Supporting Information

Crown ether-cycloparaphenylene hybrid multimacrocycles: Insights into supramolecular gas sensing and biological potential

Yaning Hu,[1] Tong Li,[2,3] Taotao Su,[1] Wudi Shi,[1] Yabing Yu,[1] Beibei Li,[1] Menghua Li,[1] Sheng Zhang,[1] Yuan-Qing Xu,[1] Qi Liu,*,[1] Di Wu,*,[2] Youzhi Xu*,[1]

[1]College of Chemistry and Molecular Sciences, Henan University, Kaifeng 475004, P. R. China. E-mail: qiliu@henu.edu.cn; youzhixu@henu.edu.cn

[2]College of Public Health, Zhengzhou University, Zhengzhou 450001, P. R. China. E-mail: wudi22@zzu.edu.cn

[3]College of Chemistry, Zhengzhou University, Zhengzhou 450001, P. R. China.

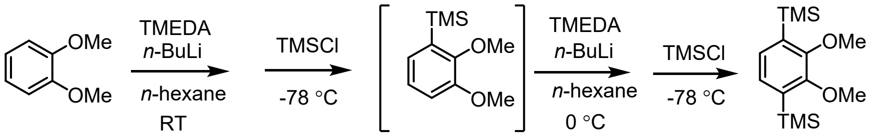
Contents

1. General Experimental Section

NMR spectra were recorded on a Bruker DRX 400 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz) or a Bruker AMX 500 (^{1}H NMR: 500 MHz, ^{13}C{^{1}H} NMR: 125 MHz) spectrometers at 298 K and referenced to the residual solvent peak (^{1}H: 7.26 ppm for $CDCl_3$, ^{13}C{^{1}H}: 77.16 ppm for $CDCl_3$, ^{1}H: 2.50 ppm for DMSO-d_6, ^{13}C{^{1}H}: 39.52 ppm for DMSO-d_6). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. High-resolution (HR) ESI mass spectra were recorded on Bruker maXis II^{TM} High Resolution LC-QTOF Mass Spectrometer. UV–Vis absorption spectra were recorded by using a Varian Cary 50 UV-Vis spectrophotometer. Steady-state excitation and emission spectra at room temperature were recorded on an Edinburgh Instruments FS5 Spectrofluorometer equipped with a Hamamatsu R928P PMT detector. A solution of quinine sulfate in 0.5 M H_2SO_4 (Φ_{lum} = 0.546, excitation wavelength at 365 nm) was used as the reference. The excited-state lifetimes were measured on a Hamamatsu C11367 Quantaurus-Tau Compact Fluorescence Lifetime Spectrometer.

2. Synthetic Procedures and Characterization Data

2.1 Synthesis of S1

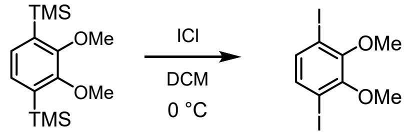


S1

S1 was prepared according to a modified published procedure. [S1]

In a 500-mL dry Schlenk flask, 1,2-Dimethoxybenzene (1.38 g, 10 mmol, 1.0 equiv.) was dissolved in a mixture of dry hexane (100 mL) and tetramethylethylenediamine (4.5 mL, 30 mmol, 3.0 equiv.), *n*-BuLi (2.4 M in hexane, 4.58 mL, 11 mmol, 1.1 equiv.) was added dropwise at room temperature. The reaction was stirred at room temperature for 12 h and cooled to −78 °C. Chlorotrimethylsilane (1.5 mL, 12 mmol, 1.2 equiv.) was slowly added and the reaction was allowed to warm to room temperature over 12 h. Then add tetramethylethylenediamine (4.5 mL, 30 mmol, 3.0 equiv.) and cooled to 0 °C, *n*-BuLi (2.4 M in hexane, 4.58 mL, 11 mmol, 1.1 equiv.) was added dropwise. The reaction was stirred at room temperature for 12 h and cooled to −78 °C. Chlorotrimethylsilane (1.5 mL, 12 mmol, 1.2 equiv.) was added dropwise. The reaction was allowed to warm to room temperature over 12 h. The reaction was quenched with water, and the aqueous layer was extracted with dichloromethane (2×50 mL), and the combined organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (dichloromethane–*n*-hexane = 1:10 v/v), and **S1** (2.43 g, 86% yield) was obtained as a colorless solid.

2.2 Synthesis of S2



S1 **S2**

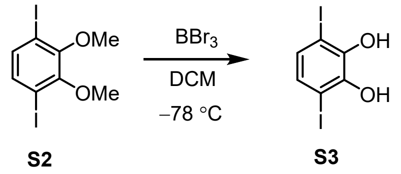
S2 was prepared according to a modified published procedure. [S1]

In a 200-mL dry Schlenk flask, 1,4-bis(trimethylsilyl)-2,3-dimethoxybenzene **S1** (2.82 g, 10 mmol, 1.0 equiv.) was dissolved in dichloromethane (100 mL) and cooled to 0 °C. A solution of iodine monochloride (3.4 g, 21 mmol, 2.1 equiv.) in dichloromethane (100 mL) was slowly added. The reaction was warmed to room temperature, stirred for 30 minutes and quenched with an aqueous solution of $Na_2S_2O_3$. Organic layer was separated and dried over $MgSO_4$.

Solvent was removed in vacuo and the crude product was purified by flash chromatography (dichloromethane–*n*-hexane = 1:10 v/v) to give **S2** (3.67 g, 94%) as a yellowish oil, which slowly solidified at room temperature.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.24 (s, 2H), 3.87 (s, 6H).

2.3 Synthesis of S3

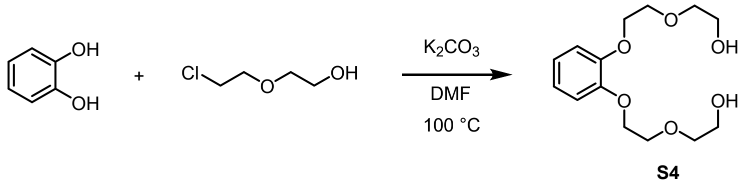


S3 was prepared according to a modified published procedure. [S1]

In a 100-mL dry Schlenk flask,1,4-diiodo-2,3-dimethoxybenzene (**S2**, 3.5 g, 8.97 mmol, 1.0 equiv.) was dissolved in dry CH_2Cl_2 (20 mL) and cooled to –78 ºC. BBr_3 (2 M in CH_2Cl_2, 21 mL, 41.3 mmol, 4.6 equiv.) was added and the reaction was allowed to warm to room temperature and stirred for 14 h. The reaction was quenched with ice water, the organic matter was extracted with ethyl acetate (3×50 mL), the organic layer is dried on anhydrous Na_2SO_4, concentrated under vacuum under reduced pressure, and purified by column chromatography (ethyl acetate–*n*-hexane = 1:1 v/v) to obtain a white solid of **S3** (2.92 g, 90% yield).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.00 (s, 2H), 5.61 (s, 2H).

2.4 Synthesis of S4

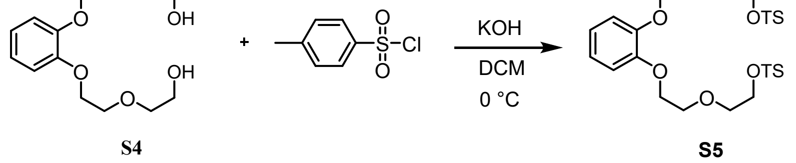


S4 was prepared according to a modified published procedure. [S2]

In a 100-mL dry Schlenk flask, 1,2-dihydroxybenzene (1.1 g, 10 mmol, 1.0 equiv.) was dissolved in 50 mL dry DMF under nitrogen atmosphere and potassium carbonate (4.14 g, 30 mmol, 3.0 equiv.) was added. After 5 minutes stirring, 2-(2-chloroethoxy) ethanol (3.73 g, 33 mmol, 3.0 equiv.) was added and the reaction stirred at 100 °C overnight. The reaction was allowed to cool down and DMF was removed in vacuum as far as possible. The residue was dissolved in water and chloroform, the phases were separated and the water layer was extracted with chloroform three more times. The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuum. To remove the rest of DMF, the residue was further dried in vacuum (oil pump) at 60 °C. The product was submitted to column chromatography on silica gel (ethyl acetate–methanol = 5:1 v/v) to obtain a yellow oil of **S4** (2.57 g, 85% yield).

^{1}H NMR (400 MHz, 298 K, CD_3OD, δ/ppm): δ = 6.98–6.96 (m, 2H), 6.91–6.89 (m, 2H), 4.13 (t, *J* = 4.0 Hz , 4H), 3.82 (t, *J* = 4.5 Hz, 4H), 3.69 (t, *J* = 4.5 Hz, 4H), 3.63(t, *J* = 4.5 Hz, 4H).

2.5 Synthesis of S5

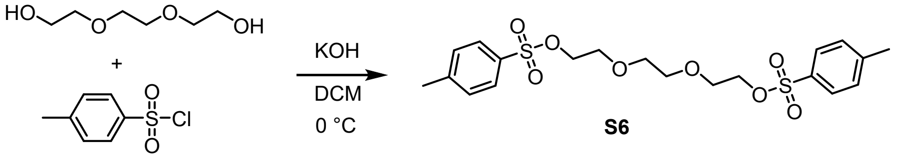


S5 was prepared according to a modified published procedure. [S2]

In a 250-mL dry Schlenk flask, **S4** (2.86 g, 10 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 under Argon. 4-Toluenesulfonyl chloride (4.18 g, 22 mmol, 2.2 equiv.) was added at 0 °C. Then, finely grinded KOH (1.34 g, 30 mmol, 3.0 equiv.) was added slowly at the same temperature. The reaction was stirred at room temperature for 3 h and filtered. The filtrate was then washed with 30 mL of water and twice with 25 mL of HCl (3 M). The organic phase was dried over $MgSO_4$. After evaporation of the solvent, the crude was purified by column chromatography on silica gel (CH_2Cl_2–*n*-hexane = 1:1 v/v) to obtain a colorless oil of **S5** (5.4 g, 91% yield).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.75 (d, *J* = 8.2 Hz, 4H), 7.26 (d, *J* = 8.0 Hz, 4H), 6.87–6.86 (m, 4H),4.15(t, *J* = 4.0 Hz, 4H), 4.03 (t, *J* = 4.4 Hz, 4H), 3.76–3.70 (m, 8H), 2.37(s, 6H).

2.6 Synthesis of S6

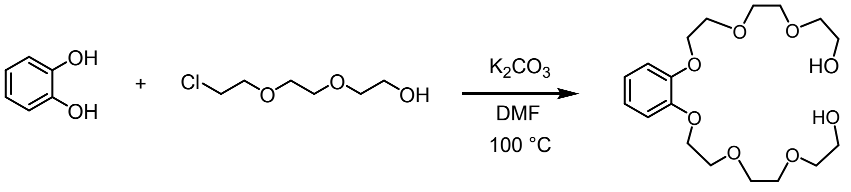


S6 was prepared according to a modified published procedure. [S3]

In a 250-mL round-bottom flask, triethylene glycol (1.5 g, 10 mmol, 1.0 equiv.) and 4-toluenesulfonyl chloride (3.99 g, 21 mmol, 2.0 equiv.) in DCM (100 mL) was slowly added freshly powdered KOH (4.48 g, 80 mmol, 8.0 equiv.) at 0 °C. The mixture was stirred for 3 h at 0 °C before ice water (200 mL) was added. The phases were separated and the organic layer was washed with water (100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was obtained as colorless solid (4.35 g, 9.5 mmol, 95% yield).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.72 (d, *J* = 8.1 Hz, 4H), 7.29 (d, *J* = 8.1 Hz, 4H), 4.08 (t, *J* = 4.8 Hz, 4H), 3.59 (t, *J* = 4.8 Hz, 4H), 3.45 (s, 4H), 2.38 (s, 6H).

2.7 Synthesis of S7



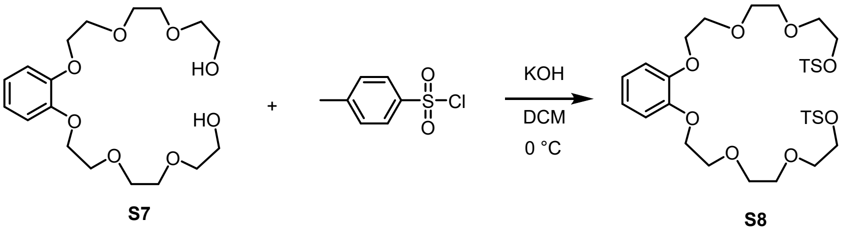
S7

S7 was prepared according to a modified published procedure. [S4]

In a 100-mL dry Schlenk flask, 1,2-dihydroxybenzene (1.1 g, 10 mmol, 1.0 equiv.) was dissolved in 50 mL dry DMF under nitrogen atmosphere and potassium carbonate (4.14 g, 30 mmol, 3.0 equiv.) was added. After 5 minutes stirring, 1,2-bis(2-chloroethoxy) ethane (3.7 g, 22 mmol, 2.2 equiv.) was added and the reaction stirred at 100 °C overnight. The reaction was allowed to cool down and DMF was removed in vacuum as far as possible. The residue was dissolved in water and chloroform, the phases was separated and the water layer was extracted with chloroform three more times. The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuum. To remove the rest of DMF, the residue was further dried in vacuum (oil pump) at 60 °C. The product was submitted to column chromatography on silica gel (ethyl acetate–methanol = 4:1 v/v) to obtain a yellow oil of **S7** (3.63 g, 97% yield).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 3.36 (s, 2H), 3.61 (m, 4H), 3.66 (m, 4H), 3.72 (m, 8H), 3.88 (m, 4H), 4.17 (m, 4H), 6.91 (m, 4H).

2.8 Synthesis of S8



S8

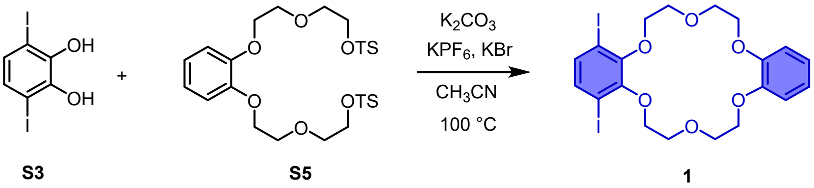
S8 was prepared according to a modified published procedure. [S4]

In a 250-mL dry Schlenk flask, **S5** (2.24 g, 6 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 under argon. 4-toluenesulfonyl chloride (2.5 g, 13.2 mmol, 2.2 equiv.) was added at 0 °C. Then, finely grinded KOH (1.34 g, 30 mmol, 5.0 equiv.) was added slowly at the same temperature. The reaction was stirred at room temperature for 3 h and filtered. The filtrate was then washed with 30 mL of water and twice with 25 mL of HCl (3 M). The organic phase was dried over $MgSO_4$. After evaporation of the solvent, the crude was purified by column chromatography on silica gel (CH_2Cl_2–*n*-hexane = 1:1 v/v) to obtain a colorless oil of **S8** (3.72 g, 91% yield).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.68 (d, *J* = 8.0 Hz, 4H), 7.22 (s, 4H), 6.86-6.75(m, 4H), 4.04(dt, *J* = 7.4, 4.7 Hz, 8H), 3.72(t, *J* = 5.0 Hz, 4H), 3.62–3.53(m, 8H), 3.49(dd, *J* = 5.8, 3.5 Hz, 4H).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 148.99, 144.85, 132.95, 129.87, 127.92, 121.67, 114.94, 70.74, 70.71, 69.80, 69.37, 68.85, 68.65, 21.60.

2.9 Synthesis of 1



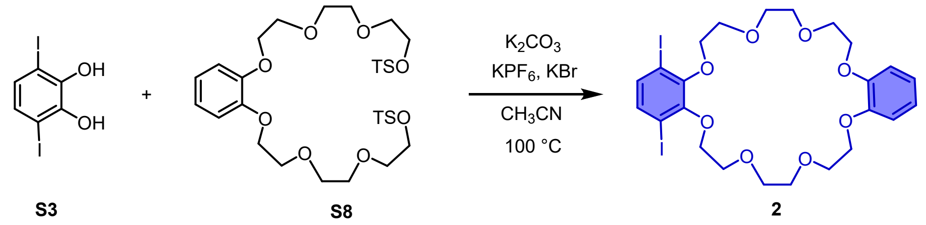
A 200-mL Schlenk flask was charge with **S3** (0.36 g, 1.0 mmol, 1.0 equiv.), **S5** (0.59 g, 1.0 mmol, 1.0 equiv.), K_2CO_3 (0.55 g, 4.0 mmol, 4.0 equiv.), KPF_6 (0.74 g, 4.0 mmol, 4.0 equiv.), KBr (2.38 mg, 0.02 mmol, 0.02 equiv.) and acetonitrile (80 mL) under N_2 atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After cooling down to room temperature, the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (petroleum ether–ethyl acetate = 5:1 v/v) to give **1** (581 mg, 95% yield) as a white solid.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.24 (s, 2H), 6.92 (s, 4H), 4.22 (t, *J* = 4.1 Hz, 8H), 4.06 (t, *J* = 4.6 Hz, 4H), 4.03–3.97 (m, 4H).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 152.31, 149.07, 135.57, 121.65, 114.58, 93.20, 77.23, 72.87, 70.62, 69.95, 69.55.

HRMS (ESI): calculated for $C_{20}H_{22}I_2O_6$ $[M+Na]^+$ 634.9398. Found: 634.9398.

2.10 Synthesis of 2



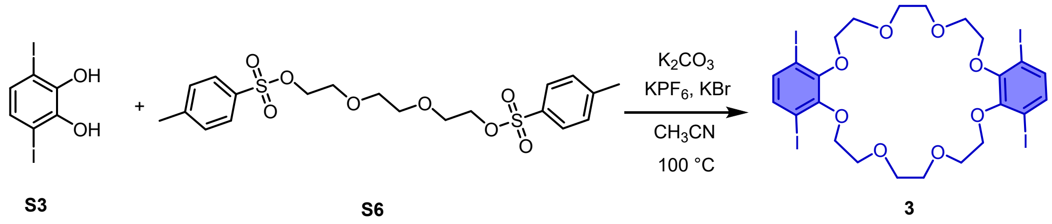
A 200-mL Schlenk flask was charge with **S3** (0.36 g, 1.0 mmol, 1.0 equiv.), **S8** (0.68 g, 1.0 mmol, 1.0 equiv.), K_2CO_3 (0.55 g, 4.0 mmol, 4.0 equiv.), KPF_6 (0.74 g, 4.0 mmol, 4.0 equiv.), KBr (2.38 mg, 0.02 mmol, 0.02 equiv.) and acetonitrile (80 mL) under N_2 atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After cooling down to room temperature, the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (CH_2Cl_2–ethyl acetate = 5:1 v/v) to give **2** (630 mg, 90 % yield) as a light yellow oil.

^{1}H NMR (500 MHz, 298 K, DMSO-*d*$_6$, δ/ppm): δ = 7.31 (s, 2H), 6.96 (dt, *J* = 7.7, 3.8 Hz, 2H,), 6.88 (dd, *J* = 6.0, 3.6 Hz, 2H), 4.07 (q, *J* = 4.6 Hz, 8H), 3.79 (dt, *J* = 12.4, 4.5 Hz, 8H), 3.71–3.62 (m, 8H).

^{13}C{^{1}H} NMR (125 MHz, 298 K, DMSO-*d*$_6$, δ/ppm): δ = 152.46, 148.91, 135.91, 121.73, 114.70, 94.28, 72.89, 70.54, 70.16, 69.58, 69.09, 60.24, 39.71.

HRMS (ESI): calculated for $C_{24}H_{30}I_2O_8$ $[M + Na]^+$ 722.9944. Found: 722.9922.

2.11 Synthesis of 3



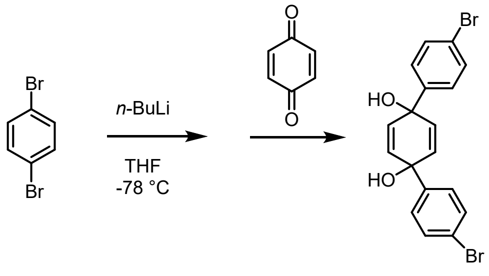
A 200-mL Schlenk flask was charge with **S3** (0.36 g, 1.0 mmol, 1.0 equiv.), **S6** (0.66 g, 1.0 mmol, 1.0 equiv.), K_2CO_3 (0.55 g, 4.0 mmol, 4.0 equiv.), KPF_6 (0.74 g, 4.0 mmol, 4.0 equiv.), KBr (2.38 mg, 0.02 mmol, 0.02 equiv.) and acetonitrile (80 mL) under N_2 atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After cooling down to room temperature, the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (*n*-hexane–ethyl acetate = 3:1 v/v) to give **3** (276 mg, 29 % yield) as a light yellow solid.

^{1}H NMR (500 MHz, 298 K, DMSO-d_6, δ/ppm): δ = 7.34 (s, 4H), 4.10–4.06 (m, 8H), 3.84– 3.80 (m, 8H), 3.66 (s, 8H).

^{13}C{^{1}H} NMR (125 MHz, 298 K, DMSO-d_6, δ/ppm): δ = 152.85, 136.13, 94.76, 73.44, 70.99, 70.04, 39.54.

HRMS (ESI): calculated for $C_{24}H_{28}I_4O_8$ [M + Na]$^+$ 974.7855. Found: 974.7876.

2.12 Synthesis of S9



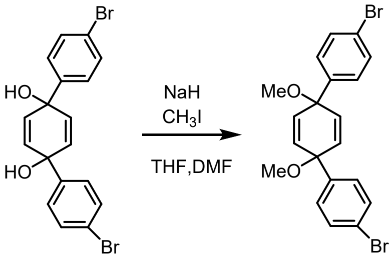
S9

S9 was prepared according to a modified published procedure. [S5]

A 200-mL dry Schlenk flask was charged with 1,4-dibromobenzene (11.8 g, 50 mmol, 1.0 equiv.) and 80 mL anhydrous THF. *n*-BuLi in *n*-hexane (22.0 mL, 2.5 mol/L, 55.0 mmol, 1.1 equiv.) was added dropwise at –78 ºC over 5 minutes under N_2 atmosphere. The reaction mixture was stirred for 1 h at –78 ºC, then 1,4-benzoquinone (2.16 g, 20.0 mmol, 0.4 equiv.) was added portionwise (ca. 0.54 g each). The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The reaction was quenched with water (40 mL) and diluted with diethyl ether (40 mL). After layer separation the aqueous layer was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over magnesium sulfate. The organic solvents were removed under reduced pressure. The crude product was precipitated from CH_2Cl_2 in petroleum ether three times and the precipitate was recrystallized from diethyl ether and *n*-hexane several times to yield the **S9** (1.26 g, 15 % yield) as a colorless crystalline solid.

^{1}H-NMR (500 MHz, 298 K, d_2-DCM, δ/ppm): δ = 7.26–7.53 (m, 8H), 6.02 (s, 4H), 2.64 (s, 2H).

2.13 Synthesis of S10



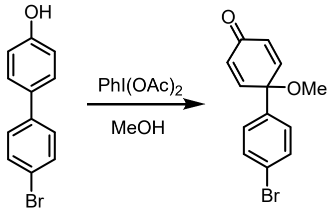
S9 **S10**

S10 was prepared according to a modified published procedure. [S5]

A 50-mL dry Schlenk flask was charged with **S9** (1.26 g, 3 mmol, 1.0 equiv.) and 20 mL anhydrous THF. Sodium hydride (480 mg, 12 mmol, 60 % in mineral oil, 4.0 equiv.), methyl iodide (0.58 mL, 9.0 mmol, 3.0 equiv.) and anhydrous DMF (2.0 mL) were added to the reaction at 0 ºC. The mixture was allowed to warm up to room temperature overnight. Deionized water (10 mL) was added carefully to quench the sodium hydride, the resulting mixture was extracted with Et_2O (3×50 mL). The combined organic layers were concentrated under reduced pressure and purified by column chromatography (CH_2Cl_2–*n*-hexane = 1:1 v/v) to give **S10** (1.32 g, 98 % yield) as a light yellow solid.

^1H NMR (500 MHz, 298 K, *d*$_2$-DCM, δ/ppm): δ = 7.20–7.49 (m, 8H), 6.07 (s, 4H), 3.40 (s, 6H).

2.14 Synthesis of S11



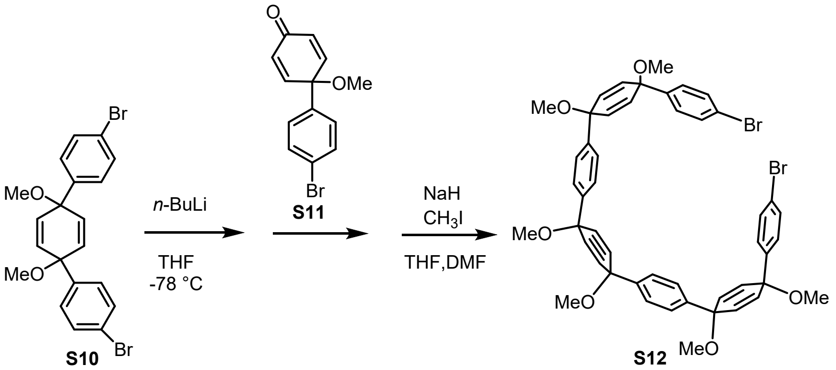
S11

S11 was prepared according to a modified published procedure. [S6]

In a 200-mL dry Schlenk flask, 4-bromo-4'-hydroxybiphenyl (12.5 g, 50 mmol, 1.0 equiv.), $PhI(OAc)_2$ (20.0 g, 62 mmol, 1.24 equiv.) was dissolved in anhydrous MeOH (100 mL). The reaction mixture was allowed to stir at room temperature under N_2 atmosphere. After stirring for 48 h, the solvent was removed under vacuum and the resulting product was extracted with CH_2Cl_2. Solvent was removed in vacuo and the crude product was purified by flash chromatography (ethyl acetate–*n*-hexane = 1:10 v/v) to give **S11** (9.16 g, 65%) as a yellow solid.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, δ/ppm): δ=7.47 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 9.6 Hz, 2H), 6.40 (d, *J* = 9.7 Hz, 2H), 3.40 (s, 3H).

2.15 Synthesis of S12

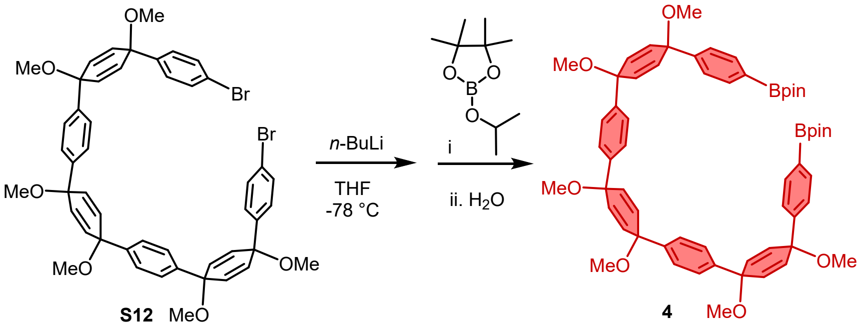


S12 was prepared according to a modified published procedure. [S7]

In a 200-mL dry Schlenk flask was charged with **S10** (1.8 g, 4.0 mmol, 1.0 equiv.) and 80 mL anhydrous THF. *n*-BuLi in *n*-hexane (4.8 mL, 2.5 M, 12.0 mmol, 3.0 equiv.) was added dropwise at –78 ºC. After stirring the mixture for 3 min at –78 °C, **S11** (3.38 g, 12.0 mmol, 3.0 equiv.) was added, and the resultant mixture was further stirred at –78 °C for 2 h. After warmed up to room temperature, the mixture was quenched with H_2O, extracted with EtOAc, dried over Na_2SO_4, and concentrated under reduced pressure. NaH (672 mg, 60 % mineral oil, 17.2 mmol, 4.2 equiv.) was suspended in 20 mL anhydrous THF and cooled to 0 °C. The above crude product was put into the cooled suspension portionwise. After 30 min stirring, MeI (1.3 mL, 21.5 mmol, 5.3 equiv.) was added dropwise. The mixture was warmed to room temperature and stirred for 8 h. The excess sodium hydride was quenched by the addition of water. After layer separation, the aqueous layer was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and the organic solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate–*n*-hexane = 1:10 v/v) to give **S12** as a white solid (2.8 g, 79%).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.47 (dd, *J* = 8.6, 6.7 Hz, 2H), 7.42 (td, *J* = 7.0, 6.4, 4.0 Hz, 4H), 7.36–7.29 (m, 6H), 7.27–7.23 (m, 4H), 6.14–6.00 (m, 12H), 3.43–3.39 (m, 15H), 3.29–3.21 (m, 3H).

2.16 Synthesis of 4

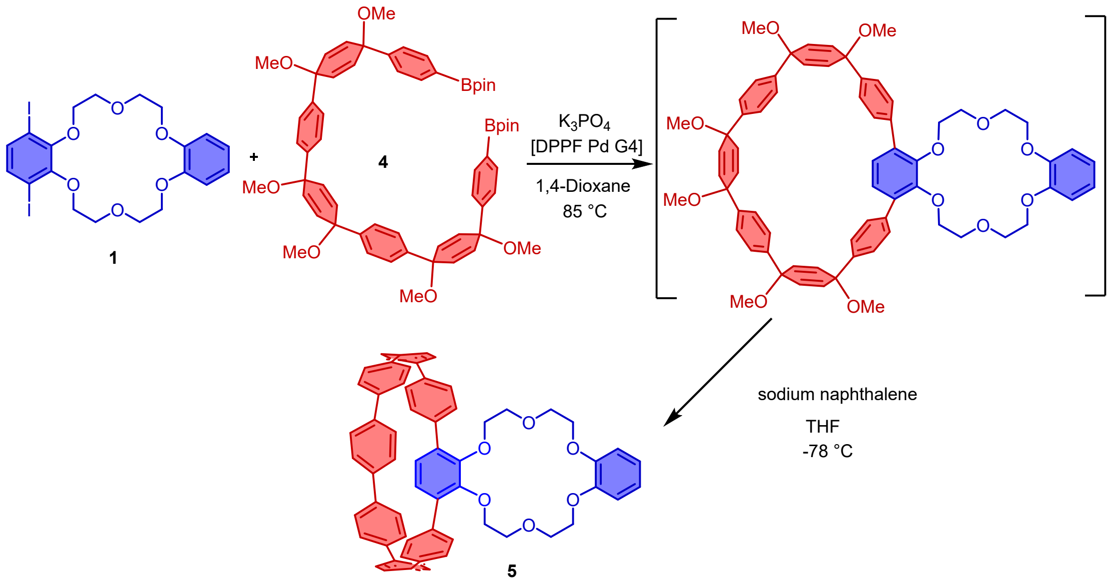


4 was prepared according to a modified published procedure. [S7]

In a 100-mL dry Schlenk flask was charged with **S12** (3.0 g, 3.4 mmol, 1.0 equiv.) and 50 mL anhydrous THF. *n*-BuLi in *n*-hexane (3.4 mL, 2.5 M, 8.54 mmol, 2.5 equiv.) was added dropwise at –78 ºC over 5 minutes under N_2 atmosphere. Isopropyl pinacol borate (2.2 mL, 10.2 mmol, 3.0 equiv.) was added immediately, and the solution was stirred for 30 min at –78 °C. The reaction was warmed up to room temperature and water (20 mL) was then added to the solution and the mixture was allowed to stir for 10 min before extracting with CH_2Cl_2 (2×20 mL). The crude product was purified by column chromatography (ethyl acetate–*n*-hexane = 1:10 v/v) to give **4** as a white solid (1.8 g, 55%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ/ppm): δ = 7.80 (m, 3H), 7.55 (m, 2H), 7.45–7.32 (m, 11H), 3.41 (s, 15H), 3.31–3.14 (m, 3H), 1.32 (s, 24H).

2.17 Synthesis of 5



A 200-mL Schlenk flask was charged with **1** (63 mg, 0.10 mmol, 1.0 equiv.), **4** (100 mg, 0.10 mmol, 1.0 equiv.), K_3PO_4 (436 mg, 2.05 mmol, 20.0 equiv.), [DPPF Pd G4] (9.4 mg, 0.01 mmol, 0.1 equiv.), 1,4-dioxane (50 mL) and deionized water (1.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 85 °C for 24 h under N_2 atmosphere. After cooling down to room temperature, the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (dichloromethane–methanol = 25:1 v/v) to give crude macrocycle as a light yellow solid.

The crude macrocycle was dissolved in 10 mL anhydrous THF under nitrogen and cooled down to –78 °C. At this point, freshly prepared sodium naphthalenide (1.0 mL, 1.0 mmol, 1.0 M in THF) was added. The reaction mixture was stirred for 2 hours at –78 °C before MeOH (5 mL) was added. Then the resulting mixture was warmed up to room temperature. After removal of the solvent under reduced pressure, the crude solid was purified by silica gel column chromatography (CH_2Cl_2–methanol = 30:1 v/v) to give **5** (17.7 mg, 20 % yield) as a yellow solid.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.67–7.32 (m, 28H), 6.92 (s, 4H), 6.58 (s, 2H), 4.35 (s, 4H), 4.22 (s, 4H), 3.98 (d, J = 13.2 Hz, 8H).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 149.49, 149.18, 139.17, 137.95, 137.85, 137.81, 137.78, 137.71, 137.38, 131.07, 128.69, 127.51, 121.73, 114.84, 73.89, 29.72.

HRMS (ESI): calculated for $C_{62}H_{50}O_6$ $[M + Na]^+$ 913.3500. Found: 913.3504.

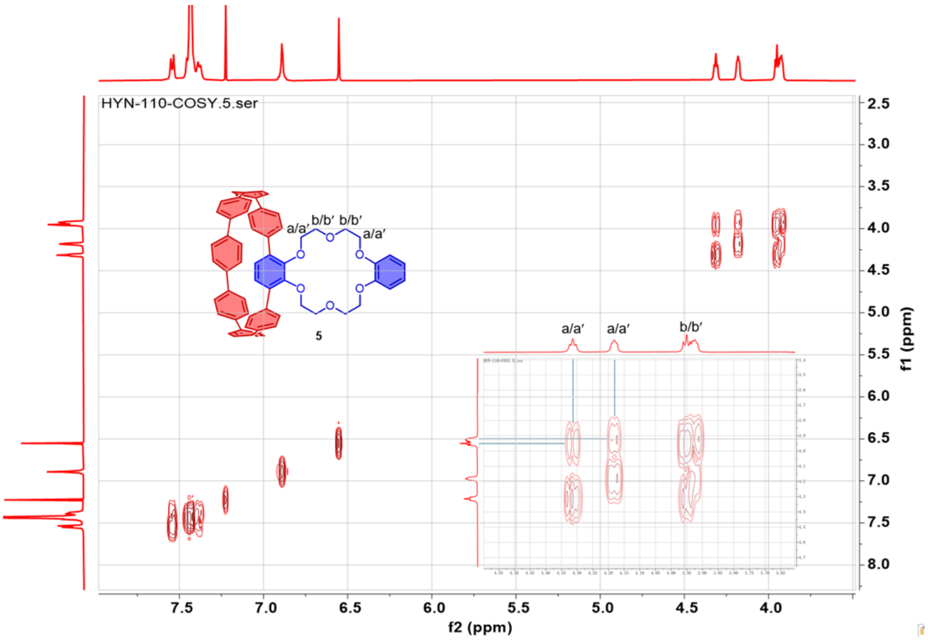


Figure S1. ^{1}H–^{1}H COSY of **5** (CDCl$_3$, 500 MHz, 298 K)

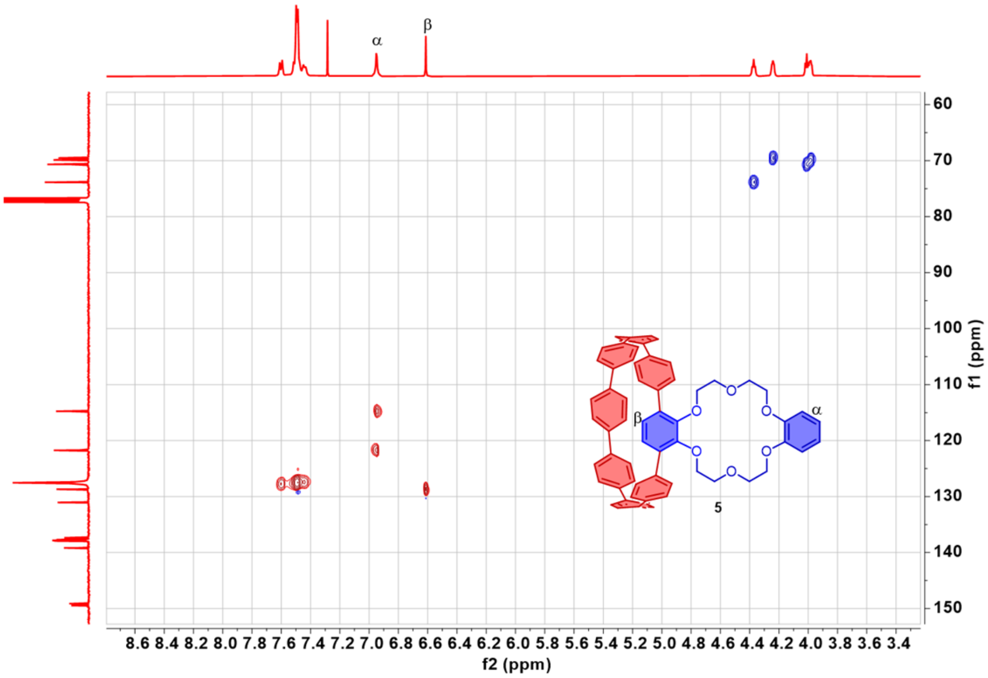
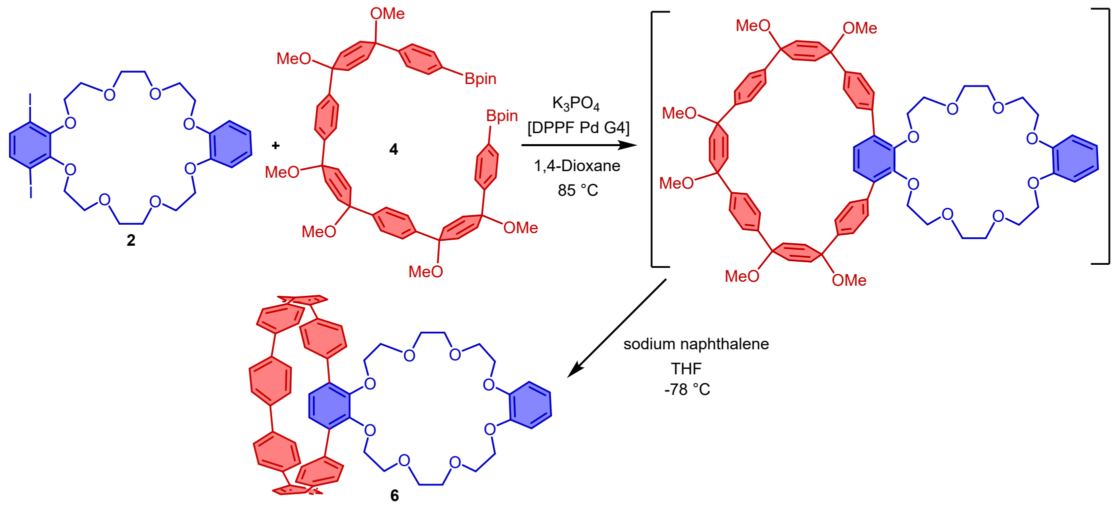


Figure S2. ^{1}H–^{13}C{^{1}H} HSQC of **5** (CDCl$_3$, 500 MHz, 298 K

2.18 Synthesis of 6



A 200-mL Schlenk flask was charged with **2** (100 mg, 0.14 mmol, 1.0 equiv.), **4** (139 mg, 0.14 mmol, 1.0 equiv.), K_3PO_4 (605 mg, 2.85 mmol, 20.0 equiv.), [DPPF Pd G4] (13 mg, 0.014 mmol, 0.1 equiv.), 1,4-dioxane (60 mL) and deionized water (1.42 mL) under N_2 atmosphere. The reaction mixture was stirred at 85 °C for 24 h under N_2 atmosphere. After cooling down to room temperature, the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (CH_2Cl_2–methanol = 20:1 v/v) to give crude macrocycle as light yellow solid.

The crude macrocycle was dissolved in 10 mL anhydrous THF under nitrogen and cooled down to –78 °C. At this point, freshly prepared sodium naphthalenide (1.0 mL, 1.0 mmol, 1.0 M in THF) was added. The reaction mixture was stirred for 2 h at –78 °C before MeOH (5 mL) was added. Then the resulting mixture was warmed up to room temperature. After removal of the solvent under reduced pressure, the crude solid was purified by silica gel column chromatography (CH_2Cl_2–methanol 30:1 = v/v) to give **6** (23.29 mg, 17% yield) as a yellow solid.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.68–7.35 (m, 28H), 6.89 (d, *J* = 3.4 Hz, 4H), 6.56 (s, 2H), 4.34 (t, *J* = 4.9 Hz, 4H), 4.19–4.10 (m, 4H), 3.92–3.87 (m, 4H), 3.83 (t, *J* = 5.6 Hz, 8H), 3.76–3.70 (m, 4H).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 149.58, 149.07, 139.12, 137.94, 137.85, 137.81, 137.78, 137.70, 137.46, 128.62, 127.51, 121.54, 114.39, 77.23, 73.88, 71.12, 70.82, 70.64, 69.90, 69.48.

HRMS (ESI): calculated for $C_{66}H_{58}O_8$ $[M + Na]^+$ 1001.4024. Found: 1001.4053.

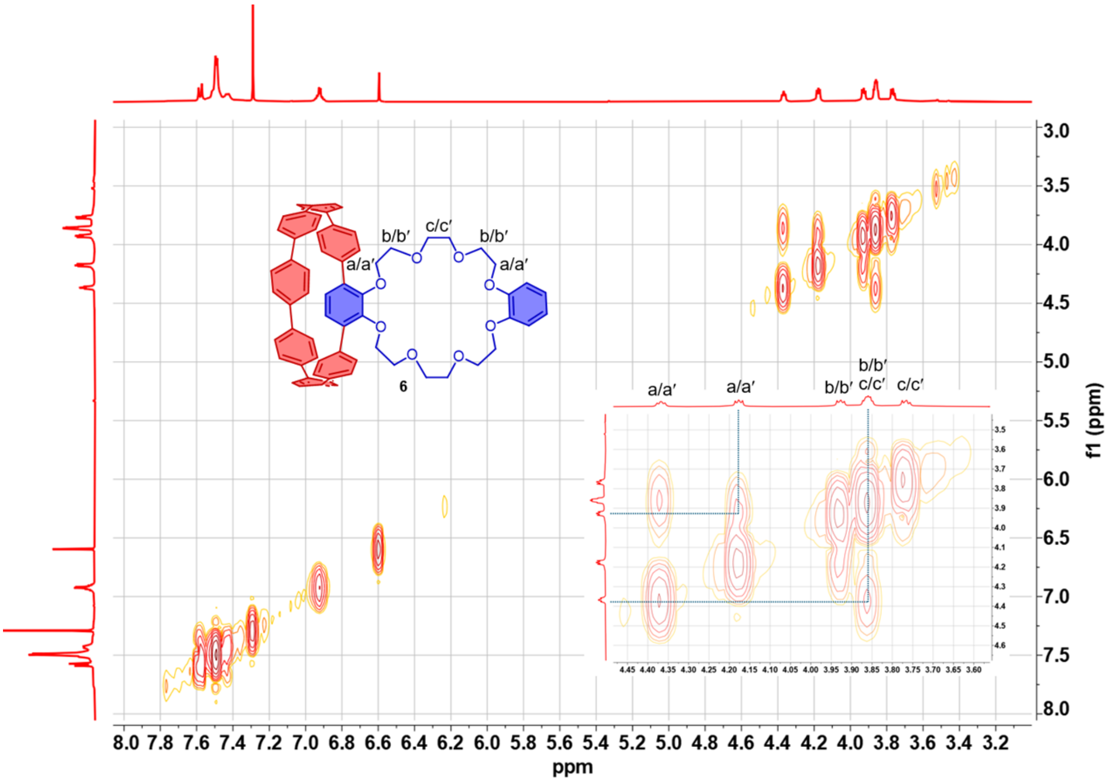
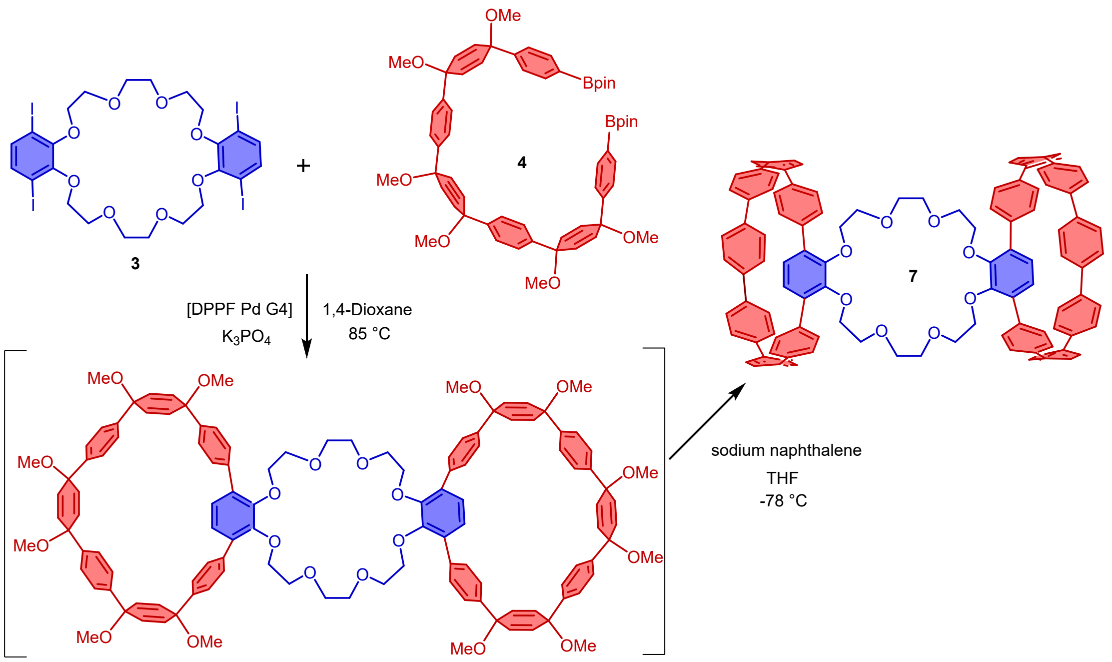


Figure S3. ^{1}H–^{1}H COSY of **6** (CDCl$_3$, 500 MHz, 298 K

2.19 Synthesis of 7



A 200-mL Schlenk flask was charged with **3** (105 mg, 0.11 mmol, 1.0 equiv.), **4** (214 mg, 0.22 mmol, 2.0 equiv.), K_3PO_4 (467 mg, 2.20 mmol, 20.0 equiv.), [DPPF Pd G4] (10.2 mg, 0.011 mmol, 0.1 equiv.), 1,4-dioxane (60 mL) and deionized water (1.1 mL) under N_2 atmosphere. The reaction mixture was stirred at 85 °C for 24 h under N_2 atmosphere. After cooling down to room temperature, the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (CH_2Cl_2–methanol = 15:1 v/v) to give crude macrocycle as a light yellow solid.

The crude macrocycle was dissolved in 10 mL anhydrous THF under nitrogen and cooled down to –78 °C. At this point, freshly prepared sodium naphthalenide (1.0 mL, 1.0 mmol, 1.0 M in THF) was added. The reaction mixture was stirred for 2 hours at –78 °C before MeOH (5 mL) was added. Then the resulting mixture was warmed up to room temperature. After removal of the solvent under reduced pressure, the crude solid was purified by silica gel column chromatography (CH_2Cl_2–methanol = 25:1 v/v) to give **7** (13.3 mg, 10 % yield) as a yellow solid.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 7.57 (d, J = 8.6 Hz, 57H), 6.59 (s, 4H), 4.33 (s, 8H), 3.85 (t, J = 4.0 Hz, 8H), 3.75 (s, 8H).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, δ/ppm): δ = 149.74, 139.30, 137.94, 137.90, 137.82, 137.77, 137.69, 137.57, 130.60, 128.60, 77.22, 74.61, 70.71, 70.52.

HRMS (ESI): calculated for $C_{108}H_{84}O_8$ $[M + Na]^+$ 1531.6058. Found:1531.6060.

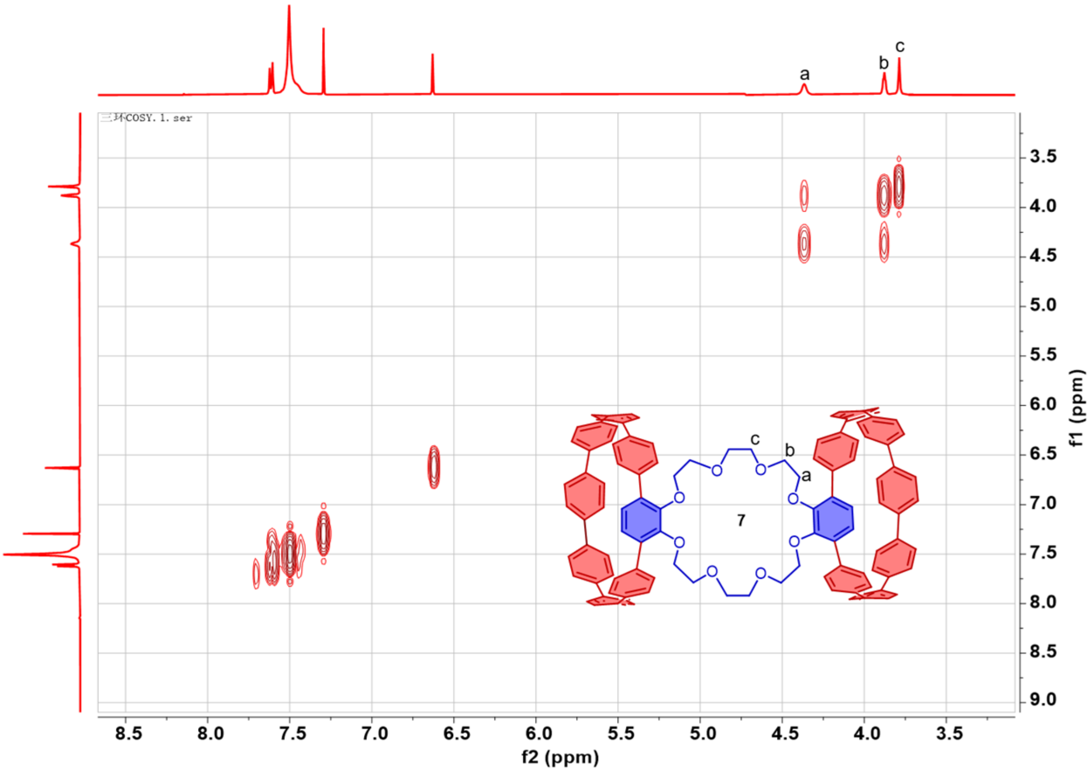


Figure S4. ^{1}H–^{1}H COSY of **7** (CDCl$_3$, 500 MHz, 298

3. X-Ray Crystallographic and Optimized Structure Details

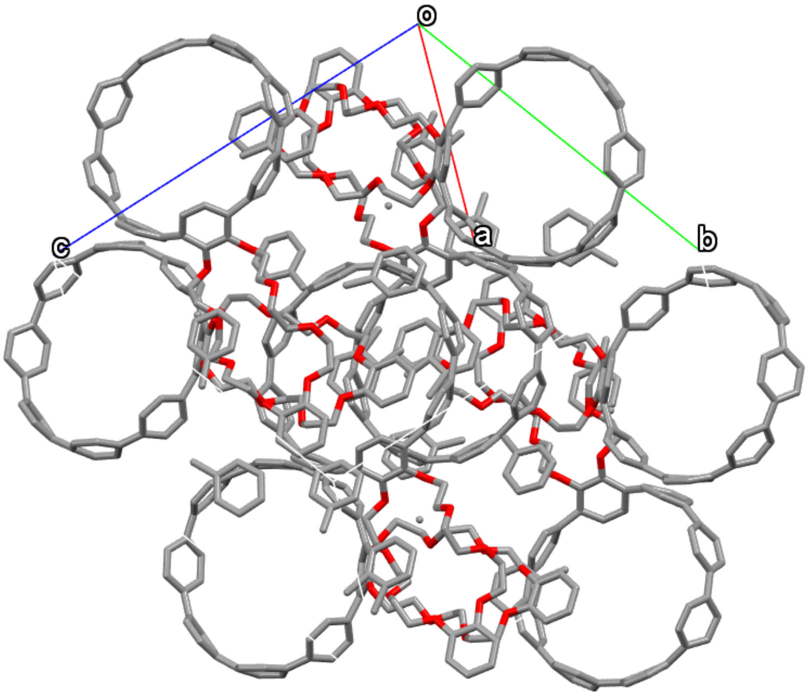


Figure S5. Solid-state structure of **6**, representation of the packing structure. The cif-file was deposited in the Cambridge Structural Database under identifier CCDC 2393490. Single crystals of **6** were prepared by slow diffusion of diisopropyl ether into toluene solution.

Table S1 Crystal data and structure refinement for 6

Empirical formula	$C_{66}H_{58}O_8$
Formula weight	1162.88
Temperature/K	150.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.9739(14)
b/Å	21.8794 (13)
c/Å	27.0805 (16)
α/°	90
β/°	106.434 (3)
γ/°	90
Volume/Å^3	12487.7 (1)
Z	8

ρ_{calc}g/cm^3	1.237
μ/mm^{-1}	0.620
F(000)	4940.0
Crystal size/mm^3	0.22 × 0.16 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.192 to 130.57
Index ranges	$-25 \leq h \leq 16$, $-23 \leq k \leq 25$, $-30 \leq l \leq 31$
Reflections collected	112251
Independent reflections	21290 [R_{int} = 0.1008, R_{sigma} = 0.0833]
Data/restraints/parameters	21290/170/1597
Goodness-of-fit on F^2	1.256
Final R indexes [I>=2σ (I)]	R_1 = 0.1140, wR_2 = 0.3217
Final R indexes [all data]	R_1 = 0.1527, wR_2 = 0.3659
Largest diff. peak/hole / e Å^{-3}	0.78/-0.50

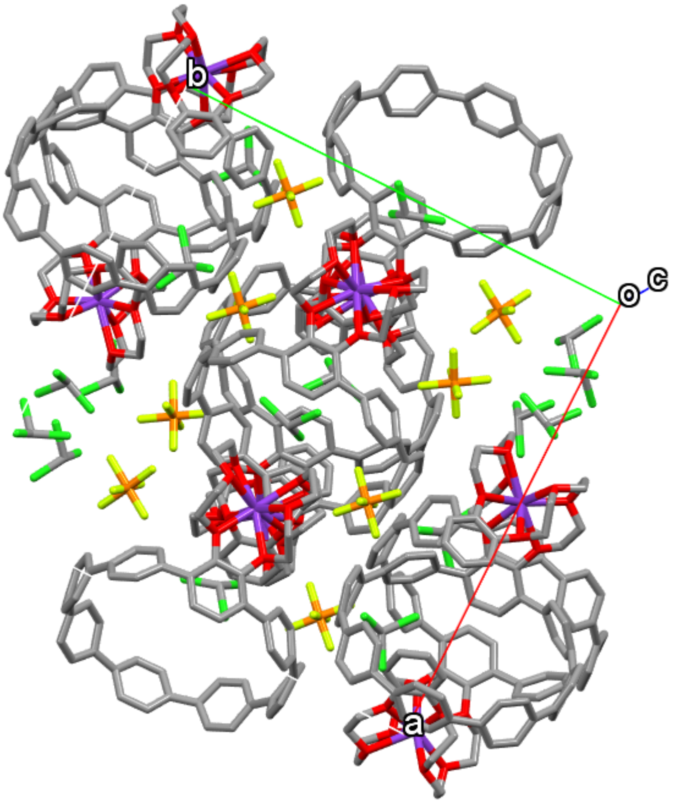


Figure S6. Solid-state structure of **6**⊃K$^+$, representation of the packing structure. The cif-file was deposited in the Cambridge Structural Database under identifier CCDC 2393489. Single crystals of **6**⊃K$^+$ were prepared by through slow evaporation of the $CHCl_3$

Table S2 Crystal data and structure refinement for 6⊃K$^+$

Empirical formula	$C_{66}H_{58}O_8K$
Formula weight	120.96
Temperature/K	150.00
Crystal system	monoclinic
Space group	*P*c
a/Å	23.096 (14)
b/Å	22.914 (16)
c/Å	25.886 (19)
α/°	90
β/°	90.17 (2)
γ/°	90
Volume/Å^3	13699 (16)

Z	8
ρ_{calc}g/cm^3	0.117
μ/mm^{-1}	0.836
F(000)	475.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	3.856 to 109.204
Index ranges	$-12 \leq h \leq 22$, $-23 \leq k \leq 22$, $-26 \leq l \leq 26$
Reflections collected	69783
Independent reflections	24391 [R_{int} = 0.0663, R_{sigma} = 0.0639]
Data/restraints/parameters	24391/2/1493
Goodness-of-fit on F^2	1.881
Final R indexes [I>=2σ (I)]	R_1 = 0.1597, wR_2 = 0.4154
Final R indexes [all data]	R_1 = 0.1861, wR_2 = 0.4383
Largest diff. peak/hole / e Å^{-3}	1.57/-1.46
Flack parameter	0.376 (4)

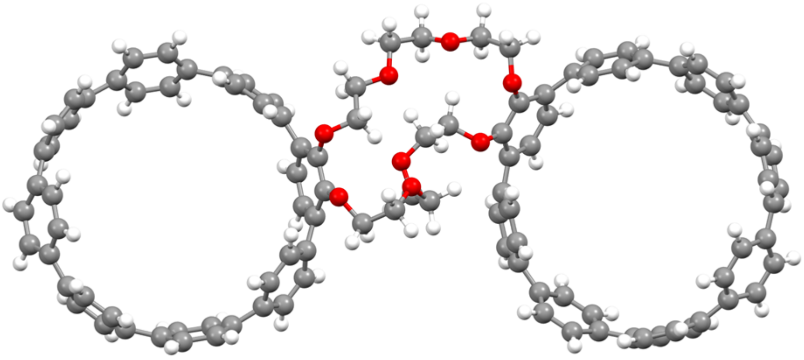


Figure S7. Optimized geometry of **7** obtained by DFT calculations at B3LYP/6-31G(d) level of theory.

Table S3. optimized structure of 7

C	13.440400	-3.039700	-1.720500
C	14.251000	-1.955600	-1.405400
C	14.508200	-1.600300	-0.069000
C	14.118900	-2.532300	0.910700
C	13.278900	-3.593300	0.598600
C	12.814100	-3.798900	-0.714100
C	10.737200	-4.122700	-2.057400
C	11.523000	-4.493500	-0.951000
C	10.886200	-5.269000	0.038000
C	9.506700	-5.452900	0.035700
C	8.700200	-4.885300	-0.966800
C	9.363300	-4.317200	-2.067500
C	7.270400	-4.549800	-0.769200
C	6.856900	-4.098500	0.496500
C	5.739400	-3.286200	0.644800
C	4.991500	-2.882200	-0.476400
C	5.270900	-3.521300	-1.698500
C	6.388500	-4.337300	-1.843500
C	3.620200	-1.107200	0.739300
C	3.360400	0.270600	0.881400
C	3.747000	1.183400	-0.121800
C	4.148700	0.637300	-1.355000
C	4.382200	-0.718300	-1.504900
C	4.230200	-1.608200	-0.425300
C	4.187400	3.563000	-0.860300
C	5.048800	4.652800	-0.771700
C	5.894000	4.817900	0.339800
C	5.682300	3.966400	1.438000
C	4.826300	2.875900	1.349800
C	4.144500	2.589100	0.153200
C	13.099200	4.452900	1.726000
C	13.696600	3.911400	0.572900
C	13.298500	4.467400	-0.656100
C	12.205100	5.321200	-0.741300
C	11.431000	5.631000	0.392900
C	11.984600	5.276700	1.637800
C	9.990200	5.974800	0.283800
C	9.297700	5.673300	-0.903300
C	7.923300	5.479800	-0.911100
C	7.169800	5.568700	0.271100
C	7.824200	6.081900	1.404700
C	9.200200	6.289900	1.407000
C	15.352900	0.734400	-0.635000
C	15.150800	2.103100	-0.476100
C	14.407000	2.610600	0.606300
C	14.071300	1.696700	1.620900
C	14.272000	0.334700	1.462600
C	14.820300	-0.193600	0.280400
O	3.379400	-1.922300	1.820900
O	2.852700	0.657800	2.088300
C	-10.029100	6.046100	-1.849900
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C	-4.040700	0.983100	-0.306100
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C	-7.567900	-5.101700	-1.430800
C	-8.913700	-5.324800	-1.154000
C	-9.484600	-4.888600	0.054600
C	-8.605400	-4.425700	1.049300
C	-7.262600	-4.200400	0.774900
C	-6.742800	-4.428600	-0.512500
C	-14.313400	0.245900	2.155500
C	-14.548400	1.054800	1.028300
C	-14.795700	0.382200	-0.181900
C	-14.575800	-0.984500	-0.305900
C	-14.060700	-1.740700	0.763900
C	-14.058300	-1.112900	2.023700
C	-13.252300	-2.965400	0.534800
C	-12.707500	-3.202600	-0.740400
C	-11.577300	-3.990000	-0.910100
C	-10.926700	-4.575100	0.188800
C	-11.591900	-4.517300	1.426100
C	-12.733900	-3.739500	1.591800
C	-13.811200	4.527200	-0.273300
C	-14.551400	3.375200	-0.019900
C	-14.200200	2.495900	1.022300
C	-13.213600	2.945300	1.917600
C	-12.477100	4.092000	1.665800
C	-12.683900	4.856100	0.503700
O	-2.900500	-1.605700	0.611300
O	-4.205400	-3.917200	1.073900
C	-4.135600	-5.349500	1.032100
C	-3.014900	-5.875000	0.155000
O	-1.772200	-5.638700	0.787500
C	-0.668900	-5.923500	-0.049300
C	0.626700	-5.663600	0.692900
O	0.724800	-4.297100	1.041200
C	2.067300	-3.849000	1.177500
C	2.052600	-2.484600	1.857400
C	-1.629700	-2.305300	0.616200
C	-0.763000	-1.978300	-0.605400
O	0.239100	-0.990100	-0.408800
C	-0.173800	0.361700	-0.339300
C	-0.809700	0.756500	0.996000
O	-0.058800	0.296600	2.117200
C	0.659900	1.275300	2.835900
C	1.928000	1.746900	2.142500
H	13.202900	-3.219200	-2.764000
H	14.575100	-1.301300	-2.208600
H	14.380600	-2.364700	1.950900
H	12.881300	-4.188800	1.413700
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H	8.780700	-3.878000	-2.871100
H	7.502300	-4.259000	1.354800
H	5.514900	-2.855900	1.612900
H	4.656300	-3.305900	-2.568100
H	6.625600	-4.745200	-2.822500
H	4.448700	1.310400	-2.151000
H	4.845100	-1.070900	-2.419700
H	3.608700	3.416300	-1.768300
H	5.124500	5.340200	-1.609900
H	6.309500	4.068900	2.318300
H	4.794200	2.159800	2.164000
H	13.437500	4.138700	2.708600
H	13.761800	4.126300	-1.576600
H	11.887200	5.653700	-1.724100
H	11.469200	5.540200	2.555200
H	9.847900	5.438200	-1.807100
H	7.454600	5.100800	-1.813800
H	7.262200	6.246400	2.320100
H	9.672600	6.621700	2.326500
H	15.866200	0.381100	-1.524900
H	15.512300	2.778500	-1.246500
H	13.503500	2.032400	2.481300
H	13.852000	-0.332800	2.206400

H	-9.866700	6.016900	-2.922300
H	-12.080400	5.511200	-2.082200
H	-10.712300	6.182800	1.935800
H	-8.465000	6.539100	1.110900
H	-8.151400	4.963200	-3.270100
H	-6.511600	6.615200	0.349700
H	-4.540000	5.205100	0.086900
H	-6.179100	3.593400	-3.539900
H	-4.618700	2.867900	0.514500
H	-4.115000	0.479700	0.650300
H	-3.483600	0.366900	-3.594100
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H	-7.175400	-5.368300	-2.408400
H	-9.547100	-5.768000	-1.917600
H	-9.007300	-4.094000	2.001700
H	-6.639300	-3.718600	1.520700
H	-14.217500	0.700300	3.136700
H	-15.034600	0.950900	-1.075100
H	-14.700200	-1.439200	-1.283200
H	-13.730900	-1.659600	2.901600
H	-13.074500	-2.650800	-1.598000
H	-11.105200	-4.021300	-1.887100
H	-11.168000	-5.025600	2.287900
H	-13.175200	-3.671100	2.581300
H	-14.069900	5.137000	-1.134300
H	-15.367000	3.119300	-0.690400
H	-12.906800	2.312800	2.742800
H	-11.627700	4.304100	2.305200
H	-5.087700	-5.775200	0.701900
H	-3.959800	-5.646100	2.068500
H	-3.052500	-5.386300	-0.831700
H	-3.164800	-6.956400	-0.006100
H	-0.688200	-6.979800	-0.368600
H	-0.707200	-5.299200	-0.956600
H	0.678700	-6.293500	1.594500
H	1.454500	-5.957200	0.028000
H	2.661400	-4.558400	1.773200
H	2.539400	-3.771800	0.188200
H	1.346200	-1.813000	1.368400
H	1.784100	-2.579500	2.912800
H	-1.813000	-3.376500	0.688200
H	-1.129700	-1.986300	1.530900
H	-0.198400	-2.874100	-0.870000
H	-1.405600	-1.707100	-1.456900
H	-0.889000	0.596700	-1.144100
H	0.741600	0.936000	-0.513700
H	-0.933100	1.850000	1.020100
H	-1.800600	0.309900	1.078400
H	0.928700	0.811700	3.790300
H	0.026800	2.154100	3.046500
H	2.382600	2.567800	2.710700
H	1.713200	2.120300	1.137700

4. Photophysical properties.

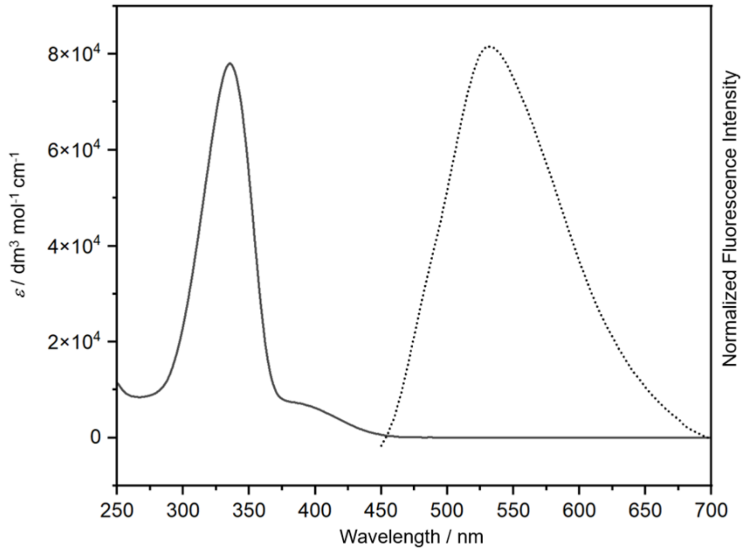


Figure S8. UV-Vis absorbance (solid lines) and fluorescence (dashed lines) spectra for **5** (conc. 1.0×10^{-6} M in dichloromethane).

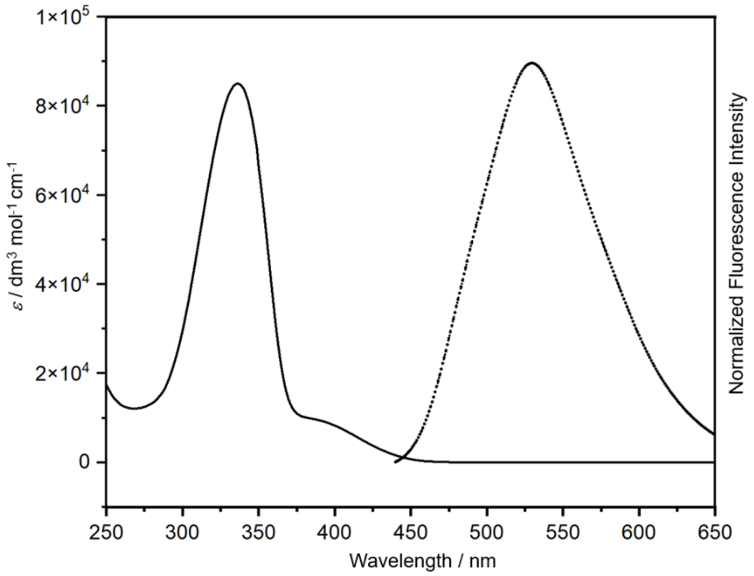


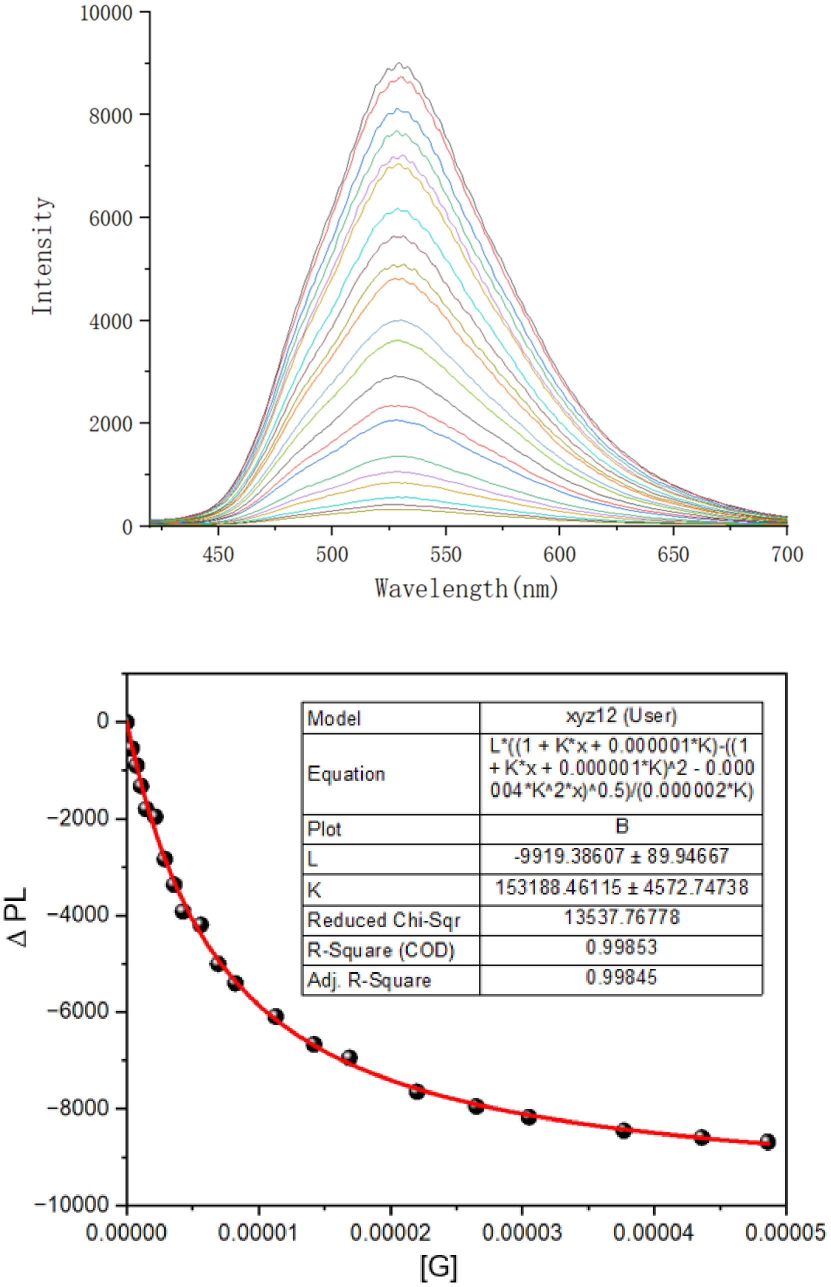
Figure S9. UV-Vis absorbance (solid lines) and fluorescence (dashed lines) spectra for **6** (conc. 5.0×10^{-6} M in dichloromethane).

5. Guest Recognition and Gas Sensing

K_{assoc} values were evaluated by applying a nonlinear curve-fitting method to photoluminescence changes (ΔPL) observed for the host molecules upon titration with C_{60} or C_{70}:

$\Delta PL = (L(1 + K_{assoc}X + K_{assoc}A) - (L^2 (K_{assoc}X + K_{assoc}A + 1)^2 - 4K_{assoc}{}^2 AXL^2)^{0.5})/2K_{assoc}A$

where X and A represent $[\mathrm{Guest}]_{total}$ and $[\mathrm{Host}]_{total}$, respectively; L denotes ΔPL at 100% complexation; L and K_{assoc} are parameters.



Model	xyz12 (User)
Equation	L*((1 + K*x + 0.000001*K)-((1 + K*x + 0.000001*K)^2 - 0.000004*K^2*x)^0.5)/(0.000002*K)
Plot	B
L	-9919.38607 ± 89.94667
K	153188.46115 ± 4572.74738
Reduced Chi-Sqr	13537.76778
R-Square (COD)	0.99853
Adj. R-Square	0.99845

Figure S10. Fluorescence spectra and fluorescence titration of C_{60} in the presence of **6** (0.0-1.0×10^{-6} M) in toluene.

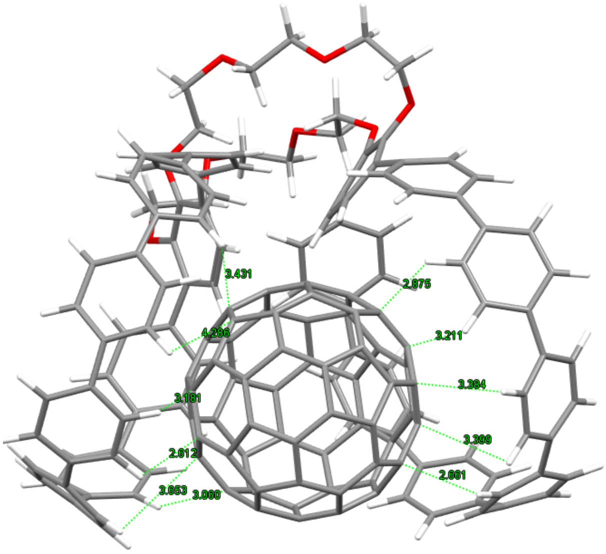


Figure S11. Optimized geometry of **7**⊃C_{60} (1:1) obtained by DFT calculations at B3LYP/6-31G(d) level of theory.

Table S4. optimized structure of 7⊃C_{60}

O	-6.393300	3.831500	0.539600
O	-8.479200	2.345200	-2.092000
O	-7.347000	-0.627800	-3.710900
O	-6.398400	-3.339300	-3.040600
O	-5.487100	4.061500	3.252500
O	-8.676500	2.336800	3.126400
O	-8.870000	-0.223300	1.746500
O	-7.257700	-2.432600	-0.650700
C	-5.539200	-2.560400	-2.304500
C	-5.968300	-2.146600	-1.029300
C	-5.071200	-1.512700	-0.149400
C	-3.830300	-1.109700	-0.658400
C	-3.426100	-1.473000	-1.931700
C	-4.226700	-2.290600	-2.743500
C	1.041900	-4.807300	-4.846800
C	-0.206600	-5.425800	-5.033100
C	-0.220000	-6.833000	-4.961200
C	0.866600	-7.537100	-4.458000
C	2.021800	-6.869900	-4.004100
C	2.130400	-5.511500	-4.345400
C	2.332400	-8.367600	-2.049900
C	2.875700	-8.579100	-0.791900
C	4.010500	-7.874100	-0.351600
C	4.679800	-7.098100	-1.318200
C	4.133700	-6.884700	-2.581400
C	2.890600	-7.437700	-2.945000
C	3.609300	-8.577800	2.042800
C	3.272700	-8.130600	3.313200
C	3.532400	-6.803400	3.712000
C	4.416500	-6.078100	2.895500
C	4.754500	-6.525600	1.623100
C	4.224300	-7.720600	1.108200
C	-1.448100	-3.217300	-5.094200
C	-2.454300	-2.440100	-4.529900
C	-3.517100	-3.027600	-3.820200
C	-3.638800	-4.425500	-3.889100
C	-2.622200	-5.198800	-4.436600
C	-1.450600	-4.619200	-4.959500
C	-5.148600	-1.551500	1.336000
C	-5.202400	-2.818600	1.941500

C	-4.663000	-3.017000	3.205600
C	-4.051900	-1.959900	3.907100
C	-4.227700	-0.662000	3.400100
C	-4.768200	-0.461400	2.130100
C	-2.988400	-2.312000	4.879400
C	-3.050400	-3.457500	5.692000
C	-1.889900	-4.076200	6.143700
C	-0.617100	-3.583400	5.795000
C	-0.572400	-2.317600	5.186500
C	-1.732500	-1.697700	4.735200
C	1.893900	-3.984300	5.636800
C	0.575100	-4.464600	5.744100
C	0.383500	-5.834300	5.493500
C	1.401100	-6.628300	4.986600
C	2.673800	-6.102600	4.699300
C	2.916700	-4.783500	5.131900
C	-3.155700	2.119100	0.406400
C	-2.753500	2.211300	1.725300
C	-3.501100	2.927200	2.667400
C	-4.768800	3.418300	2.280200
C	-5.178800	3.315000	0.929000
C	-4.332700	2.731500	-0.031900
C	-7.307000	2.864200	-0.030700
C	-7.856000	3.390500	-1.357900
C	-7.546900	1.507000	-2.754200
C	-8.308200	0.366000	-3.407200
C	-7.895300	-1.820800	-4.229200
C	-6.785000	-2.849600	-4.328900
C	-6.909500	3.884800	3.326700
C	-7.304800	2.416000	3.478000
C	-9.361700	1.200400	3.619300
C	-8.820100	-0.143800	3.156900
C	-8.452900	-1.493800	1.266100
C	-8.016900	-1.305400	-0.182500
C	-0.935800	2.820600	-4.933500
C	-2.012600	3.724800	-4.915800
C	-1.799300	4.978300	-5.517900
C	-0.523800	5.384500	-5.893700
C	0.596400	4.557000	-5.682400
C	0.337100	3.226500	-5.314500
C	2.096800	6.422900	-5.025700
C	3.254500	6.847200	-4.390700
C	4.346000	5.982200	-4.195700
C	4.282700	4.734100	-4.845500
C	3.119800	4.307300	-5.481000
C	1.961500	5.107600	-5.502200
C	5.416100	7.571100	-2.547000
C	5.795700	7.754700	-1.223600
C	6.093300	6.654300	-0.396300
C	6.270300	5.420000	-1.041800
C	5.873600	5.231500	-2.360800
C	5.302200	6.279700	-3.101800
C	-3.512700	2.152700	-3.625500
C	-4.112600	1.907000	-2.395400
C	-4.384100	2.955800	-1.503900
C	-4.258600	4.268800	-1.983600
C	-3.642000	4.512300	-3.207500
C	-3.144700	3.457800	-3.996500
C	-2.747400	3.324000	3.886100
C	-1.870300	2.421700	4.512300
C	-0.737600	2.866600	5.184300
C	-0.417200	4.236300	5.231400
C	-1.417800	5.132300	4.808700
C	-2.567300	4.688600	4.162800
C	0.984400	4.707200	5.366800
C	2.035000	3.836400	5.028200
C	3.266800	4.315800	4.602500
C	3.513100	5.694800	4.501000
C	2.554100	6.549600	5.078600
C	1.320200	6.068200	5.501900

C	4.255700	7.328000	2.783200
C	4.537500	6.182200	3.547100
C	5.637200	5.404100	3.137700
C	6.283300	5.646300	1.929200
C	5.860100	6.677300	1.068200
C	4.899200	7.568800	1.577500
H	-3.132700	-0.617400	0.006800
H	-2.416800	-1.248400	-2.249200
H	1.134700	-3.732800	-4.945800
H	-1.120800	-7.381100	-5.219100
H	0.781300	-8.612800	-4.336700
H	3.021200	-4.957000	-4.075400
H	1.376600	-8.825800	-2.278900
H	2.319600	-9.193700	-0.093000
H	5.603000	-6.588700	-1.058500
H	4.648300	-6.216300	-3.265400
H	3.304900	-9.576400	1.744500
H	2.717800	-8.796600	3.966400
H	4.727400	-5.082000	3.183600
H	5.307500	-5.856600	0.975500
H	-0.610500	-2.717700	-5.571400
H	-2.367500	-1.357100	-4.563000
H	-4.471600	-4.909500	-3.390900
H	-2.686200	-6.275900	-4.326400
H	-5.536700	-3.670900	1.357800
H	-4.564800	-4.030700	3.581500
H	-3.852800	0.193500	3.952700
H	-4.783800	0.536100	1.710300
H	-4.013400	-3.915600	5.901000
H	-1.972500	-5.001300	6.706500
H	0.383900	-1.878800	4.927800
H	-1.640500	-0.812900	4.114300
H	2.113700	-2.950300	5.886000
H	-0.613100	-6.257000	5.561200
H	1.152700	-7.638400	4.681600
H	3.900500	-4.342700	5.004300
H	-2.500100	1.677600	-0.330500
H	-1.787600	1.826900	2.019600
H	-8.106800	2.670900	0.691300
H	-6.770100	1.927300	-0.195500
H	-7.039500	3.844600	-1.934100
H	-8.623400	4.150900	-1.186100
H	-6.966100	2.074700	-3.495500
H	-6.827500	1.061400	-2.055800
H	-8.837500	0.696800	-4.314300
H	-9.059900	-0.015200	-2.700400
H	-8.688200	-2.204000	-3.568400
H	-8.332500	-1.650900	-5.228800
H	-7.139000	-3.725700	-4.879400
H	-5.923600	-2.426100	-4.857100
H	-7.207000	4.456200	4.208400
H	-7.400000	4.303300	2.449000
H	-7.138000	2.072200	4.510400
H	-6.696500	1.784400	2.816700
H	-10.393300	1.314700	3.274300
H	-9.360400	1.202400	4.722900
H	-7.786100	-0.295800	3.506400
H	-9.438700	-0.931600	3.620700
H	-9.269200	-2.228500	1.348700
H	-7.604400	-1.865900	1.847500
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H	-8.884100	-1.192800	-0.841100
H	-1.055300	1.834700	-4.495500
H	-2.626900	5.675100	-5.617200
H	-0.386300	6.389600	-6.281300
H	1.160900	2.537600	-5.173800
H	1.235700	7.082300	-5.019100
H	3.248200	7.821300	-3.914700
H	5.126300	4.052600	-4.793000
H	3.093400	3.307200	-5.904100

H	5.113500	8.437300	-3.127300
H	5.771400	8.756600	-0.805000
H	6.561600	4.552100	-0.465100
H	5.868700	4.221400	-2.755900
H	-3.238200	1.310100	-4.254400
H	-4.275800	0.884000	-2.081700
H	-4.500800	5.100200	-1.328600
H	-3.400200	5.536800	-3.472500
H	-2.021000	1.354100	4.389700
H	-0.050300	2.130000	5.589100
H	-1.234000	6.200900	4.849400
H	-3.256700	5.411000	3.738500
H	1.847900	2.772800	4.947100
H	3.986200	3.608400	4.203900
H	2.743400	7.618200	5.123900
H	0.580400	6.775400	5.864800
H	3.419500	7.962200	3.057700
H	5.945700	4.550700	3.734300
H	7.078400	4.974800	1.618300
H	4.538600	8.380800	0.955300
C	5.754300	-2.592700	-0.830300
C	6.409900	-1.527400	-0.086900
C	6.016400	-1.644200	1.309400
C	5.117200	-2.781000	1.428300
C	4.954400	-3.366600	0.106000
C	3.714200	-3.871400	-0.283400
C	2.584100	-3.820200	0.631200
C	2.738800	-3.256800	1.896700
C	4.031800	-2.725500	2.302800
C	3.800900	-1.531700	3.100500
C	4.662800	-0.439800	2.986200
C	5.793600	-0.497100	2.071900
C	5.953400	0.817800	1.470300
C	6.328400	0.928900	0.130700
C	6.562700	-0.267100	-0.664300
C	6.067200	-0.018200	-2.010200
C	5.526700	1.332200	-2.047600
C	5.685500	1.914100	-0.723100
C	4.693800	2.745200	-0.204700
C	4.305700	2.635400	1.191700
C	4.921600	1.689400	2.011900
C	4.124100	0.911600	2.949900
C	2.745900	1.112800	3.024600
C	1.846600	-0.025200	3.148900
C	2.363200	-1.321300	3.182300
C	1.707200	-2.388900	2.439700
C	0.561200	-2.116900	1.693900
C	0.399400	-2.702900	0.370300
C	1.389200	-3.536900	-0.150100
C	1.782300	-3.415700	-1.545900
C	1.171100	-2.467500	-2.364800
C	0.141600	-1.597900	-1.824300
C	-0.233800	-1.712600	-0.485500
C	-0.463800	-0.515300	0.307500
C	0.024700	-0.764200	1.655600
C	0.651600	0.259800	2.367100
C	0.817000	1.573900	1.761500
C	2.106900	2.102000	2.168800
C	2.869000	2.850400	1.273300
C	2.374200	3.100900	-0.072800
C	3.504100	3.039700	-0.987100
C	3.349400	2.479900	-2.254600
C	4.382300	1.608100	-2.796800
C	3.727800	0.541500	-3.540500
C	2.290300	0.752900	-3.456400
C	2.057900	1.951100	-2.661800
C	0.973100	2.008300	-1.788800
C	1.135600	2.594100	-0.466000
C	0.347400	1.811100	0.470500
C	-0.302100	0.742500	-0.271100

C	0.078400	0.866400	-1.669300	C	4.244700	-0.754500	-3.503900
C	0.297700	-0.282300	-2.430100	C	5.439600	-1.040100	-2.723300
C	1.428100	-0.339900	-3.346100	C	5.279800	-2.354700	-2.120600
C	1.968200	-1.690900	-3.304800	C	3.985700	-2.881400	-2.526500
C	3.346700	-1.893300	-3.383900	C	3.219700	-3.622700	-1.626500

Fabrication of gas sensors

The fabrication process of film electrodes involved a straightforward solution-based quasi-Langmuir-Shäfer (QLS) technique (**Figure S6**).[S8] Firstly, the **7**⊃C_{60} complex was ultrasonically dissolved in chloroform. A small amount of the dispersion was then gently dropped onto the surface of ultrapure water. As the chloroform evaporated, the **7**⊃C_{60} complex or **7** self-assembled to dense thin film at the ultrapure water interface. Subsequently, the film was easily transferred from the water surface onto the substrate of ITO IDEs, resulting in the **7**⊃C_{60} complex or **7** QLS film electrodes.

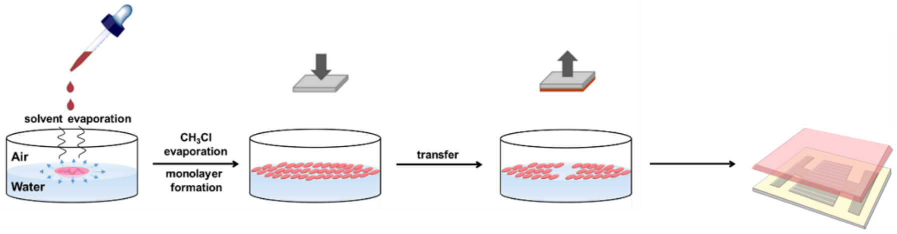

Figure S12. The fabrication of film electrodes by QLS method.

I-V test

The current-voltage (***I-V***) characteristics were obtained using a Keysight B2911B Precision Source/Measurement Unit system at room temperature in air. Current-voltage (I-V) curves were registered in the -10 to 10 V voltage range, starting and finishing at 0 V bias to avoid irreversible polarization effects.

The conductivity can be calculated according to the following equation:

$$\sigma = \frac{dI}{(2n-1)LhV} \quad (1)$$

where d is the interelectrode spacing, I the current, n the number of electrode digits, L the overlapping length of the electrodes, and h the electrode thickness as the microstructures thickness exceeds that of the ITO electrodes in the present case.

The gas sensing performance test

The sensing performance of the fabricated sensors was monitored at room temperature. The fabricated sensors were connected to the precision measurement system (Keysight B2911B). The gas inlet and outlet are mounted at the opposite ends of the chamber through which the analyte can pass. The NO_2 and NH_3 were diluted directly to the desired concentration by mixing with dry synthetic air. The vapor of methyl alcohol (MeOH), ethyl alcohol (EtOH), triethylamine (TEA), tetrahydrofuran (THF), H_2O were obtained by volatilization of the compound liquid and diluted with dry synthetic air to the desired concentrations. The steady-state baseline resistance curve of the fabricated sensor was recorded in the dry air first under a constant applied voltage of 10 V, and then the analytes was injected into the chamber and the corresponding resistance change of the fabricated sensor was test and record under a constant applied voltage of 10 V. The interval for recording resistance was set 0.5 s. The response in this work is defined as $(R_t\text{-}R_0)/R_0 \times 100\%$. R_0: initial resistance; R_t: real time resistance.

Data processing

The theoretical limits of detection (LOD) were calculated using reported protocols.[S9] The noise-based deviation in $\Delta R/R_0$ (%) was calculated as the root mean squared (rms) value of the baseline trace before exposure to analyte. The sum of squared residuals (SSR) V_x^2 was then calculated using Equation (2), where y_i is measured $\Delta R/R_0$ (%) and y is the value calculated from the polynomial fit. The root-mean-square deviation (rms_{noise}) was calculated by Equation (3).

$$V_x^2 = \sum (y_i - y)^2 \quad (2)$$

$$rms_{noise} = \sqrt{\frac{V_x^2}{N}} \quad (3)$$

The plots for concentration of analyte versus response ($\Delta R/R_0$ (%)) after a specific exposure time were isolated wherein this relationship was linear (slope = m). The theoretical LOD was calculated from Equation 4.

$$LOD = 3 \times \frac{rms_{noise}}{m} \quad (4)$$

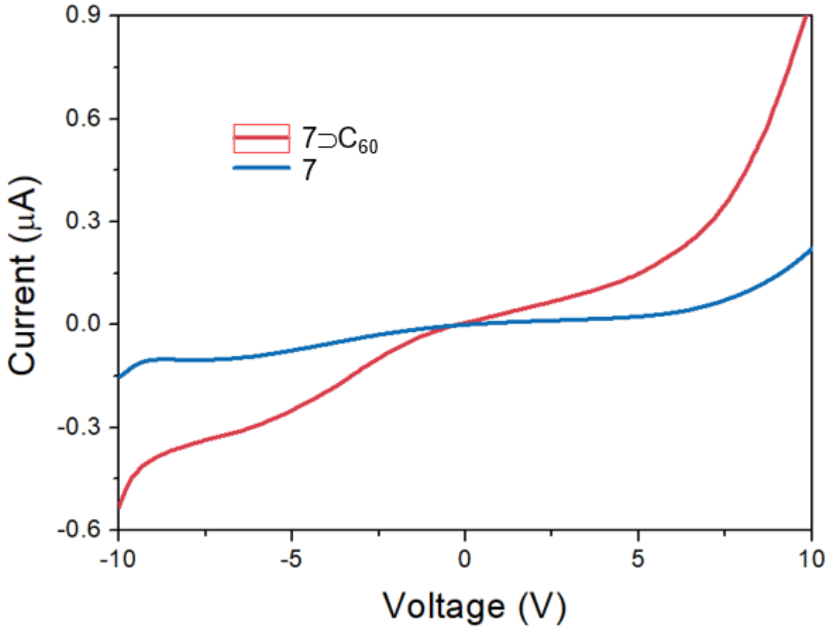

Figure S13. *I–V* curves of the **7**⊃C_{60} complex and **7**

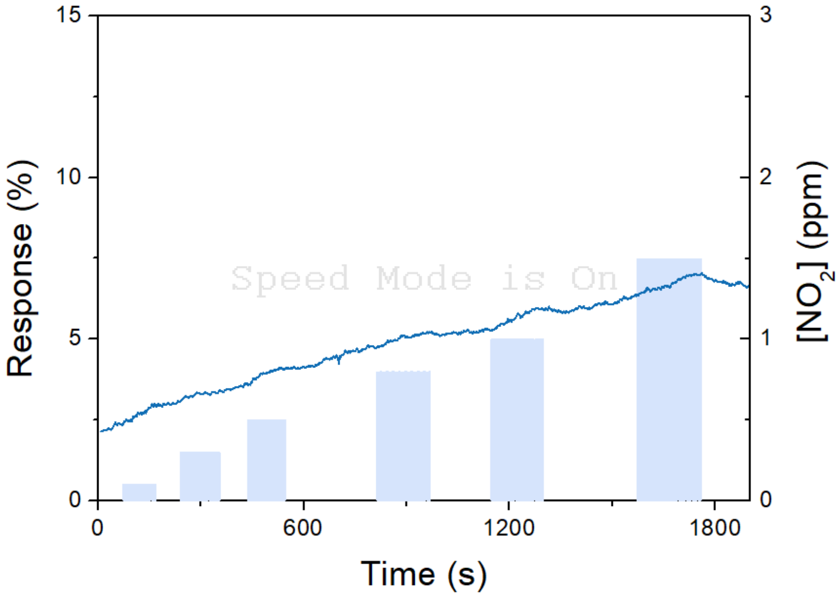

Figure S14. Dynamic response curves of **7** toward 0.1–1.5 ppm NO_2

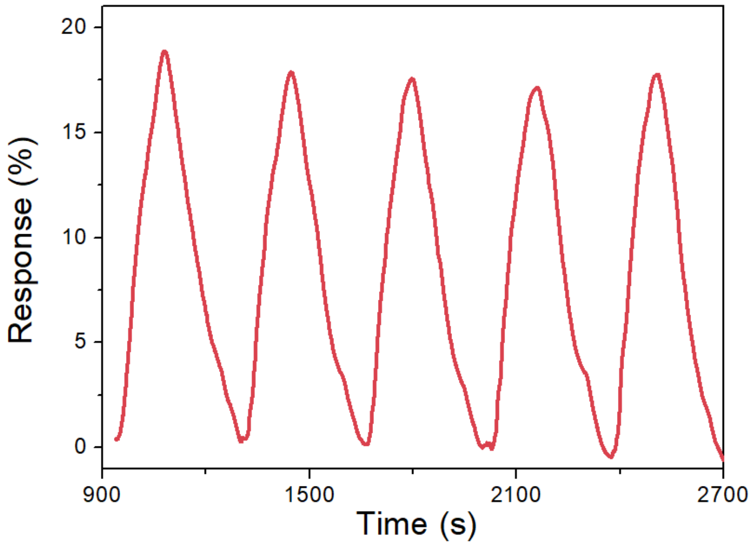

Figure S15. Reproducibility of the **7**$\supset$$C_{60}$ complex for 1 ppm NO_2.

6. NMR Spectra

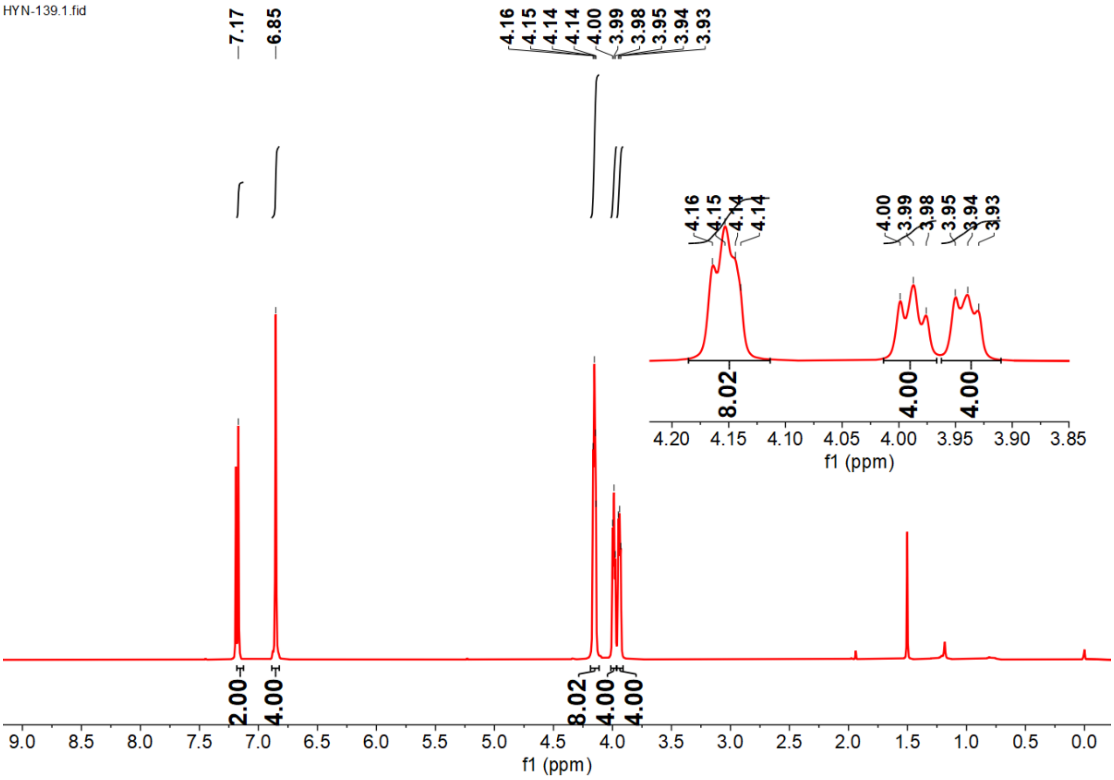

Figure S16. ^{1}H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of **1**.

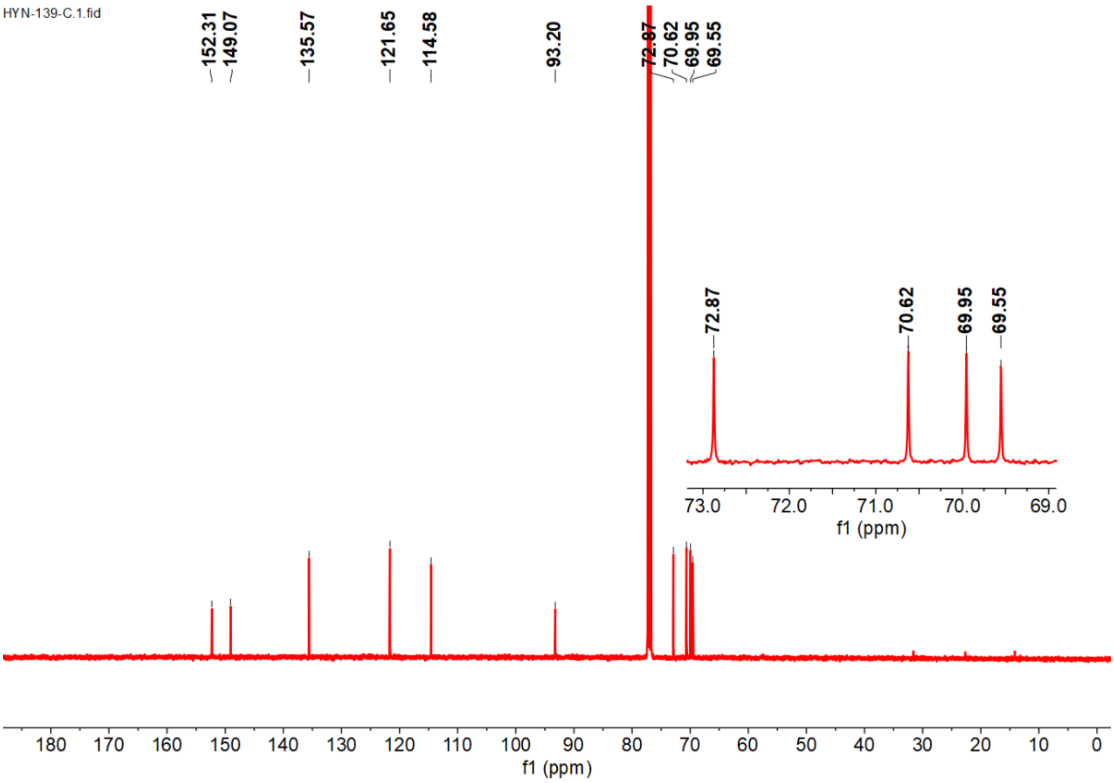

Figure S17. ^{13}C{^{1}H} NMR spectrum (125 MHz, 298 K, CDCl$_3$) of **1**.

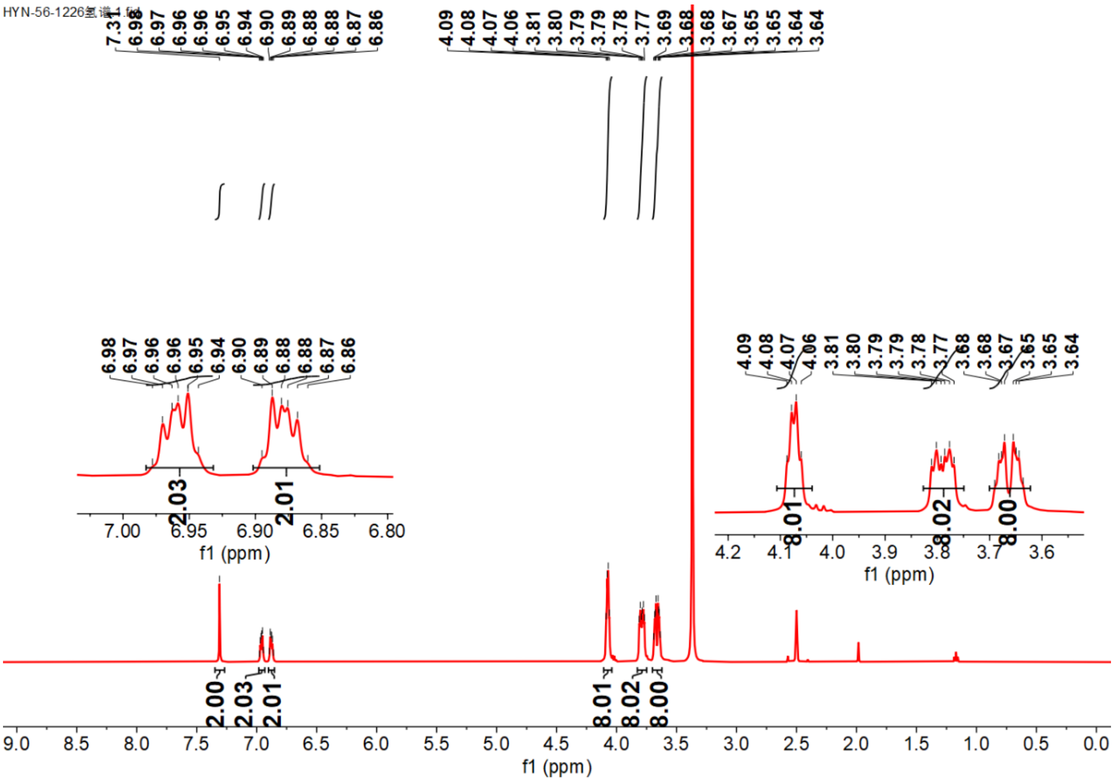

Figure S18. ^{1}H NMR spectrum (500 MHz, 298 K, DMSO-d_6) of **2**.

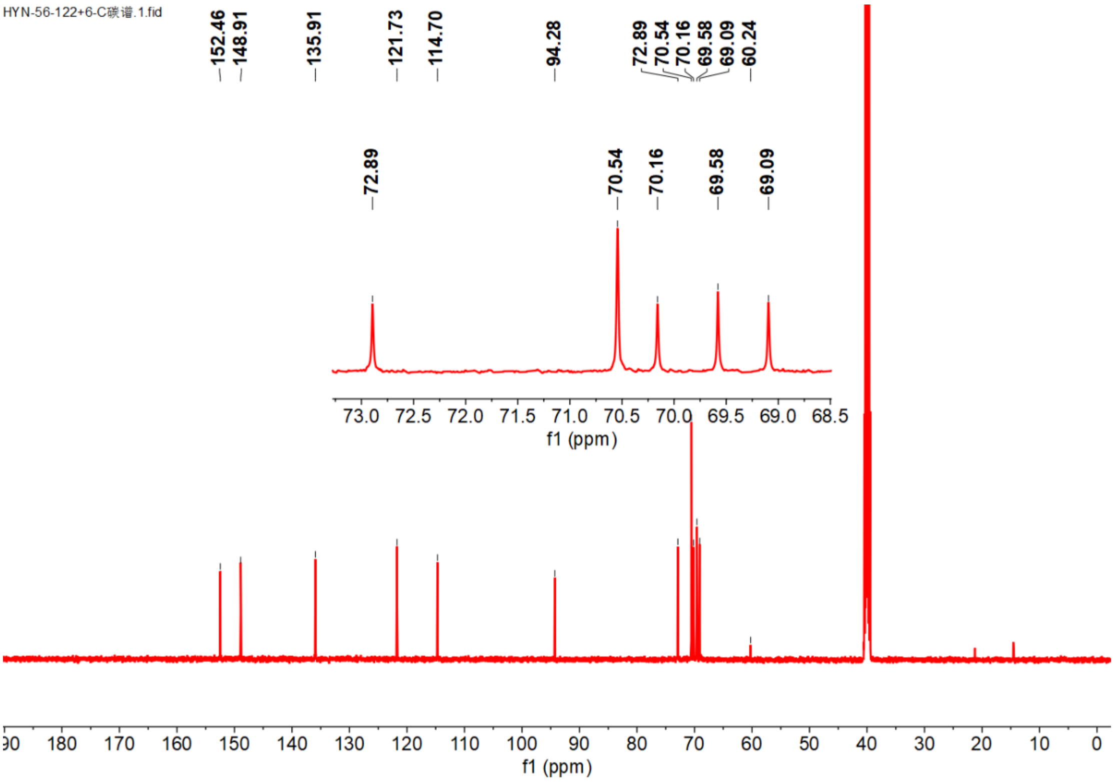

Figure S19. ^{13}C{^{1}H} NMR spectrum (125 MHz, 298 K, DMSO-d_6) of **2**.

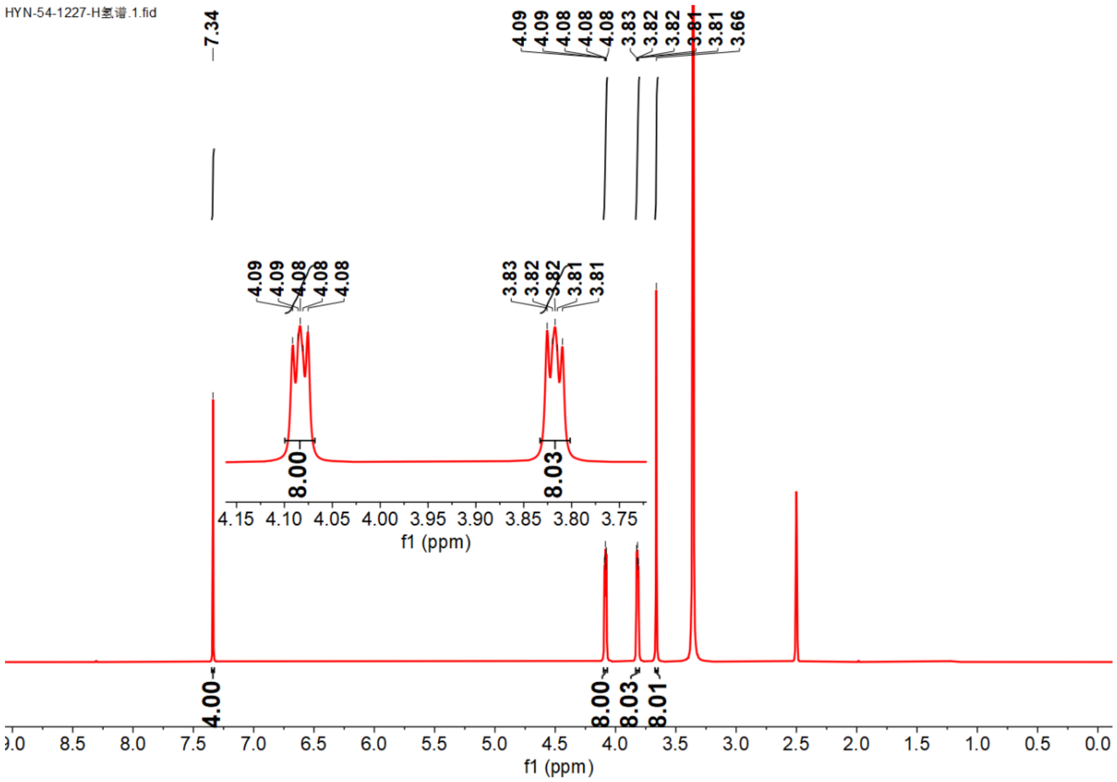

Figure S20. ^{1}H NMR spectrum (500 MHz, 298 K, DMSO-d_6) of **3**.

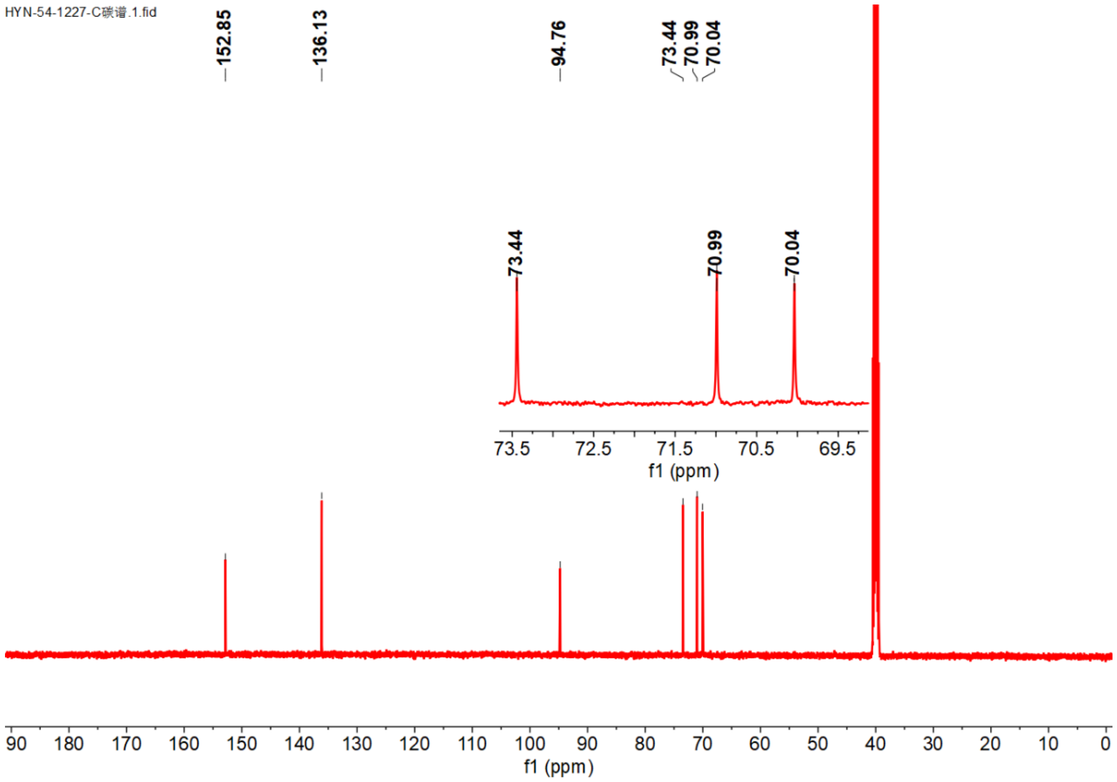

Figure S21. ^{13}C{^{1}H} NMR spectrum (125 MHz, 298 K, DMSO-d_6) of **3**.

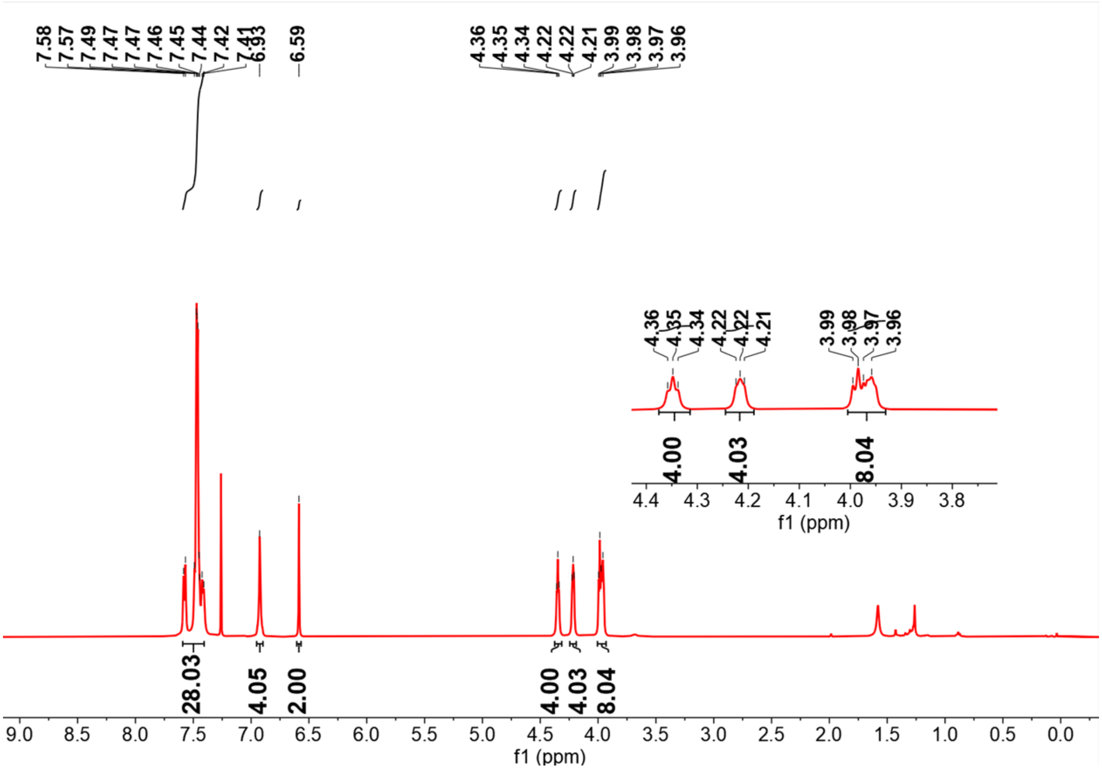

Figure S22. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **5**.

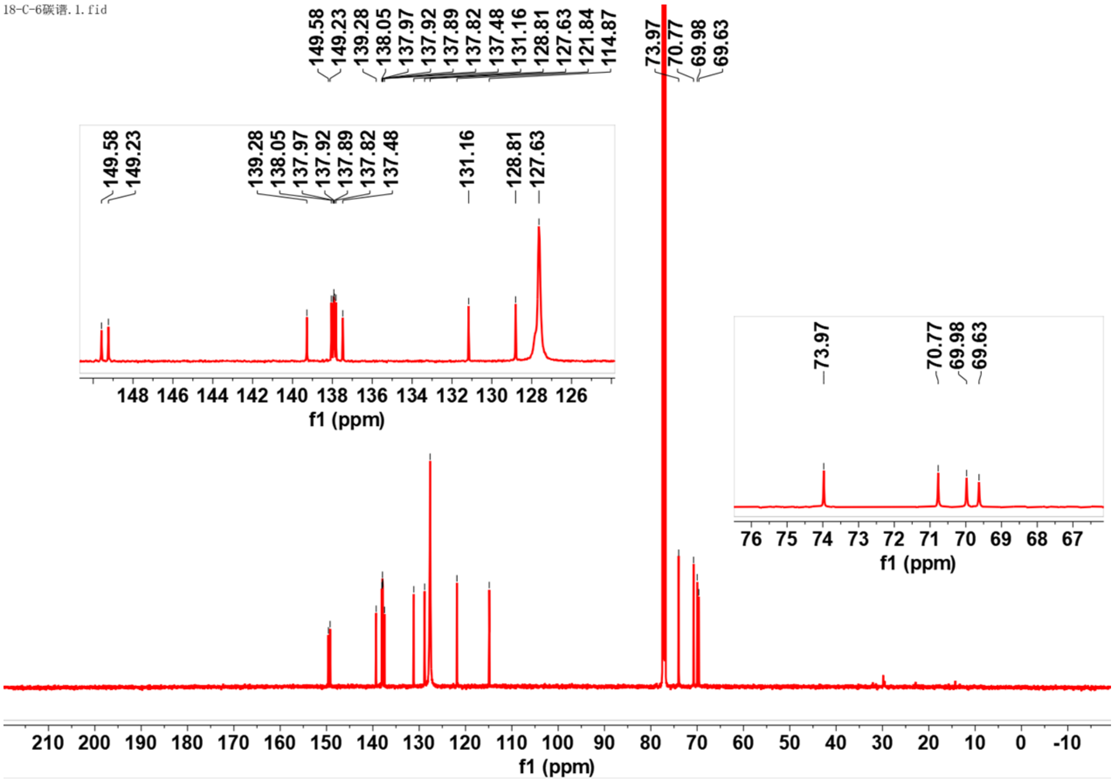

Figure S23. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **5**.

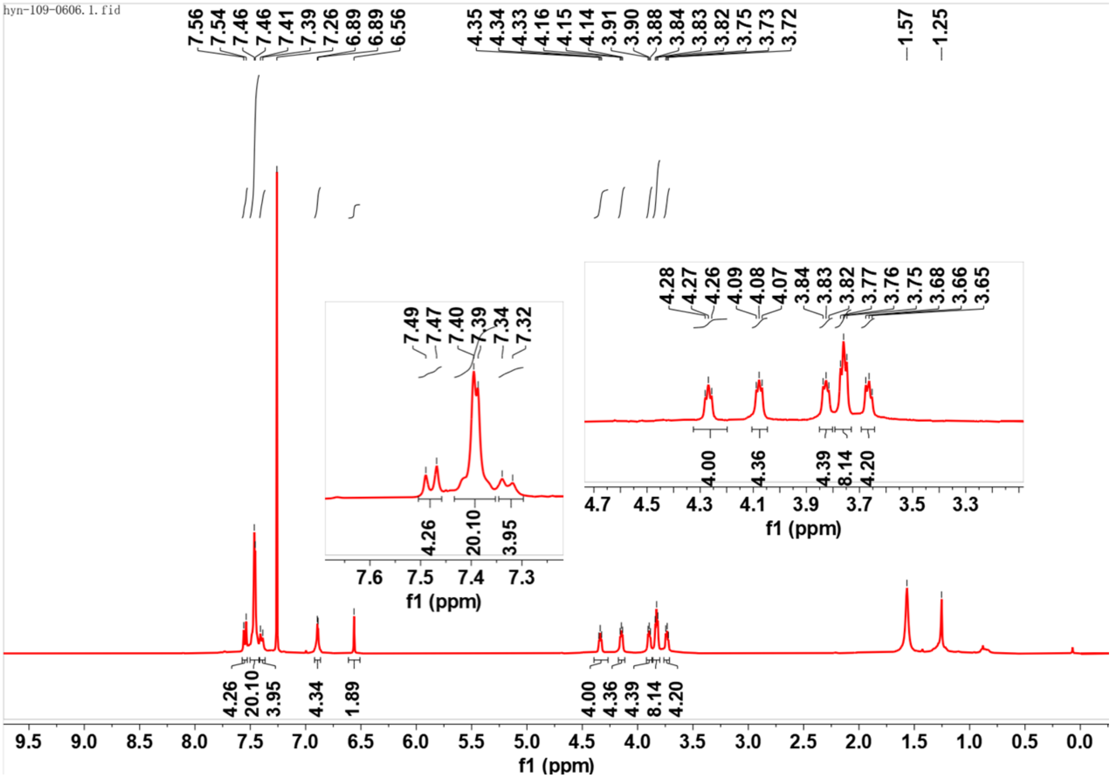

Figure S24. ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **6**.

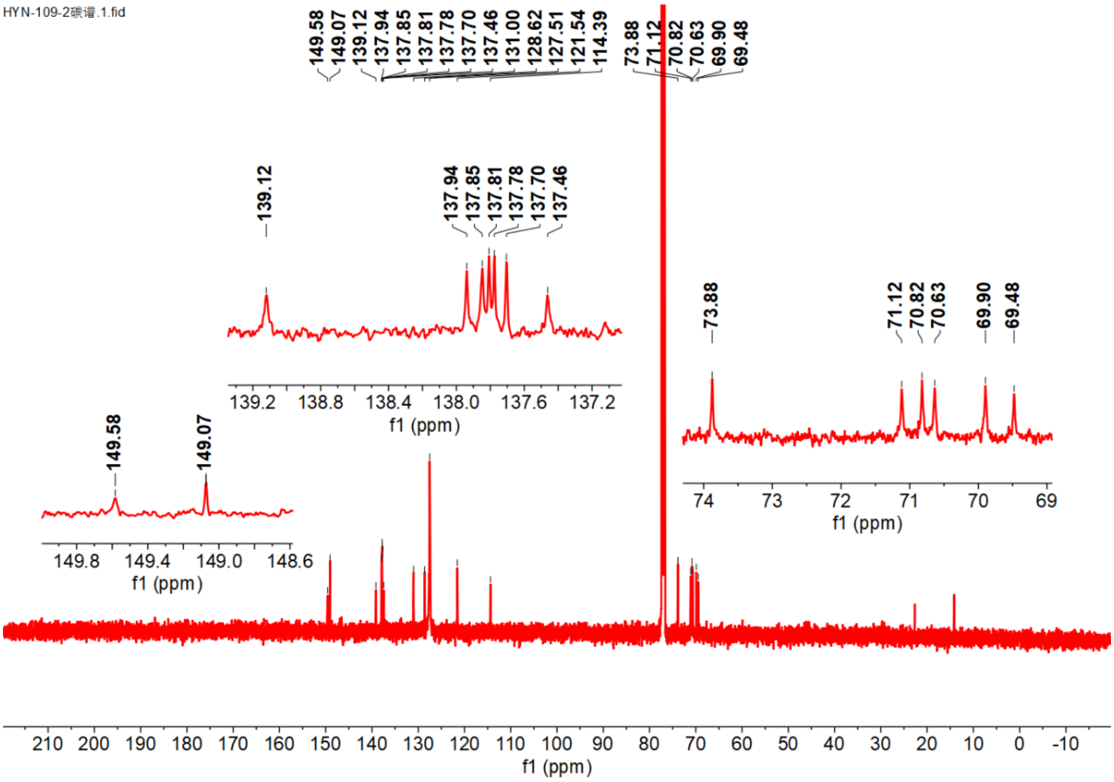

Figure S25. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **6**.

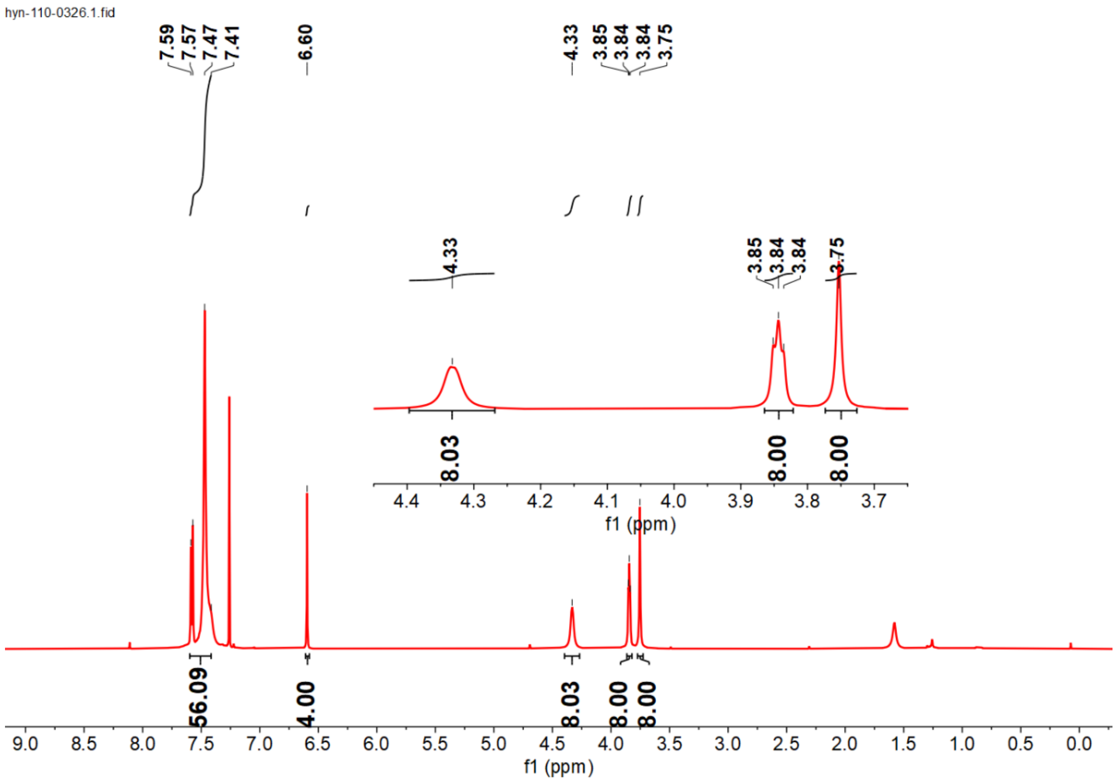

Figure S26. ^{1}H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of **7**.

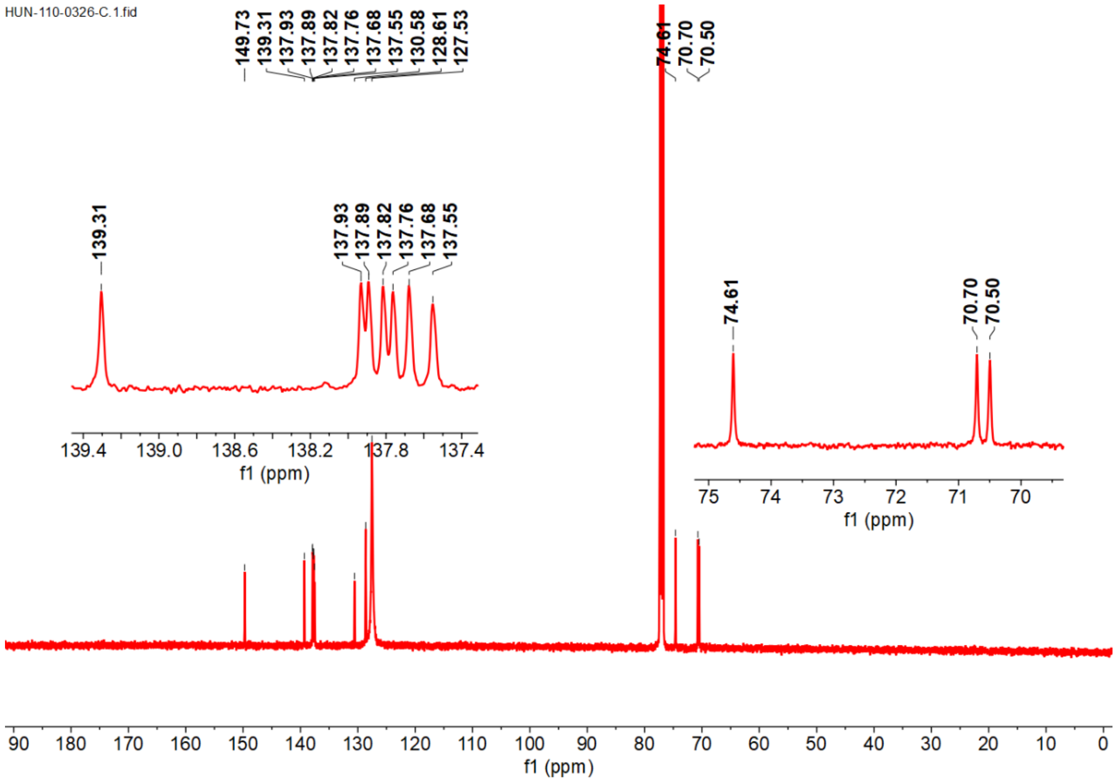

Figure S27. ^{13}C{^{1}H} NMR spectrum (125 MHz, 298 K, CDCl$_3$) of **7**.

7. References

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