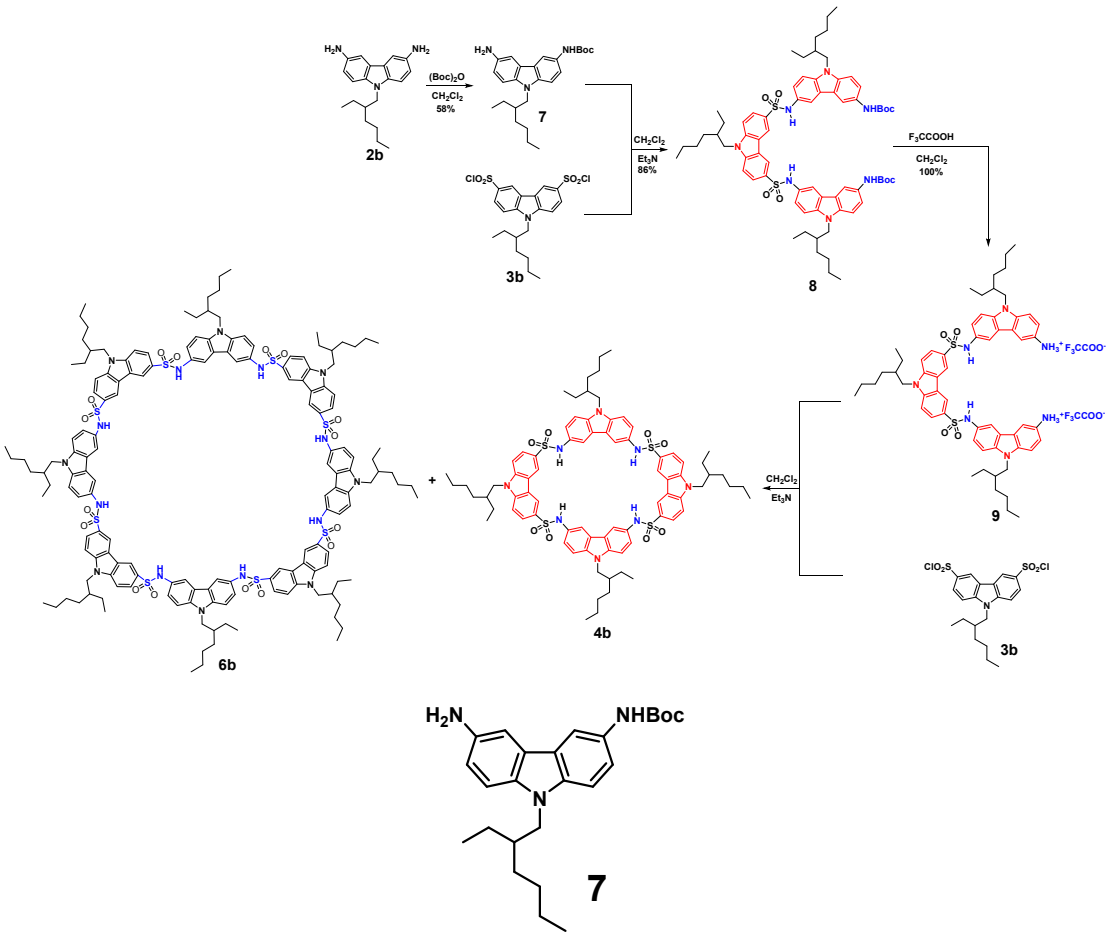
3. Fragment Coupling Strategy for the Synthesis of Macrocycles



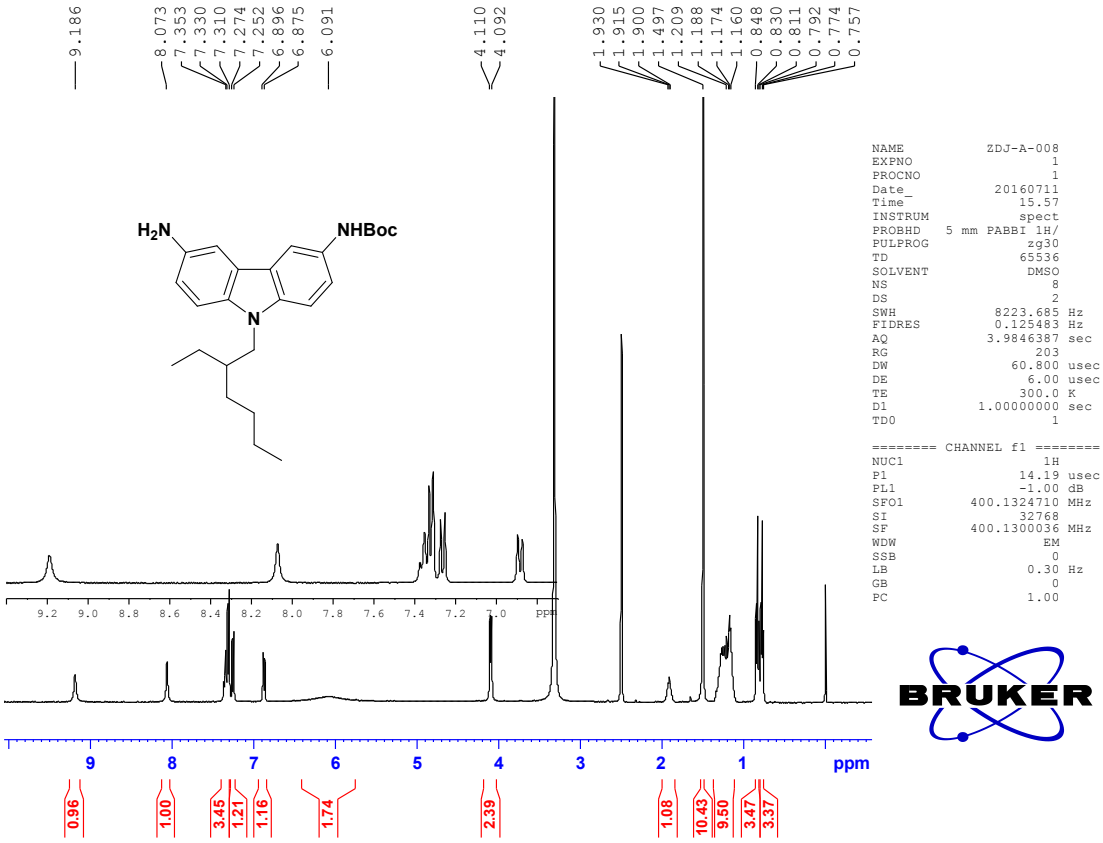
A solution of 3, 6-diamino-9-(2-ethylhexyl)carbazole **2b** (3.106 g, 10 mmol) in CH_2Cl_2 (150 mL) was stirred at room temperature. And then a solution of di-*tert*-butyl dicarbonate (2.183 g, 10 mmol) in CH_2Cl_2 (30 mL) was added dropwise into above solution. After complete addition, the mixture was stirred at room temperature for 2 hours. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, petroleum ether: CH_2Cl_2: ethyl acetate = 3:2:2 as eluent) to provide the product as a white solid (2.367 g, 58%).

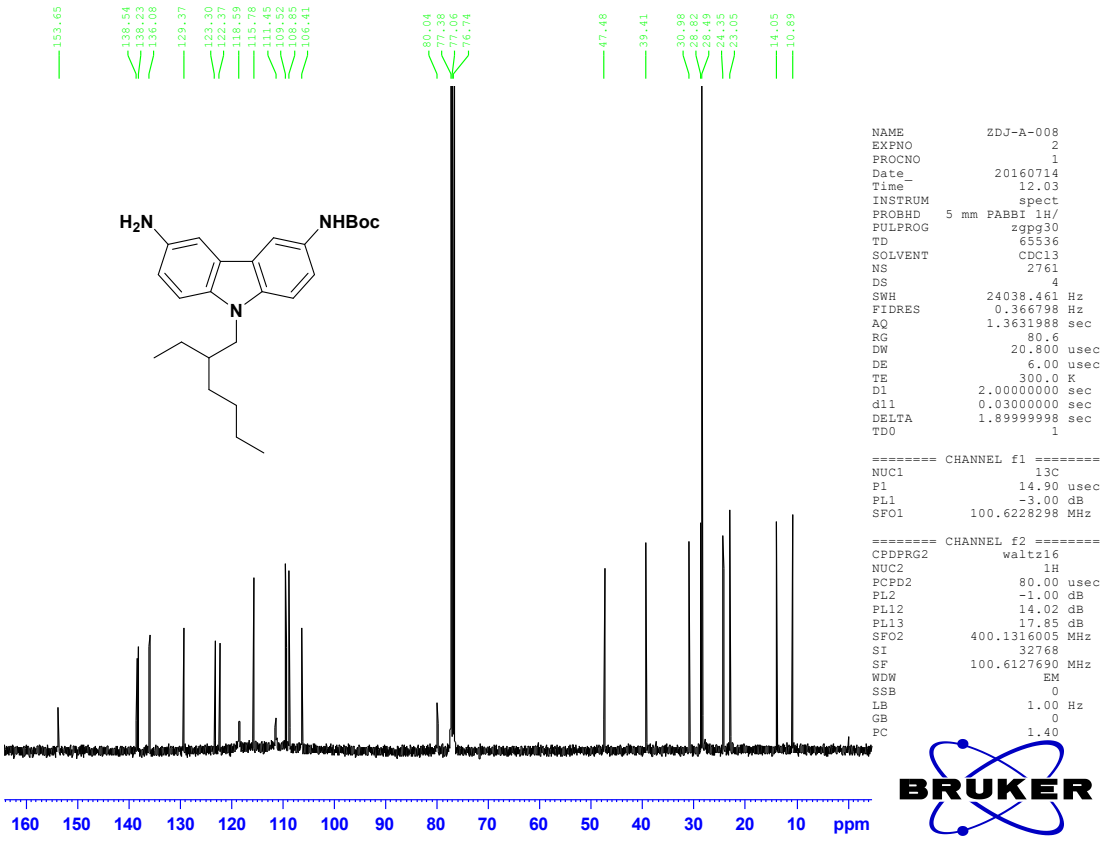
M.p: 141.4-142.0 ºC.

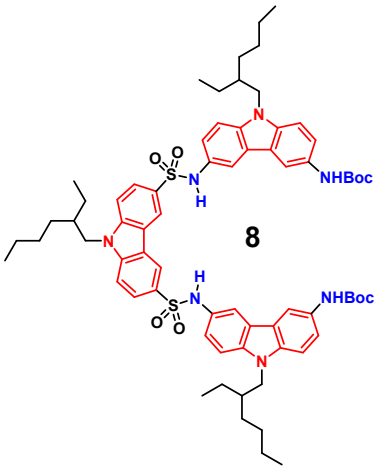
^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.19 (s, 1H, BocN*H*), 8.07 (s, 1H, Ar*H*), 7.40-7.30 (m, 3H, Ar*H*), 7.26 (d, *J* = 8.6 Hz, 1H, Ar*H*), 6.89 (dd, *J* = 1.5 Hz, *J* = 8.6 Hz, 1H, Ar*H*), 6.42-5.76 (br, 2H, NH_2), 4.10 (d, *J* = 7.3 Hz, 2H, NCH_2), 2.00-1.85 (m, 1H, NCH$_2$C*H*), 1.50 (s, 10H, CO(CH_3)$_3$), 1.36-1.11 (m, 8H, CH_2), 0.83 (t, *J* = 7.4 Hz, 3H, CH_3), 0.77 (t, *J* = 6.9 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 153.6, 138.5, 138.2, 136.1, 129.4, 123.3, 122.4, 118.6, 115.8, 111.5,109.5, 108.9, 106.4, 80.0, 47.5, 39.4, 31.0, 28.8, 28.5, 24.4, 23.0, 14.1, 10.9.

HRMS (ESI^+) calcd. for $[C_{25}H_{35}N_3O_2+H]^+$ 410.2802, found: 410.2803; calcd. for $[C_{25}H_{35}N_3O_2+Na]^+$ 432.2621, found: 432.2622.







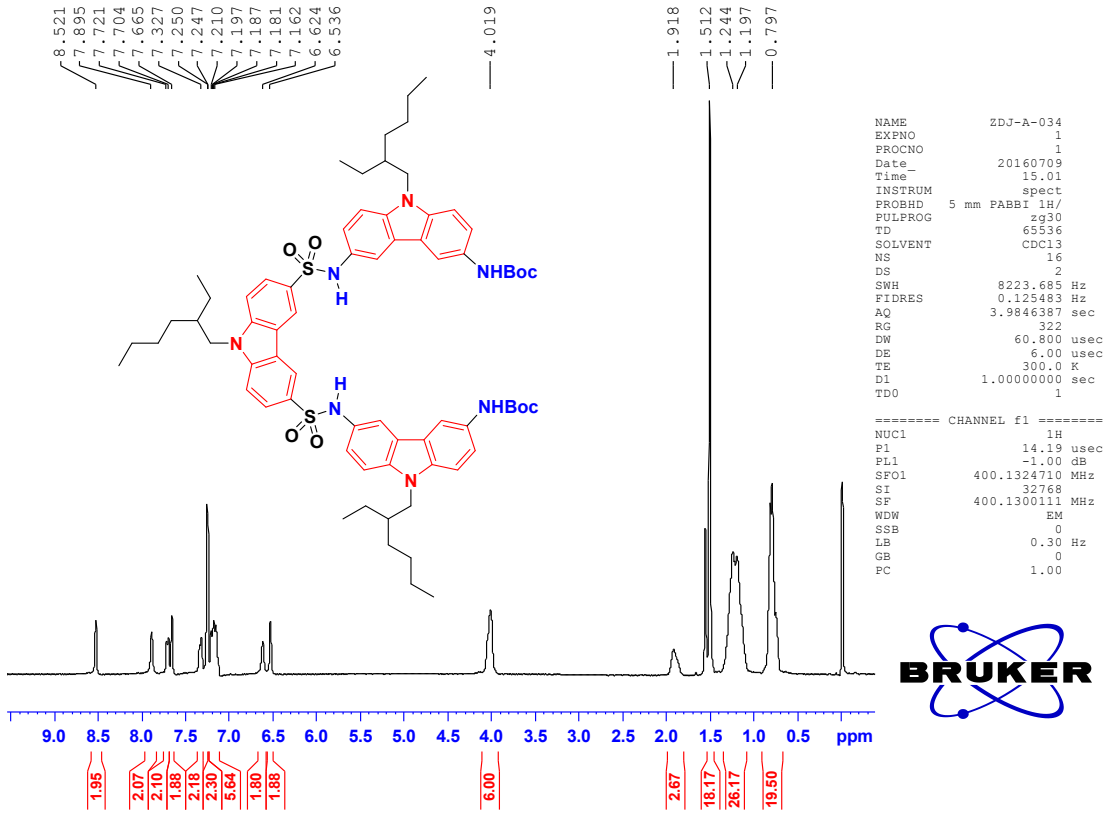
A solution of mono Boc protected 3, 6-diamino-9-(2-ethylhexyl)carbazole **7** (2.253 g, 5.5 mmol) and triethylamine (1.51 mL, 11 mmol) in dry CH_2Cl_2 (60 mL) was stirred at room temperature. A solution of 3, 6-di(chlorosulfonyl)-9-(2-ethylhexyl)carbazole **3b** (1.310 g, 2.75 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise into above solution. After addition, the mixture was stirred for 4 hours at room temperature. The reaction mixture was then concentrated under reduced pressure and purified by column chromatography (silica gel, petroleum ether: ethyl acetate = 3:1 as eluent) to provide the product as a white solid (2.881 g, 86%).

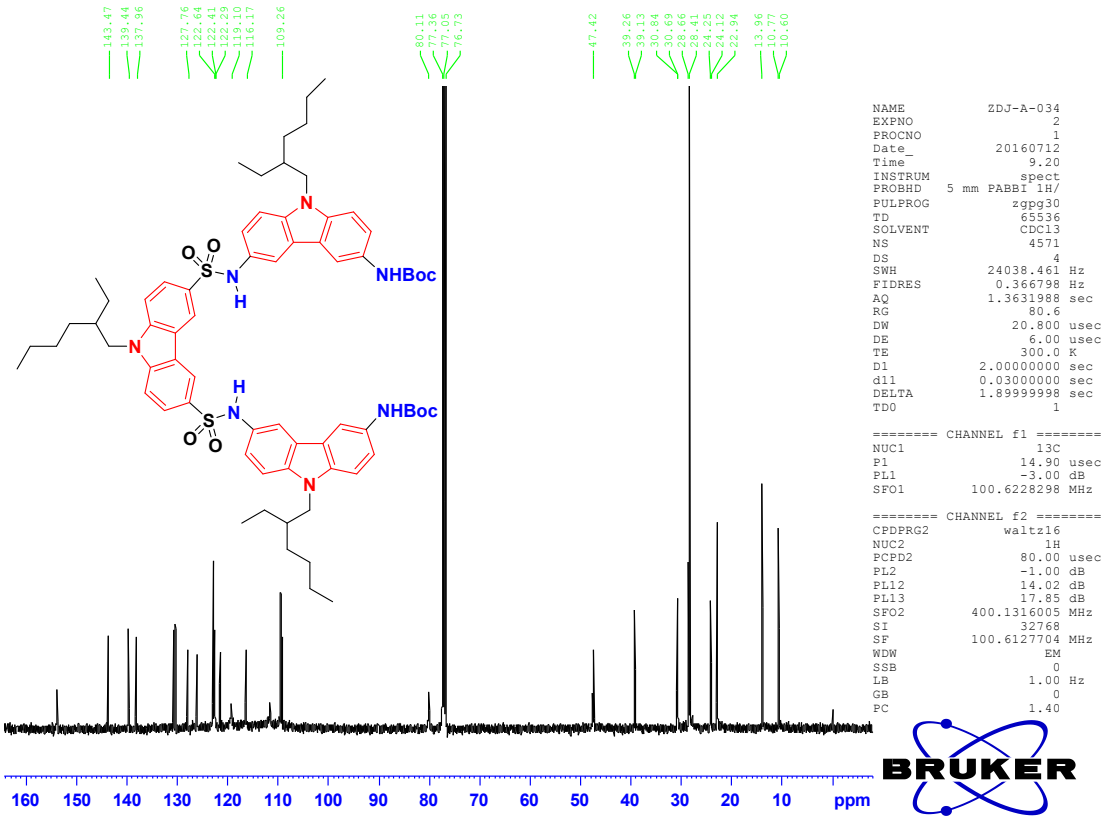
M.p: 154.0-155.0 ºC.

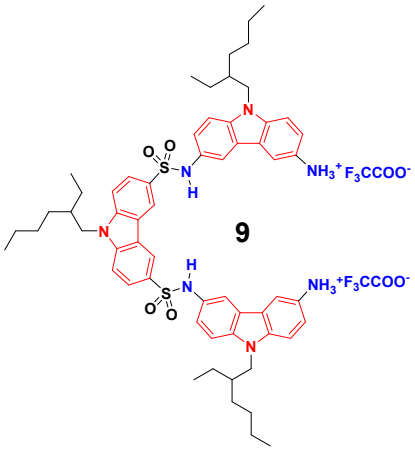
^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.52 (s, 2H, N*H*), 7.89 (s, 2H, Ar*H*), 7.71 (d, *J* = 6.96 Hz, 2H, Ar*H*), 7.67 (s, 2H, Ar*H*), 7.33 (s, 2H, Ar*H*), 7.25 (s, 2H, Ar*H*), 7.23-7.12 (m, 6H, Ar*H*), 6.62 (s, 2H, Ar*H*), 6.54 (s, 2H, Ar*H*), 4.02 (s, 6H, NCH_2), 1.92 (s, 3H, NCH_2CH), 1.51 (s, 18H, CCH_3), 1.35-1.08 (m, 26H, CH_2), 0.91-0.71 (m, 20H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 153.6, 143.5, 139.4, 138.0, 130.5, 130.1, 127.8, 125.9, 122.6, 122.4, 122.3, 121.3, 119.1, 116.2, 111.5, 109.3, 109.0, 80.1, 47.7, 47.4, 39.3, 39.1, 30.8, 30.7, 28.7, 28.4, 27.8, 24.3, 24.1, 22.9, 22.8, 13.96, 13.86, 10.8, 10.6.

HRMS (MALDI$^+$) calcd. for $[C_{70}H_{91}N_7O_8S_2+Na]^+$ 1244.6, found: 1244.5; calcd. for $[C_{70}H_{91}N_7O_8S_2+K]^+$ 1260.6, found: 1260.5.







9

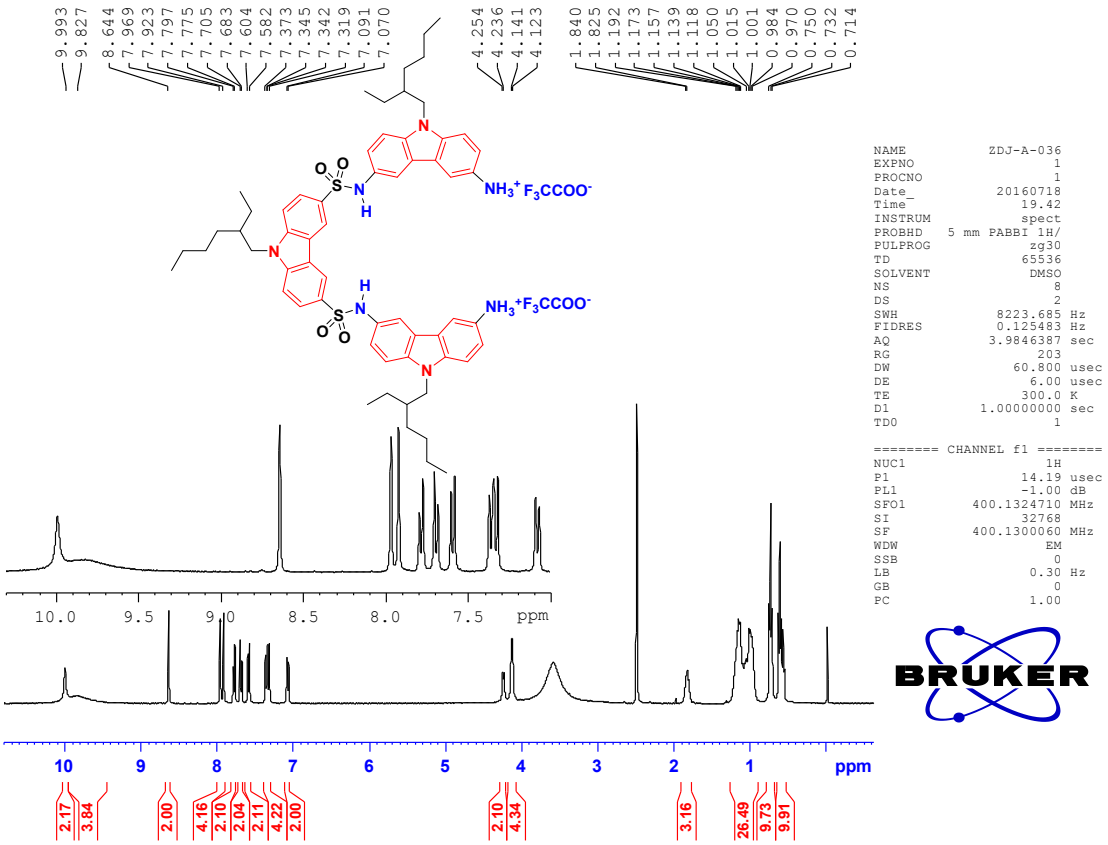
A solution of Boc protected "2+1" fragment **8** (1.834 g, 1.5 mmol) in CH_2Cl_2 (120 mL) was stirred at room temperature. Trifluoroacetic acid (9 mL) was added into the above solution. After 4 hours, the reaction solvent was removed under reduced pressure and the residue was triturated with petroleum ether and a little ethyl acetate to give the white product (1.873 g, almost quantitative yield).

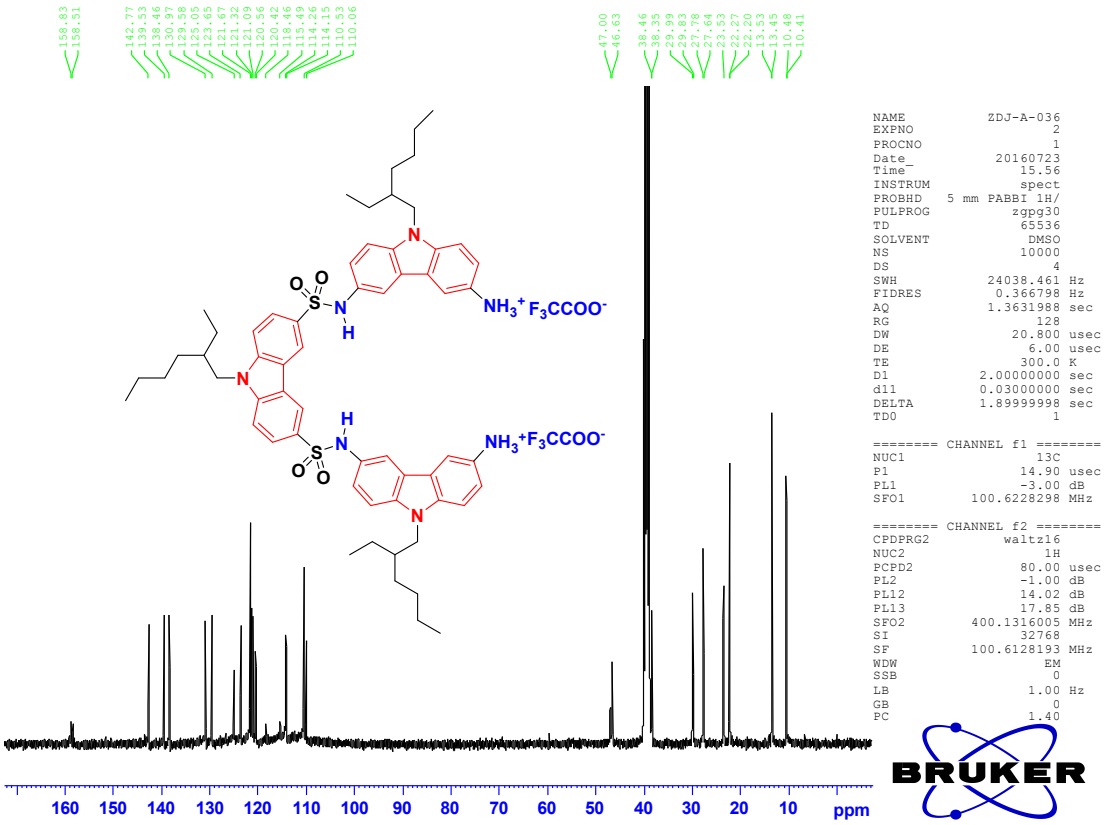
M.p: 179.1-180.0 ºC.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.99 (s, 2H, N*H*), 9.95-9.44 (br, 4H, NH_2), 8.64 (s, 2H, Ar*H*), 7.97 (s, 2H, Ar*H*), 7.92 (s, 2H, Ar*H*), 7.79 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.69 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.59 (d, *J* = 8.7 Hz, 2H, Ar*H*), 7.39-7.31 (m, 4H, Ar*H*), 7.08 (d, *J* = 8.7 Hz,

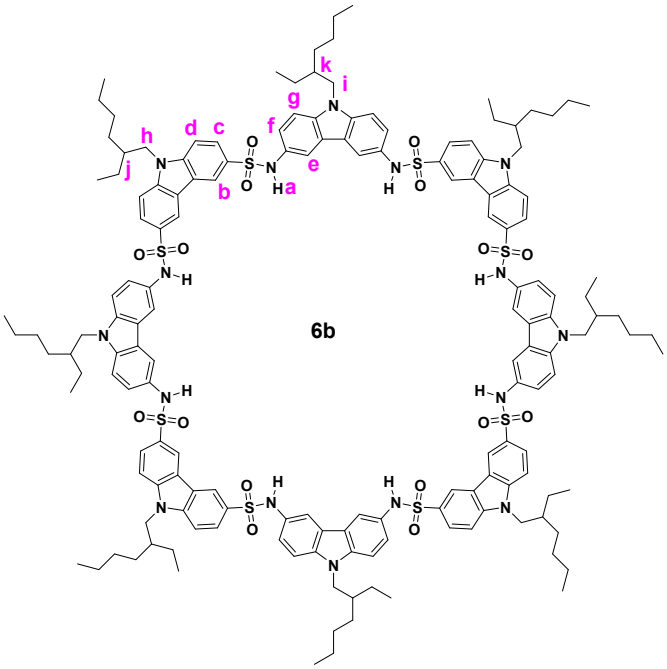
2H, Ar*H*), 4.25 (d, *J* = 7.0 Hz, 2H, NCH_2), 4.13 (d, *J* = 7.1 Hz, 4H, NCH_2), 1.90-1.78 (m, 3H, NCH$_2$C*H*), 1.27-0.90 (m, 24H, CH_2), 0.73 (t, *J* = 7.3 Hz, 9H, CH_3), 0.65-0.63 (m, 9H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 158.8, 158.5, 142.8, 139.5, 138.5, 131.0, 129.6, 125.1, 123.7, 121.7, 121.3, 121.1, 120.6, 120.4, 118.5, 115.5, 114.3, 114.1, 110.5, 110.1, 47.0, 46.6, 38.5, 38.3, 30.0, 29.8, 27.8, 27.6, 23.5, 22.27, 22.20, 13.5, 13.4, 10.5, 10.4.





A suspension of "2+1" fragment **9** (250 mg, 0.2 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature. Triethylamine (0.11 mL, 0.8 mmol) was added into the above solution. The suspension became clear quickly. Then the clear solution was stirred at -12 °C. A solution of 3, 6-di(chlorosulfonyl)-9-(2-ethylhexyl)carbazole **3b** (95 mg, 0.2 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise into the above solution. The mixture was stirred for 2 hours and then allowed to reach room temperature over a period of 6-8 hours. The mixture was heated under reflux for another 10 hours. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, CH_2Cl_2: CH_3OH = 90:1 as eluent) to give the "2+2" product **4b** (65 mg, 23%). Further purification was achieved via trituration with hot methanol. Eluting with CH_2Cl_2: CH_3OH = 50:1 afforded the "4+4" product **6b** (63 mg, 22%).

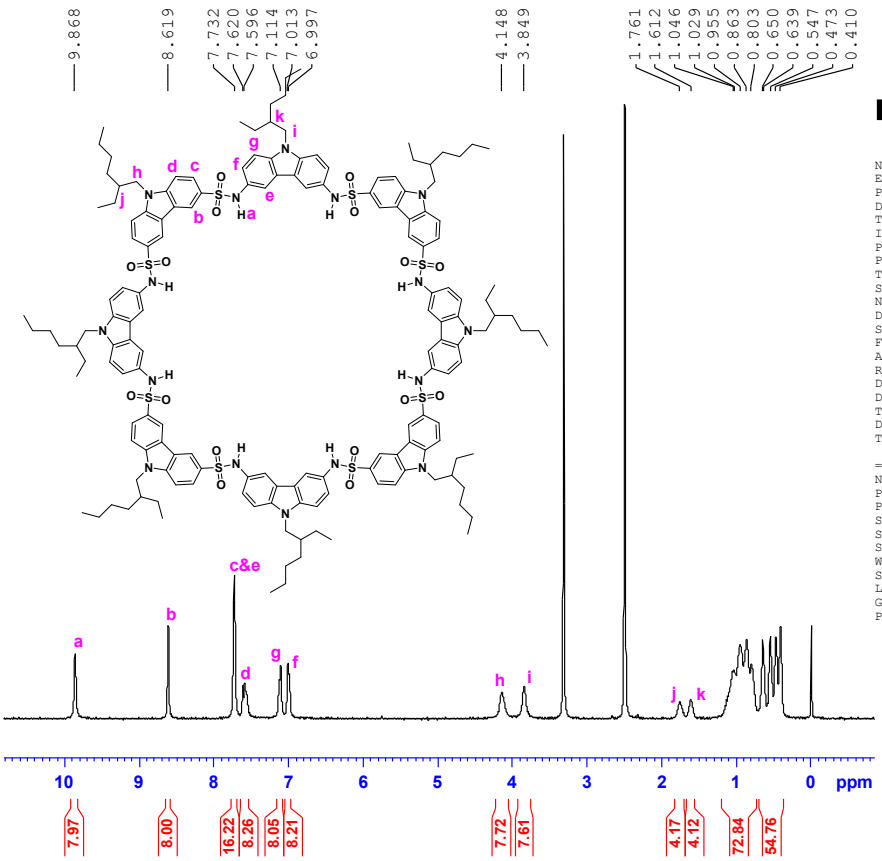


M.p: > 225 ºC.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.87 (s, 8H, NH^{a}), 8.62 (s, 8H, ArH^{b}), 7.73 (s, 16H, Ar$H^{c\&e}$), 7.64-7.54 (m, 8H, ArH^{d}), 7.12 (d, J = 6.3 Hz, 8H, ArH^{g}), 7.00 (d, J = 6.3 Hz, 8H, ArH^{f}), 4.15 (s, 8H, NCH_2^{h}), 3.85 (s, 8H, NCH_2^{i}), 1.76 (s, 4H, NCH$_2$CH^{j}), 1.61 (s, 4H, NCH$_2$CH^{k}), 1.19-0.73 (m, 73H, CH_2), 0.69-0.36 (m, 55H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 143.2, 138.7, 131.5, 129.6, 125.5, 122.1, 121.6, 120.8, 114.6, 110.8, 110.0, 47.5, 46.9, 38.8, 30.4, 28.1, 23.9, 22.6, 13.87, 13.84, 10.8.

HRMS (MALDI^{+}) calcd. for [$C_{160}H_{192}N_{16}O_{16}S_8$+Na]$^{+}$ 2872.2, found: 2874.5.

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PROCNO                  1
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DS                      2
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FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                   1030
DW                 60.800 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec
TD0                     1

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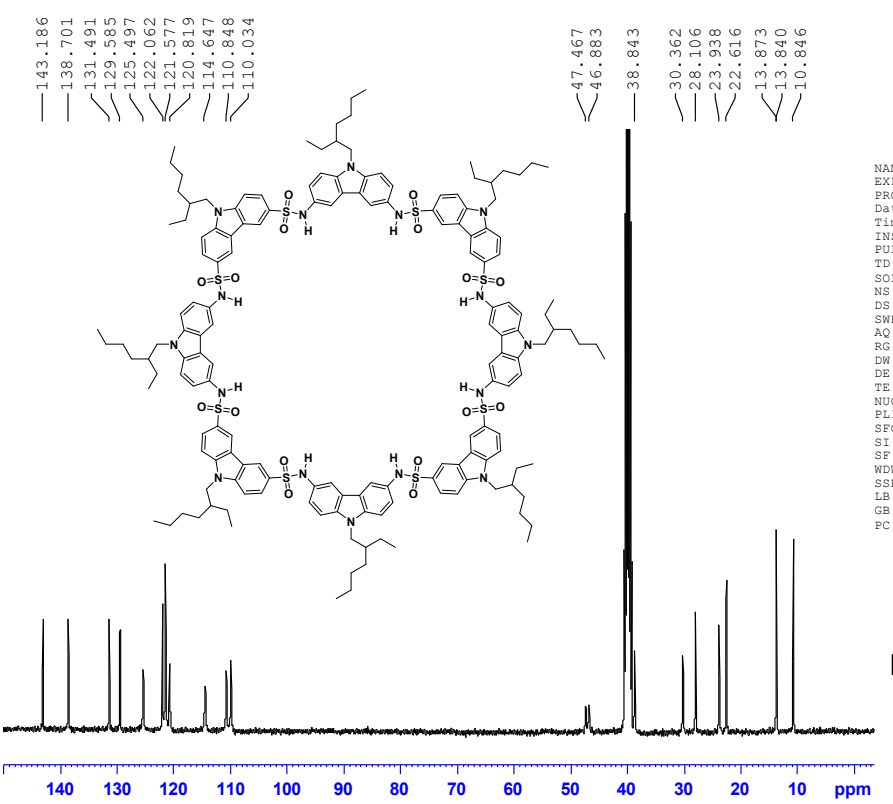


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PROCNO                  1
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DS                      0
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AQ               0.7999841 sec
RG                   72.9
DW                 18.399 usec
DE                  30.00 usec
TE                 293.1 K
NUC1                  13C
PL1                120.00 dB
SFO1         100.6333528 MHz
SI                  131072
SF           100.6220325 MHz
WDW                    EM
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GB                    0.1
PC                   1.00
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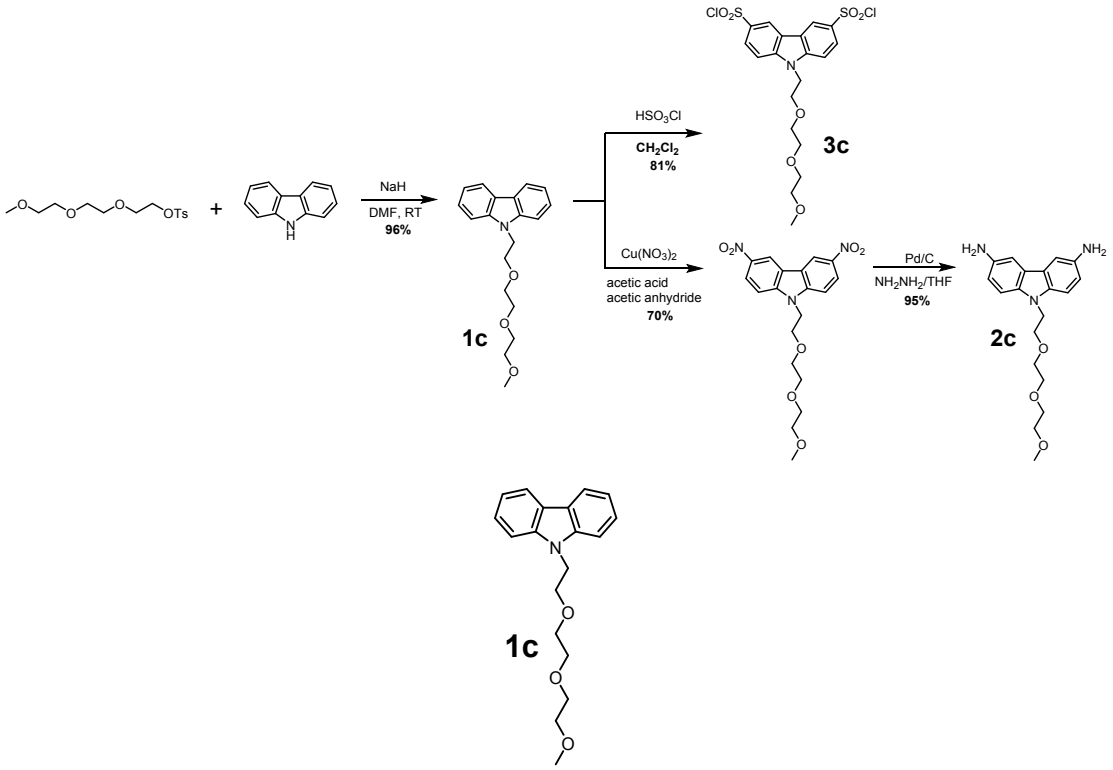
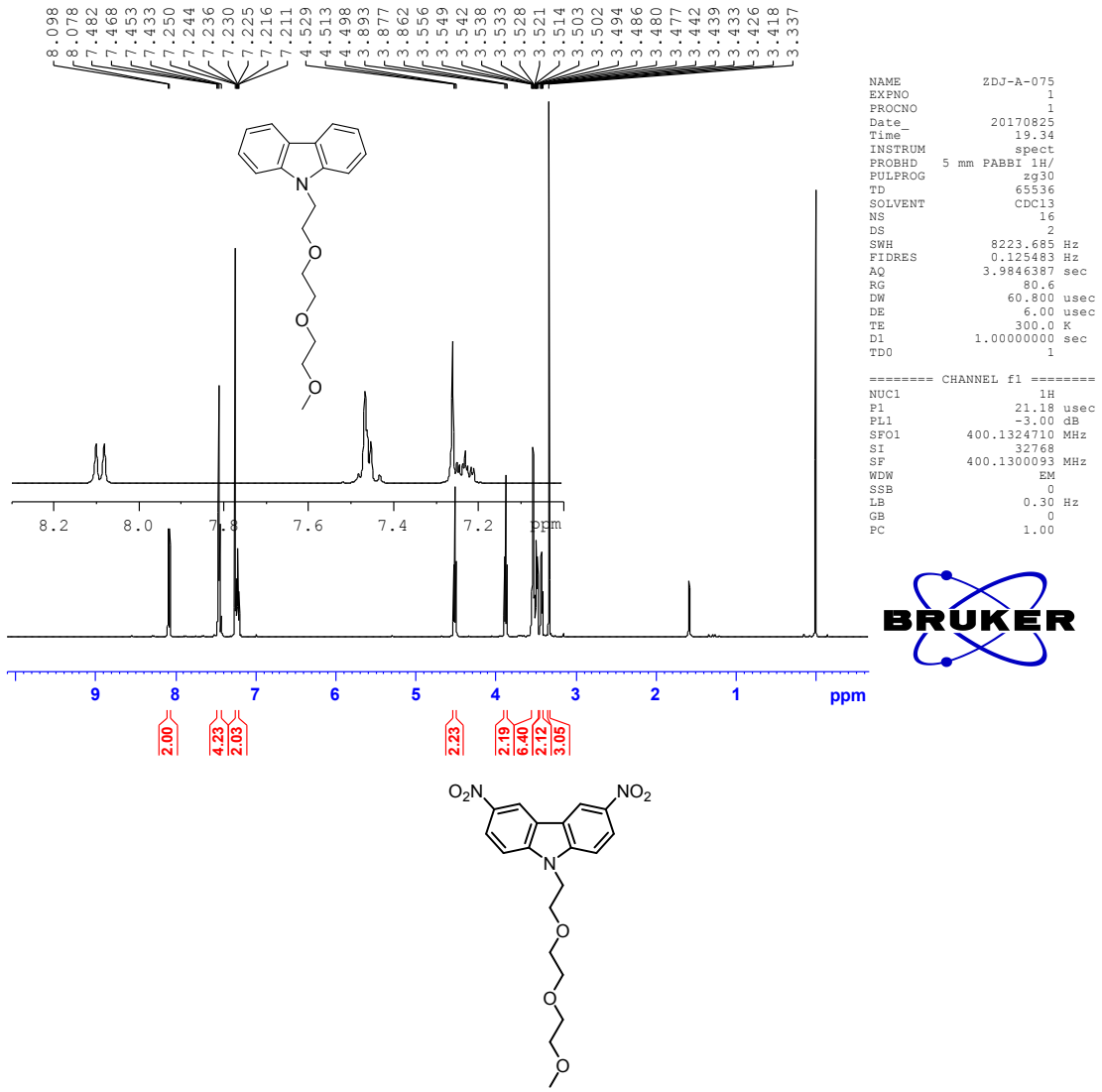
4. One Pot Synthesis of Macrocycles with Amphiphilic Periphery Tails



In a 50 mL round bottom flask, carbazole (167.2 mg, 1 mmol), NaH (56 mg, 1.4 mmol) and DMF (10 mL) were combined. The mixture was stirred for 30 minutes at room temperature under a nitrogen atmosphere. And then 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (382.1 mg, 1.2 mmol) was added into the above solution. The mixture was stirred for 2 hours at room temperature and then H_2O (50 mL) was added. The aqueous solution was extracted three times with CH_2Cl_2. The combined organic phase was washed with brine and water, and then dried over anhydrous Na_2SO_4. The organic phase was then concentrated under reduced pressure and purified by column chromatography (silica gel, petroleum ether: ethyl acetate = 2:1 as eluent) to provide the product as a yellow oil (300 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.09 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.49-7.43 (m, 4H, Ar*H*), 7.25-7.20 (m, 2H, Ar*H*), 4.51 (t, *J* = 6.1 Hz, 2H, NCH_2), 3.88 (t, *J* = 6.1 Hz, 2H, NCH$_2$CH_2), 3.56-3.47 (m, 6H, CH_2), 3.45-3.41 (m, 2H, CH_2), 3.34 (s, 3H, CH_3).



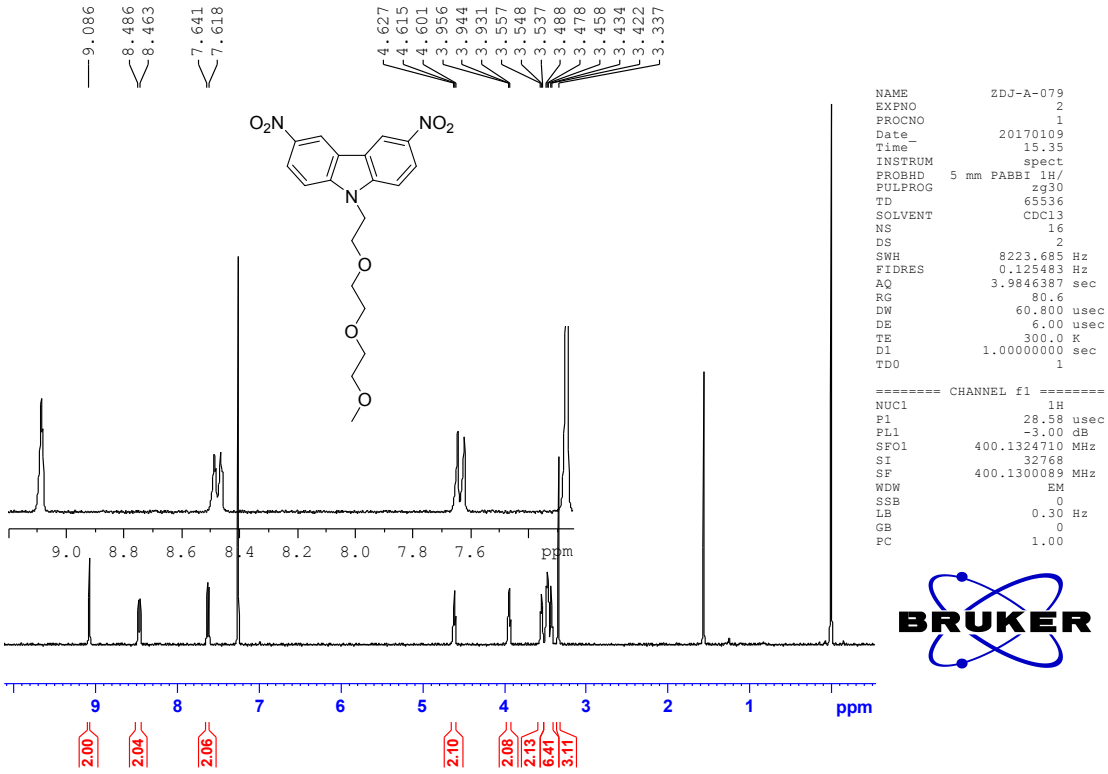
$Cu(NO_3)_2{\cdot}3H_2O$ (362 mg, 1 mmol) was added into a mixture of acetic acid (15 mL) and acetic anhydride (30 mL) at room temperature. The mixture was stirred for 10 min. Compound **1c** (313 mg, 1 mmol) was added slowly in portions over 5 minutes. Heat was generated during the addition, and an additional 15 mL of acetic acid was added. The mixture was stirred at this temperature for 2 hours and then poured into water. The aqueous solution was extracted three times with CH_2Cl_2. The combined organic phase was washed with brine and water, and then dried over anhydrous Na_2SO_4. The organic phase was then concentrated under reduced pressure and purified by column chromatography (silica gel, dichloromethane: ethyl acetate = 14:1 as eluent) to provide the product as a yellow solid (283 mg, 70%).

M.p: 150.2-151.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 9.09 (s, 2H, Ar*H*), 8.47 (d, *J* = 9.0 Hz, 2H, Ar*H*), 7.63 (d, *J* = 9.2 Hz, 2H, Ar*H*), 4.61 (t, *J* = 5.1 Hz, 2H, NCH_2), 3.94 (t, *J* = 5.1 Hz, 2H, NCH$_2$CH_2), 3.58-3.52 (m, 2H, OCH_2), 3.51-3.40 (m, 6H, CH_2), 3.34 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 145.1, 141.9, 122.8, 122.5, 117.4, 110.2, 71.8, 70.9, 70.6, 70.5, 69.4, 59.0, 44.6.

HRMS (ESI$^+$) calcd. for $[C_{19}H_{21}O_7N_3+Na]^+$ 426.1277, found: 426.1272.

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PROCNO                  1
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FIDRES           0.125483 Hz
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RG                   80.6
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D1             1.00000000 sec
TD0                     1

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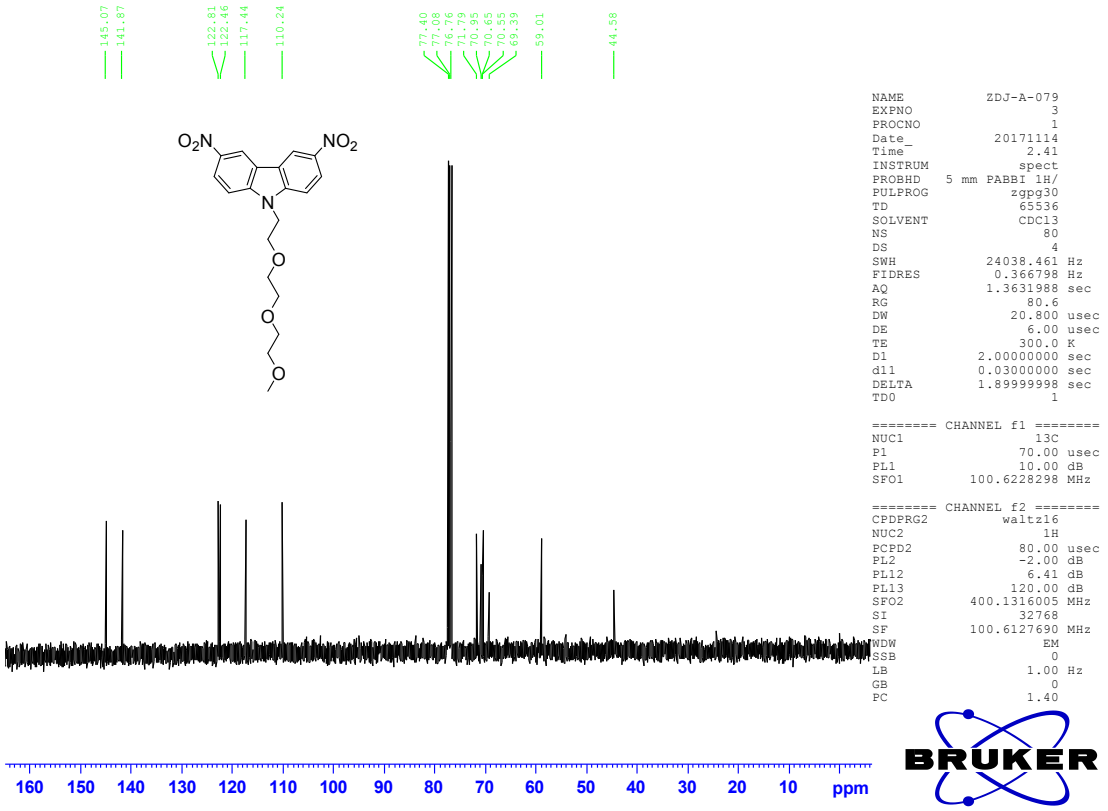


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TD                  65536
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NS                     80
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FIDRES           0.366798 Hz
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RG                   80.6
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DE                 6.00 usec
TE                300.0 K
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d11            0.03000000 sec
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TD0                     1

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PL1                10.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
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PL12                6.41 dB
PL13              120.00 dB
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SF            100.6127690 MHz
WDW                    EM
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GB                      0
PC                   1.40
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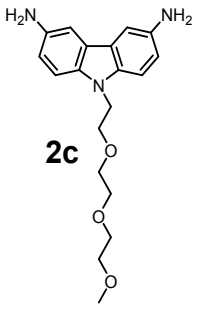


2c

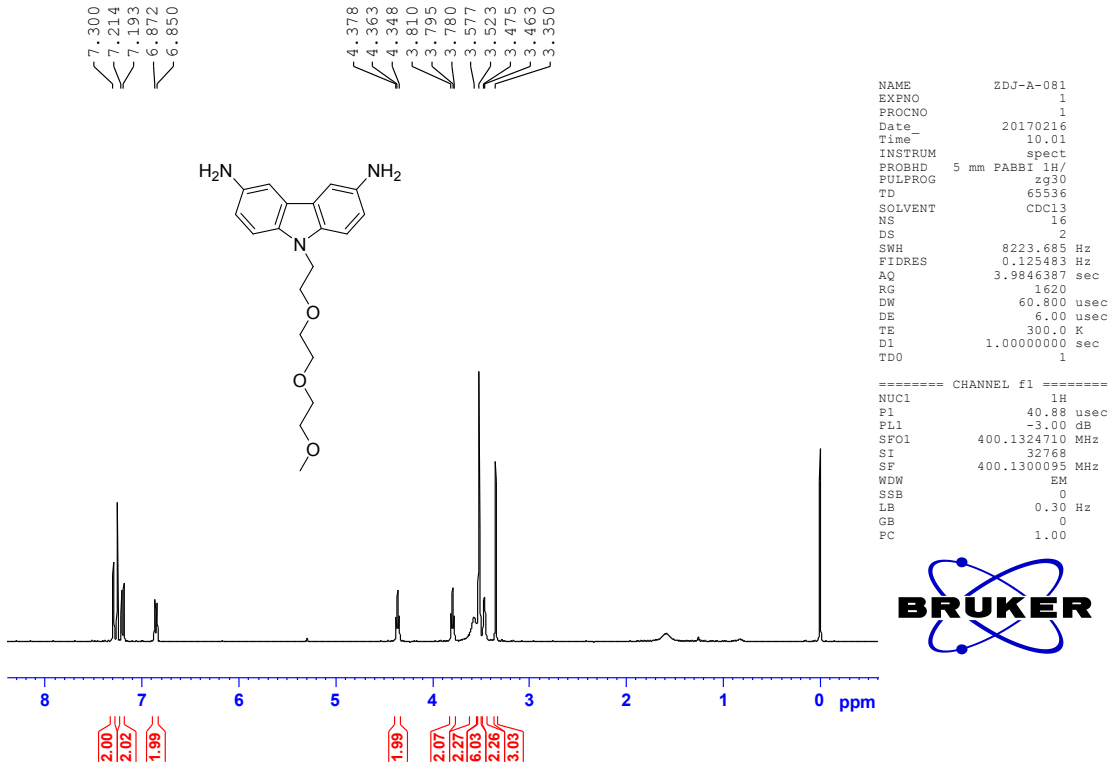
Palladium on active charcoal (10%, 400 mg) was added in portions to a hot solution of 9-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3,6-dinitro-9H-carbazole (5.316 g, 13.178 mmol) and hydrazine monohydrate (33 mL) in THF (200 mL) and the mixture was heated under reflux over night. Palladium on charcoal was filtered off. After concentration of the filtrate under reduced pressure, the residue was dissolved in CH_2Cl_2 and the organic phase was washed with water. The organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was triturated with petroleum ether to give the product as a gray solid (4.313 g, 95%).

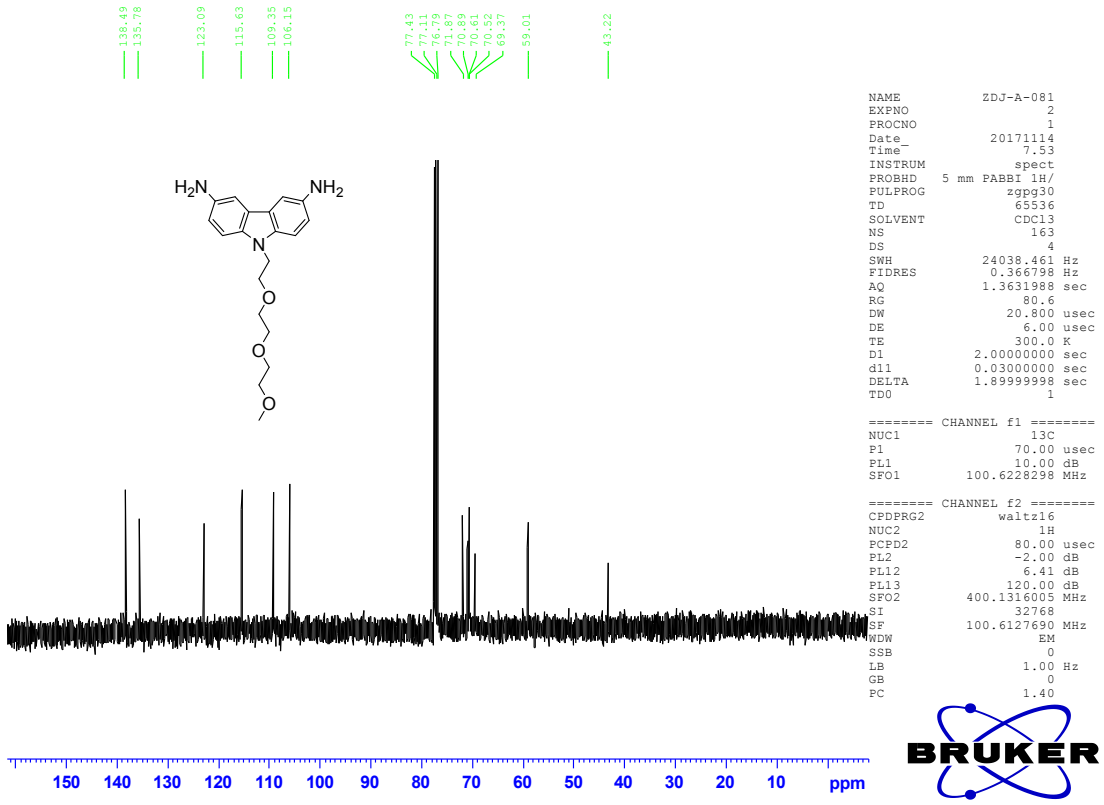
M.p: 84.6-85.1 ºC.

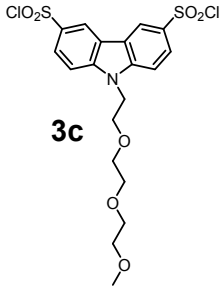
^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 7.30 (s, 2H, Ar*H*), 7.20 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.86 (d, *J* = 8.6 Hz, 2H, Ar*H*), 4.36 (t, *J* = 6.1 Hz, 2H, NCH_2), 3.79 (t, *J* = 6.2 Hz, 2H, NCH$_2$CH_2), 3.62-3.55 (br, 2H, NH_2), 3.52 (s, 6H, CH_2), 3.49-3.44 (m, 2H, CH_2), 3.35 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 138.5, 135.8, 123.1, 115.6, 109.4, 106.1, 71.9, 70.9, 70.6, 70.5, 69.4, 59.0, 43.2.

HRMS (ESI$^+$) calcd. for $[C_{19}H_{25}O_3N_3+Na]^+$ 366.1794, found: 366.1788.







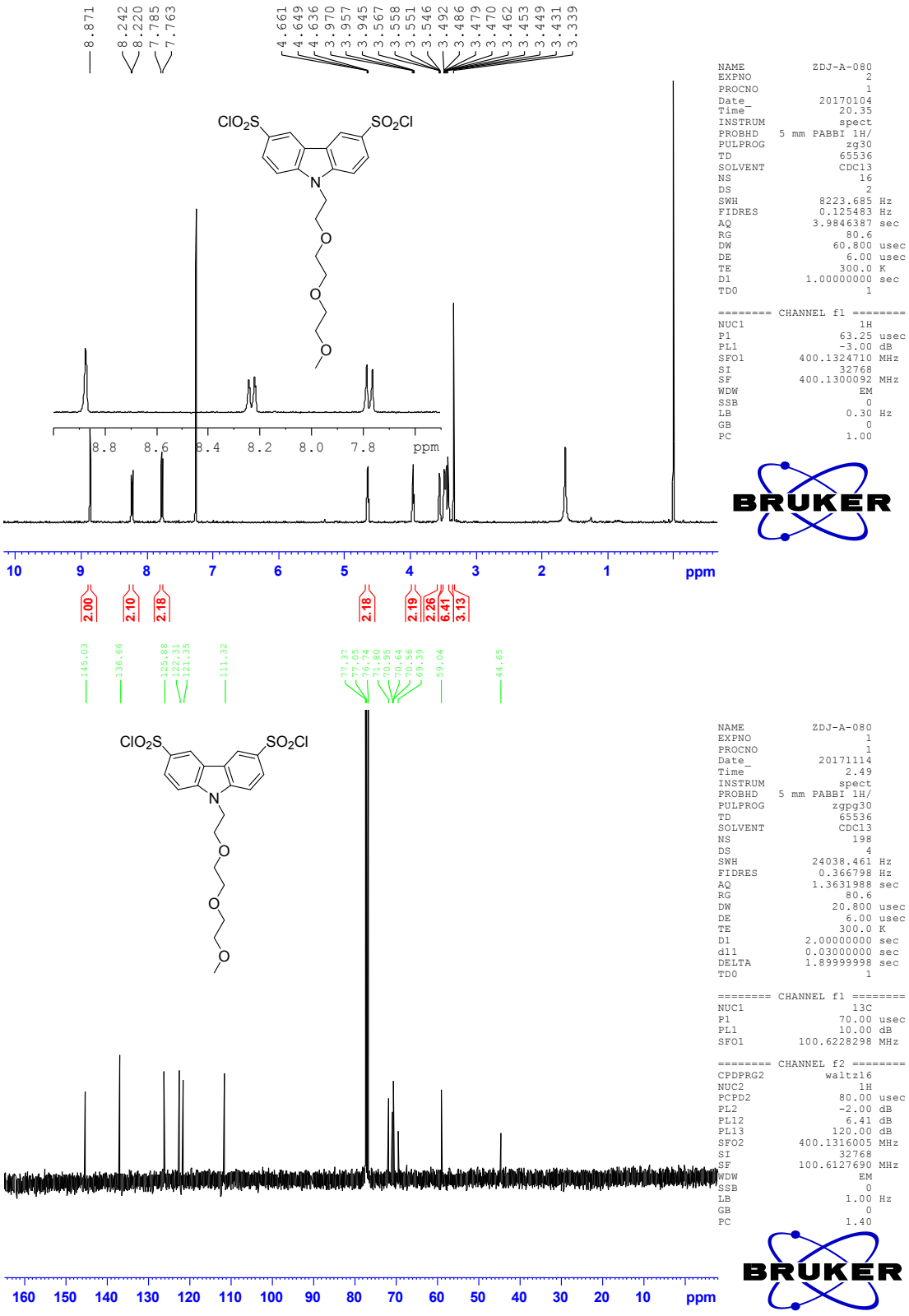
A solution of chlorosulphonic acid (8 mL, 120 mmol) in CH_2Cl_2 (30 mL) was added dropwise into a stirred solution of compound **1c** (4.701 g, 15 mmol) in CH_2Cl_2 (50 ml) at -5 °C over a period of 1.5 hours. The mixture was allowed to reach room temperature and stirred for another 3 hours. The reaction mixture was poured into ice water and extracted three times with CH_2Cl_2. The combined organic phase was washed with brine and water, and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was triturated with petroleum ether to give the product as a light yellow solid (6.23 g, 81%).

M.p: 123.2-124.0 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.87 (s, 2H, Ar*H*), 8.23 (d, *J* = 8.9 Hz, 2H, Ar*H*), 7.77 (d, *J* = 8.9 Hz, 2H, Ar*H*), 4.65 (t, *J* = 5.0 Hz, 2H, NCH_2), 3.96 (t, *J* = 5.0 Hz, 2H, NCH$_2$CH_2), 3.58-3.53 (m, 2H, OCH_2), 3.51-3.41 (m, 6H, CH_2), 3.34 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 145.0, 136.7, 125.9, 122.3, 121.3, 111.3, 71.8, 70.9, 70.64, 70.56, 69.4, 59.0, 44.6.

HRMS (ESI$^+$) calcd. for $[C_{19}H_{21}O_7NCl_2S_2+Na]^+$ 532.0034, found: 532.0029.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2.26
6.41
3.13
145.03
136.66
125.88
122.31
121.35
111.32
77.37
77.05
76.74
71.88
70.95
70.64
70.56
69.39
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44.65
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SO2Cl
N
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PROCNO 1
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PCPD2 80.00 usec
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PL13 120.00 dB
SFO2 400.1316005 MHz
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SF 100.6127690 MHz
WDW EM
SSB 0
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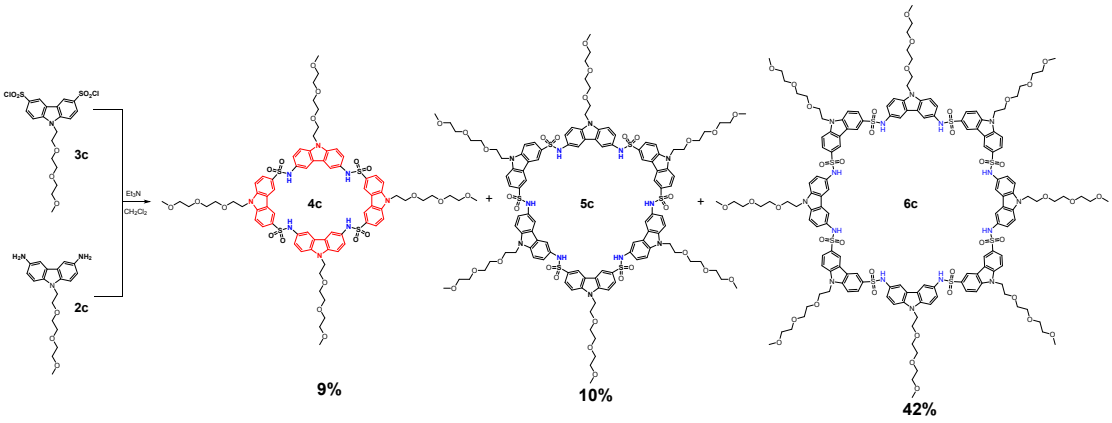
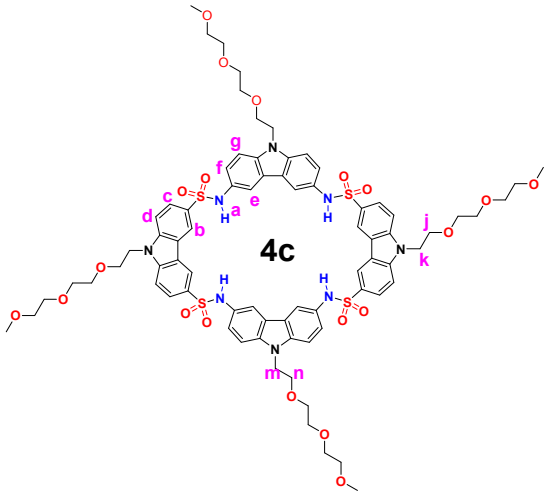
10
ppm



A solution of triethylamine (1.10 mL, 8 mmol) in CH_2Cl_2 (400 mL) was stirred at -12 °C. Compound **3c** (2.042 g, 4 mmol) and Compound **2c** (1.374 g, 4 mmol) in solid state were added into above solution in one portion. The mixture was stirred for 4 hours and then allowed to reach room temperature over a period of 6 hours. The mixture was then heated to reflux for 24 hours. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel). Eluting with CH_2Cl_2: CH_3OH = 38:1 afforded the "2+2" product **4c**. Further purification was achieved *via* trituration with hot methanol (274 mg, 9%). Eluting with CH_2Cl_2: CH_3OH = 35:1 gave the "3+3" product **5c**. Further purification via trituration with methanol was also successful (300 mg, 10%). Eluting with CH_2Cl_2: CH_3OH = 20:1 gave the "4+4" product **6c** (1.302 g, 42%). Further purification could be achieved *via* trituration with hot methanol.

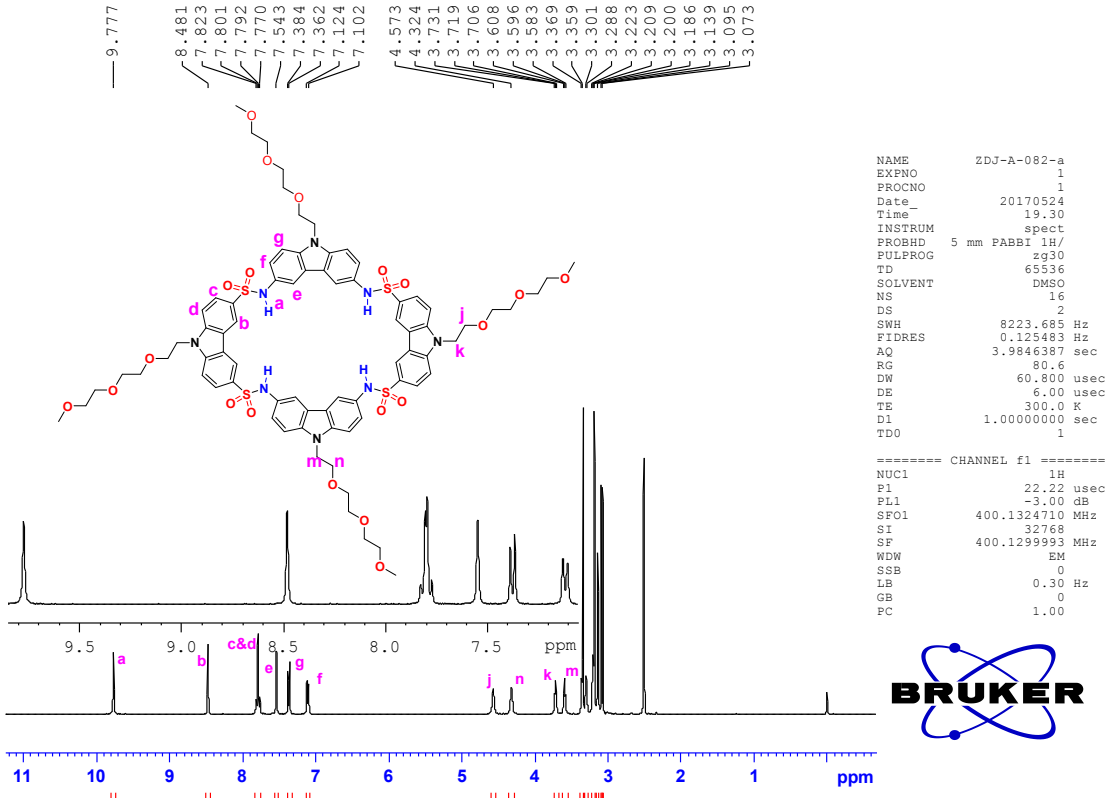


M.p: 153.0-153.9 ºC.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.77 (s, 4H, NH^a), 8.47 (s, 4H, ArH^b), 7.83-7.75 (m, 8H, Ar$H^{c\&d}$), 7.54 (s, 4H, ArH^e), 7.37 (d, J = 8.8 Hz, 4H, ArH^g), 7.11 (d, J = 8.8 Hz, 4H, ArH^f), 4.57 (s, 4H, OCH_2^j), 4.32 (s, 4H, OCH_2^n), 3.72 (t, J = 4.8 Hz, 4H, NCH_2^k), 3.60 (t, J = 5.1 Hz, 4H, NCH_2^m), 3.38-3.34 (m, 4H, CH_2), 3.32-3.28 (m, 4H, CH_2), 3.23-3.17 (m, 16H, CH_2), 3.16-3.12 (m, 8H, CH_2), 3.09 (s, 6H, CH_3), 3.07 (s, 6H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 143.3, 138.7, 131.3, 129.7, 125.4, 122.1, 121.9, 121.7, 121.0, 114.4, 111.2, 110.4, 71.5, 70.5, 70.3, 70.1, 70.0, 69.2, 58.4, 43.8, 43.2.

HRMS (ESI$^+$) calcd. for $[C_{76}H_{88}O_{20}N_8S_4+Na]^+$ 1583.4895, found: 1583.4890.

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FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   80.6
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TE                 300.0 K
D1            1.00000000 sec
TD0                     1

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PL1                 -3.00 dB
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SI                  32768
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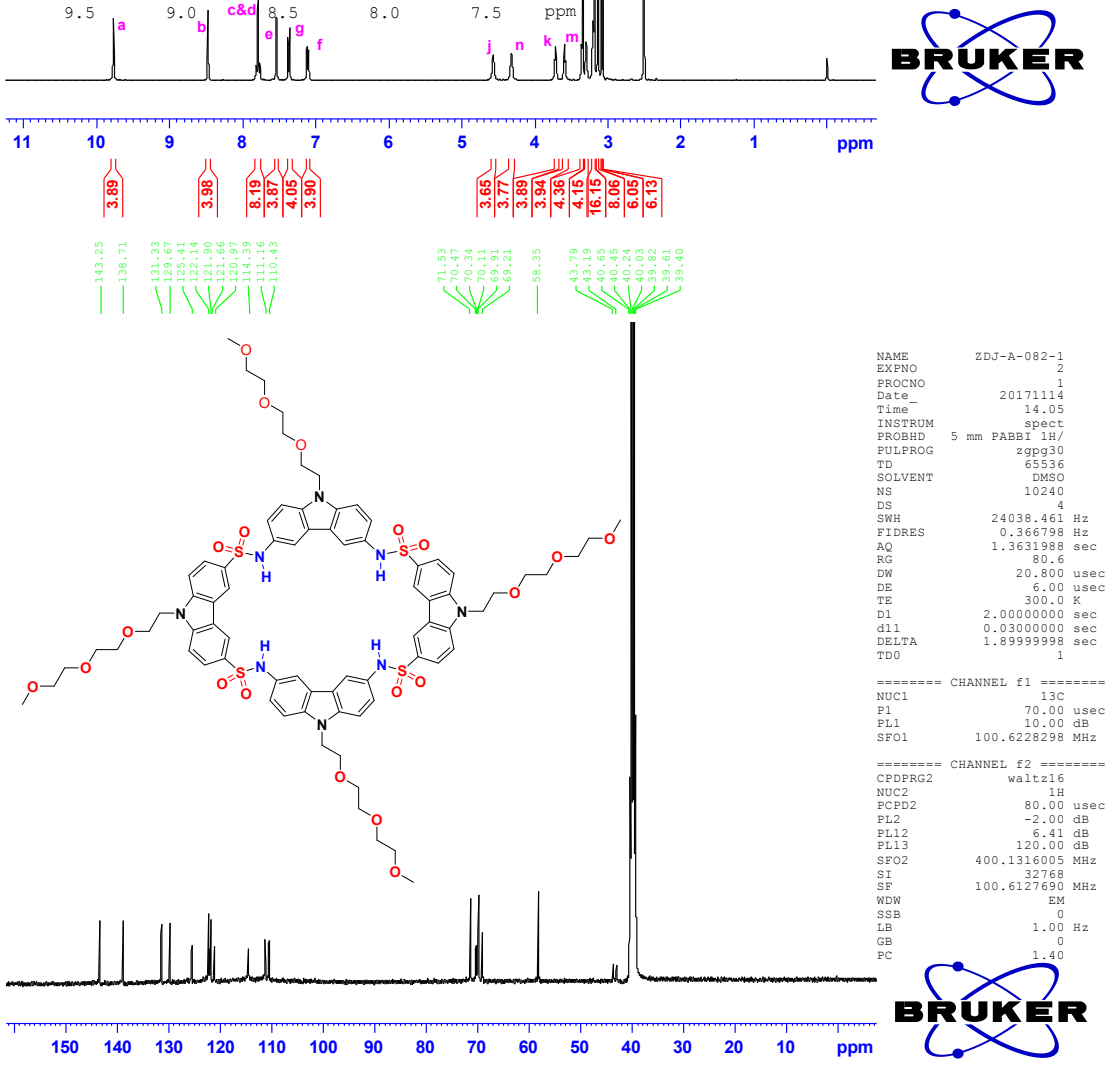


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SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   80.6
DW                 20.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

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PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                 6.41 dB
PL13               120.00 dB
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SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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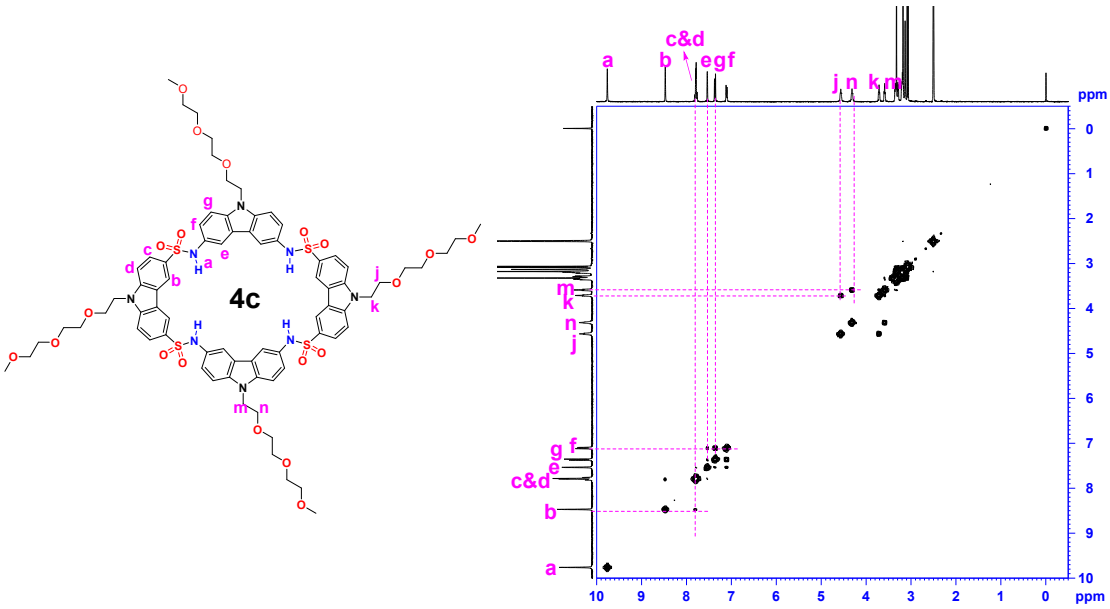
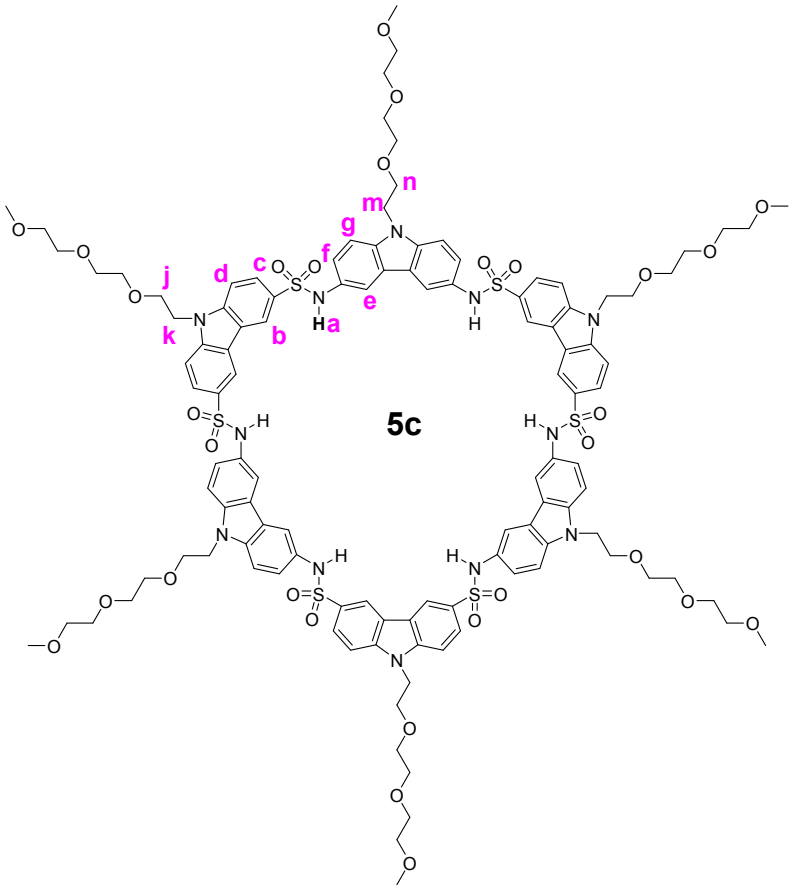


COSY spectrum for macrocycle **4c**, DMSO-d_6, 298 K, 400 MHz.



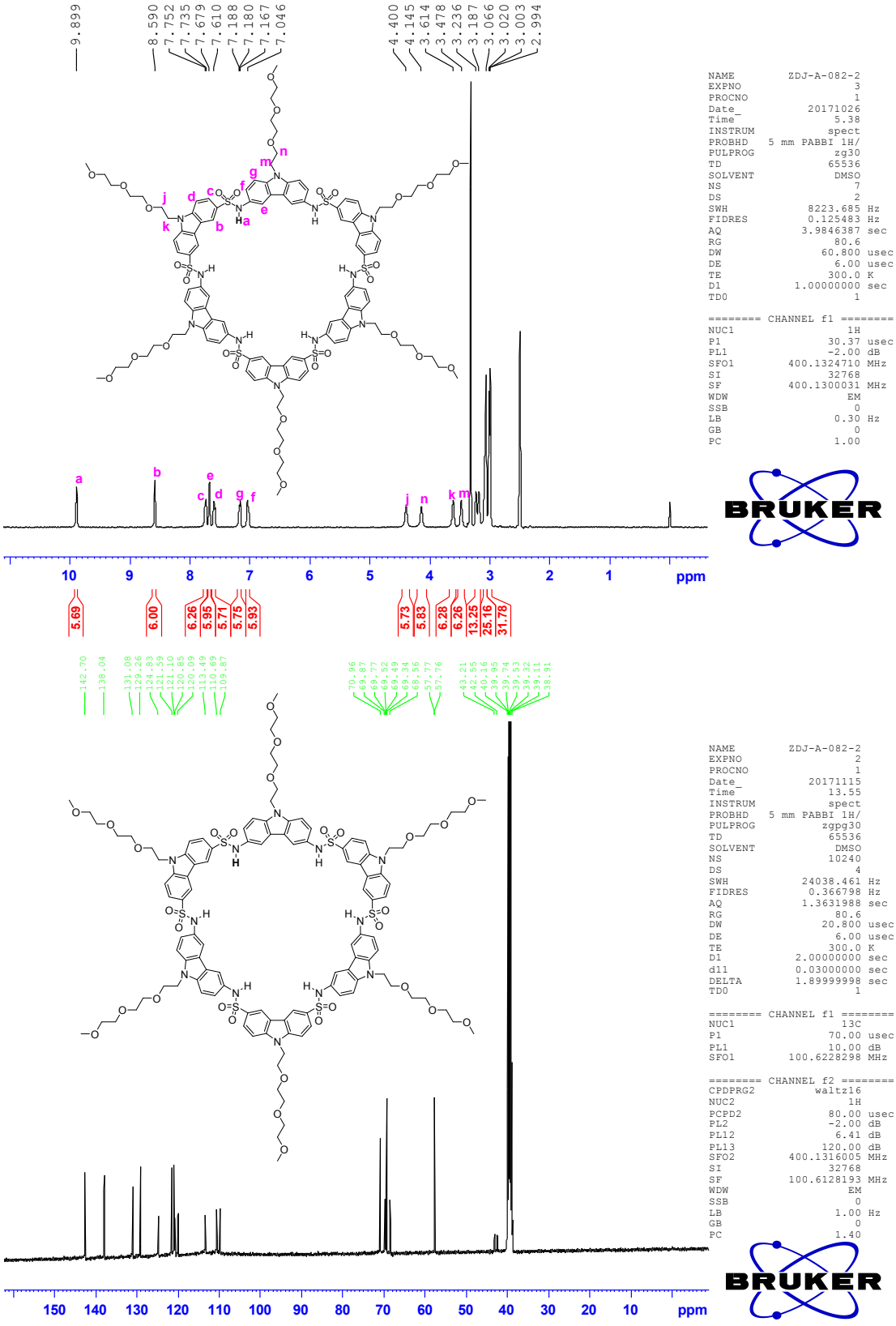
M.p: 212.1-213.0 ºC.

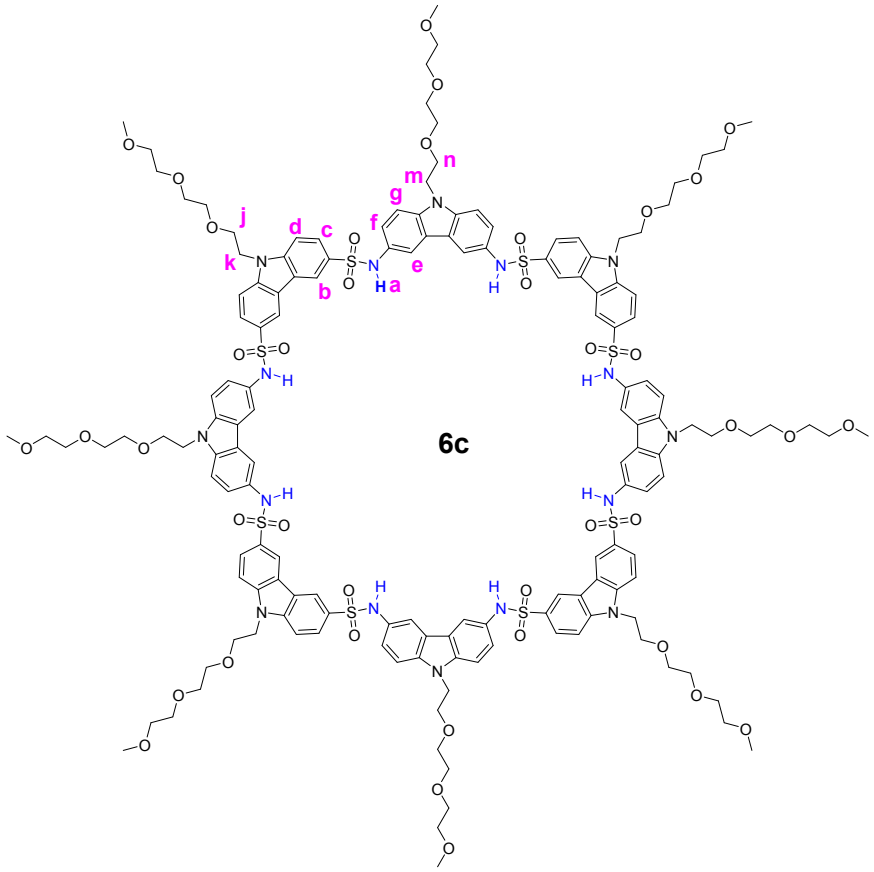
^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.90 (s, 6H, NH^a), 8.59 (s, 6H, ArH^b), 7.74 (d, J = 6.6 Hz, 6H, ArH^c), 7.68 (s, 6H, ArH^e), 7.60 (d, J = 8.4 Hz, 6H, ArH^d), 7.17 (d, J = 5.2 Hz, 6H, ArH^g), 7.04 (d, J = 7.0 Hz, 6H, ArH^f), 4.40 (s, 6H, OCH$_2^j$), 4.15 (s, 6H, OCH$_2^n$), 3.61 (s, 6H, NCH$_2^k$), 3.48 (s, 6H, NCH$_2^m$), 3.26-3.16 (m, 12H, CH$_2$), 3.11-3.05 (m, 24H, CH$_2$), 3.04-2.97 (m, 32H, CH$_2$&CH$_3$).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 142.7, 138.0, 131.1, 129.3, 124.8, 121.6, 121.1,

120.9, 120.1, 113.5, 110.7, 109.9, 71.0, 69.9, 69.8, 69.51, 69.48, 69.3, 68.6, 57.8, 43.2, 42.6.

HRMS (ESI$^+$) calcd. for $[C_{114}H_{132}O_{30}N_{12}S_6+Na]^+$ 2363.7394, found: 2363.7389.



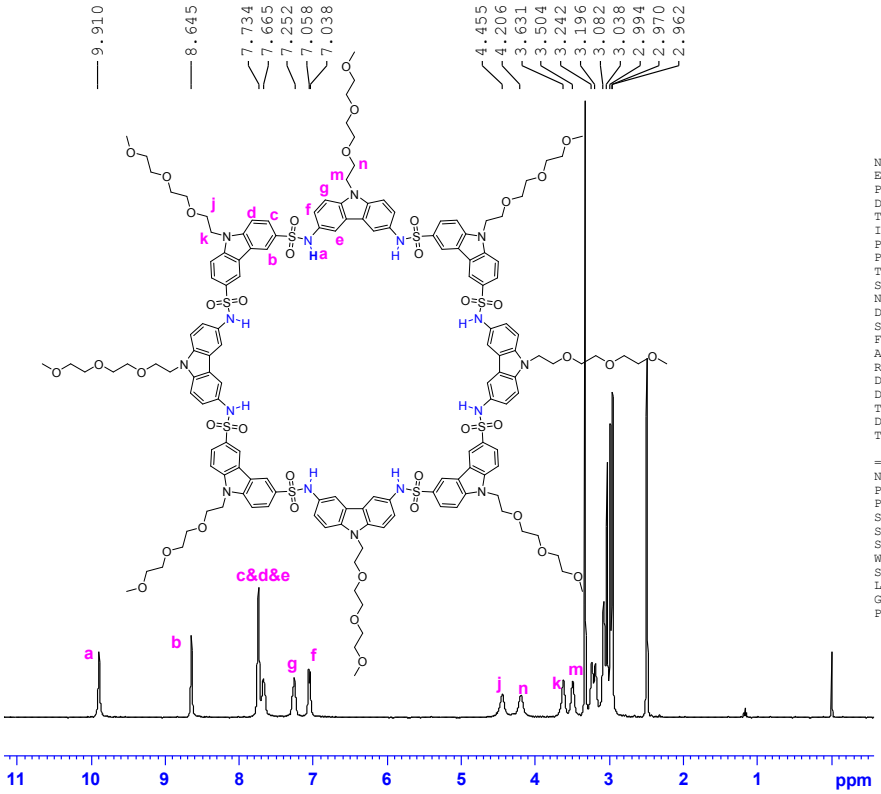


M.p: 151.3-152.2 ºC.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.91 (s, 8H, NH^{a}), 8.64 (s, 8H, ArH^{b}), 7.78-7.62 (m, 24H, Ar$H^{c\&d\&e}$), 7.25 (s, 8H, ArH^{g}), 7.05 (d, J = 3.9 Hz, 8H, ArH^{f}), 4.45 (s, 8H, OCH_2^{j}), 4.21 (s, 8H, OCH_2^{n}), 3.63 (s, 8H, NCH_2^{k}), 3.50 (s, 8H, NCH_2^{m}), 3.28-3.16 (m, 18H, CH_2), 3.11-2.95 (m, 76H, CH_2&CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 143.3, 138.7, 131.6, 129.8, 125.4, 122.2, 121.7, 121.4, 120.6, 114.2, 111.2, 110.4, 71.5, 70.4, 70.3, 70.0, 69.8, 69.1, 58.2, 43.8, 43.2.

HRMS (ESI^{+}) calcd. for $[C_{152}H_{176}O_{40}N_{16}S_8+2Na]^{2+}$ 1583.4890, found: 1584.4919; calcd. for $[C_{152}H_{176}O_{40}N_{16}S_8+Na]^{+}$ 3143.9888, found: 3144.9940.

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TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                   80.6
DW                60.800 usec
DE                 6.00 usec
TE                 300.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  22.22 usec
PL1                 -3.00 dB
SFO1          400.1324710 MHz
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SF            400.1300031 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
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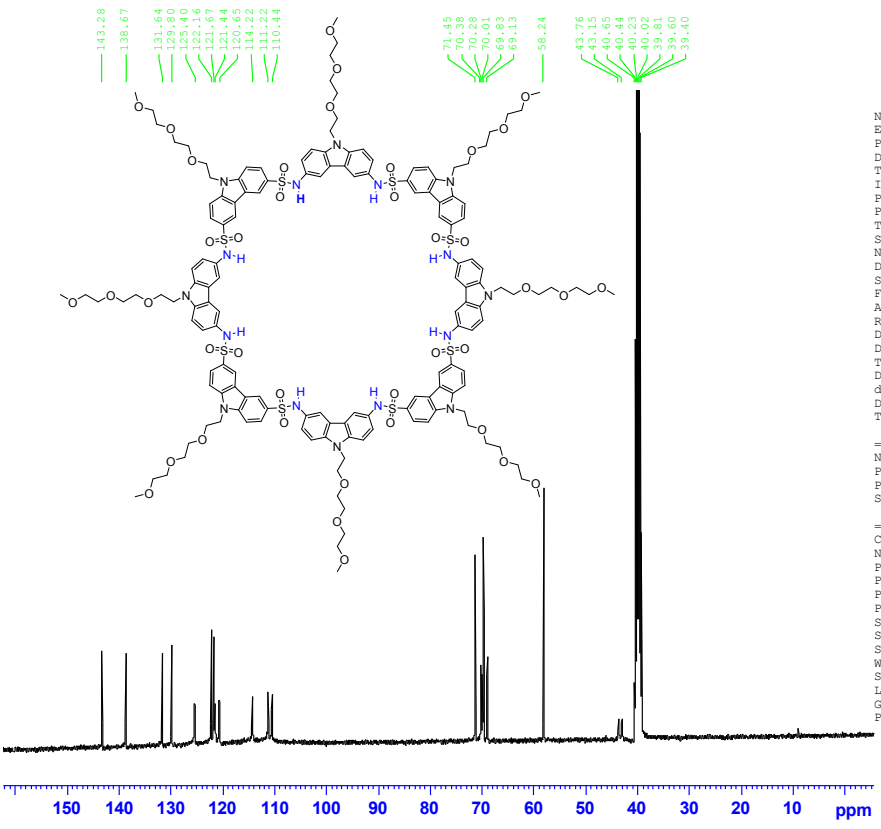


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PULPROG           zgpg30
TD                  65536
SOLVENT              DMSO
NS                  10370
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                   80.6
DW                20.800 usec
DE                 6.00 usec
TE                 300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
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P1                  70.00 usec
PL1                 10.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                 6.41 dB
PL13                120.00 dB
SFO2          400.1316005 MHz
SI                   32768
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WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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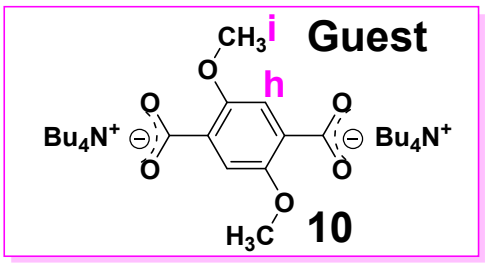
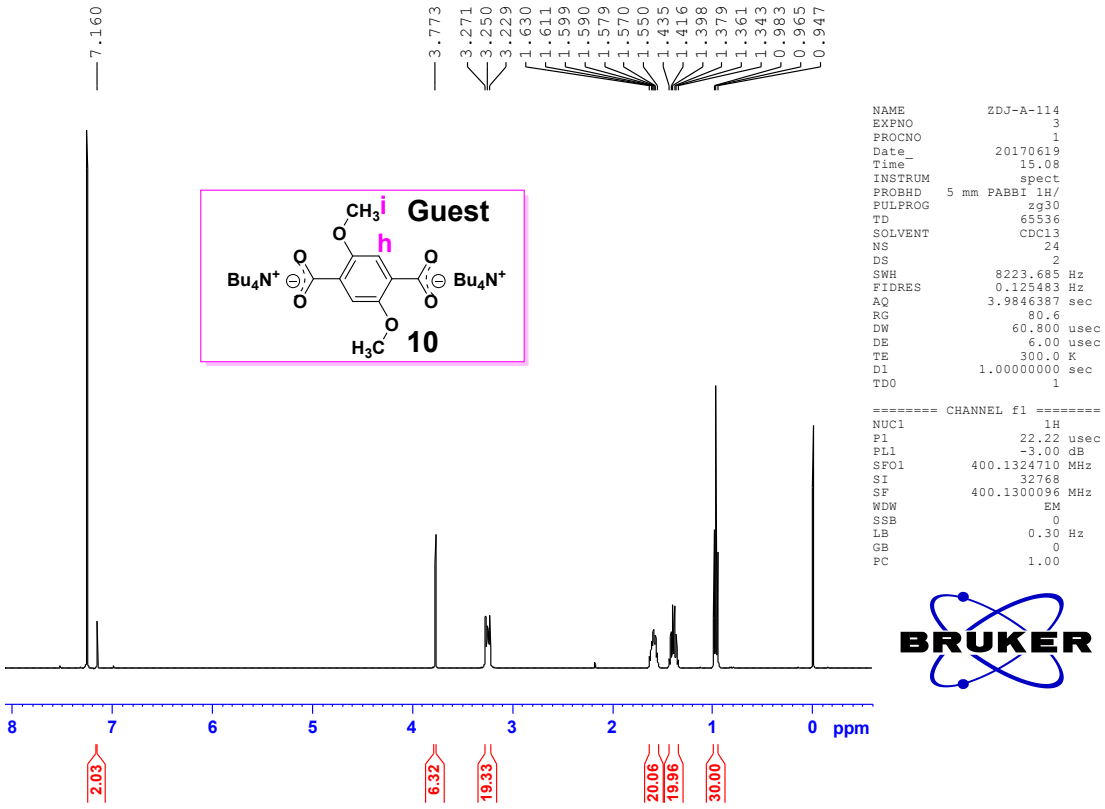
5. Synthesis of Guest **10**



A solution of 2, 5-dimethoxyterephthalic acid[S3] (339 mg, 1.5 mmol) and tetrabutylammonium hydroxide (1.946 g, 3 mmol) in methanol (20 mL) was stirred at room temperature overnight. The solvent was removed under reduced pressure and the residue was triturated with petroleum ether to give the product as a gray white solid (1.064 g, almost quantitative yield).

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 7.17 (s, 2H, Ar*H*), 3.78 (s, 6H, OCH_3), 3.26 (t, J = 8.5 Hz, 16H, NCH_2), 1.64-1.55 (m, 16H, NCH_2CH_2), 1.45-1.34 (m, 16H, CH_2), 0.97 (t, J = 7.3 Hz, 24H, CH_3).



6. UV-vis absorption spectra and FL emission spectra of **4c**, **5c** and **6c**

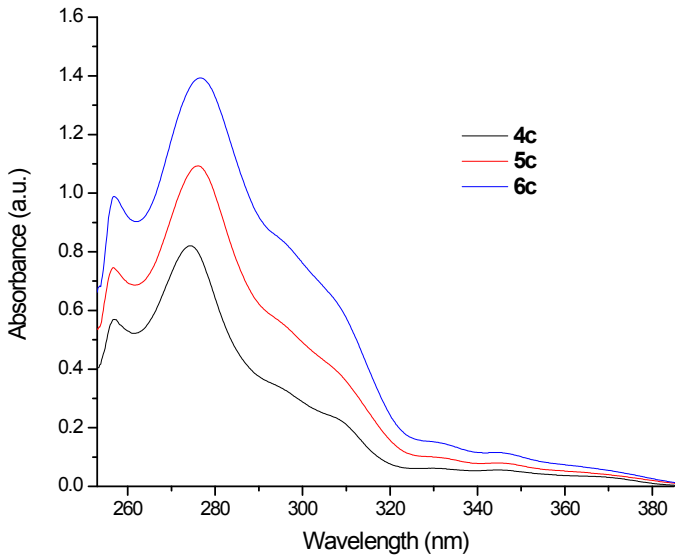


Fig. S1. UV-vis absorption spectra for macrocycles **4c**, **5c** and **6c**, recorded in DMSO, 298 K, concentration: 6.0×10^{-6} M.

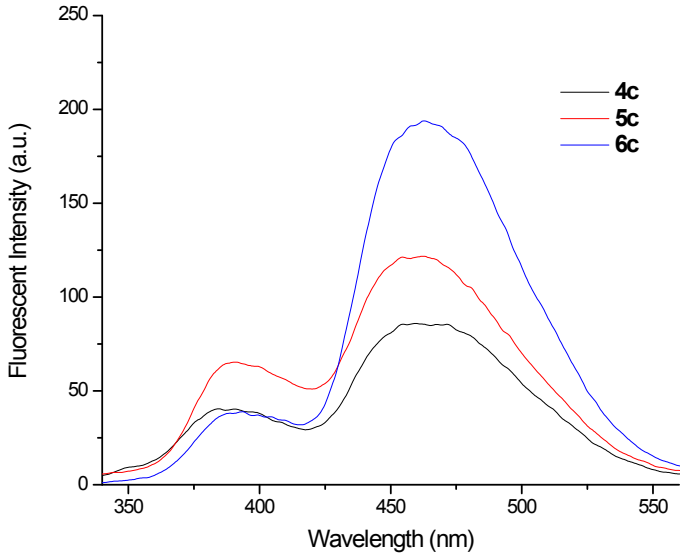


Fig. S2. Fluorescence spectra for macrocycles **4c**, **5c** and **6c**, recorded in DMSO, 298 K, concentration: 6.0×10^{-6} M, λ_{ex} = 285 nm.

7. Complexation Study of Macrocycle **4c** and Guest **10**

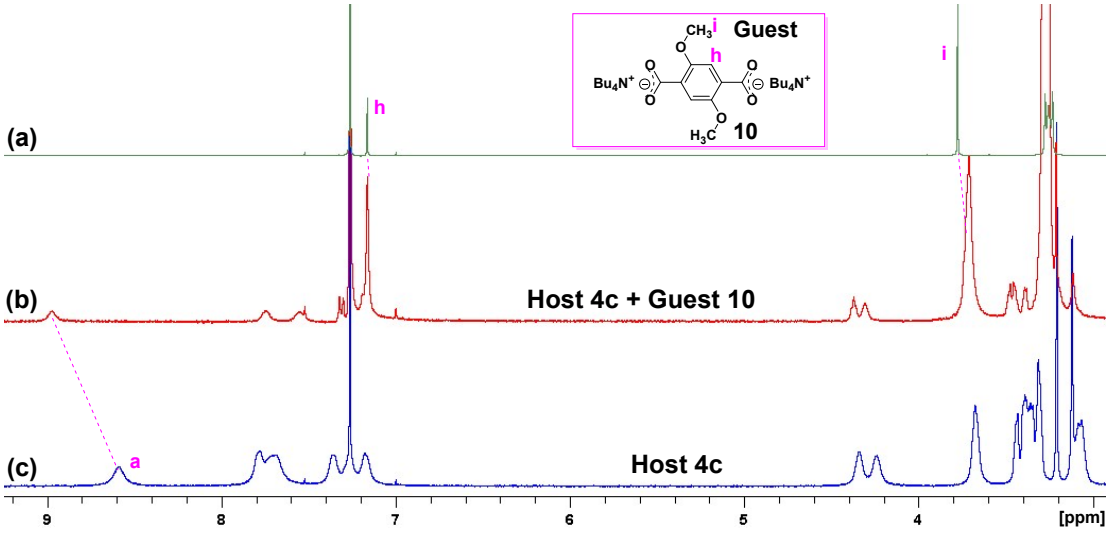


Fig. S3. Stacked partial ^{1}H NMR spectra for 14 mM **10** (a), 4 mM **4c** + 14 mM **10** (b), and 4 mM **4c** (c), in $CDCl_3$, 298 K, 400 MHz.

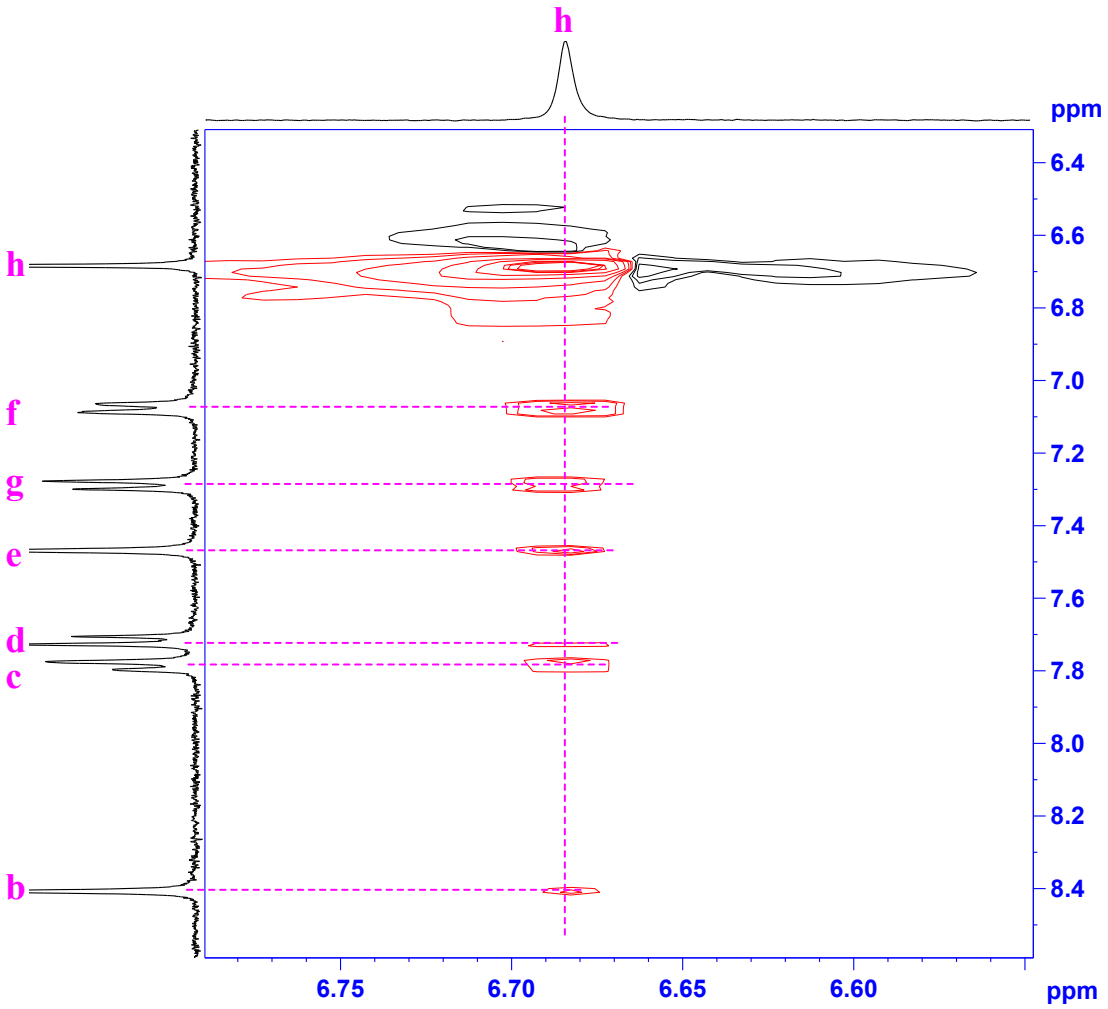


Fig. S4. Partial NOESY spectrum of 4 mM Host **4c** and 12 mM Guest **10**, in DMSO-d_6, 298 K, 400 MHz, showing cross contacts between H^h on guest **10** and H^b, H^c, H^d, H^e, H^g, and H^f on host **4c**.

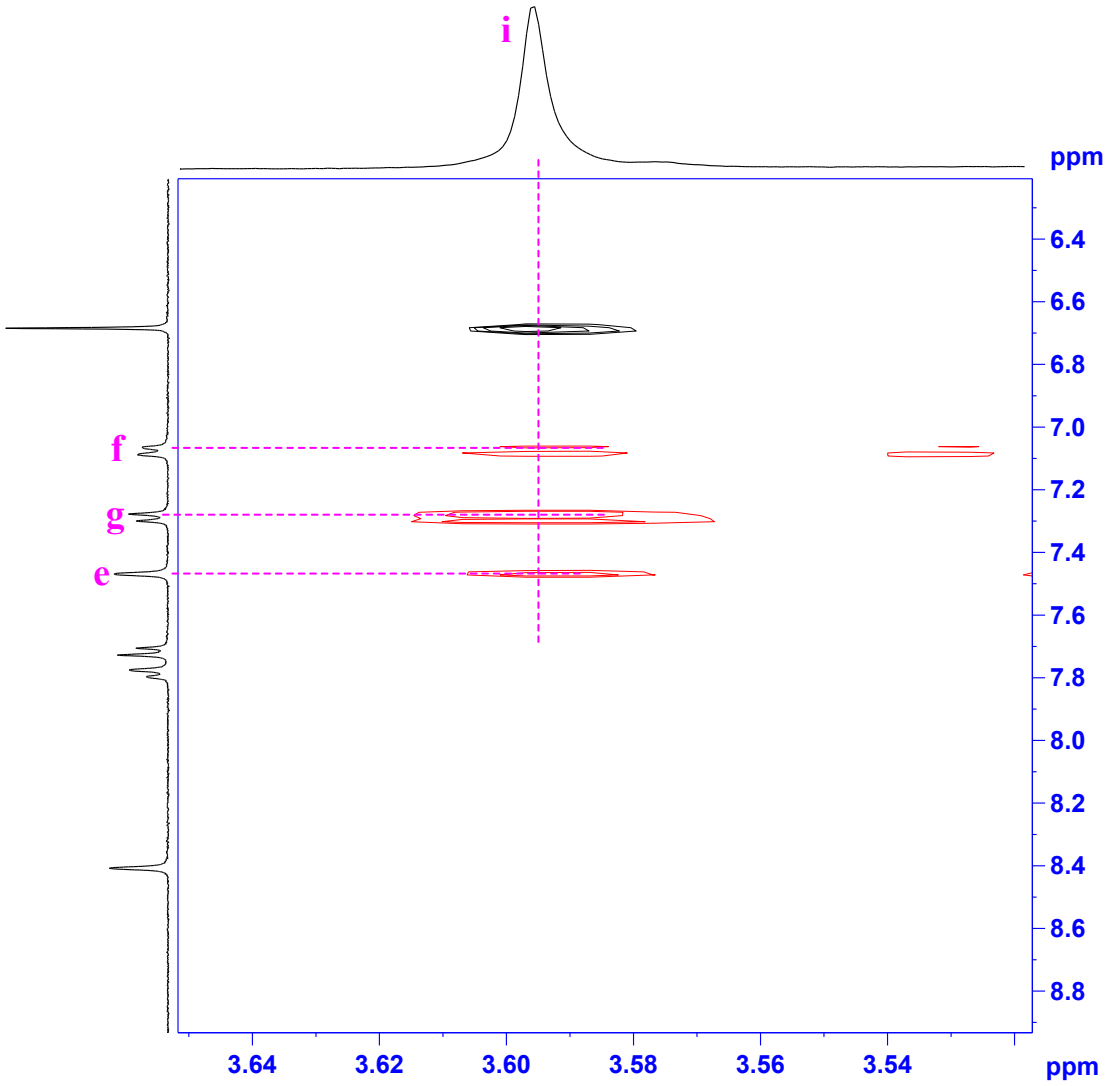


Fig. S5. Partial NOESY spectrum of 4 mM Host **4c** and 12 mM Guest **10**, in DMSO-d_6, 298 K, 400 MHz, showing cross contacts between H^i on guest **10** and H^e, H^g, and H^f on host **4c**.

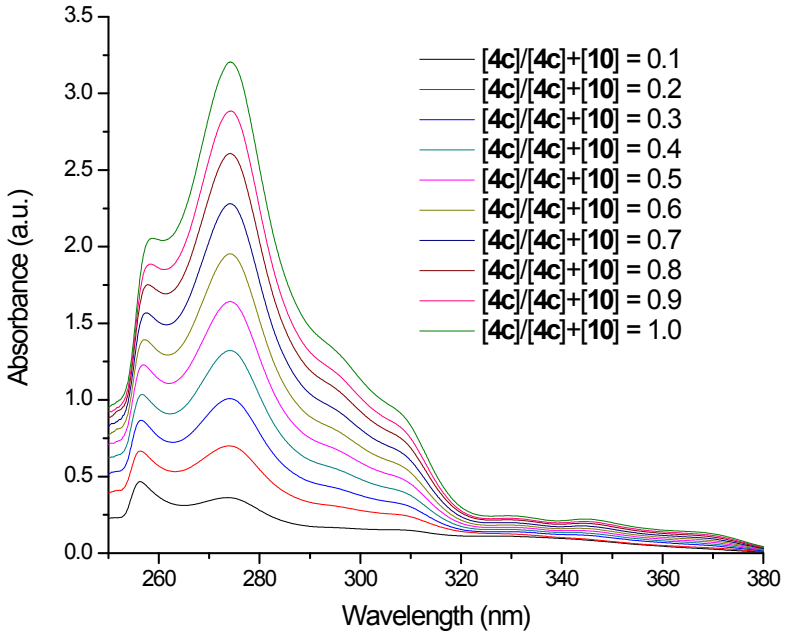


Fig. S6. UV-vis spectra of a mixture of host **4c** and guest **10** with different ratios in DMSO, with the total concentration fixed at 2.5×10^{-5} M.

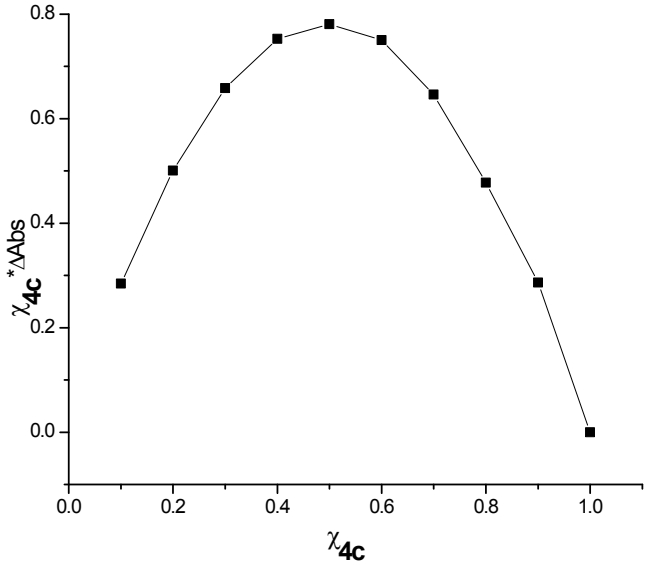


Fig. S7. Job-plot for the complex between host **4c** and guest **10** in DMSO using UV-vis absorption value at λ = 275 nm, showing a 1:1 stoichiometry.

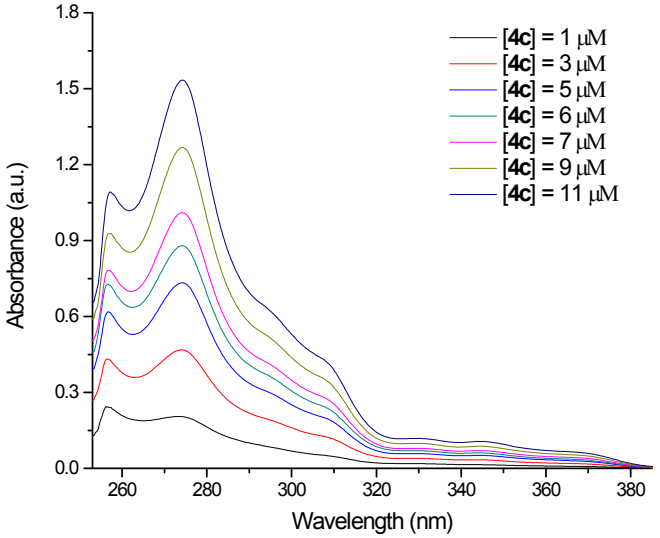


Fig. S8. UV-vis spectra of macrocycle **4c** at different concentrations (1 ~ 11 μM) in DMSO, 298 K.

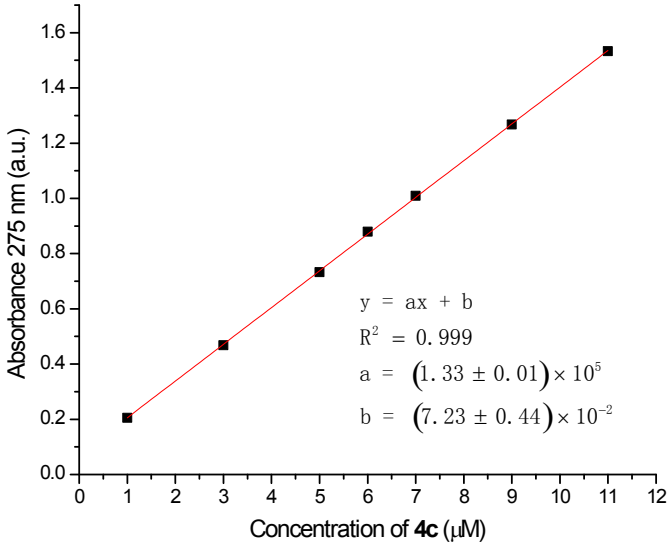


Fig. S9. UV-vis absorption of macrocycle **4c** in DMSO as function of its concentration, λ = 275 nm.

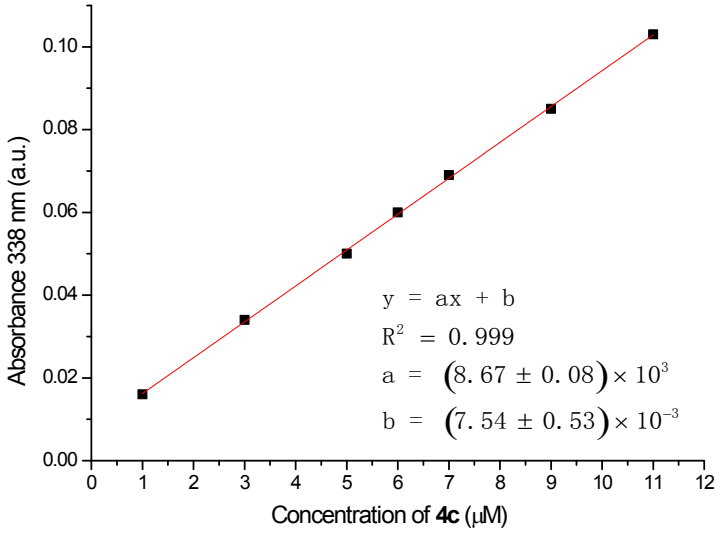


Fig. S10. UV-vis absorption of macrocycle **4c** in DMSO as function of its concentration, λ = 338 nm.

*NOTE: The linear relationship of A_{275nm} and A_{338nm} versus the concentration of **4c** (1 ~ 11 μM) in above Figures indicated that **4c** did not aggregate at 6 μM.*

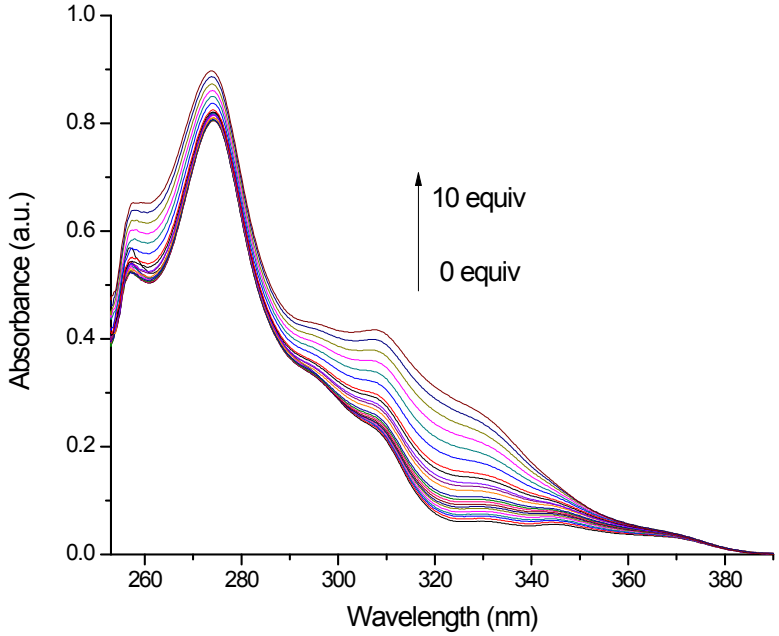


Fig. S11. Titration curves of host **4c** (fixed at 6.0×10^{-6} M in DMSO) with guest **10**, 298 K.

Determination of association constant (K_a) of macrocycles **4c**, **5c**, **6c** and the guest **10** from UV-vis titration data was based on the following equation.[S4]

$$H + G \rightleftharpoons HG$$

$$K_a = \frac{[HG]}{[H][G]}$$

$$[H] = [H]_0 - [HG]$$

$$[G] = [G]_0 - [HG]$$

$$[HG] = \frac{[G]_0 + [H]_0 + \frac{1}{K_a} - \sqrt{([G]_0 + [H]_0 + \frac{1}{K_a})^2 - 4[G]_0[H]_0}}{2}$$

$$A_{obs} = \varepsilon_1[H] + \varepsilon_2[HG]$$

$$= \varepsilon_1([H]_0 - [HG]) + \varepsilon_2[HG]$$

$$= \varepsilon_1[H]_0 + (\varepsilon_2 - \varepsilon_1)[HG] \qquad A_0 = \varepsilon_1[H]_0$$

$$A_{obs} - A_0 = (\varepsilon_2 - \varepsilon_1)[HG]$$

$$\Delta A = A_{obs} - A_0 \qquad C = \varepsilon_2 - \varepsilon_1$$

$$\Delta A = C\frac{[G]_0 + [H]_0 + \frac{1}{K_a} - \sqrt{([G]_0 + [H]_0 + \frac{1}{K_a})^2 - 4[G]_0[H]_0}}{2} \qquad \text{(Eq. S1)}$$

$[H]_0$: the initial concentration of Host

[H]: the concentration of free Host

$[G]_0$: the initial concentration of Guest

[G]: the concentration of free Guest

[HG]: the concentration of Host-Guest complex

K_a: association constant

ε_1: molar absorption coeffcient of Host

ε_2 : molar absorption coeffcient of Host-Guest complex HG

A_0: the initial absorption value of Host

A_{obs}: absorption value measured for each titration

ΔA : changes for absorption value

C : constant

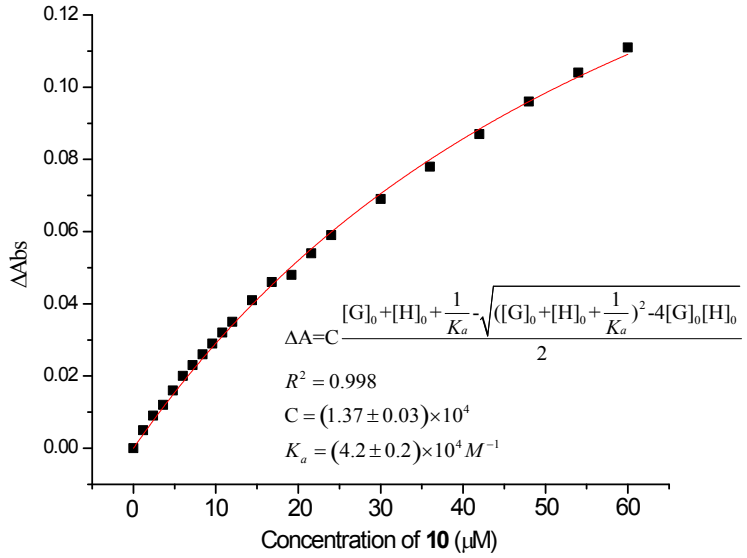


Fig. S12. Plot of the absorption intensity changes at λ = 338 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant K_a = (4.2 ± 0.2) × 10^4 M^{-1}.

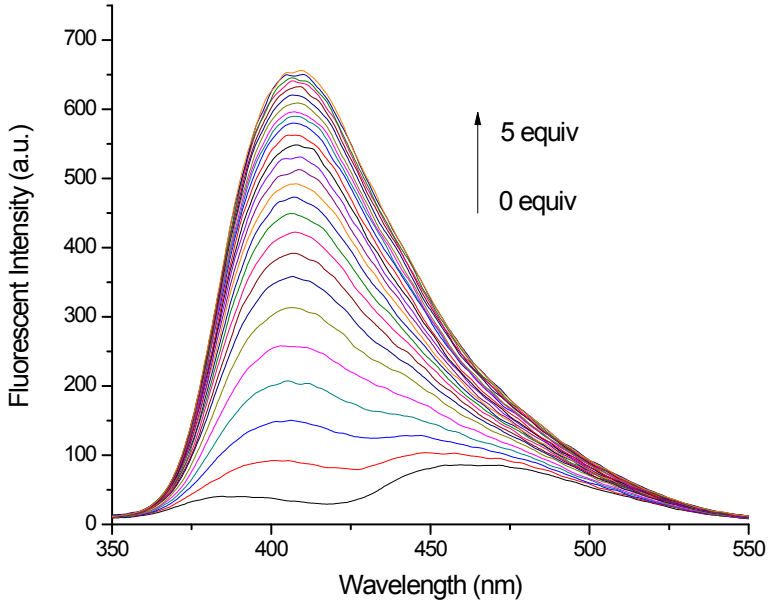


Fig. S13. Fluorescence spectra for a 6.0 × 10^{-6} M solution of host **4c** in DMSO with addition of different equivalents of guest **10**, λ_{ex} = 285 nm.

Determination of association constant (K_a) of macrocycles **4c**, **5c**, **6c** and the guest **10** from FL titration data was based on the following equation[S4].

$$\Delta F = \frac{a \times [G]_0}{\frac{1}{K_a} + [G]_0} \qquad \text{(Eq. S2)}$$

$[G]_0$: initial concentration of guest

K_a: association constant

ΔF: changes of fluorescence intensity

a : constant

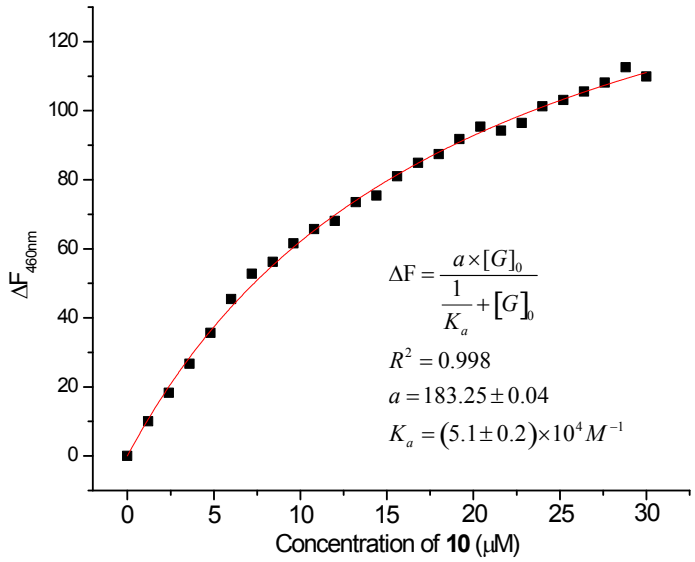


Fig. S14. Plot of fluorescence intensity of $\Delta F_{460\ nm}$ *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S2, yielding an association constant K_a = (5.1 ± 0.2) × 10^4 M^{-1}.

8. Complexation Study of Macrocycle **5c** and Guest **10**

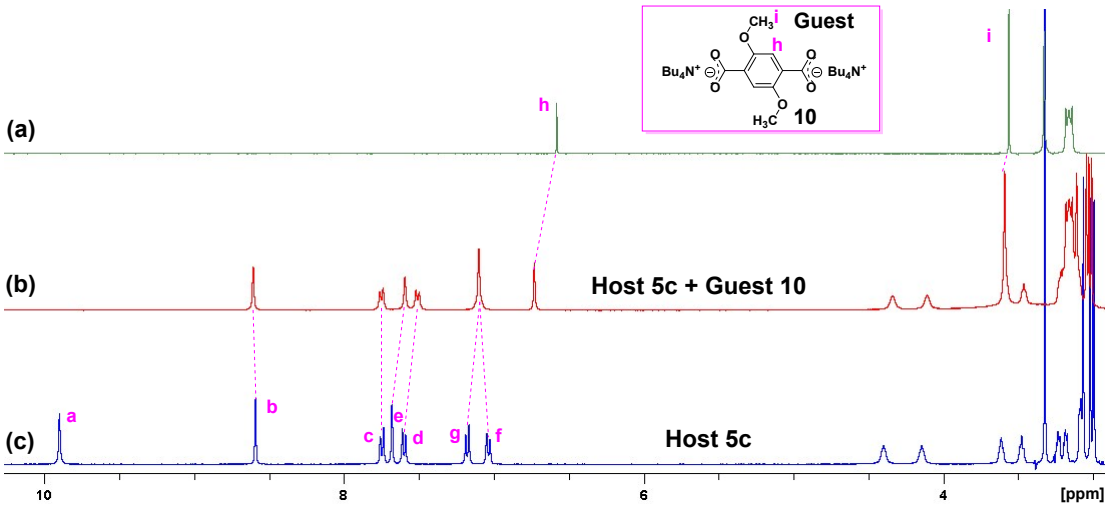


Fig. S15. Stacked partial ^{1}H NMR spectra for 4 mM **10** (a), 4 mM **5c** + 12 mM **10** (b) and 4 mM **5c** (c), DMSO-d_6, 298 K, 400 MHz. H^h: $\Delta\delta$ = 6.73 – 6.58 = 0.15 ppm; H^i: $\Delta\delta$ = 3.59 – 3.56 = 0.03 ppm.

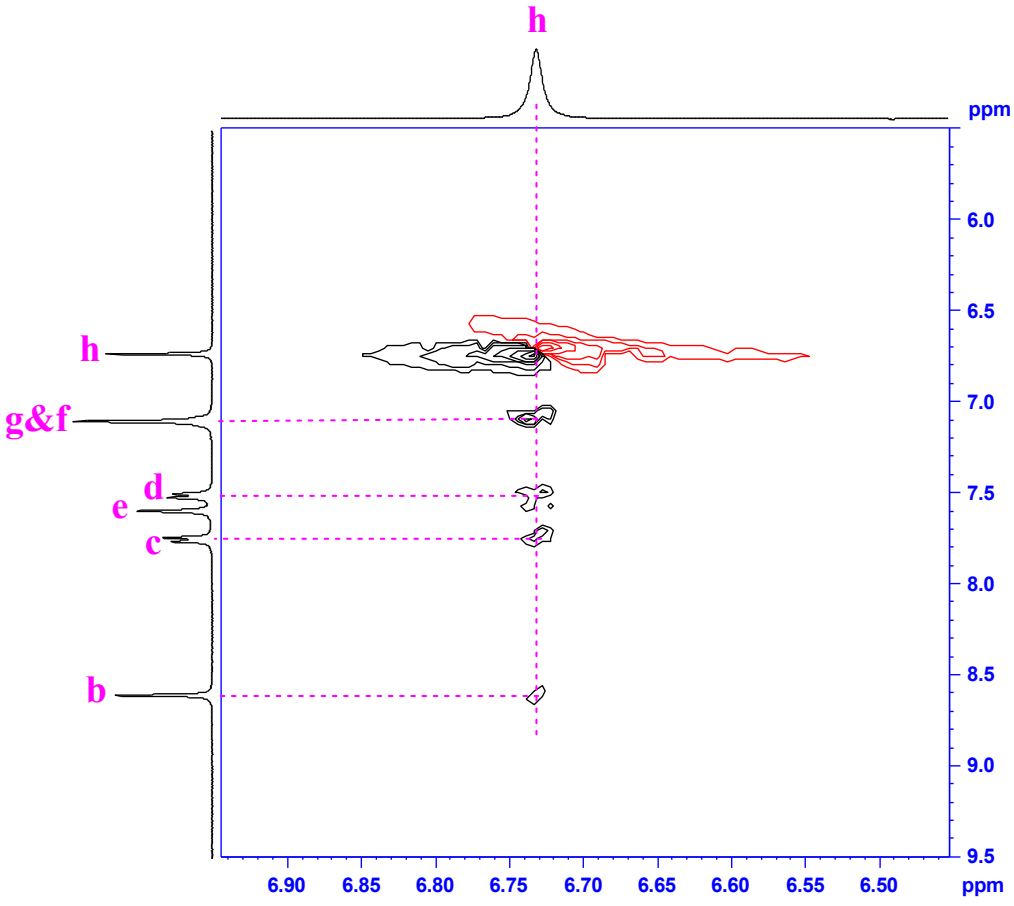


Fig. S16. Partial NOESY spectrum of 4 mM Host **5c** and 12 mM Guest **10**, in DMSO-d_6, 298 K, 400 MHz, showing cross contacts between H^h on guest **10** and H^b, H^c, H^d, H^g, H^f on host **5c**.

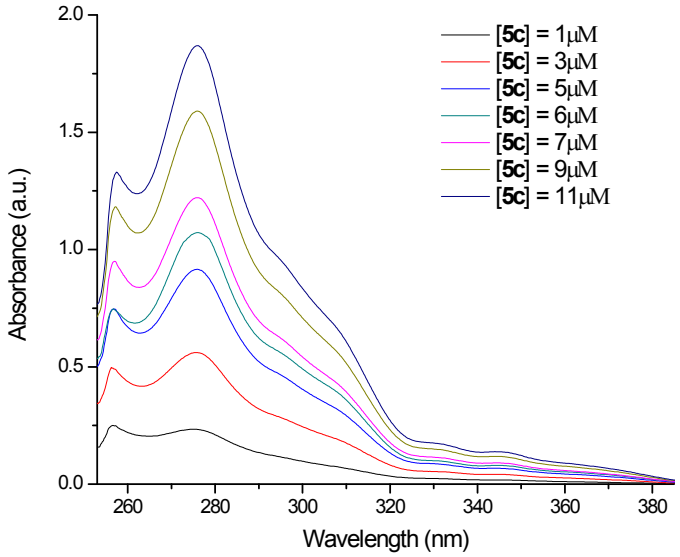


Fig. S17. UV-vis spectra of macrocycle **5c** at different concentrations (1 ~ 11 μM) in DMSO, 298 K.

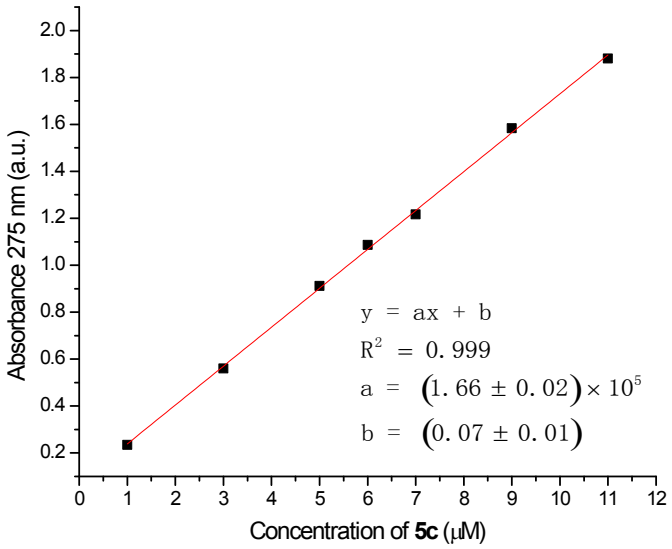


Fig. S18. UV-vis absorption of macrocycle **5c** in DMSO as function of its concentration, λ = 275 nm.

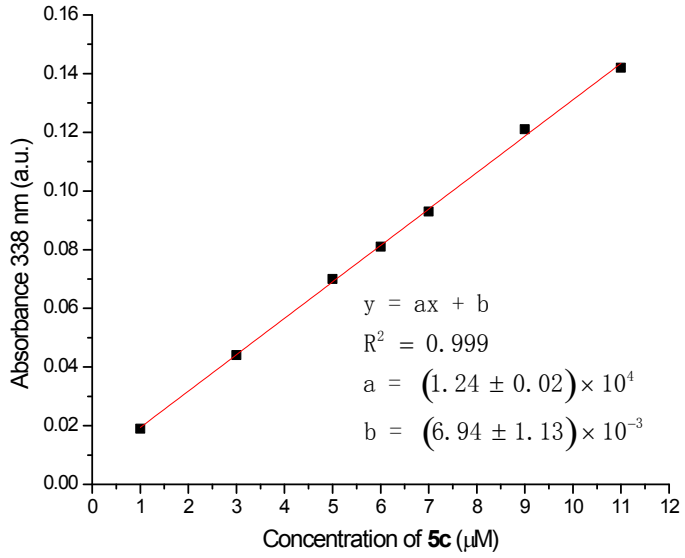


Fig. S19. UV-vis absorption of macrocycle **5c** in DMSO as function of its concentration, λ = 338 nm.

*NOTE: The linear relationship of A_{275nm} and A_{338nm} versus the concentration of **5c** (1 ~ 11 μM) in above Figures indicated that **5c** did not aggregate at 6 μM.*

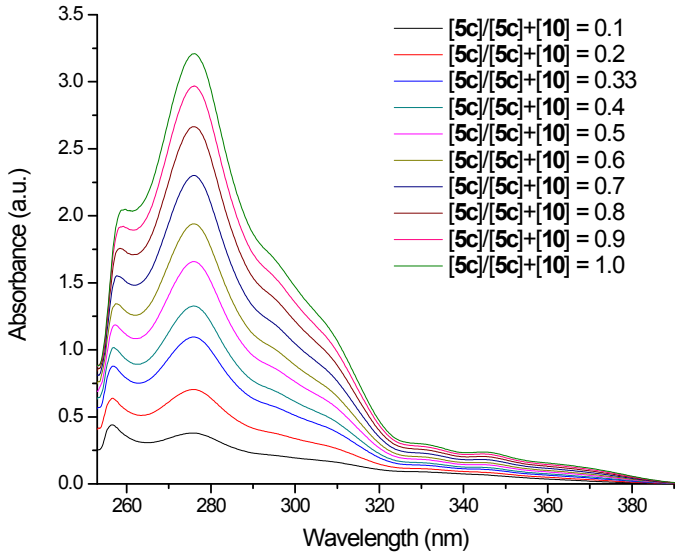


Fig. S20. UV-vis spectra of a mixture of host **5c** and guest **10** with different ratios in DMSO, 298 K, with the total concentration fixed at 1.8×10^{-5} M.

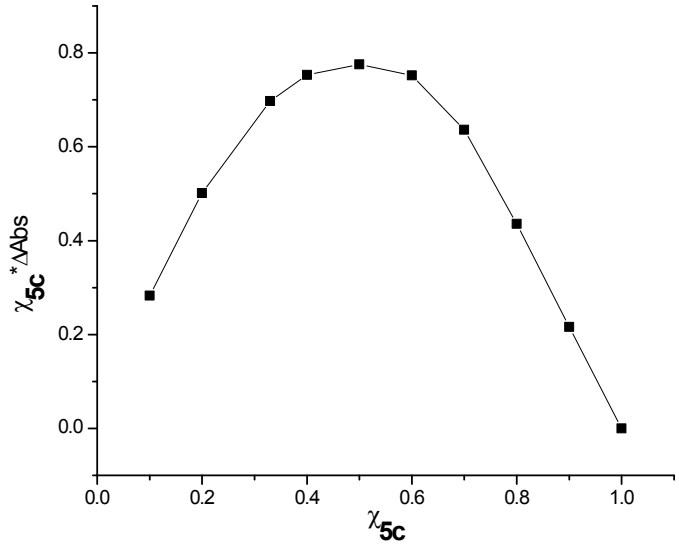


Fig. S21. Job-plot for the complex between host **5c** and guest **10** in DMSO using UV-vis absorption value at λ = 275 nm, showing a 1:1 stoichiometry.

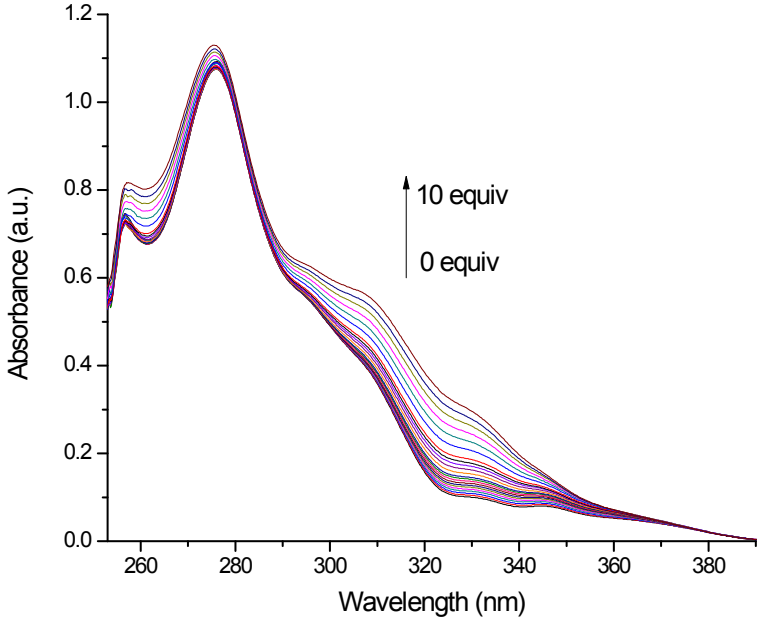


Fig. S22. Titration curves of host **5c** (fixed at 6.0 × 10^{-6} M) with guest **10**, 298 K, DMSO.

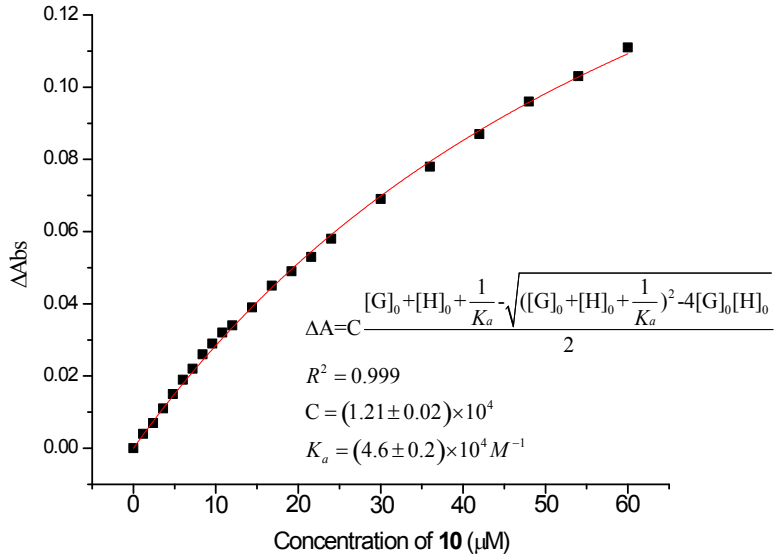


Fig. S23. Plot of the absorption intensity changes at λ = 338 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant K_a = (4.6 ± 0.2) × 10^4 M^{-1}.

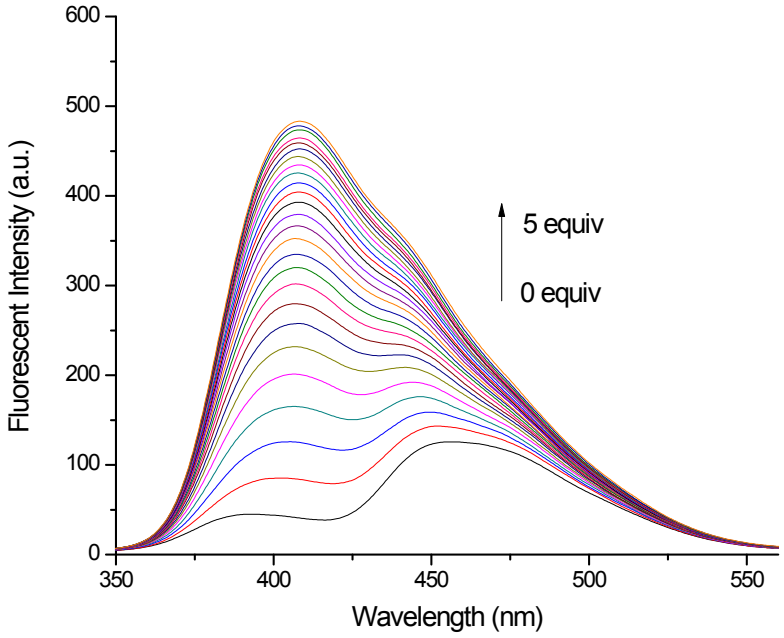


Fig. S24. Fluorescence spectra for a 6.0 × 10^{-6} M solution of host **5c** in DMSO with addition of different equivalents of guest **10**, 298 K, λ_{ex} = 285 nm.

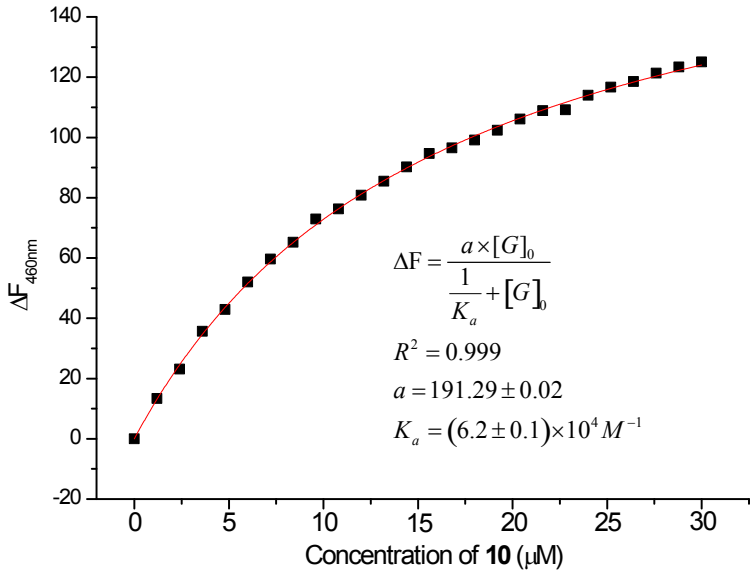


Fig. S25. Plot of fluorescence intensity of $\Delta F_{460\ nm}$ *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S2, yielding an association constant $K_a = (6.2 \pm 0.1) \times 10^4\ M^{-1}$.

9. Complexation Study of Macrocycle **6c** and Guest **10**

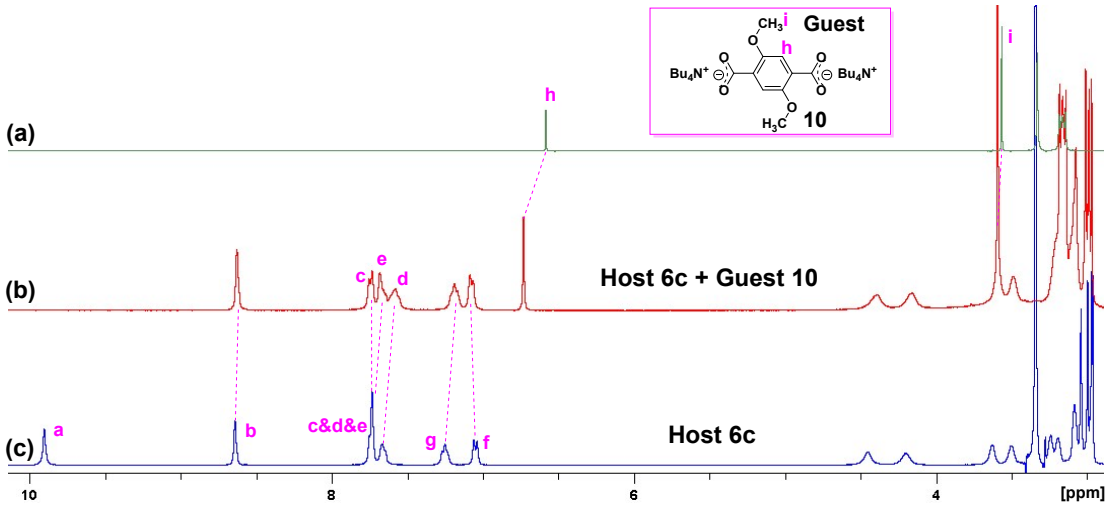


Fig. S26. Stacked partial ^{1}H NMR spectra for 4 mM **10** (a), 4 mM **6c** + 12 mM **10** (b) and 4 mM **6c** (c), DMSO-d_6, 298 K, 400 MHz. H^h: $\Delta\delta$ = 6.73 – 6.58 = 0.15 ppm; H^i: $\Delta\delta$ = 3.59 – 3.56 = 0.03 ppm.

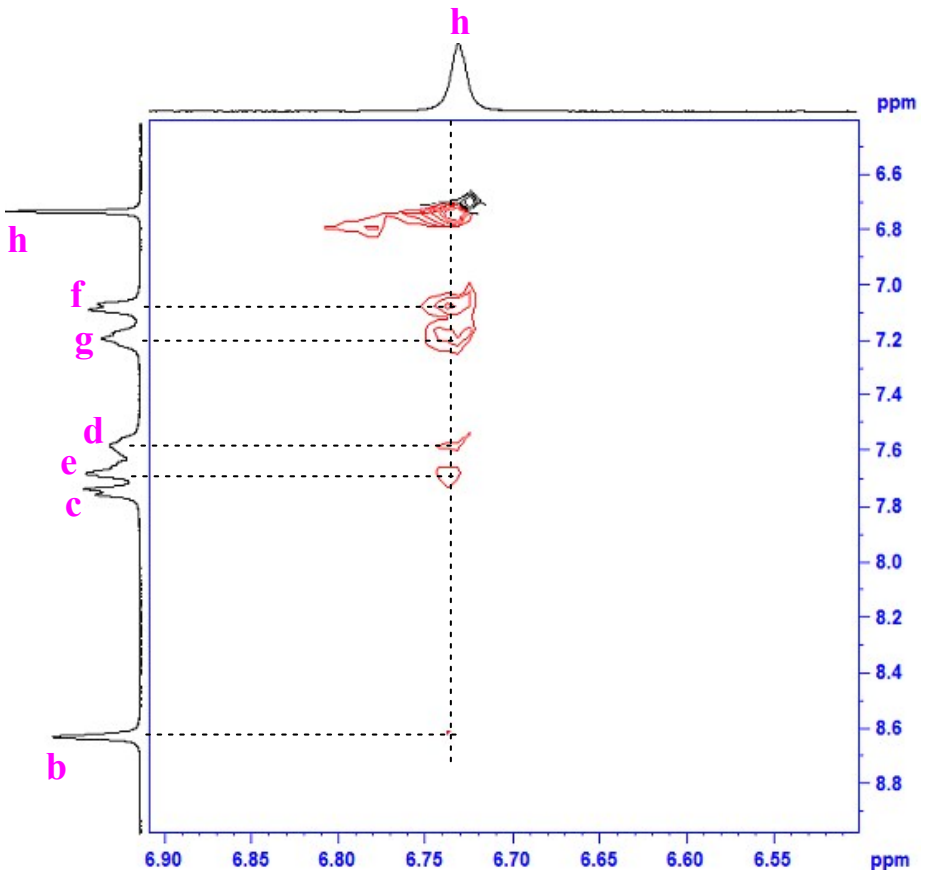


Fig. S27. Partial NOESY spectrum of 4 mM Host **6c** and 12 mM Guest **10**, in DMSO-d_6, 298 K, 400 MHz, showing cross contacts between H^h on guest **10** and H^b, H^d, H^e, H^g, H^f on host **6c**.

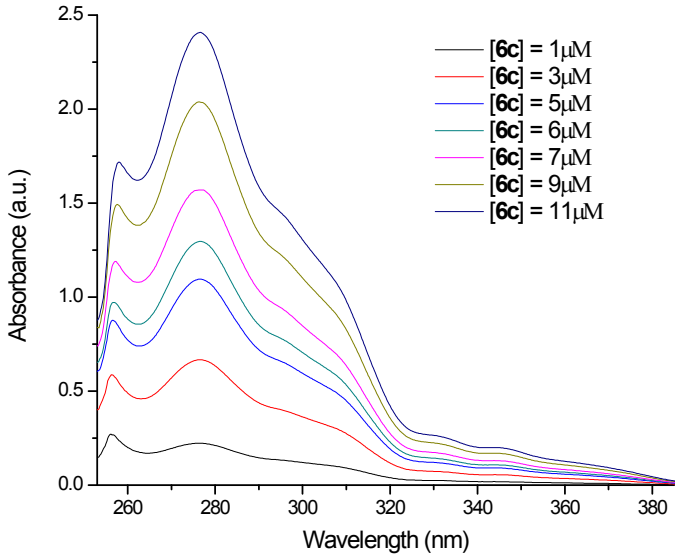


Fig. S28. UV-vis spectra of macrocycle **6c** at different concentrations (1 ~ 11 μM) in DMSO, 298 K.

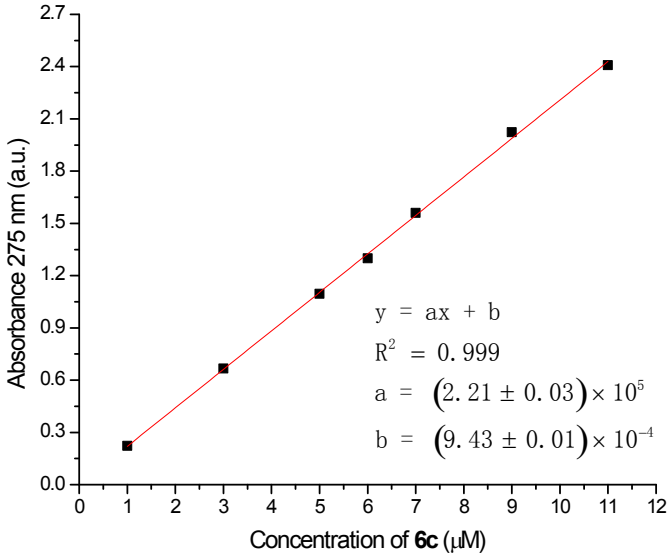


Fig. S29. UV-vis absorption of macrocycle **6c** in DMSO as function of its concentration, λ = 275 nm.

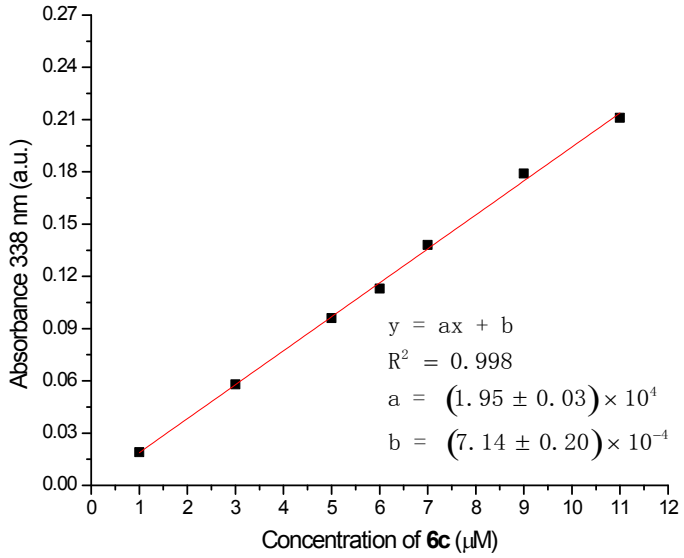


Fig. S30. UV-vis absorption of macrocycle **6c** in DMSO as function of its concentration, λ = 338 nm.

NOTE: The linear relationship of A_{275nm} and A_{338nm} versus the concentration of ***6c*** *(1 ~ 11 μM) in above Figures indicated that* ***6c*** *did not aggregate at 6 μM.*

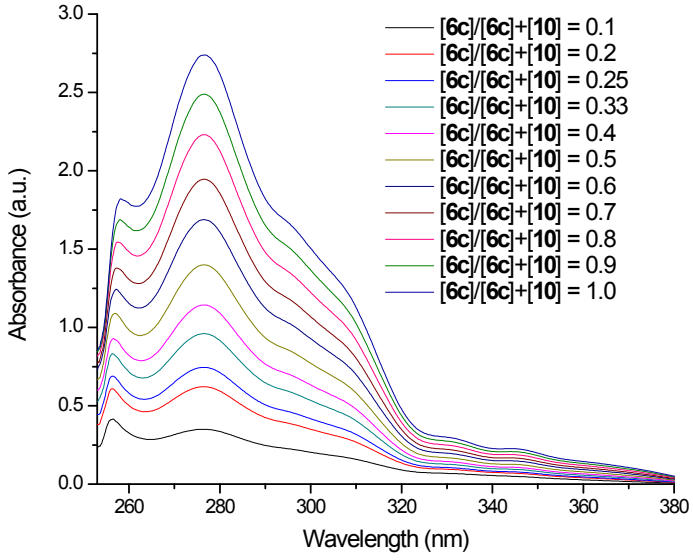


Fig. S31. UV-vis spectra of a mixture of host **6c** and guest **10** with different ratios in DMSO, with the total concentration fixed at 1.2×10^{-5} M, 298 K.

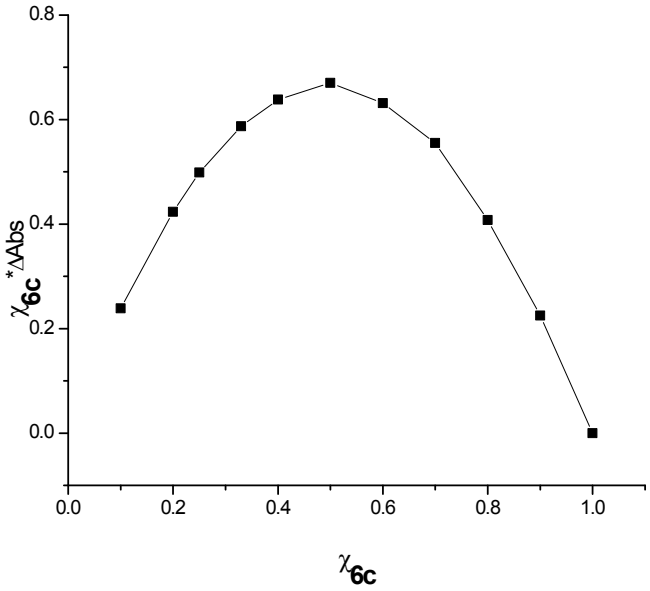


Fig. S32. Job-plot for the complex between host **6c** and guest **10** in DMSO using UV-vis absorption value at λ = 275 nm, showing a 1:1 stoichiometry.

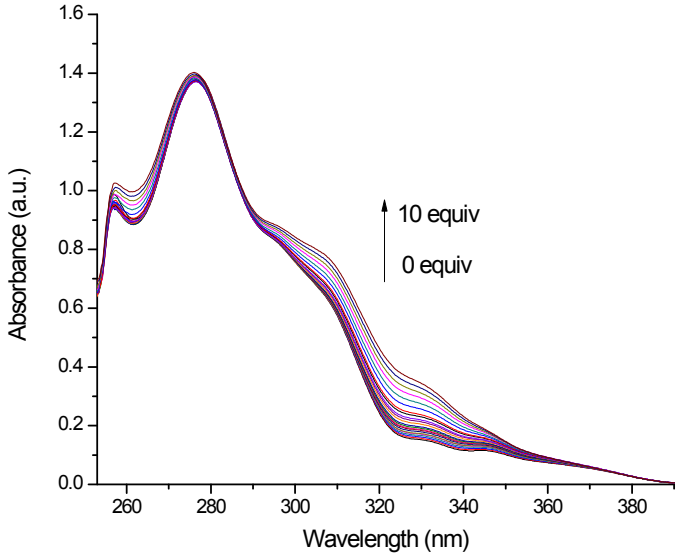


Fig. S33. Titration curves of host **6c** (fixed at 6.0×10^{-6} M) with guest **10**, 298 K, DMSO.

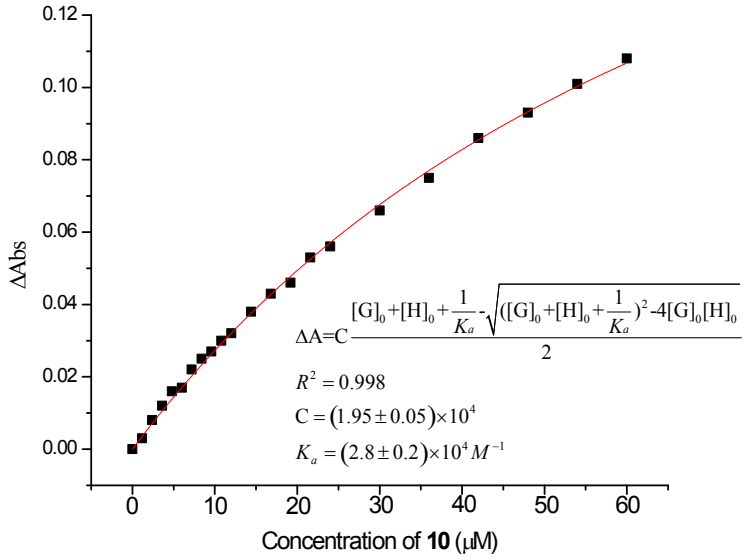


Fig. S34. Plot of the absorption intensity changes at λ = 338 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant K_a = (2.8 ± 0.2) × 10^4 M^{-1}.

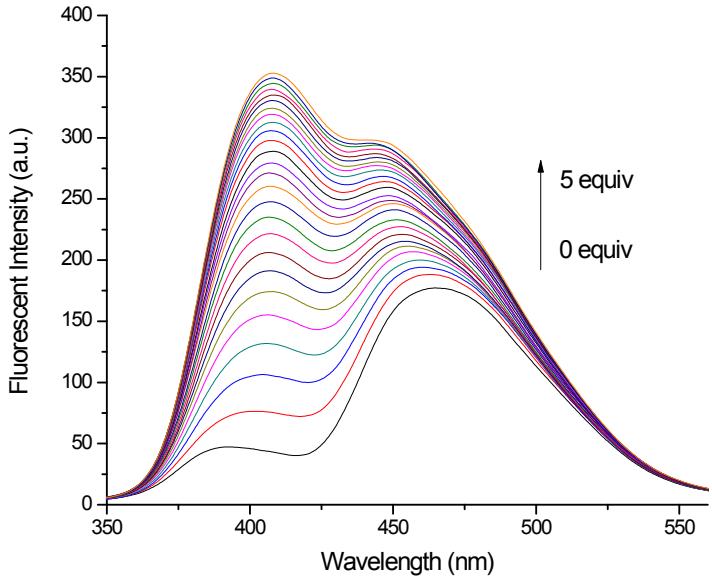


Fig. S35. Fluorescence spectra for a 6.0 × 10^{-6} M solution of host **6c** in DMSO with addition of different equivalents of guest **10**, 298 K, λ_{ex} = 285 nm.

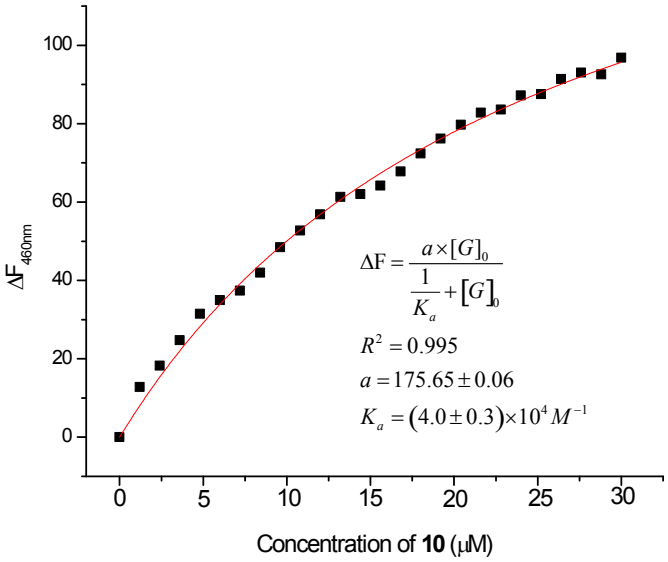


Fig. S36. Plot of fluorescence intensity of $\Delta F_{460\ nm}$ *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S2, yielding an association constant $K_a = (4.0 \pm 0.3) \times 10^4\ M^{-1}$.

References:

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S2: Meng, H.; Chen, Z. K.; Liu, X. L.; Lai, Y. H.; Chua, S. J.; Huang, W. *Phys. Chem. Chem. Phys.*, **1999**, *1*, 3123-3127.

S3: Zhang, Y. W.; Shen, X. C.; Feng, X.; Xia, H.; Mu, Y.; Liu, X. M. *Chem. Commun.*, **2016**, *52*, 11088-11091.

S4: (a) Hirose, K. in *Analytical Methods in Supramolecular Chemistry*, ed. Schalley, C. Wiley-VCH, **2012**, Vol. 1, pp. 27-66. (b) Connors, K. A. *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley: New York, **1987**.