Supplementary Information for

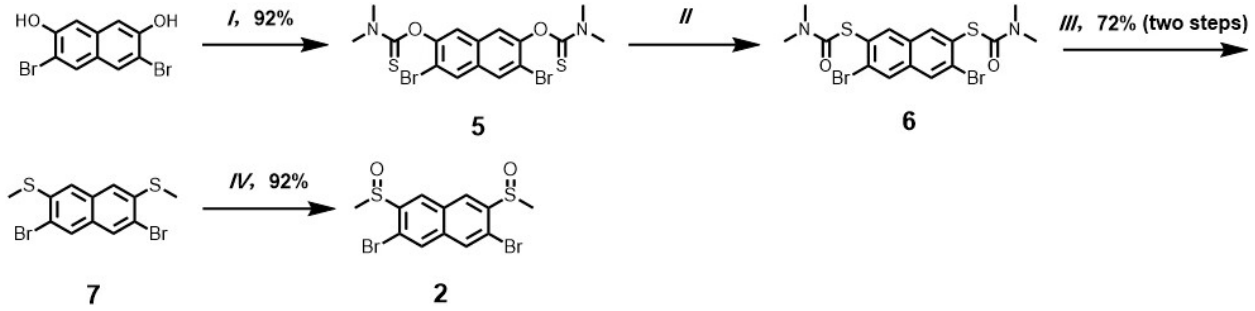
A π-Extended Molecular Belt with Selective Binding Capability for Fullerene C_{70}

Section A. Materials and General Methods

2-Butyl-3-methoxyphenol[S1] and 1,5-dibromo-2,4-bis(methylsulfinyl) benzene (compound **B**) [S2,S3] were synthesized according to literatures. All other reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Reaction progress was monitored by thin layer chromatography (TLC) or on an Advion Plate Express® Automated TLC plate reader (TLC/CMS). Flash column chromatography was performed over silica gel (200-300 mesh). NMR spectra were recorded on a JEOL 400YH instrument. NMR spectra were internally referenced to tetramethylsilane (^{1}H) or alternatively, to the residual proton solvent signal (^{13}C). All ^{13}C NMR spectra were recorded with complete proton decoupling. UV-vis absorbance spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Fluorescent spectroscopy were recorded on a Shimadzu RF-6000 spectro fluorophotometer. ESI-MS data were recorded either on an Advion Expression^{L} CMS instrument or a Thermo Fisher Scientific LTQ Orbitrap Elite LC/MS (ESI). MALDI-TOF MS experiments were carried out on a Bruker ultraflex matrix assisted laser desorption-ionization TOF mass spectrometer with DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as supporting matrix.

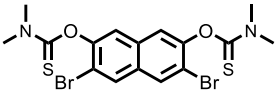
Section B. Synthesis and Characterization of compounds

Scheme S1. Synthesis of 2,7-dibromo-3,6-bis(methylsulfinyl)naphthalene (2)



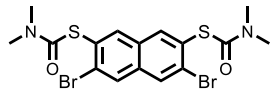
Conditions: *i*) Dimethylaminothioformyl chloride, DABCO, DMF, RT, 20 h; *ii*) *N*,*N*-dimethylaniline, 220 °C, 2 h; *iii*) (a) NaOH, CH_3OH, 70 °C, 20 h; (b) CH_3I, RT, 20 h; *iv*) H_2O_2, CH_3COOH, RT, 20 h.

O,O'-(3,6-dibromonaphthalene-2,7-diyl) bis(dimethylcarbamothioate) (5)



A solution of 3,6-dibromonaphthalene-2,7-diol (13.041 g, 41 mmol) in DMF (130 ml) was prepared, followed by the addition of DABCO (13.821 g, 123 mmol) at 0 °C under a nitrogen atmosphere. The reaction mixture was then allowed to reach room temperature and was stirred for 30 minutes. Subsequently, a DMF solution (60 mL) of dimethylaminothioformyl chloride (15.207 g, 123 mmol) was added dropwise, and the reaction was carried out at room temperature for 20 hours. Upon completion of the reaction, DMF was removed using a rotary evaporator, hydrochloric acid was added, and extraction was performed using DCM. The organic phase was dried with Na_2SO_4 and concentrated by rotary evaporation. Compound **5** (19.757 g, 92% yield) was obtained through recrystallization from ethanol followed by filtration. HRMS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{16}Br_2N_2O_2S_2^+$, 490.9093, found: 490.9095.

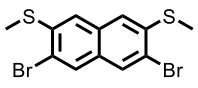
S,S'-(3,6-dibromonaphthalene-2,7-diyl) bis(dimethylcarbamothioate) (6)



Compound **5** (8.868g, 17.0mmol) was dissolved in tetra-ethylene glycol dimethyl ether (60 mL) and subjected to reflux at 240 °C for 2 hours under a nitrogen atmosphere. After completion of the reaction by TLC monitoring, the reaction mixture was quenched by addition to ice water and filtered to isolate **6** which was directly used in the subsequent step without further purification. HRMS (m/z): $[M+H]^+$ calcd. for

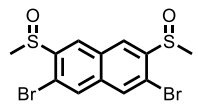
$C_{16}H_{16}Br_2N_2O_2S_2^+$, 490.9093, found: 490.9097.

(3,6-dibromonaphthalene-2,7-diyl)bis(methylsulfane) (7)



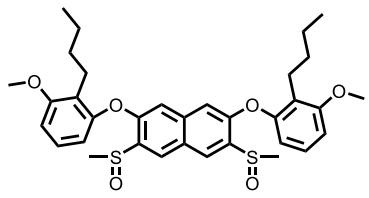
Compound **6** (8.868 g, 17.0 mmol), along with KOH (9.520 g, 170.0 mmol), and CH_3OH (100.0 ml), were combined in a three-neck flask under a nitrogen atmosphere. The mixture was then refluxed at 70°C overnight. Monitoring by TLC indicated the disappearance of the starting material. After cooling to room temperature, CH_3I (9.656g, 68 mmol) was slowly introduced into the flask. The CH_3OH was removed under vacuum, and the resulting residue was dissolved in CH_2Cl_2. The organic phase was dried over Na_2SO_4, and the solvent was evaporated under vacuum. The crude product was subsequently purified by column chromatography on silica gel, using a eluent mixture of petroleum ether/dichloromethane (20/1), yielding the product **7** (4.623g, 72% yield over 2 steps). HRMS (m/z): $[M+H]^+$ calcd. for $C_{12}H_{10}Br_2S_2^+$, 374.8507, found: 374.8505.

2,7-dibromo-3,6-bis(methylsulfinyl)naphthalene (2)



A solution of **7** (3.781 g, 10.0 mmol, 1.0 equiv) in 100 mL of glacial acetic acid was prepared in a 250 mL round-bottom flask. Hydrogen peroxide (35%, 2.429 g, 25 mmol, 2.5 equiv) was then added drop-wise at room temperature, and the resulting mixture was stirred for 20 hours at ambient conditions. Afterward, the glacial acetic acid was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2, followed by several washes with water. The organic phase was subsequently treated with aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and then the solvent was evaporated under vacuum. The crude product obtained was subjected to purification by column chromatography on silica gel, using a eluent mixture of CH_2Cl_2/CH_3OH (40/1), resulting in the isolation of product **5** (3.691 g, 90% yield) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (s, 2H), 8.04 (s, 2H), 2.90 (s, 2H) and (s, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.2, 137.0, 131.1, 127.1, 117.6, 117.6, 42.5, 42.5. HRMS (m/z): $[M+Na]^+$ calcd. for $C_{12}H_{10}Br_2O_2S_2Na^+$, 430.8381, found: 430.8387.

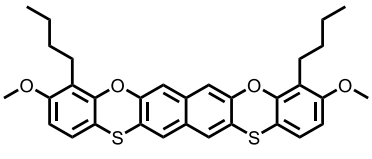
2,7-bis(2-butyl-3-methoxyphenoxy)-3,6-bis(methylsulfinyl)naphthalene (3)



In a 250 mL dry Schlenk flask, 2-butyl-3-methoxyphenol (3.960 g, 11 mmol, 2 equiv), **2** (1.356 g, 5mmol, 1.0 equiv), Cs_2CO_3 (4.888 g, 15 mmol, 3.0 equiv), and anhydrous DMAC (60 mL) were

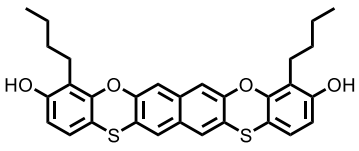
combined. The reaction mixture was then stirred at 120 °C for 26 hours under a nitrogen atmosphere. Upon cooling to room temperature, the reaction was quenched by adding an aqueous solution of HCl (1 M) and extracted with three portions of CH_2Cl_2. The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude product underwent purification by column chromatography on silica gel, utilizing a eluent mixture of CH_2Cl_2/CH_3OH (40/1), resulting in the isolation of product **3** (2.800 g, 92% yield) as a reddish brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 2H), 7.17 (t, J = 8.2 Hz, 2H), 6.76 (d, J = 9.0 Hz, 2H), 6.66 (s, 2H), 6.60 (d, J = 8.2 Hz, 2H), 3.86 (s, 6H), 2.95 (s, 4H), 2.94 (s, 2H), 2.58–2.45 (m, 4H), 1.50–1.35 (m, 4H), 1.30–1.20 (m, 4H), 0.82 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.3, 153.5, 152.8, 137.7, 134.6, 127.4, 126.6, 125.4, 124.4, 113.2, 109.6, 107.8, 55.9, 42.0, 31.9, 23.7, 22.9, 14.0. HRMS (m/z): $[M+H]^+$ calcd. for $C_{34}H_{41}O_6S_2^+$, 609.2339, found: 609.2337.

4,9-dibutyl-3,10-dimethoxyphenoxathiino[2,3-b]phenoxathiine (4)



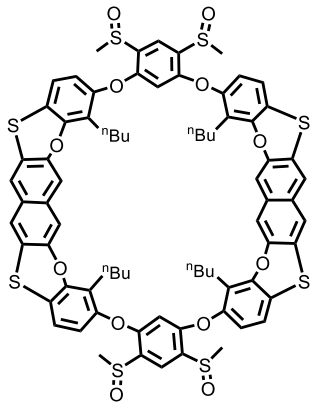
In a dry 500 mL round-bottom flask under an N_2 atmosphere, **3** (3.211 g, 5.27 mmol, 1.0 equiv) and anhydrous dichloromethane (100 mL) were combined. Trifluoromethanesulfonic anhydride (14.868 g, 52.7 mmol, 10.0 equiv) was then added in one portion. The reaction mixture was stirred for 10 hours at room temperature before being cooled to 0°C in an ice bath. Subsequently, 110 mL of pyridine was added drop-wise to the cold solution with stirring. The reaction mixture was then warmed to room temperature and stirred for another 10 hours. After removal of the solvent under reduced pressure, the crude product underwent purification by column chromatography on silica gel using a eluent mixture of petroleum ether/dichloromethane (20/1), resulting in the isolation of product **4** (2.440 g, 85% yield) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (s, 2H), 7.33 (s, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.6 Hz, 2H), 3.81 (s, 6H), 2.85-2.78 (m, 4H), 1.61-1.54 (m, 8H), 1.48-1.41 (m, 4H), 0.99 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.8, 151.1, 150.9, 132.8, 128.7, 123.9, 123.7, 122.1, 121.7, 112.9, 111.2, 106.8, 55.97, 31.9, 23.2, 22.9, 14.2. HRMS (m/z): $[M]^+$ calcd. for $C_{32}H_{32}O_4S_2^+$, 544.1736, found:544.1735.

4,9-dibutylphenoxathiino[2,3-b]phenoxathiine-3,10-diol (A)



In a dry 500 mL round-bottom flask under an N_2 atmosphere, compound **4** (2.723 g, 5.0 mmol, 1.0 equiv) and 200 mL anhydrous CH_2Cl_2 were introduced. A CH_2Cl_2 solution (1.0 M) of BBr_3 solution (50 mL, 10.0 equiv) was then added dropwise at -15 ^oC over a period of 10 minutes and stirred for an additional 30 minutes. Subsequently, the reaction mixture was slowly warmed to room temperature and stirred for a further 20 hours. The reaction was halted by the addition of ice water and then extracted with three portions of CH_2Cl_2. After combining the organic layers, they were dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude product underwent purification by column chromatography on silica gel using a eluent mixture of petroleum ether/dichloromethane (1/1), resulting in the isolation of product A (2.144 g, 83% yield) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (s, 2H), 7.32 (s, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.53 (d, J = 8.4 Hz, 2H), 4.70 (s, 2H), 2.84-2.80 (m, 4H), 1.65-1.60 (m, 4H), 1.50-1.45 (m, 4H), 0.99 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.7, 151.2, 151.0, 132.8, 128.8, 124.2, 123.7, 122.0, 119.6, 112.9, 111.5, 111.1, 31.7, 23.3, 22.9, 14.2. HRMS (m/z): $[M+H]^+$ calcd. for $C_{30}H_{29}O_4S_2^+$,517.1502 found: 517.1502.

Synthesis of Compound 1



In a 100 mL dry Schlenk flask, **A** (258 mg, 0.5 mmol, 1.0 equiv), **B** (180 mg, 0.5 mmol, 1.0 equiv), Cs_2CO_3 (328 mg, 1.0 mmol, 2.0 equiv), and degassed anhydrous dimethylacetamide (40 mL) were combined. The reaction mixture was stirred at 150 °C for 48 hours under an N_2 atmosphere. Upon cooling to room temperature, the solvent was evaporated under reduced pressure, and the resulting residue underwent purification by column chromatography on silica gel using (CH_2Cl_2/CH_3OH = 30/1) as eluent, affording product **1** (78.3 mg, 22% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50–8.43 (m, 2H), 7.23–7.15 (m, 4H), 7.09–7.02 (m, 4H), 6.90–6.80 (m, 4H), 6.58–6.43 (m, 4H), 5.46–5.18 (m, 2H), 2.94–2.87 (m, 12H), 1.51–1.18 (m, 24H), 0.95–0.87 (m, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.60–157.3 (m), 151.5–150.0 (m), 132.7, 128.8–127.5 (m), 125.8–125.6 (m), 124.9–124.5 (m), 123.9–123.6 (m), 120.8–120.7 (m), 119.0–118.3 (m), 117.4–116.8 (m), 112.8, 100.8–100.4 (m), 41.8–41.6(m),

32.2–31.5 (m), 30.4–29.4 (m), 24.2–23.9(m), 23.0–22.6 (m), 14.0–14.1 (m). HRMS (m/z): $[M]^+$ calcd. for $C_{76}H_{68}O_{12}S_8^+$, 1428.2471, found: 1428.2474.

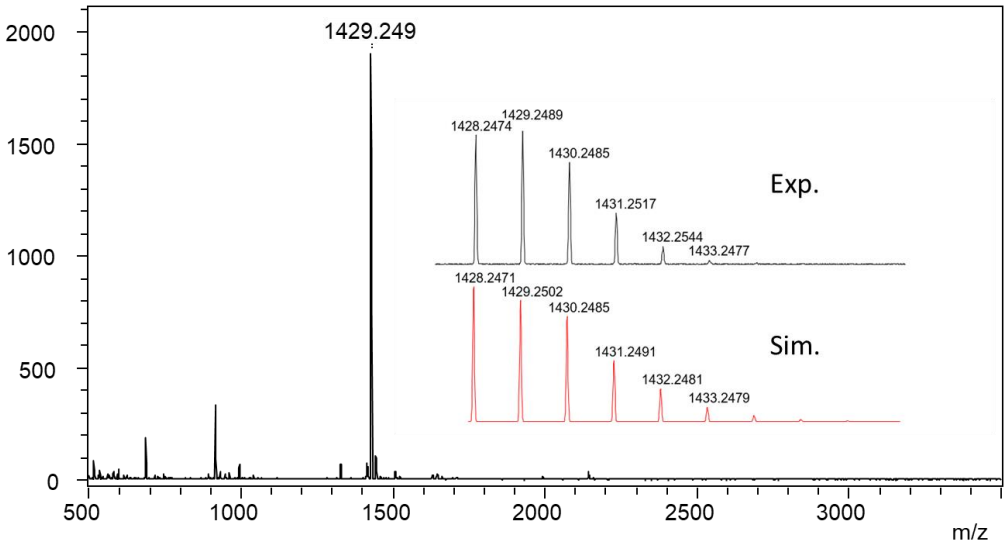
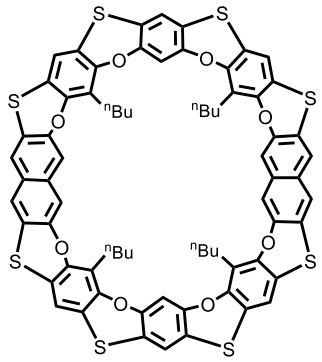


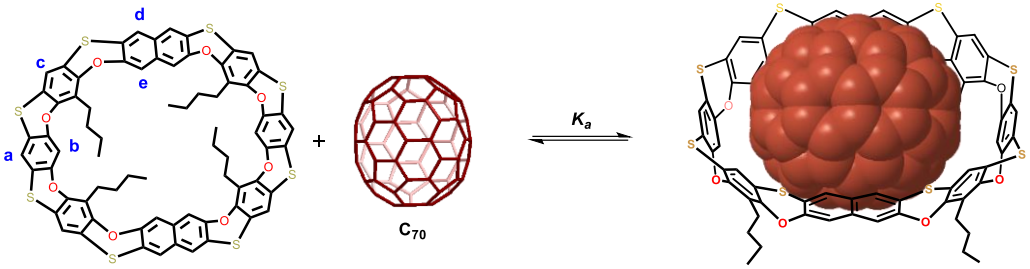
Figure S1. MALDI-TOF Mass spectra of compound **1**.

Synthesis of [8]NCP



In a 50 mL dry round-bottom flask under an N_2 atmosphere, compound **1** (71.4 mg, 0.05 mmol, 1.0 equiv) was combined with 10 mL of trifluoromethanesulfonic acid. The reaction mixture was stirred at 80 °C for 48 hours. Upon cooling to room temperature, the mixture was gradually added to 30 mL of pyridine/ice water (V/V=1/1). The resulting mixture was stirred at 105 °C for an additional 15 hours. After returning to room temperature, excess pyridine was evaporated under reduced pressure, and the residue was filtered to obtain a crude product which was further purified by column chromatography on silica gel using (dichloromethane/cyclohexane = 1/5) as eluent, yielding the product **[8]NCP** (5.2 mg, 8% yield) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 4H), 7.36 (s, 4H), 6.98 (s, 2H), 6.92 (s, 4H), 6.83 (s, 2H), 2.99-2.91 (m, 8H), 1.50-1.39 (m, 16H), 0.95 (t, J = 7.2 Hz, 12H). HRMS (m/z): $[M]^+$ calcd. for $C_{72}H_{52}O_8S_8^+$, 1300.1422, found: 1300.1505.

Section C. Host-guest chemistry of [8]NCP with C_{70}



Fluorescence titration experiments for binding C_{70} with **[8]NCP** were carried out in tetrachloroethane at 298K. A stock solution of **[8]NCP** (0.08 mM, 5 mL) was prepared (Solution **A**). Then prepare another stock solution of C_{70} (0.40 mM) using **A** as solvent (solution **B**). The Titration was performed by continuously adding solution **B** to 2 mL (1.0 cm path cuvette) of solution **A**, resulting in a perturbation of fluorescence intensity. After each addition, stir the resulting solution for at least 2 min to reach equilibrium. That is, keeping the **[8]NCP** (0.08 mM) concentration unchanged, record the emission spectrum of the solution when adding 0, 0.20, 0.40, 0.60, 0.80, 1.00, 1.10, 1.20, 1.30, 1.50, 1.80, 2.00 equivalents of C_{70}, respectively. Finally, according to the change in emission intensity at 402 nm, an association constant K_a of 1.3×10^6 M^{-1} was obtained by a curve fitting of the extracted data with a 1:1 binding model using Bindfit[S4-S5].

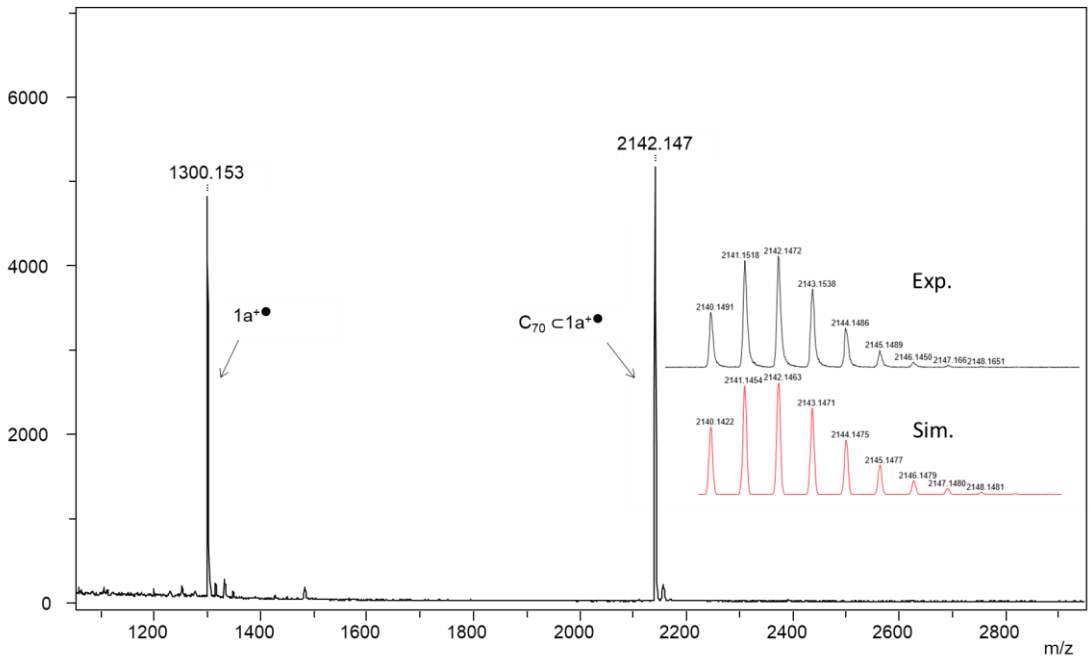


Figure S2. MALDI-TOF-Mass spectrum of a mixed sample of **[8]NCP** and **C_{70}** with a mole ratio of 1:1 in tetrachloroethane. The isotope distribution of the observed peaks for the 1:1 complex was amplified.

Section D. Host-guest Chemistry of [8]NCP with C_{60}

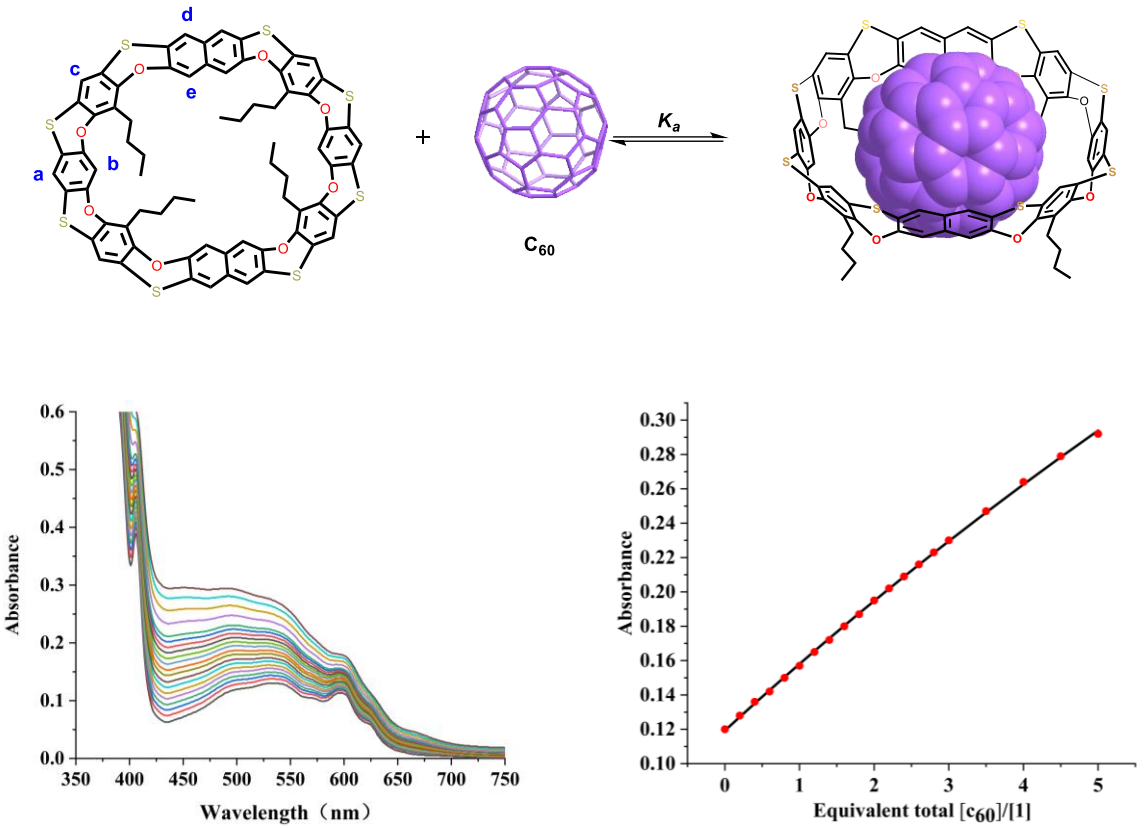


Figure S3. Titration experiments for host 1 and C_{60} were carried out in tetrachloroethane at 298K. A stock solution of guest C_{60} (0.15 mM, 5 mL) was prepared (Solution A). Then prepare another stock solution of the host 1 (1.60 mM) and C_{60} (0.08 mM) (solution B). The Titration was performed by continuously adding solution B to 2 mL (1.0 cm path cuvette) of solution A, resulting in a perturbation of the guest absorption spectrum. After each addition, stir the resulting solution for at least 2 min to reach equilibrium. That is, keeping the C_{60} (0.08 mM) concentration unchanged, test the absorption spectrum of the solution when adding 0, 0.20, 0.40, 0.60, 0.80, 1.00, 1.20, 1.40, 1.60, 1.80, 2.00, 2.20, 2.40, 2.60, 2.80, 3.00, 3.50, 4.00, 4.50, 5.00 equivalents of 1, respectively. Finally, according to the change in ΔAbs at 500 nm, association constants K = 176 M^{-1} was obtained by a curve fitting with a 1:1 binding model using Bindfit[S4-S5].

Section E. Details of X-ray Crystallography

Suitable crystals were frozen in paratone oil inside a cryoloop under a cold stream of N_2. Reflection data were collected either on a Rigaku SuperNova, Dual, AtlasS2 diffractometer using monochromatized Cu Kα radiation or on a BRUKER D8 VENTURE PHOTON II diffractometer using MoKα radiation. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved using OLEX^2 crystallography software.[S5,S6] When practical, non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in idealized positions and refined using a riding model. Figures were drawn with Diamond software. Details can be obtained from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk for CCDC accession numbers 2346199 and 2346200.

Table S1. Crystal Data, Solution and Refinement Parameters.

	[8]NCP·$(C_6H_5NO_2)_2$	C_{70}@**[8]NCP**
CCDC number	2346199	2346200
formula	$C_{84}H_{62}N_2O_{12}S_8$	$C_{142}H_{52}O_8S_8$
formula weight	1547.83	2142.31
crystal system	Monoclinic	Monoclinic
space group	Cc	$P2_1/n$
T (K)	150(2)	193(2)
a (Å)	27.458(6)	17.1449(6)
b (Å)	23.377(12)	33.6954(12)
c (Å)	11.615(3)	21.4769(7)
α (º)	90.00	90.00
β (º)	90.454(9)	92.559(2)
γ (º)	90.00	90.00
V (Å^3)	7455(3)	12394.9(7)
Z	4	4
ρ/g cm^{-3}	1.379	1.148
μ/mm^{-1}	0.305	1.775

reflections used	15085	21795
variables	856	2063
restraints	523	13251
R_1 [$I > 2\sigma(I)$][a]	0.0714	0.0932
R_1 (all data)	0.0884	0.1545
R_2w[$I > 2\sigma(I)$][b]	0.1736	0.2816
R_2w (all data)	0.1914	0.3397
GoF on F^2	1.037	1.034

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; [b] $R_{2w} = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2)+(aP)^2 + bP]^{-1}$

Section F. NMR spectra of compounds.

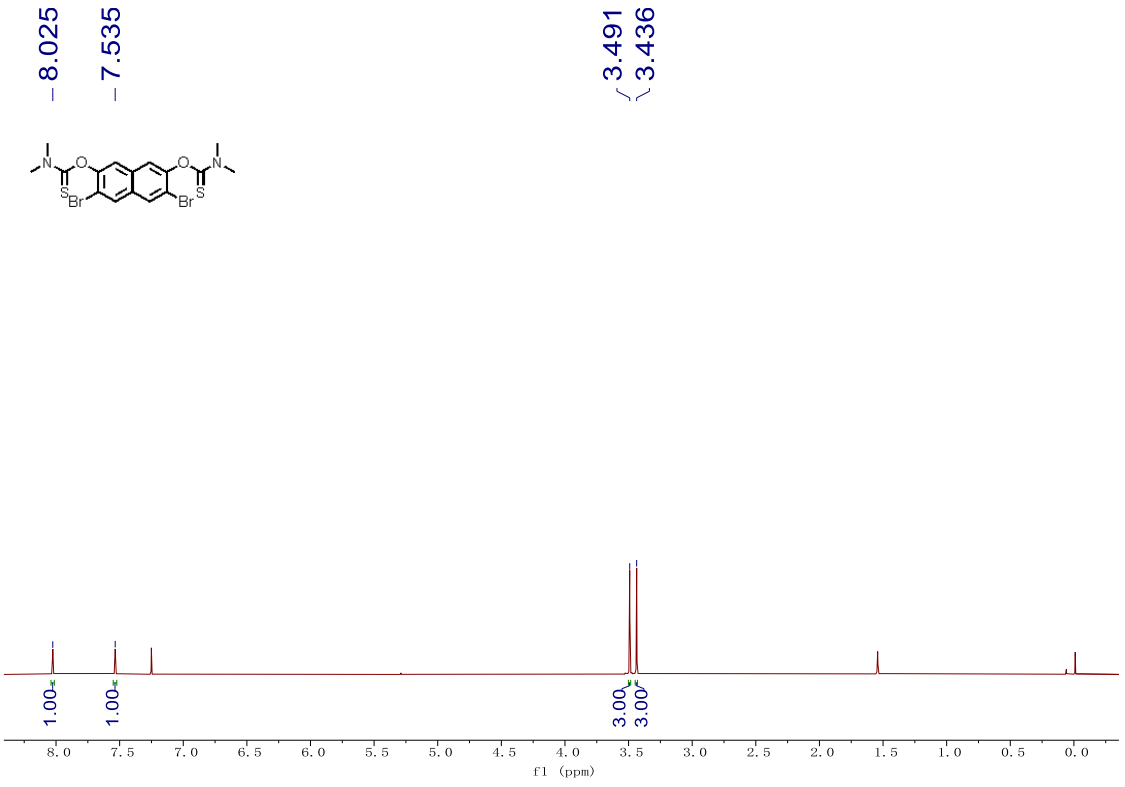


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **5**.

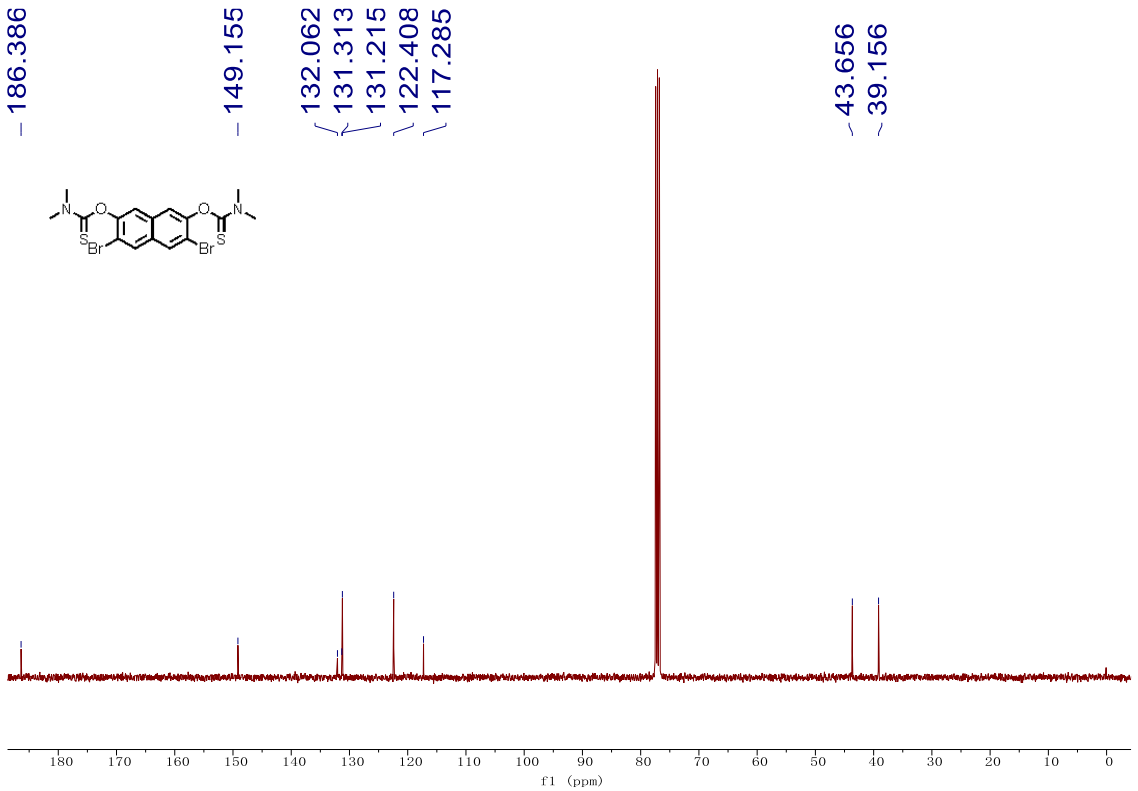


Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **5**.

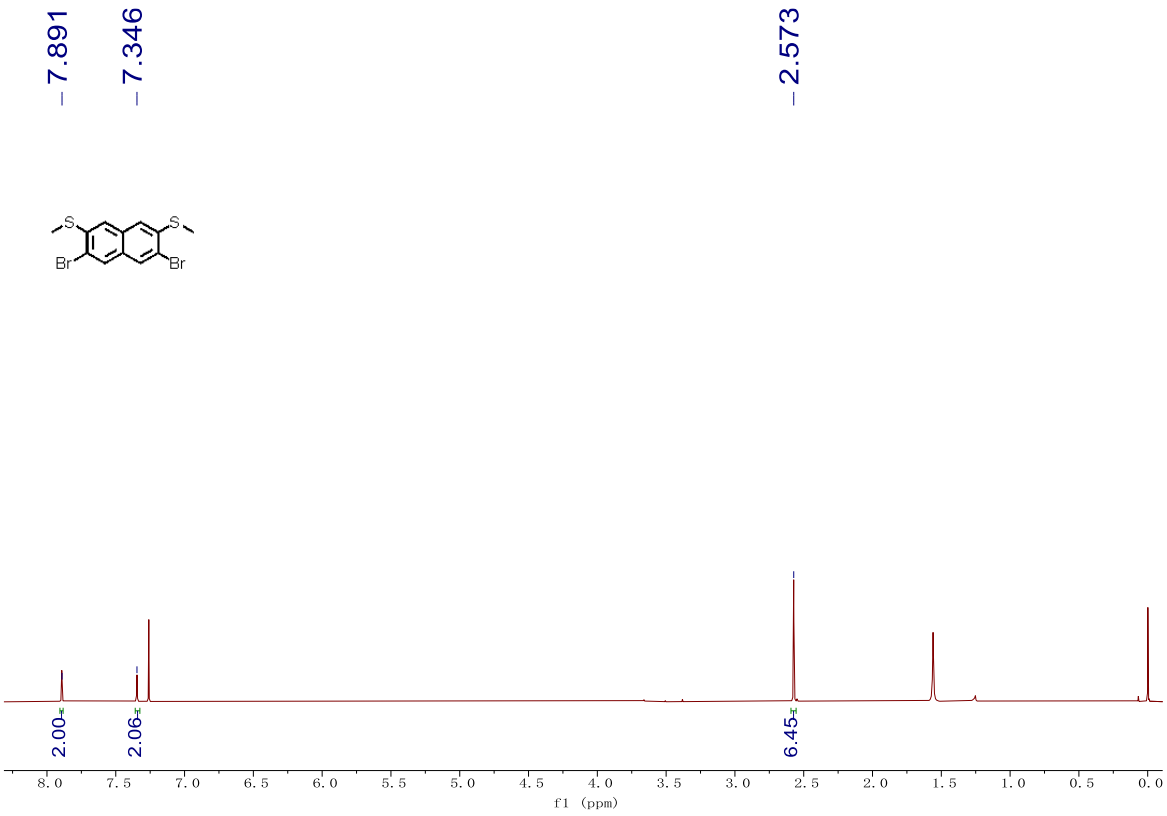


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **7**.

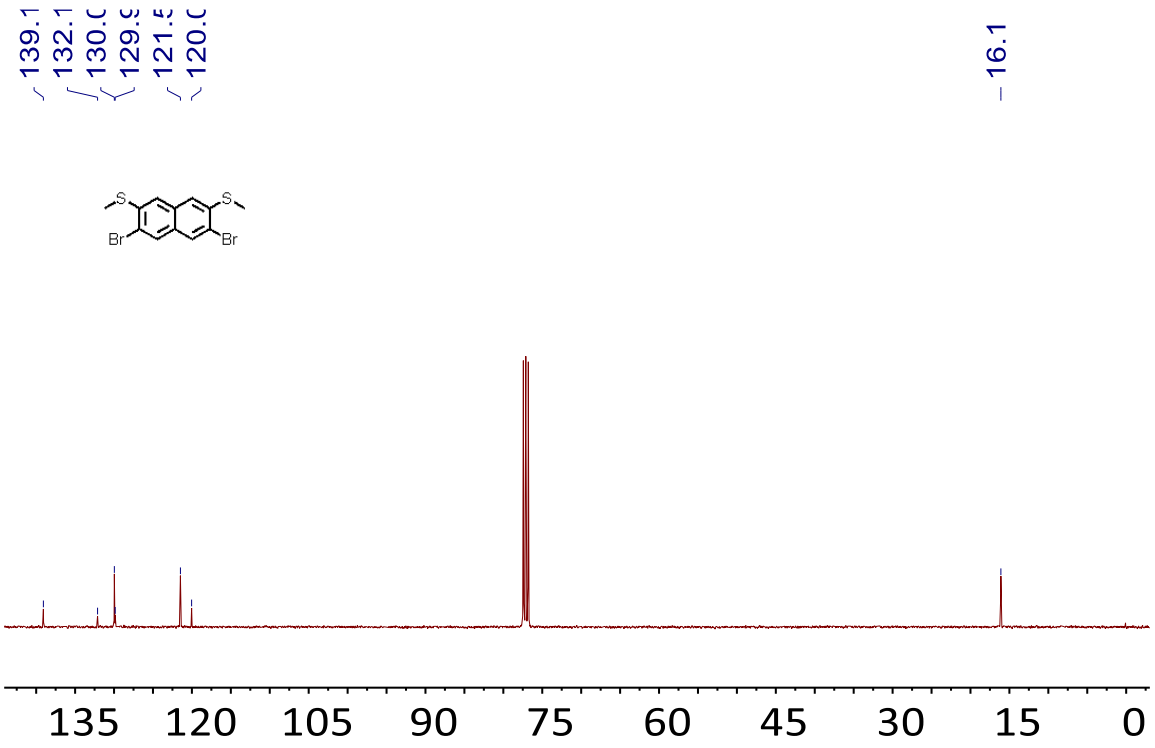


Figure S7. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **7**.

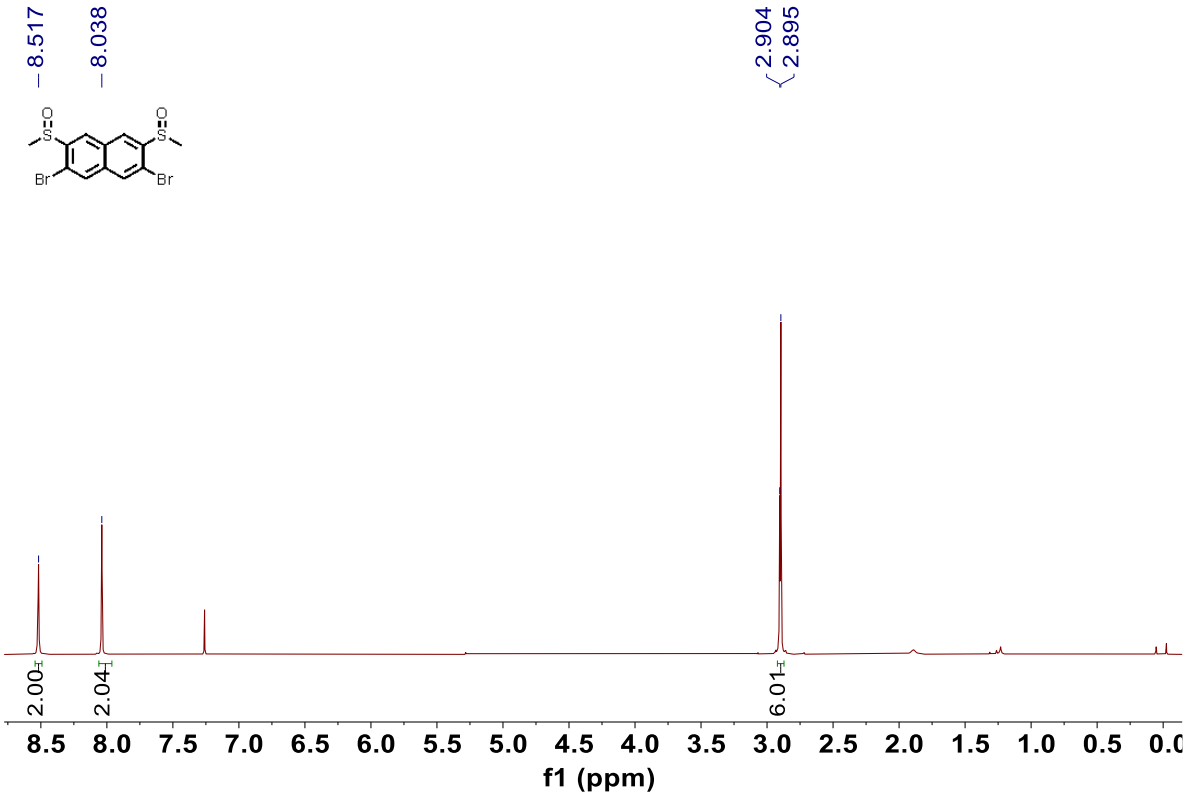


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **2**.

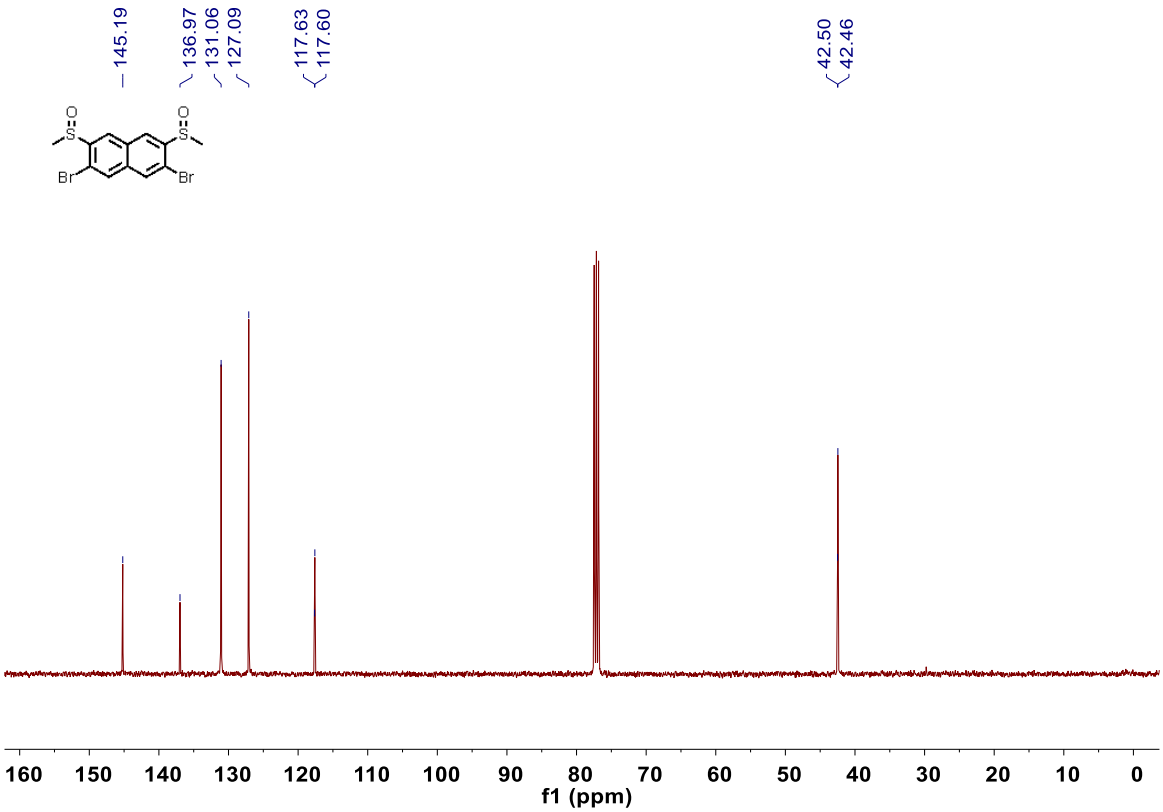


Figure S9. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **2**.

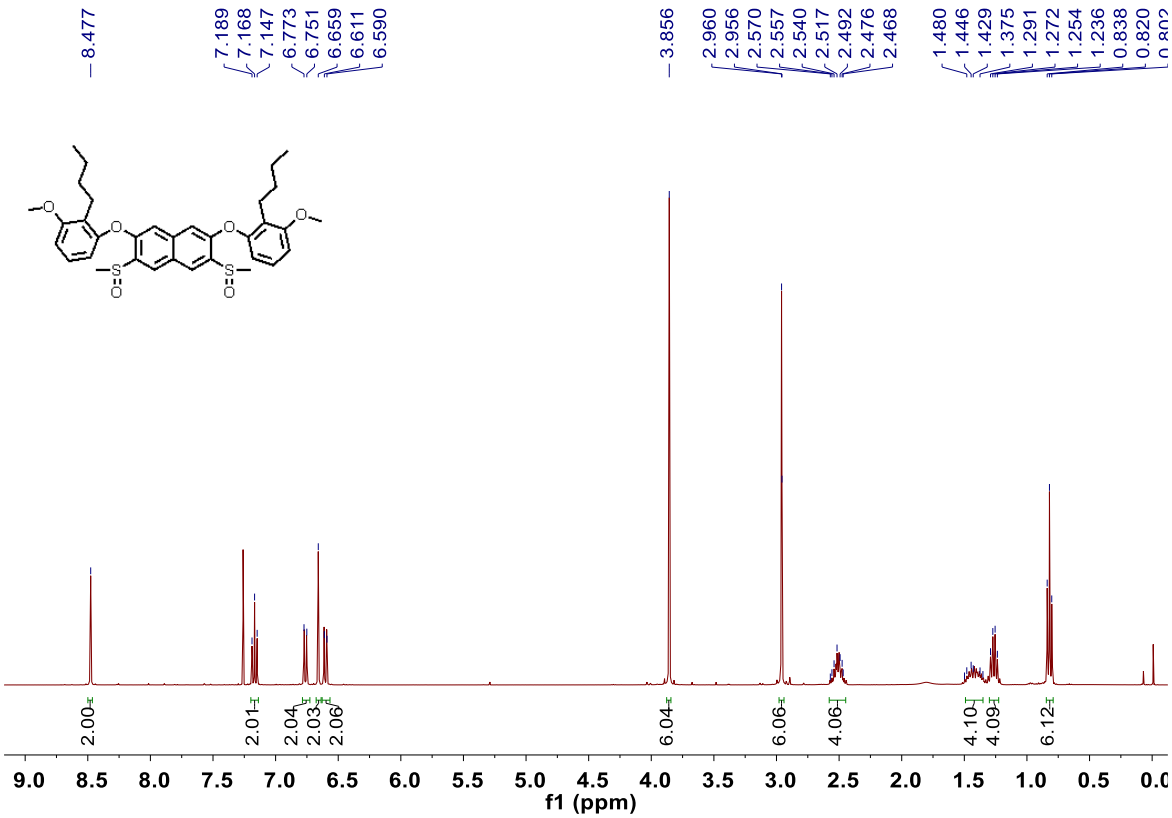


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3**.

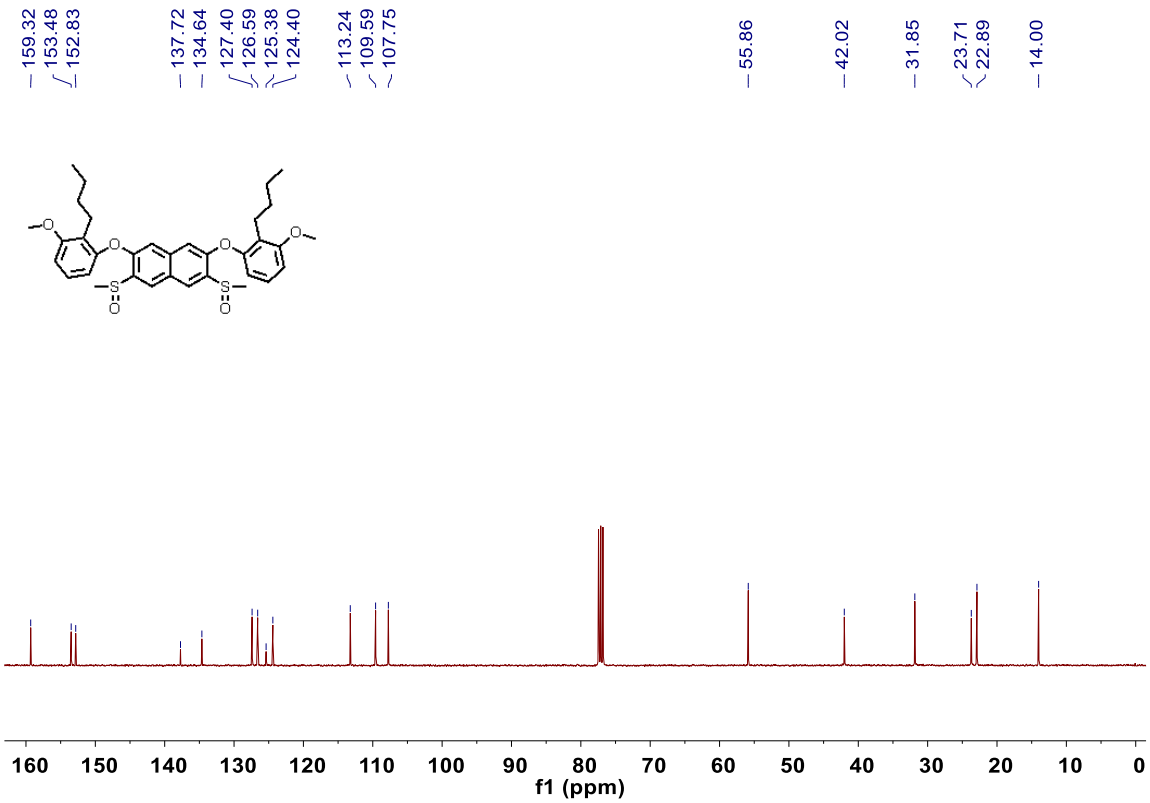


Figure S11. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **3**.

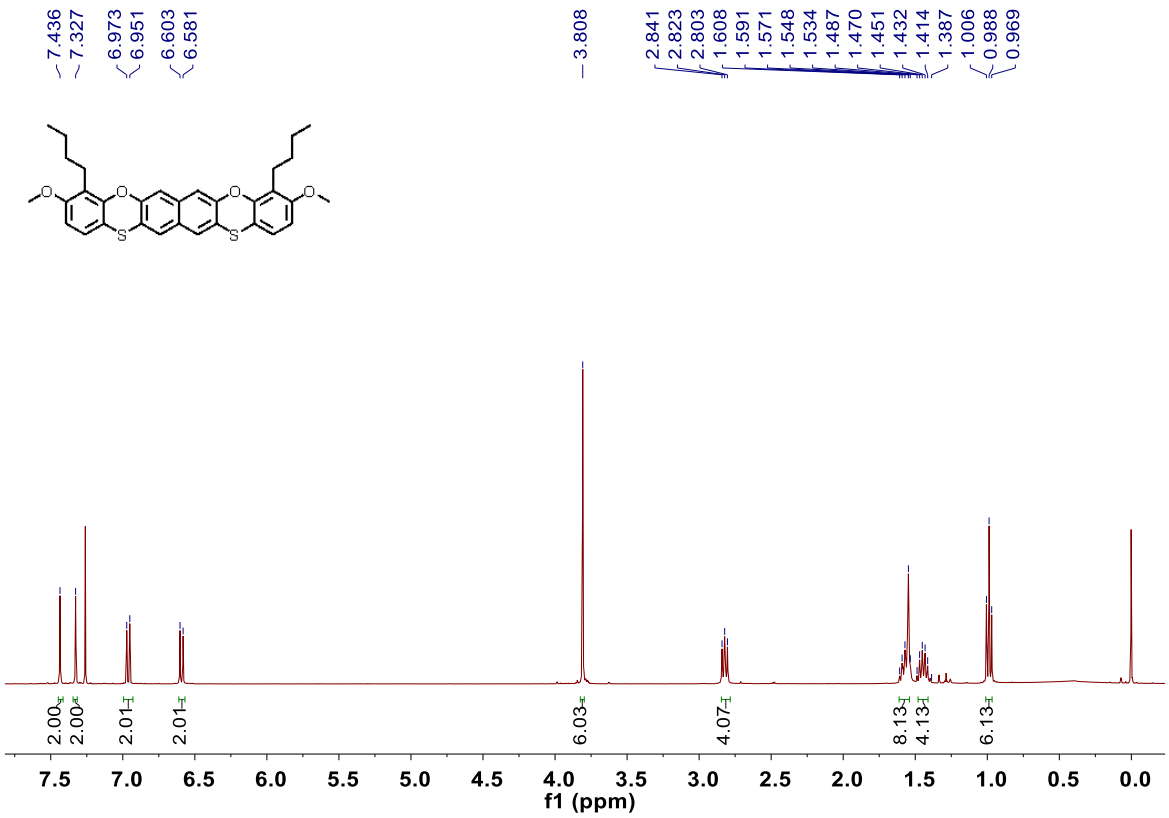


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **4**.

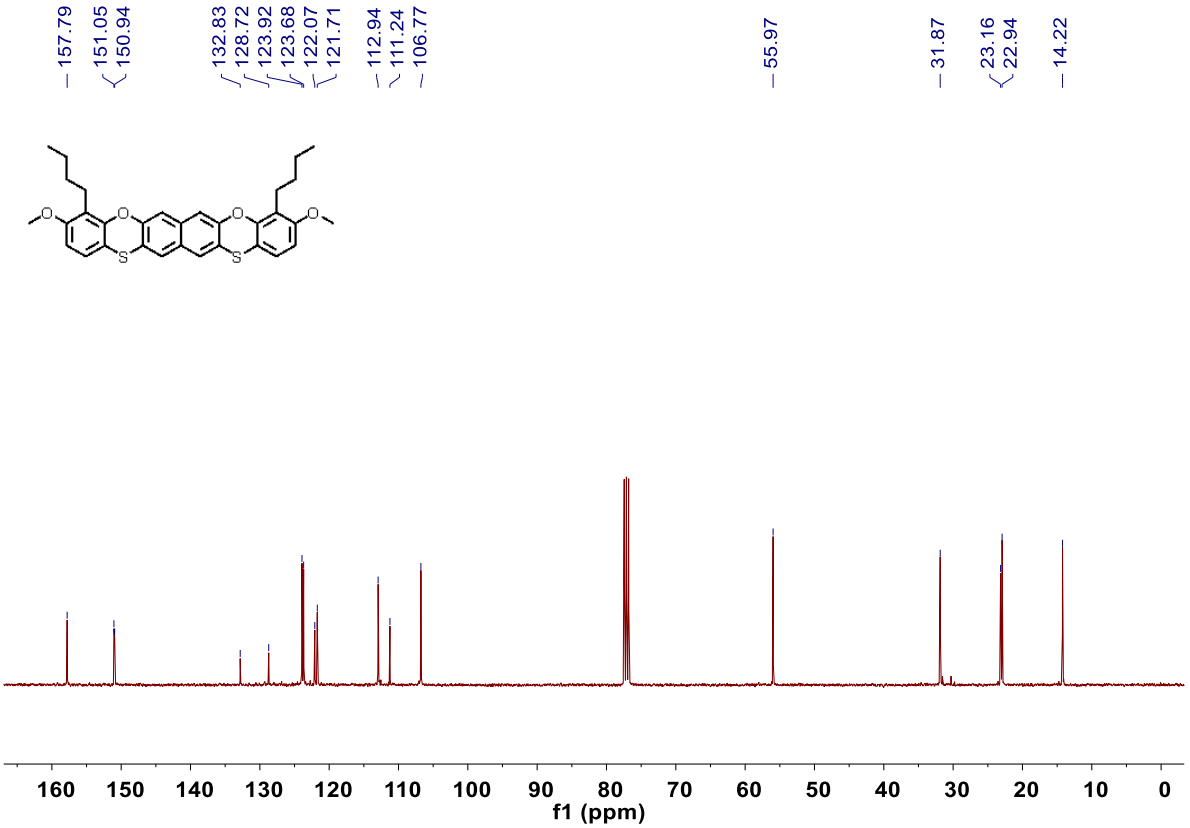


Figure S13. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **4**.

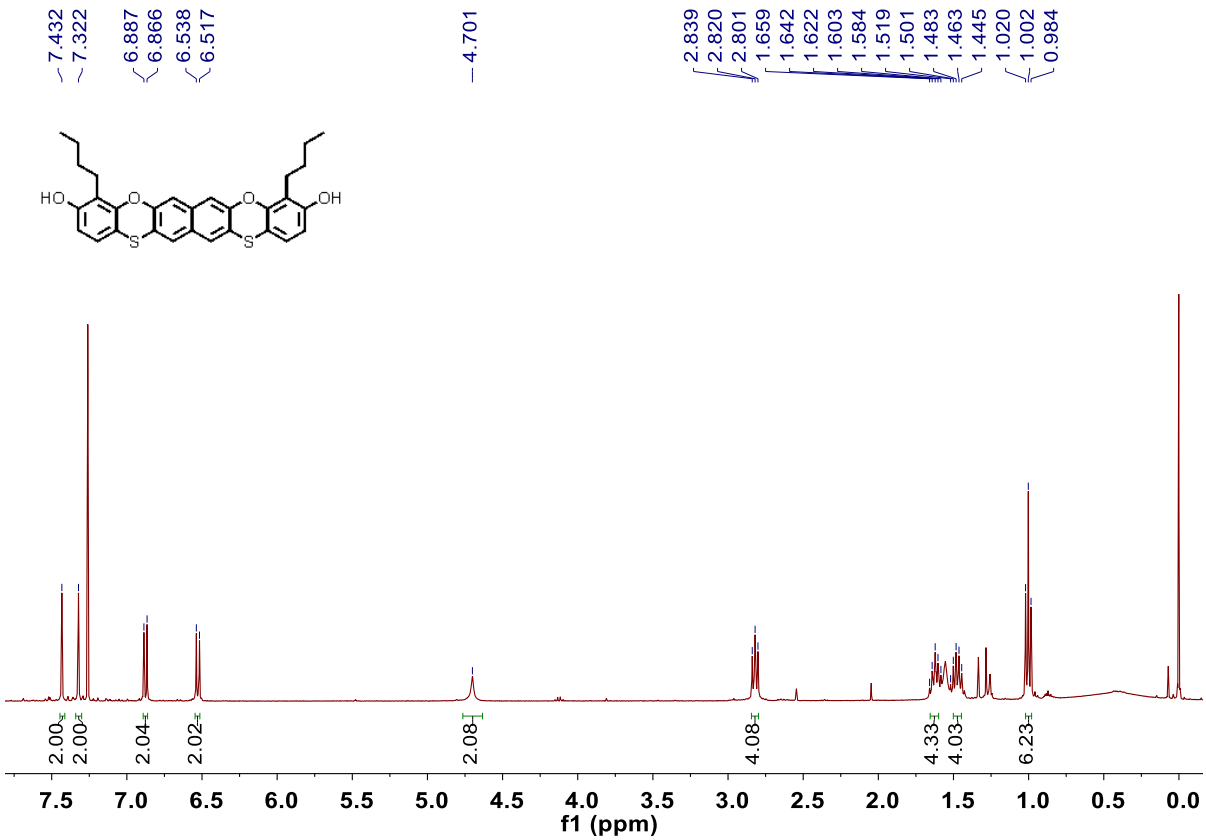


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **A**.

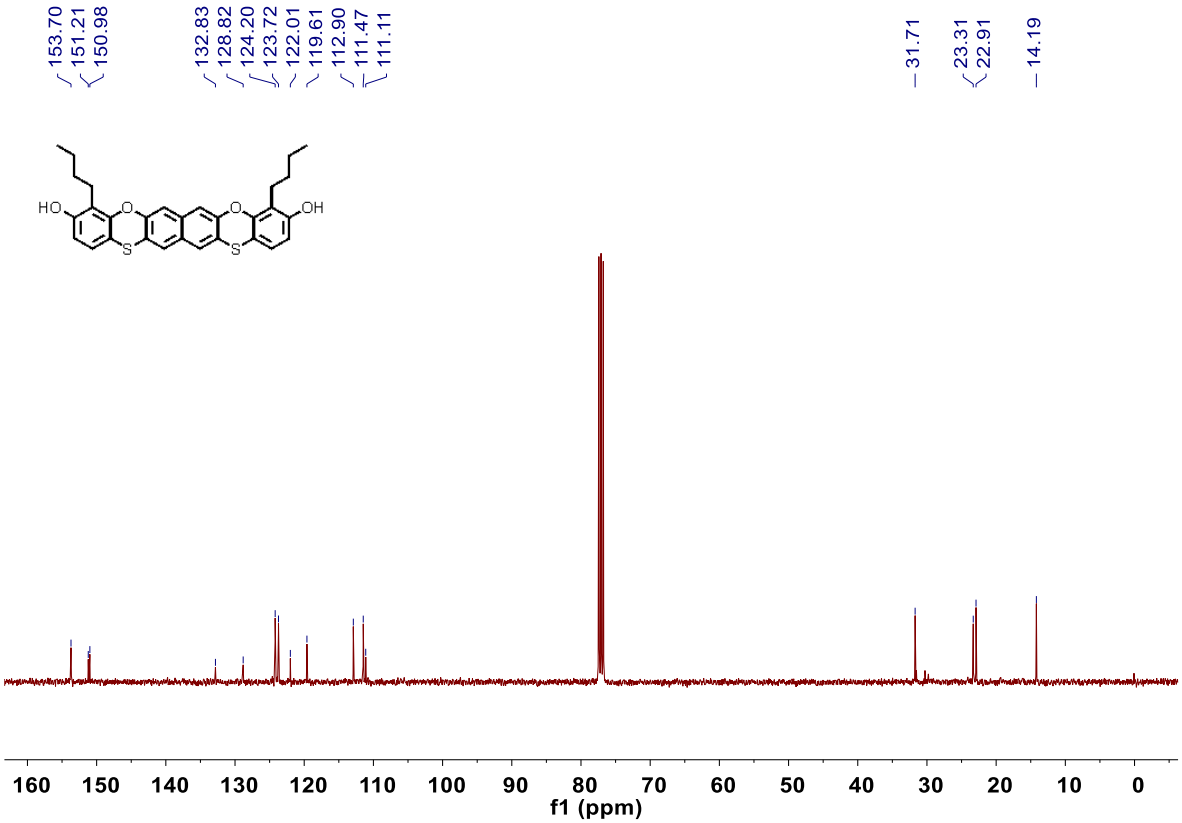


Figure S15. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **A**.

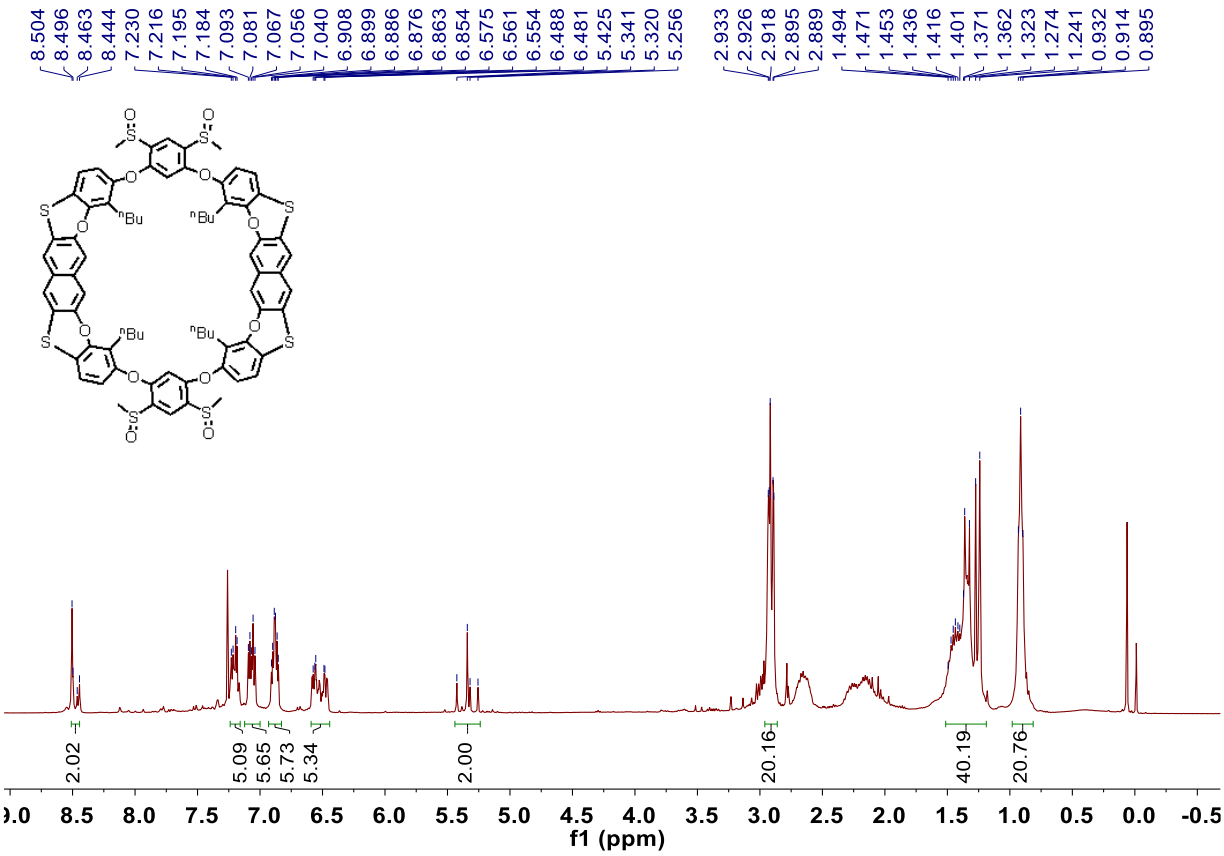


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **1**.

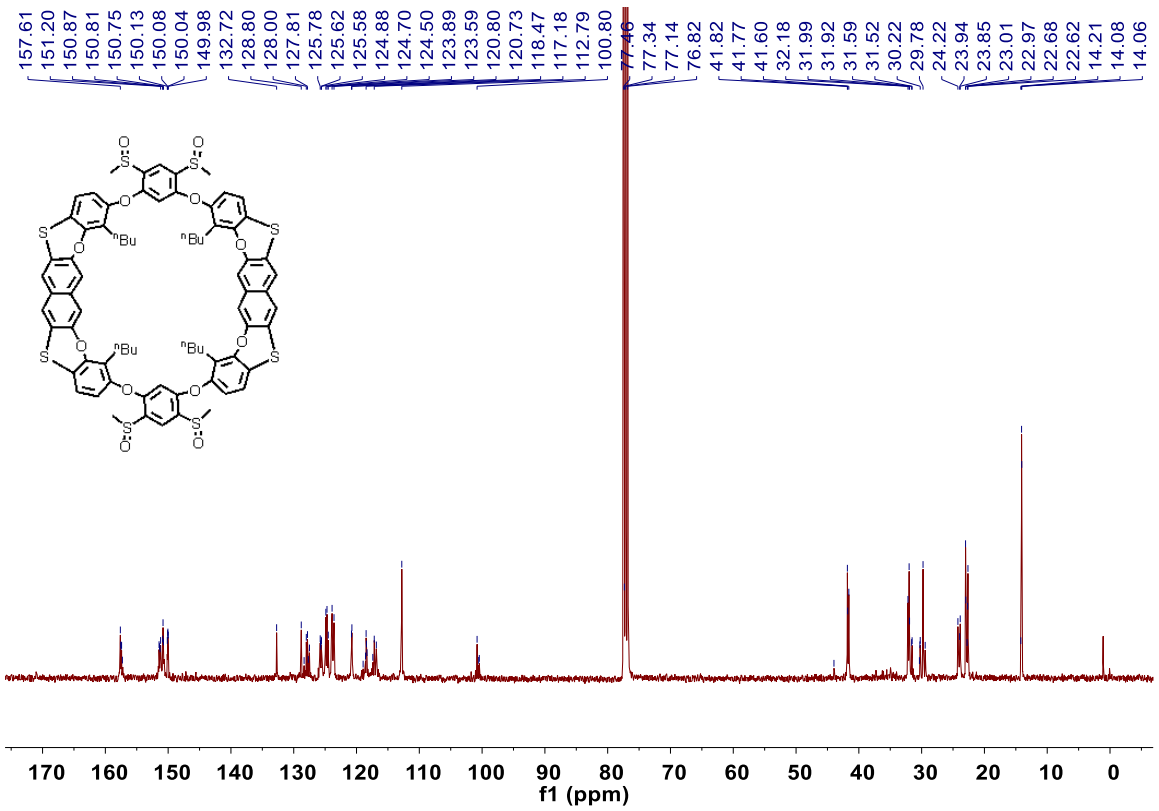


Figure S17. ^{13}C NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **1**.

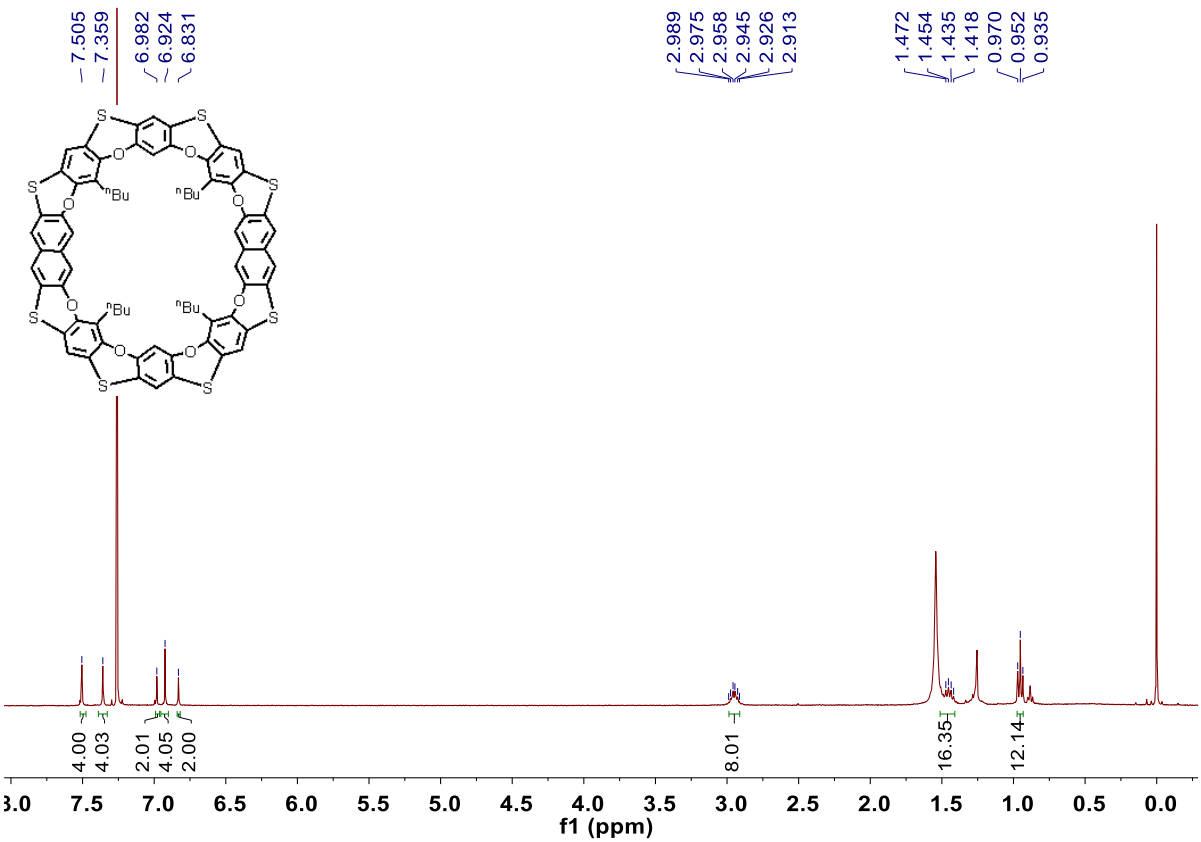


Figure S18. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298 K) of **[8]NCP**.

References

[S1] U. Azzena, G. Melloni, L. Pisano, *J. Chem. Soc. Perk. T, 1* **1995**, 3, 261-266.

[S2] 36. Xie, J.-L.; Li, X.; Wang, S.-H.; Li, A.-Q; Jiang, L.; Zhu, K.-L. Nat. Commun. 2020, 11, 3348.

[S3] Miyatake, K.; Hay, A. S.; Mitsuhashi, F.; Tsuchida, E. Macromolecules 2001, 34, 2385-2388.

[S4] Thordarson, K., Bindfit, http://app.supramolecular.org/bindfit/

[S5] Hibbert, D. B.; Thordarson, P. *Chem. Commun.* **2016**, *52*, 12792-12805.