Supporting Information for

Metal-Organic Macrocycles with Tunable Pore Microenvironments for Selective Anion Transmembrane Transport

Yingguo Li, Lei Jia, Xianhui Tang, Jinqiao Dong, Yong Cui, and Yan Liu*

School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

Email: liuy@sjtu.edu.cn.

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1. Materials and general procedures

All of the chemicals are commercial available, and used without further purification. Elemental analysis of C and H were performed with an EA1110 CHNS-0 CE elemental analyzer. The FT-IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. ^{1}H and ^{13}C NMR experiments were carried out on a Bruker 400/500 spectrometer operating at resonance frequencies of 400/500 MHz. Mass spectra were recorded on a Finnigan LCQ mass spectrometer or Bruker fourier transform ion cyclotron resonance mass spectrometer (FT-ICRMS). The fluorescence measurements were performed with a PTI-QM/TM/IM steady-state and time-resolved fluorescence spectrofluorometer (USA/CAN) Photon Technology International (PTI) Laserstrobe fluorescence. Fluorescence laser scan confocal microscopy was conducted on Leica TCS SP8 STED 3X. UV-Vis experiments were performed on a Lambda 35 UV/Vis spectrometer.

Single-crystal X-ray diffraction. Single-crystal XRD data for metallacycle **2** was collected at the BL17B macromolecular crystallography beamline National Facility for Protein Science in Shanghai Synchrotron Radiation Facility (SSRF) at 173 K. The collected diffraction data were processed with the HKL3000 software program. The structure were solved by direct methods with SHELXT-2014 and refined with SHELXL-2018 (Sheldrick, G. M. SHELXT-2014, **2013**) using OLEX 2-1.3 (Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339-341). All the non-hydrogen atoms except guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters, and the hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms, treated as riding atoms. DFIX, SADI, FLAT and SIMU restrains were used to obtain reasonable parameters due to the poor quality of crystal data. The solvent molecules were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these highly disordered solvent molecules were removed using the SQUEEZE routine of PLATON; structures were then refined again using the data generated.

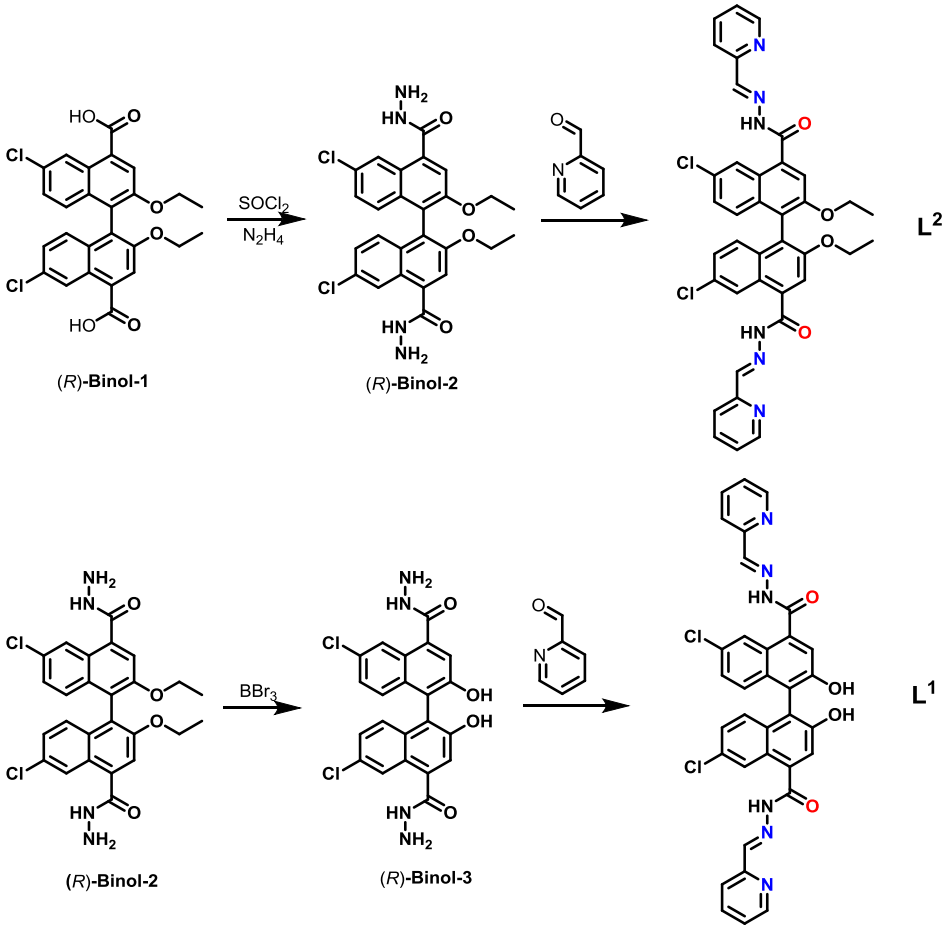
Due to the crystals lose crystallinity rapidly once outside the mother liquor, the crystals were placed in the oil for single-crystal XRD test. However, the crystals still lose crystallinity in several minutes, and leading to the weak diffraction and bad data quality. Moreover, the exposure of several low-angle x-ray diffraction spots overflowed. The above two reasons make the completeness of diffraction data has only 89.4%.

Crystal data and refinement results are shown in **Table S1**, while the selected bond distances and angles are presented in **Table S2**. The CIF files have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number

2103358 (**2**).

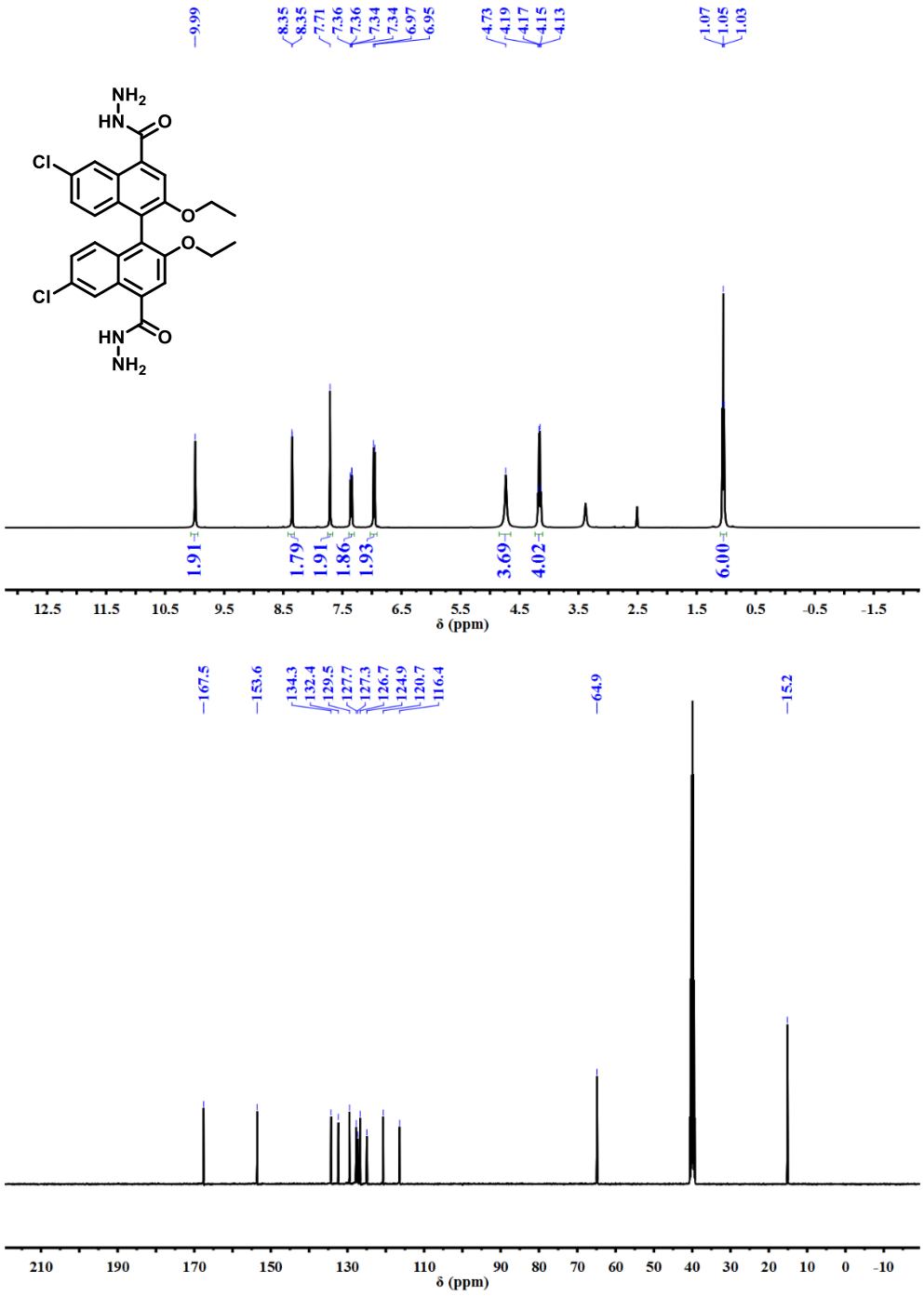
2. Synthesis

2.1 Synthesis of L^1 and L^2



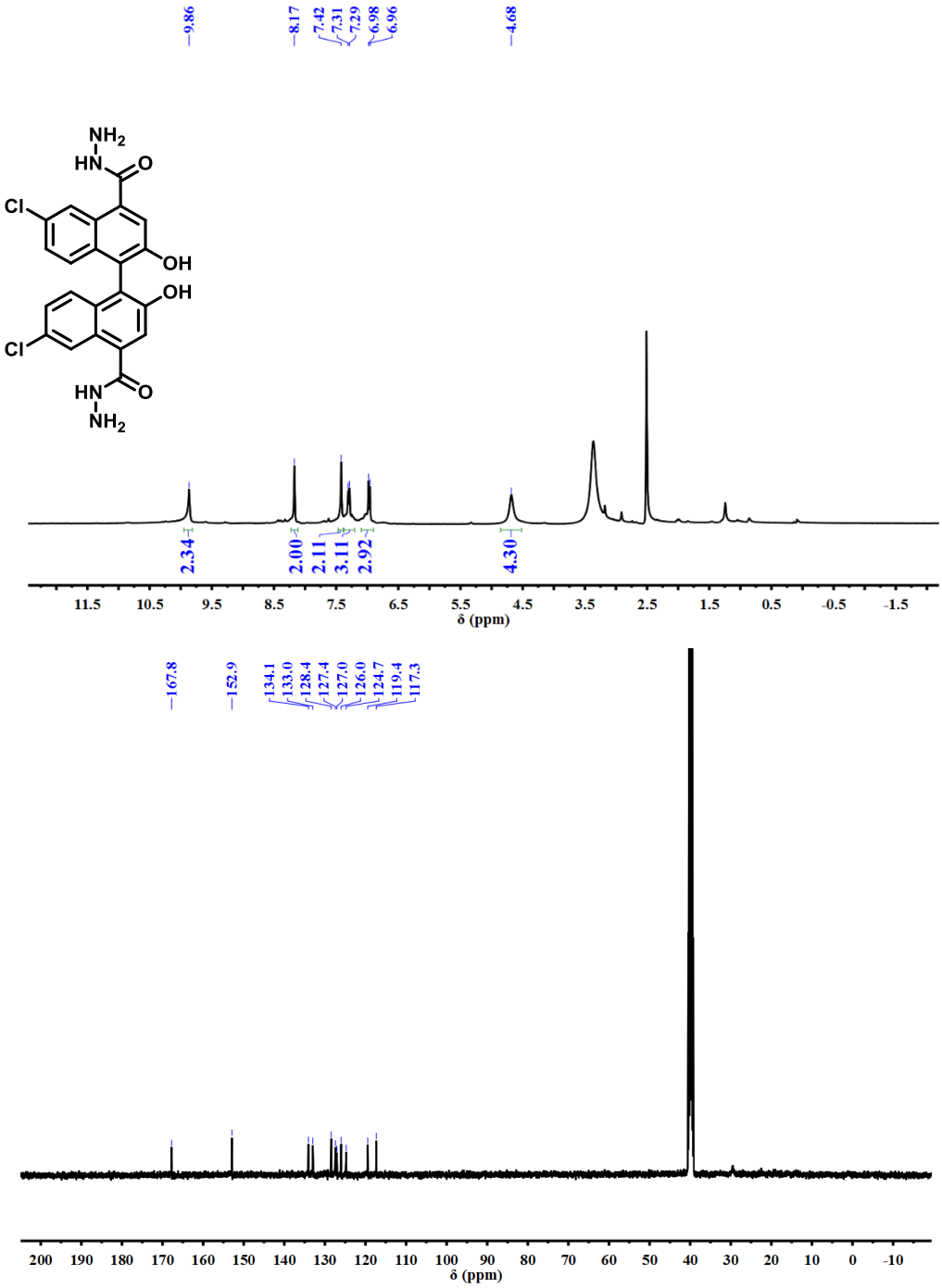
(*R*)-**Binol-1** was synthesized according to the literature.[1]

Synthesis of (*R*)-**Binol-2.** A 50 mL flame-dried round-bottom flask was charged with (*R*)-Binol-**1** (0.50 g, 1 mmol), 5 drops DMF and 10 mL $SOCl_2$, the mixture was heated at 80 °C for 4 h. The excess $SOCl_2$ was evaporated under the reduced pressure. The residue was washed with petroleum ether three times. Then the obtained solid was added to the hydrazine hydrate (10 mL, 85%) slowly, and the mixture was heated at 130 °C for 12 h. After cooling to the room temperature, the mixture was filtered and the solid was washed with H_2O three times. After that, the solid was dried in vacuum and get the product as white solid. Yield: 0.31 g, 58%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 2H), 8.35 (d, J = 2.1 Hz, 2H), 7.71 (s, 2H), 7.35 (dd, J = 9.1, 2.2 Hz, 2H), 6.96 (d, J = 9.1 Hz, 2H), 4.73 (s, 4H), 4.16 (q, J = 6.9 Hz, 4H), 1.05 (t, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.5, 153.6, 134.3, 132.4, 129.5, 127.7, 127.3, 126.7, 124.9, 120.7, 116.4, 64.9, 15.2. (*S*)-**Binol-2** was synthesized in the same way.



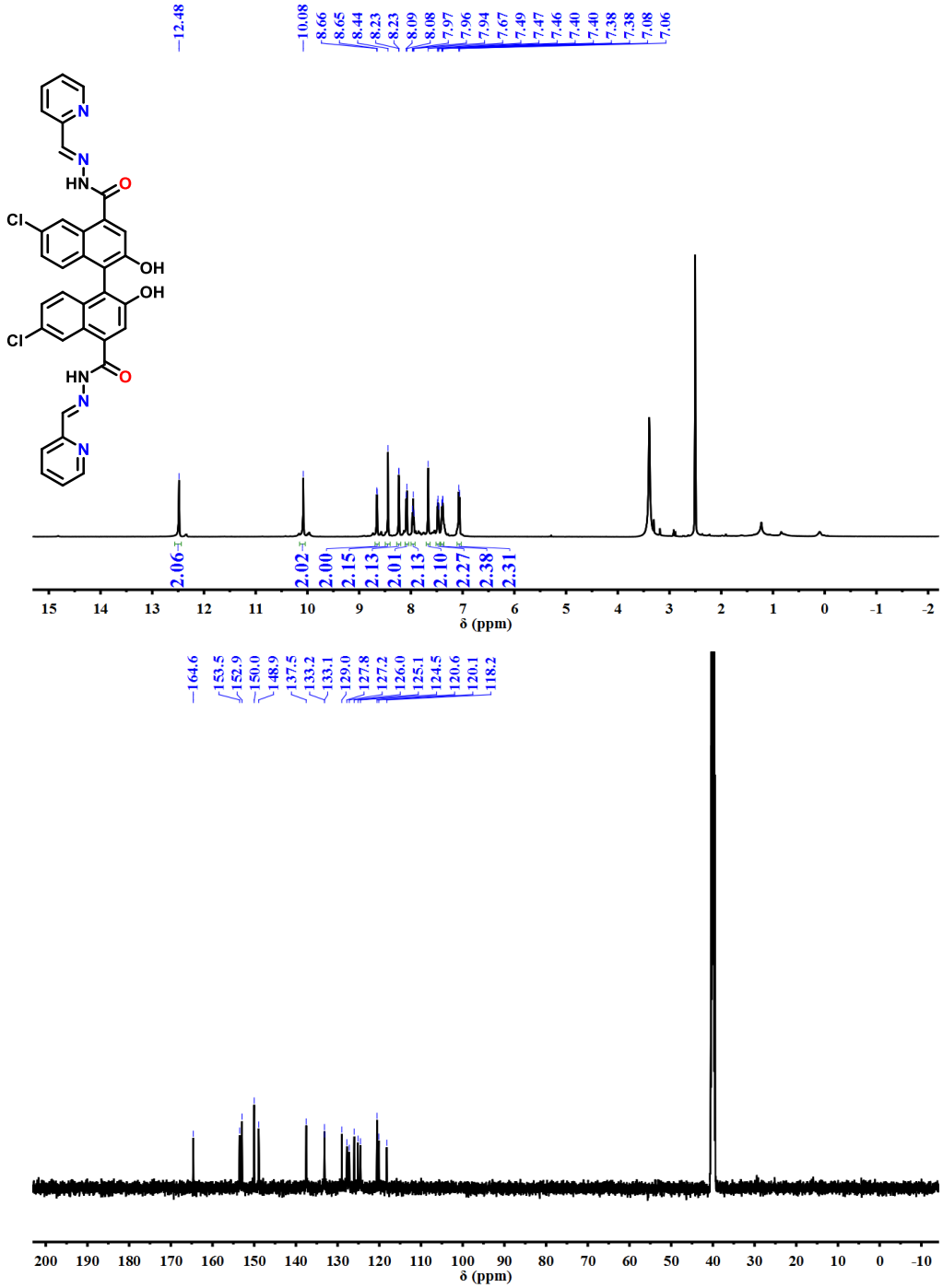
Synthesis of (*R*)-**Binol-3.** A 50 mL flame-dried round-bottom flask was charged with (*R*)-**Binol-2** (0.36 g, 0.68 mmol) and CH_2Cl_2 (20 mL). BBr_3 (2 mL, 20.8 mmol) was slowly added to the mixture at 0 °C, then the mixture was refluxed overnight. After cooling to the room temperature, saturated $NaHCO_3$ aqueous (20 mL) was added at 0 °C and the mixture was stirred for 30 min. The mixture was filtered and the solid was washed with H_2O and CH_2Cl_2. After that, the solid was dried in vacuum and get the product as pale solid. Yield: 0.30 g, 93%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.86 (s, 2H), 8.17 (s, 2H), 7.42 (s, 2H), 7.30 (m, 3H), 6.97 (m, 3H), 4.68 (br, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.8, 152.9, 134.1, 133.0, 128.4, 127.4, 127.0, 126.0, 124.7,

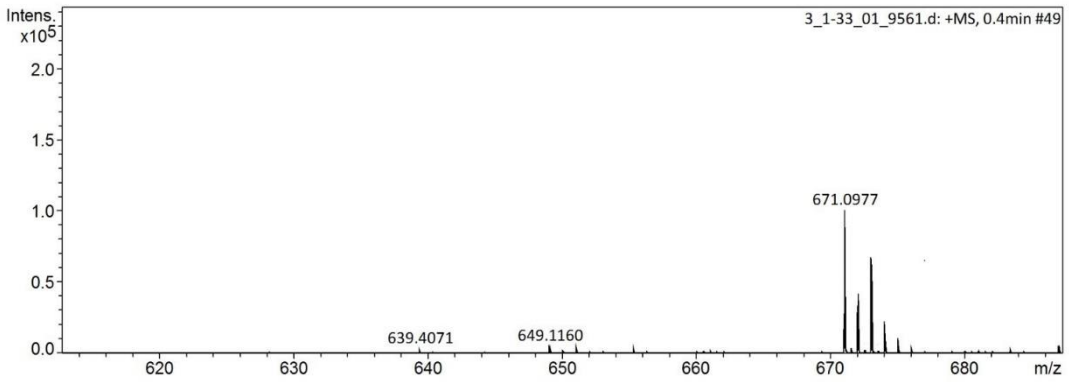
119.4, 117.3. (*S*)-**Binol-3** was synthesized in the same way.



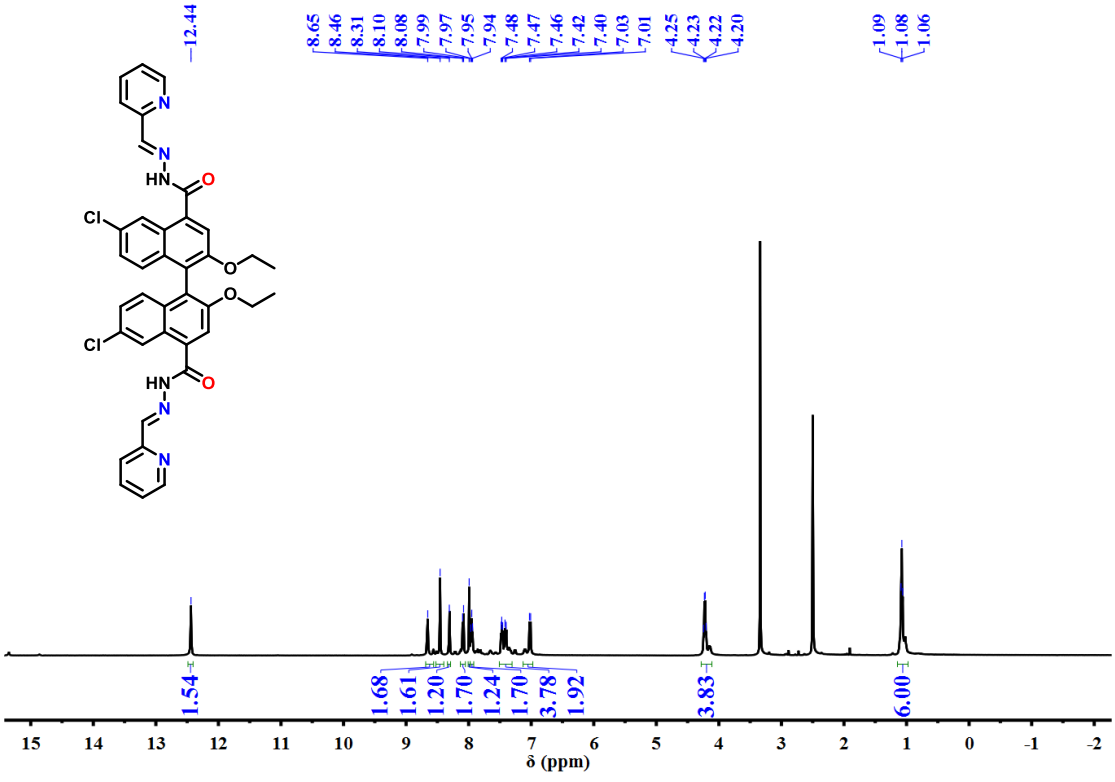
Synthesis of (*R*)-**L[1].** (*R*)-**Binol-3** (0.47 g, 1 mmol) was added to an ethanol solution (10 mL) containing 2-pyridylaldehyde (0.23 g, 2.2 mmol). After 2 drops of acetic acid was added, the mixture was held at 80 °C under magnetic stirring for 12 h. After cooling to the room temperature, the yellow solid was collected by filtration, washed with ethanol, the solid was further purified by recrystallization and dried in vacuum. Yield: 0.61 g, 94%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.48 (s, 2H), 10.08 (s, 2H), 8.66 (d, J = 4.5 Hz, 2H), 8.44 (s, 2H), 8.23 (s, 2H), 8.08 (d, J = 7.8 Hz, 2H), 7.96 (t, J = 7.4 Hz, 2H), 7.67 (s, 2H), 7.51 – 7.44 (m, 2H), 7.39 (dd, J = 9.0, 1.6 Hz, 2H), 7.07 (d, J = 9.1

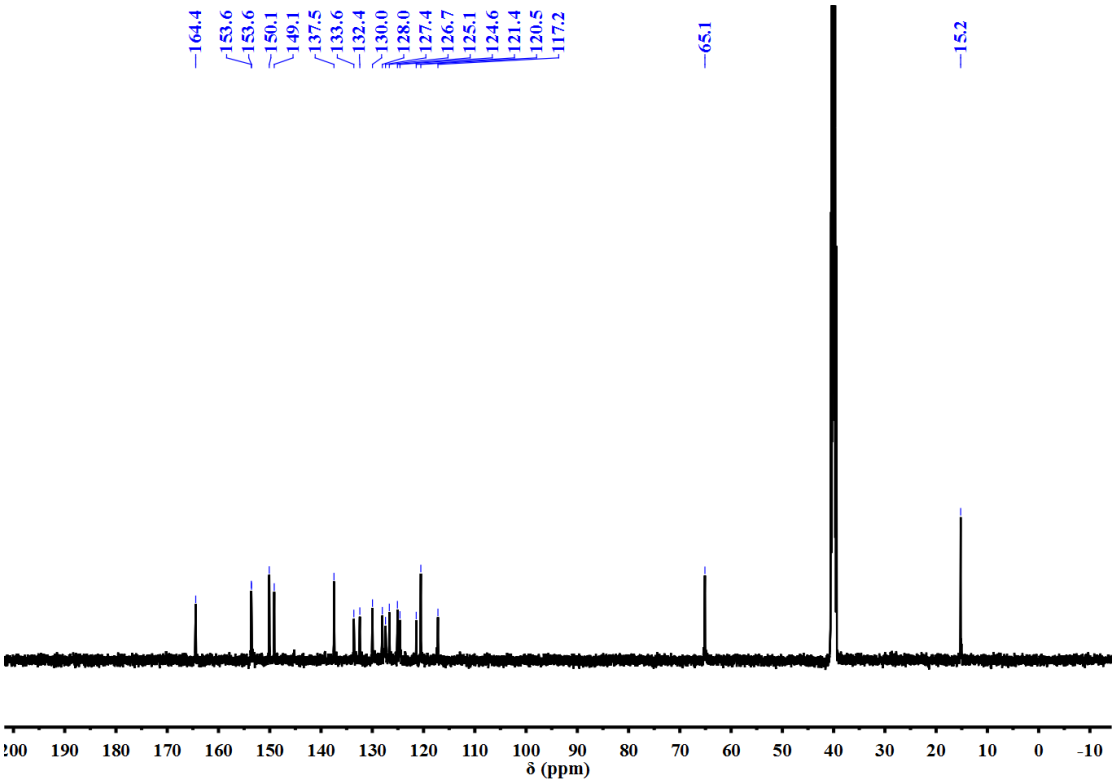
Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 164.6, 153.5, 152.9, 150.0, 148.9, 137.5, 133.2, 133.1, 129.0, 127.8, 127.2, 126.0, 125.1, 124.5, 120.6, 120.1, 118.2. ESI-MS: m/z 671.0977 (Calcd m/z 671.0977 for [$\mathbf{L^1}$+Na]$^+$). (*S*)-$\mathbf{L^1}$ was synthesized in the same way.

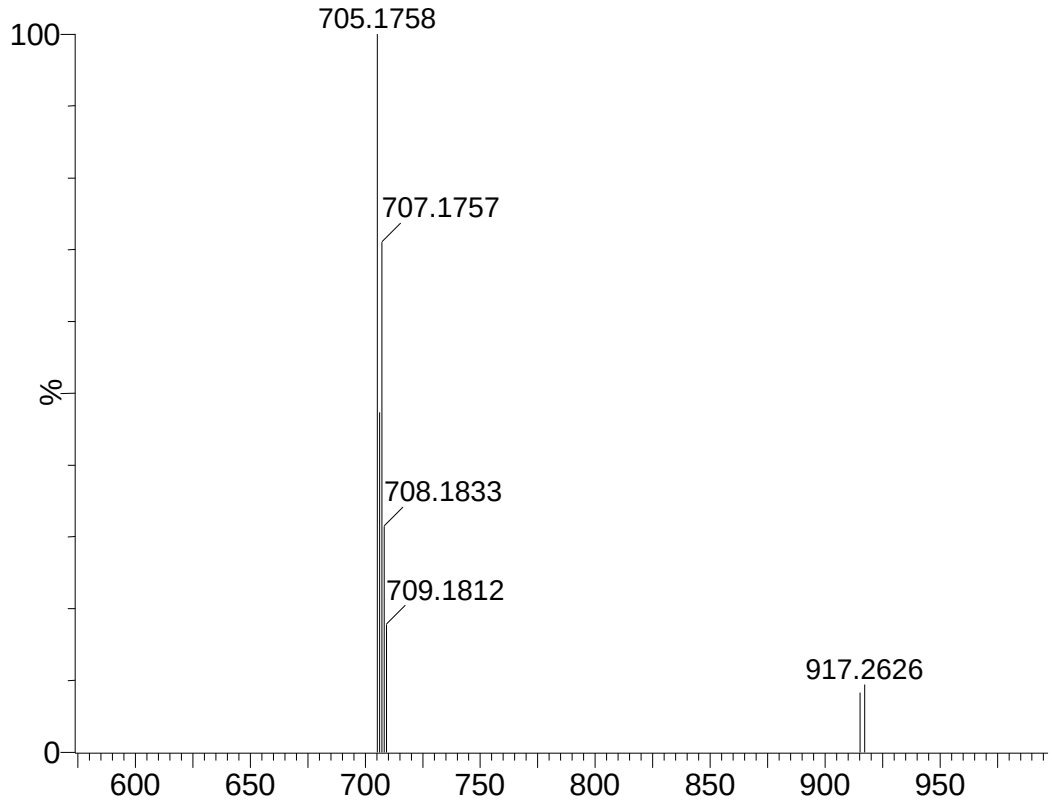




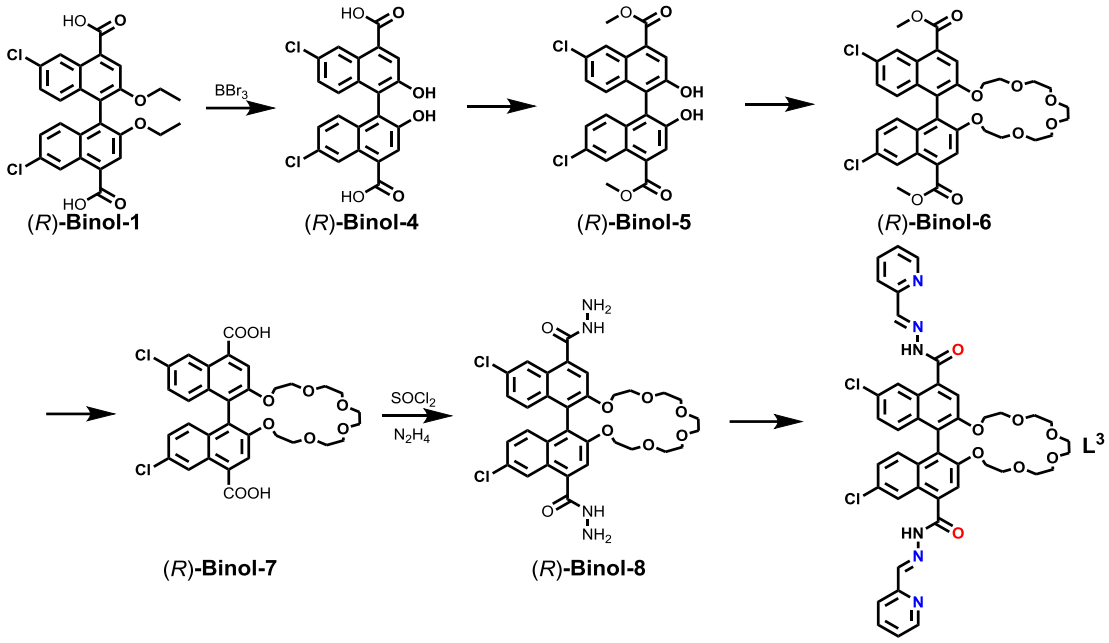
Synthesis of (*R*)-**L²**. (*R*)-**Binol-2** (0.53 g, 1 mmol) was added to an ethanol solution (10 mL) containing 2-pyridylaldehyde (0.23 g, 2.2 mmol). After 2 drops of acetic acid was added, the mixture was held at 80 °C under magnetic stirring for 12 h. After cooling to the room temperature, the yellow solid was collected by filtration, washed with ethanol, the solid was further purified by recrystallization and dried in vacuum. Yield: 0.52 g, 73%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.44 (s, 2H), 8.65 (s, 2H), 8.46 (s, 2H), 8.31 (s, 1H), 8.09 (d, J = 7.8 Hz, 2H), 7.99 (s, 1H), 7.95 (t, J = 7.1 Hz, 2H), 7.51 – 7.31 (m, 4H), 7.02 (d, J = 9.1 Hz, 2H), 4.22 (q, J = 5.6 Hz, 4H), 1.08 (t, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 164.4, 153.60, 153.57, 150.1, 149.1, 137.5, 133.6, 132.4, 130.0, 128.0, 127.4, 126.7, 125.1, 124.6, 121.4, 120.5, 117.2, 65.1, 15.2. ESI-MS: m/z 705.1758 (Calcd m/z 705.1706 for [**L²**+H]$^{+}$). (*S*)-**L²** was synthesized in the same way.



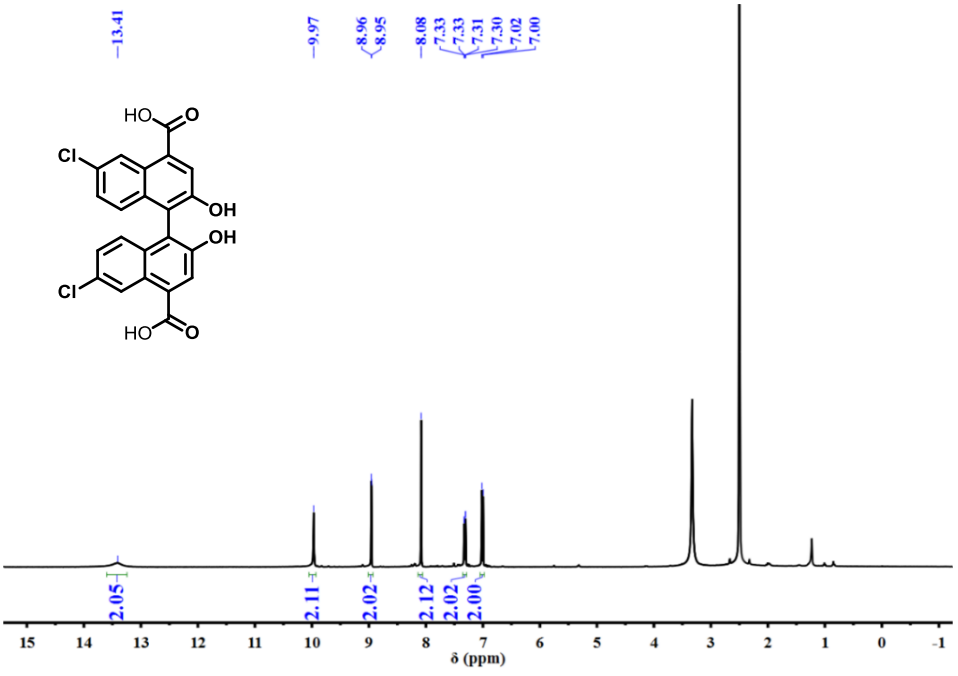


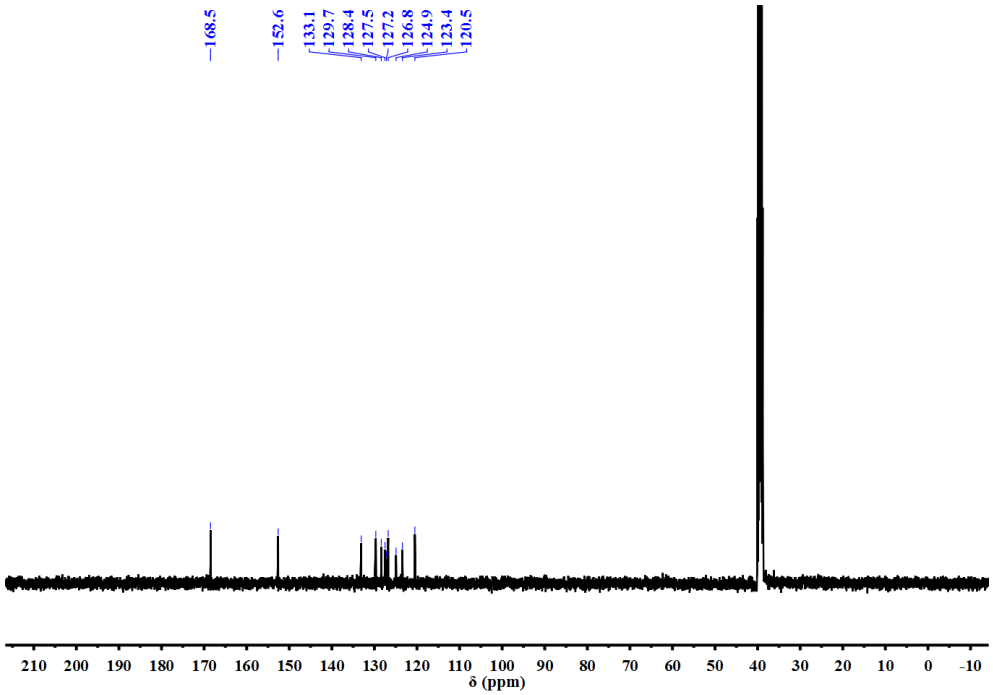


2.2 Synthesis of L^3

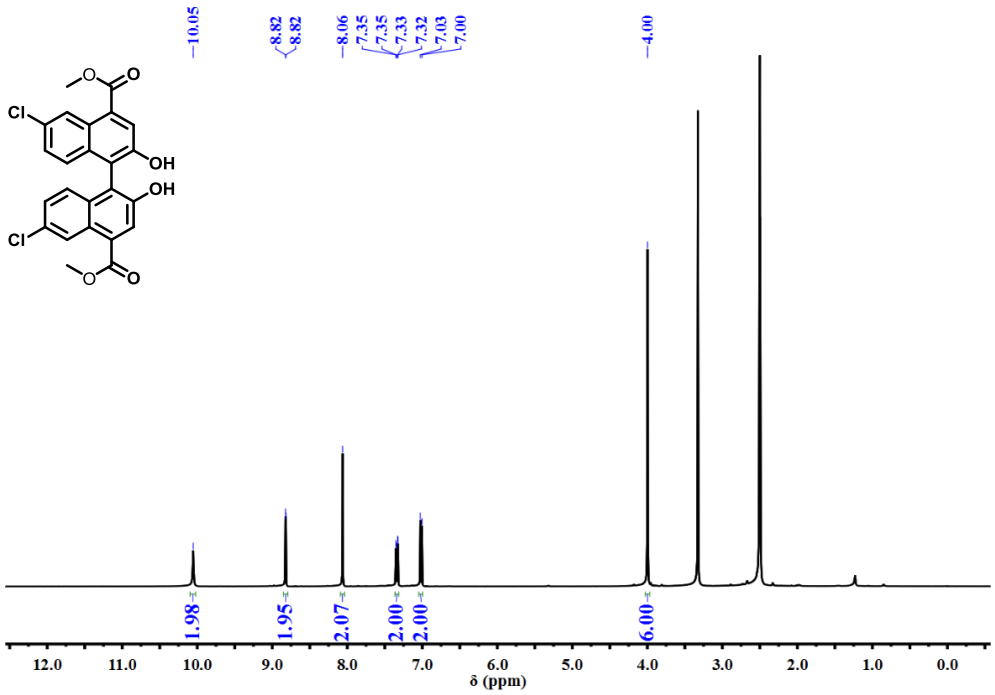


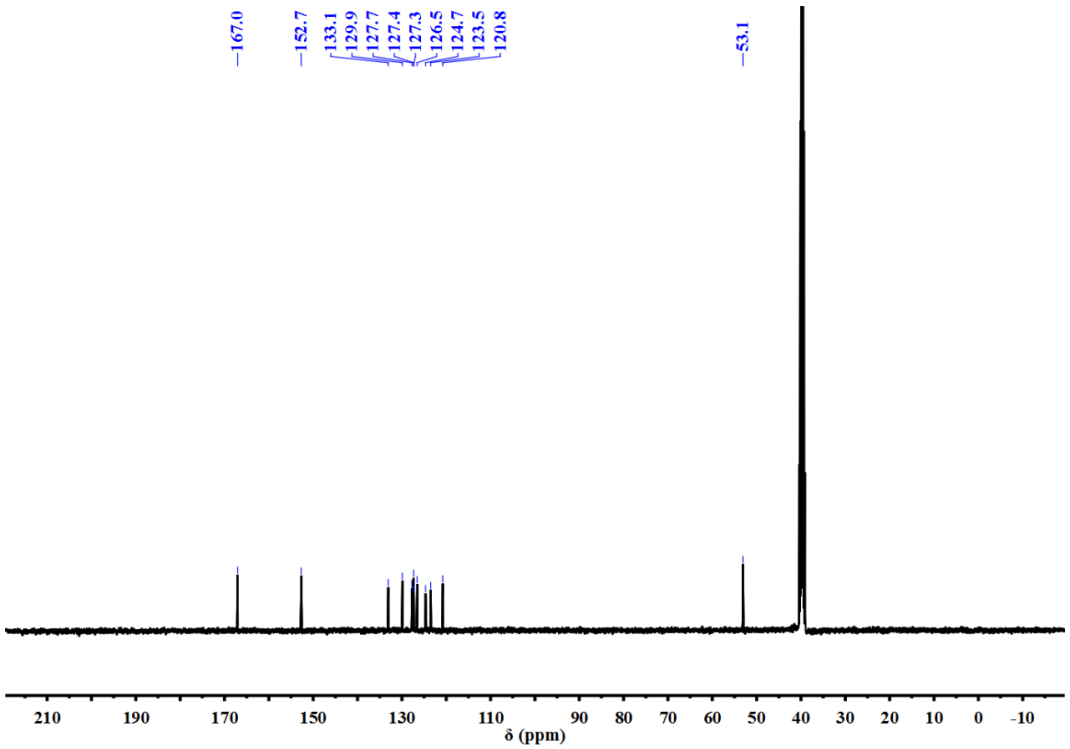
Synthesis of (*R*)-**Binol-4**. A 100 mL flame-dried round-bottom flask was charged with (*R*)-**Binol-1** (0.50 g, 1 mmol) and CH_2Cl_2 (15 mL). Then the BBr_3 (1.5 g, 6 mmol) was slowly added to the mixture at -78 ^oC. The mixture was stirred overnight, then H_2O (10 mL) was added at 0 ^oC and the mixture was stirred for 30 min. The mixture was filtered and the solid was washed with H_2O and CH_2Cl_2. After that, the solid was dried in vacuum and get the product as yellow solid. Yield: 0.40 g, 90%. ^1H NMR (400 MHz, DMSO-d_6) δ 13.41 (br, 2H), 9.97 (s, 2H), 8.96 (d, J = 2.2 Hz, 2H), 8.08 (s, 2H), 7.32 (dd, J = 9.1, 2.2 Hz, 2H), 7.01 (d, J = 9.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.5, 152.6, 133.1, 129.7, 128.4, 127.5, 127.2, 126.8, 124.9, 123.4, 120.5. (*S*)-**Binol-4** was synthesized in the same way.



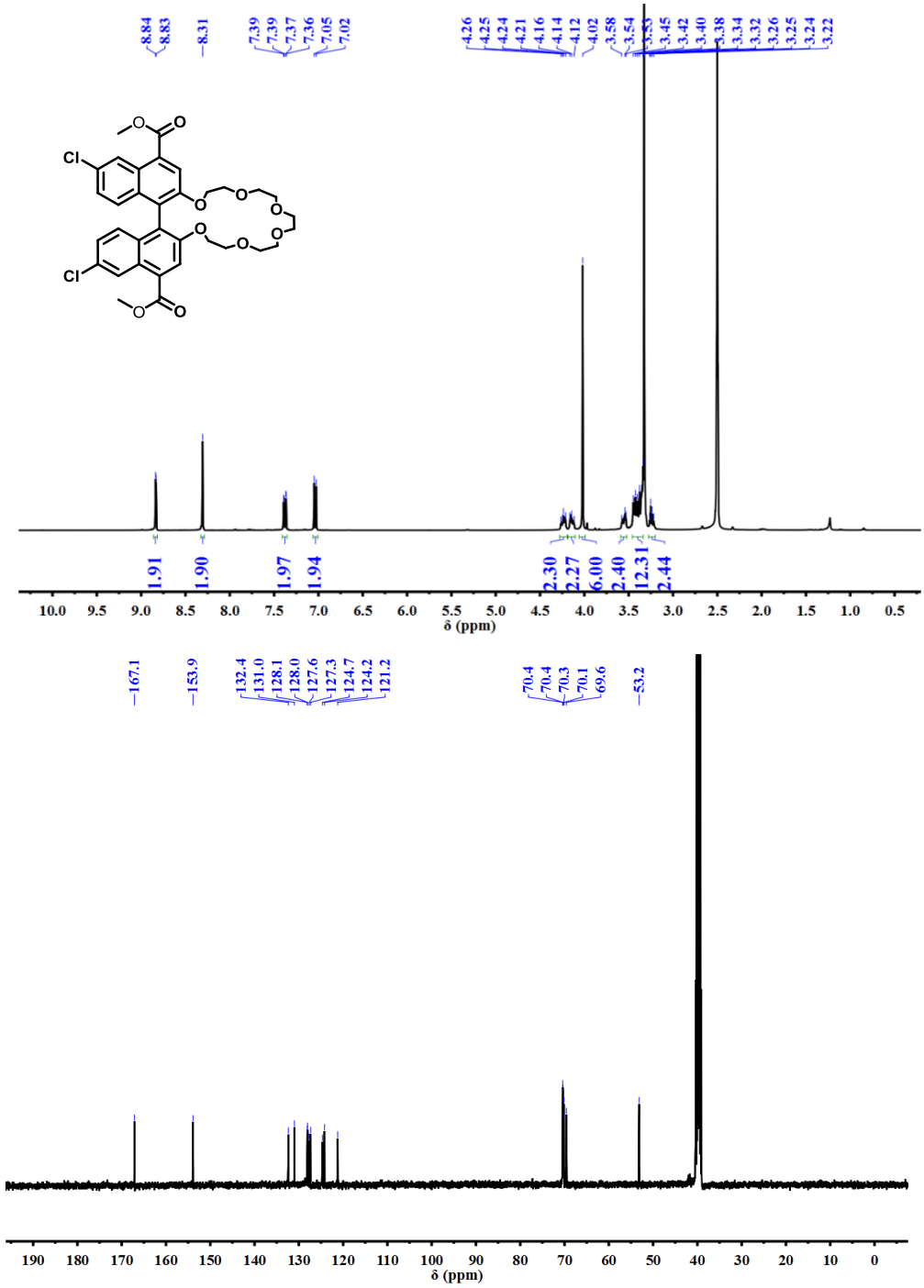


Synthesis of (*R*)-**Binol-5**. (*R*)-Binol-**4** (0.44 g, 1 mmol) was dissolved in CH_3OH (20 mL), then con. H_2SO_4 (0.2 mL) was added slowly, the mixture was heated at 90 °C for 24 h. After cooling to the room temperature, the mixture was filtered and the solid was washed with CH_3OH three times. After that, the solid was dried in vacuum and get the product as white solid. Yield: 0.43 g, 95%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 2H), 8.82 (d, J = 2.2 Hz, 2H), 8.06 (s, 2H), 7.34 (dd, J = 9.1, 2.2 Hz, 2H), 7.02 (d, J = 9.1 Hz, 2H), 4.00 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.0, 152.7, 133.1, 129.9, 127.7, 127.4, 127.3, 126.5, 124.7, 123.5, 120.8, 53.1. (*S*)-**Binol-5** was synthesized in the same way.



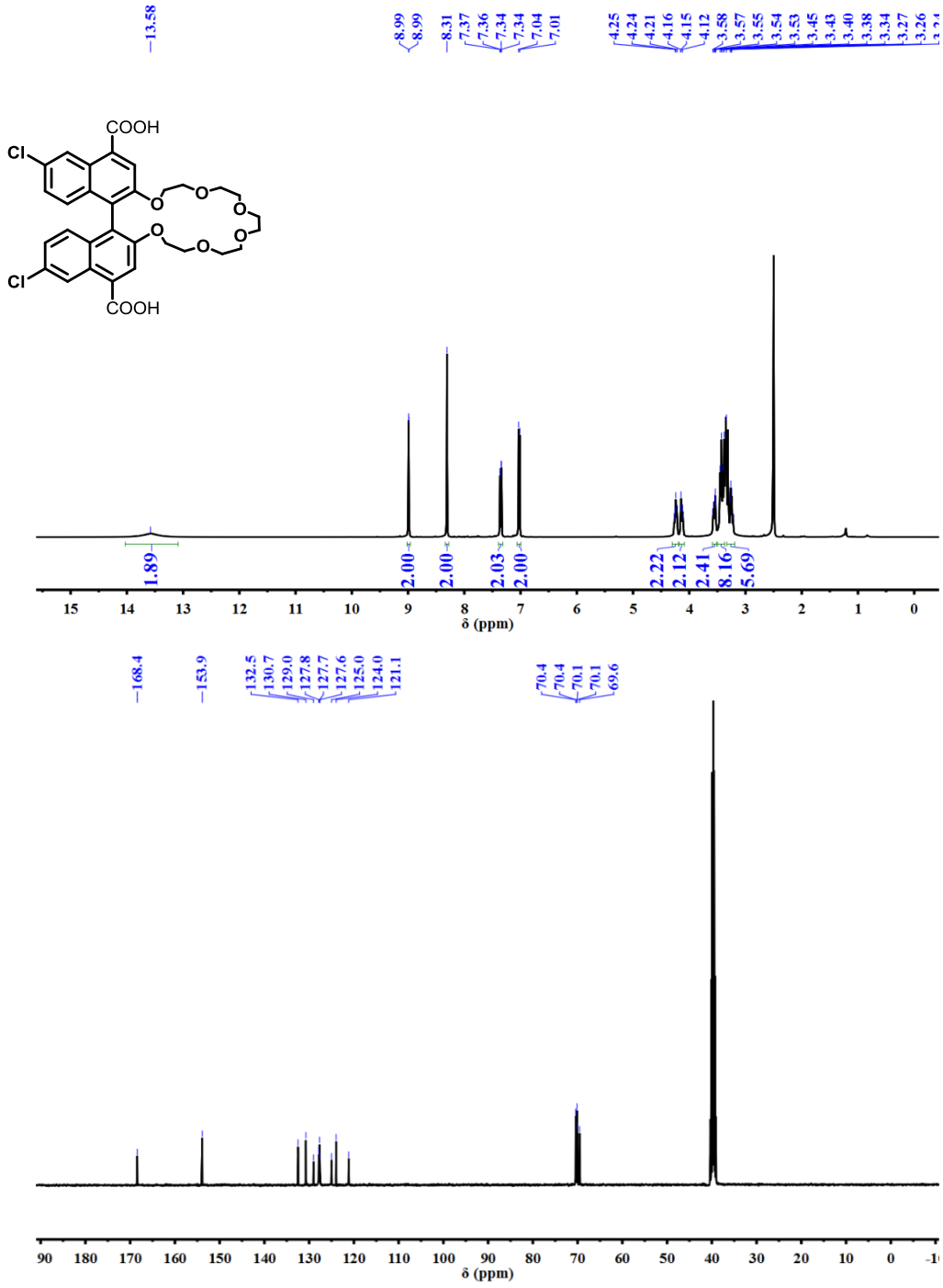


Synthesis of (*R*)-**Binol-6**. A 100 mL flame-dried round-bottom flask was charged with (*R*)-**Binol-5** (0.47 g, 1.0 mmol), NaH (0.084 g, 2.2 mmol, 60% in oil). The mixture was degassed and refilled with N_2 for three times, and then 20 mL of dry THF was added. The mixture was stirred 0.5 h at room temperature. Then 3,6,9,12-tetraoxatetradecane-1,14-diyl bis(4-methylbenzenesulfonate) (0.62 g, 1.1 mmol) was added. The suspension was heated at 65 °C for 24 h. After cooling to the room temperature, the mixture was evaporated under reduced pressure. Then the residue was extract with ethyl acetate and water, the organic phase was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude solid was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:1, v/v, R_f = 0.4) to afford (*R*)-**Binol-6** as a pale yellow solid. Yield: 0.33 g, 51%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (d, *J* = 2.1 Hz, 2H), 8.31 (s, 2H), 7.38 (dd, *J* = 9.1, 2.2 Hz, 2H), 7.04 (d, *J* = 9.2 Hz, 2H), 4.26 – 4.21 (m, 2H), 4.16 – 4.12 (m, 2H), 4.02 (s, 6H), 3.58 – 3.53 (m, 2H), 3.45 – 3.34 (m, 12H), 3.26 – 3.22 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.1, 153.9, 132.4, 131.0, 128.1, 128.0, 127.6, 127.3, 124.7, 124.2, 121.2, 70.44, 70.42, 70.3, 70.1, 69.6, 53.2. (*S*)-**Binol-6** was synthesized in the same way.



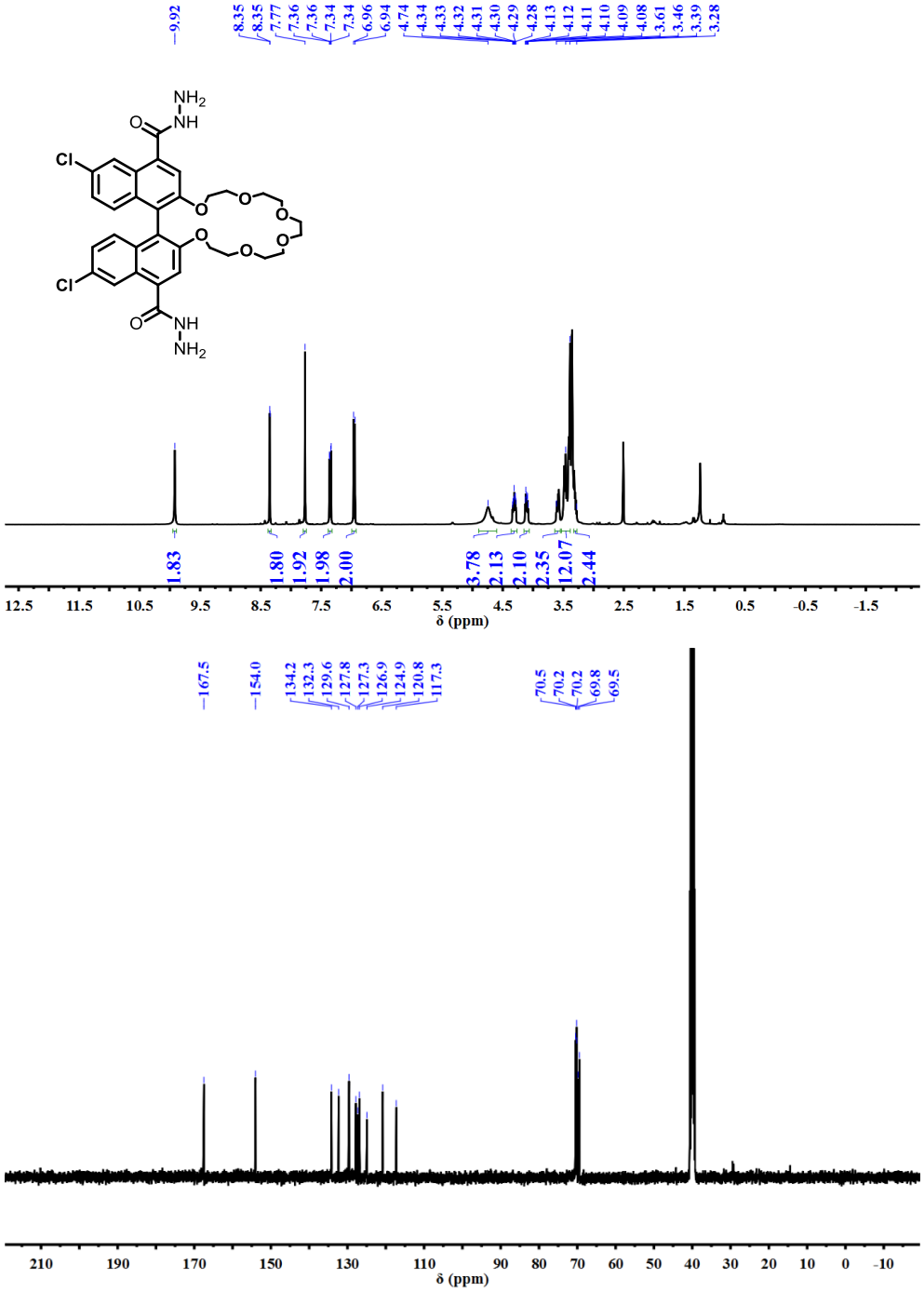
Synthesis of (*R*)-**Binol-7.** A solution of (*R*)-Binol-**6** (1.34 g, 2.0 mmol) and LiOH·H_2O (0.84 g, 20 mmol) in THF (15 mL), MeOH (45 mL) and H_2O (45 mL) was heated at 75 °C for 24 h. The solution was cooled to room temperature, acidified to pH = 1-2 with 6 M HCl and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to give a white solid of (*R*)-**Binol-7**. Yield: 1.21 g, 93%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.58 (br, 2H), 8.99 (d, *J* = 2.2 Hz, 2H), 8.31 (s, 2H), 7.35 (dd, *J* = 9.1, 2.2 Hz, 2H), 7.02 (d, *J* = 9.1 Hz, 2H), 4.27 – 4.21 (m, 2H), 4.16 – 4.11 (m, 2H), 3.59 – 3.51 (m, 2H), 3.45 – 3.22 (m, 14H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.4, 153.9, 132.5, 130.7, 129.0, 127.8, 127.7,

127.6, 125.0, 124.0, 121.1, 70.44, 70.42, 70.13, 70.11, 69.6. (*S*)-**Binol-7** was synthesized in the same way.



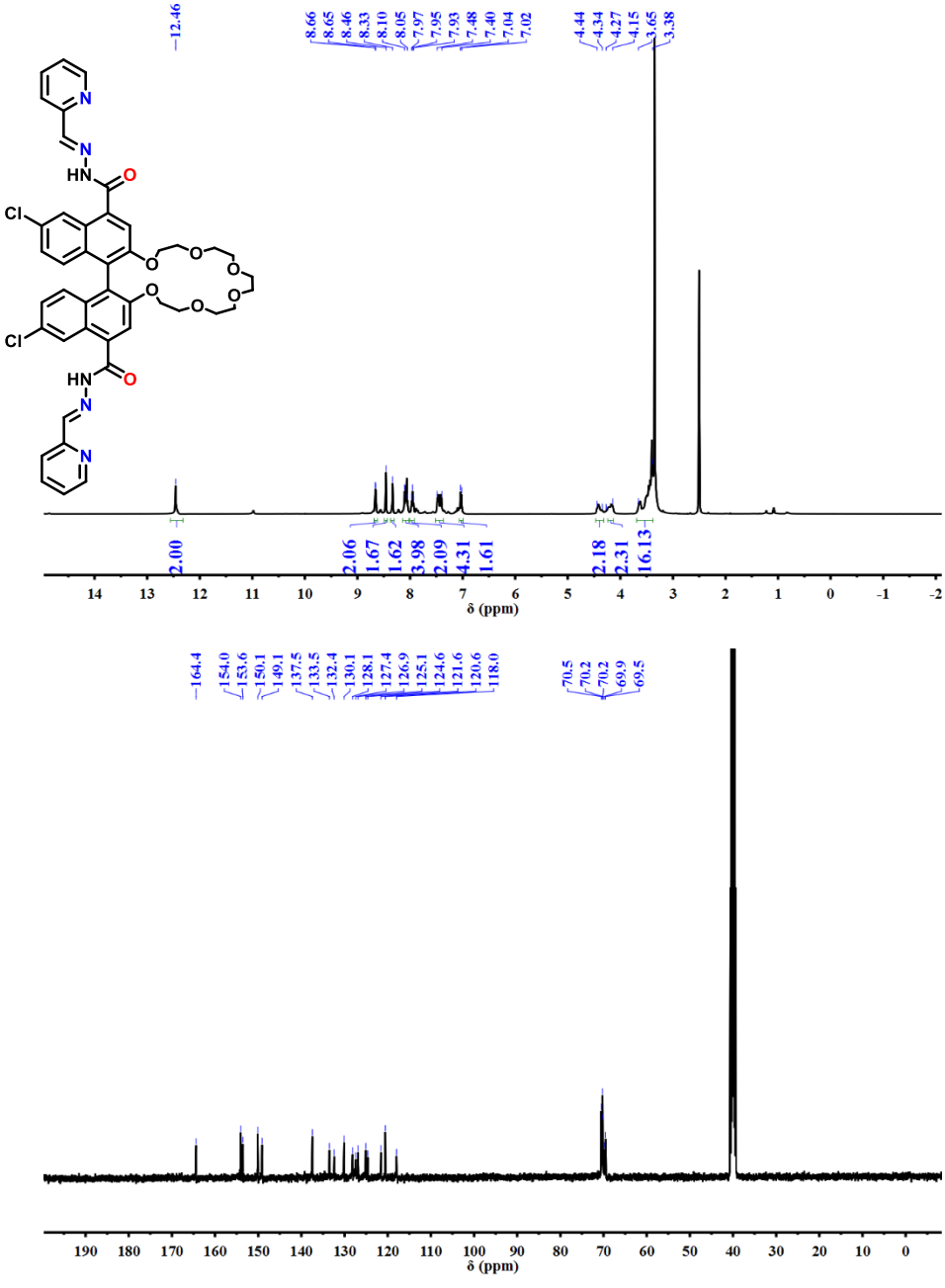
Synthesis of (*R*)-**Binol-8**. A 50 mL flame-dried round-bottom flask was charged with (*R*)-**Binol-7** (0.64 g, 1 mmol), 5 drops DMF and 10 mL $SOCl_2$, the mixture was heated at 80 ^oC for 4 h. The excess $SOCl_2$ was evaporated under the reduced pressure. The residue was washed with petroleum ether three times. Then the obtained solid was added to the hydrazine hydrate (10 mL, 85%) slowly, and the mixture was heated at 130 ^oC for 12 h. After cooling to the room temperature, the mixture was filtered and the solid was washed with H_2O three times. After that, the solid was dried in vacuum and

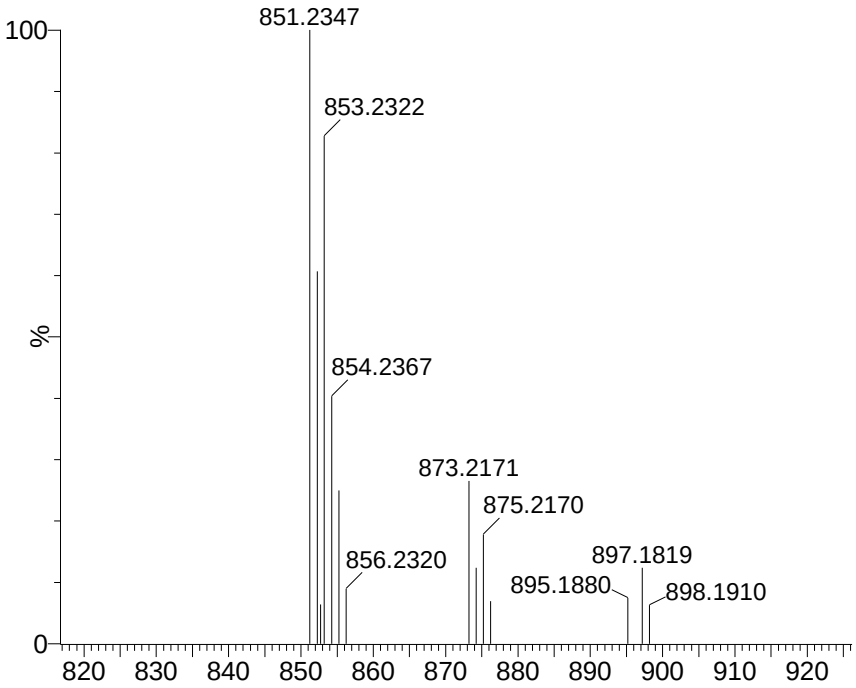
get the product as white solid. Yield: 0.42 g, 63%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.92 (s, 2H), 8.35 (d, J = 2.2 Hz, 2H), 7.77 (s, 2H), 7.35 (dd, J = 9.1, 2.2 Hz, 2H), 6.95 (d, J = 9.1 Hz, 2H), 4.74 (br, 4H), 4.34 – 4.28 (m, 2H), 4.13 – 4.08 (m, 2H), 3.61 – 3.28 (m, 16H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.5, 154.0, 134.2, 132.3, 129.6, 127.8, 127.3, 126.9, 124.9, 120.8, 117.3, 70.5, 70.19, 70.16, 69.8, 69.5. (*S*)-**Binol-8** was synthesized in the same way.



Synthesis of (*R*)-**L^{3}.** (*R*)-**Binol-8** (0.67 g, 1 mmol) was added to an ethanol solution (10 mL) containing 2-pyridylaldehyde (0.23 g, 2.2 mmol). After 2 drops of acetic acid was added, the mixture was held at 85 °C under magnetic stirring for 12 h. After cooling

to the room temperature, the yellow solid was collected by filtration, washed with ethanol, the solid was further purified by recrystallization and dried in vacuum. Yield: 0.75 g, 88%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.46 (s, 2H), 8.66 (d, J = 4.3 Hz, 2H), 8.46 (s, 2H), 8.33 (s, 2H), 8.10 – 8.05 (m, 4H), 7.95 (t, J = 7.2 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.03 (d, J = 9.1 Hz, 2H), 4.44 – 4.34 (m, 2H), 4.27 – 4.15 (m, 2H), 3.65 – 3.38 (m, 16H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.4, 154.0, 153.6, 150.1, 149.1, 137.5, 133.5, 132.4, 130.1, 128.1, 127.4, 126.9, 125.1, 124.6, 121.6, 120.6, 118.0, 70.5, 70.23, 70.18, 69.9, 69.5. ESI-MS: m/z 851.2347 (Calcd m/z 851.2285 for [**L**^{3}+H]$^{+}$). (*S*)-**L**^{3} was synthesized in the same way.





2.3 Synthesis of metallacycles 1, 2 and 3

Synthesis of the metallacycle 1. $\mathbf{L^1}$ (13 mg, 0.02 mmol) and $Zn(ClO_4)_2$ (7.5 mg, 0.02 mmol) were dissolved in CH_3CN (1 mL) to give a yellow solution and stirred at room temperature for 4 h. The powder was obtained by added Et_2O to the CH_3CN solution of **1** and filtrated the mixture. The solid was washed with the mixture solution of Et_2O and CH_3CN (V:V = 9:1), and dried in vacuum. Yield: 18.2 mg, 88%. ^{1}H NMR (500 MHz, CD_3CN) δ 13.20 (br, 6H), 9.01 (br, 8H), 8.65 (br, 8H), 8.34 (s, 8H), 8.20 (br, 16H), 7.94 (s, 8H), 7.83 (s, 16H), 7.23 – 7.20 (m, 16H). ^{13}C NMR (126 MHz, CD_3CN) δ 169.2, 152.3, 150.4, 146.1, 145.6, 142.7, 132.9, 131.0, 129.1, 128.6, 128.3, 126.7, 126.3, 124.0, 121.7, 119.7. ESI-MS: m/z = 1085.3119 [**1** - $4ClO_4^-$ - H^+]$^{3+}$,1118.9598 [**1** - $3ClO_4^-$]$^{3+}$. Elemental Analysis: Anal (%). Calcd for $C_{136}H_{88}Cl_8N_{24}O_{16}Zn_4(ClO_4)_8$: C, 44.69; H, 2.43; N, 9.20. Found: C, 44.61; H, 2.40; N, 9.14. FTIR (KBr, cm^{-1}): 3198 (br), 1634 (s), 1596 (s), 1521 (s), 1475 (w), 1446 (w), 1387 (m), 1336 (m), 1295 (m), 1244 (m), 1185 (m), 1143 (s), 1085 (s), 926 (m), 771 (m), 616 (s).

Synthesis of the metallacycle 2. $\mathbf{L^2}$ (14 mg, 0.02 mmol) and $Zn(ClO_4)_2$ (7.5 mg, 0.02 mmol) were dissolved in CH_3CN (1 mL) to give a yellow solution and stirred at room temperature for 4 h. The powder was obtained by added Et_2O to the CH_3CN solution of **1** and filtrated the mixture. The solid was washed with the mixture of Et_2O and CH_3CN (V:V = 9:1), and dried in vacuum. Yield: 17.7 mg, 81%. The single crystal of **2** was obtained by using liquid-liquid diffusion method. $\mathbf{L^2}$ (1.4 mg, 0.002 mmol) and $Zn(ClO_4)_2$ (1 mg, 0.0027 mmol) were dissolved in CH_3OH (1 mL), then dioxane (1 mL) was added to the mixture slowly. The yellow crystals were obtained after

standing the solution for several days at room temperature. Yield: 54%. ^{1}H NMR (500 MHz, CD_3CN) δ 13.15 (br, 8H), 9.07 (s, 8H), 8.67 (s, 8H), 8.35 (s, 10H), 8.23 – 8.14 (m, 22H), 7.83 (s, 8H), 7.22 – 7.06 (m, 16H), 4.23 (s, 16H), 1.08 (m, 24H). ^{13}C NMR (126 MHz, CD_3CN) δ 169.3, 153.4, 150.4, 146.2, 145.6, 142.7, 132.4, 131.4, 129.3, 128.6, 128.2, 127.3, 126.5, 124.6, 123.9, 118.3, 65.5, 14.2. ESI-MS: m/z = 1026.1225 [**2** - $8ClO_4^-$ - $5H^+$]$^{3+}$, 1059.7734 [**2** - $7ClO_4^-$ - $4H^+$]$^{3+}$, 1093.0120 [**2** - $6ClO_4^-$ - $3H^+$]$^{3+}$. Elemental Analysis: Anal (%). Calcd for $C_{152}H_{120}Cl_8N_{24}O_{16}Zn_4(ClO_4)_8$: C, 47.06; H, 3.12; N, 8.67. Found: C, 46.99; H, 3.05; N, 8.51. FTIR (KBr, cm^{-1}): 3449 (br), 2984 (w), 1638 (w), 1579 (s), 1516 (m), 1479 (w), 1433 (w), 1374 (m), 1320 (s), 1282 (m), 1252 (m), 1219 (m), 1190 (w), 1093 (w), 1093 (s), 1052 (s), 930 (w), 779 (m), 636 (s).

Synthesis of the metallacycle 3. $\mathbf{L^3}$ (17 mg, 0.02 mmol) and $Zn(ClO_4)_2$ (7.5 mg, 0.02 mmol) were dissolved in CH_3CN (1 mL) to give a yellow solution and stirred at room temperature for 4 h. The powder was obtained by added Et_2O to the CH_3CN solution of **1** and filtrated the mixture. The solid was washed with the mixture of Et_2O and CH_3CN (V:V = 9:1), and dried in vacuum. Yield: 20.5 mg, 84%. The single crystal of **3** was obtained by using liquid-liquid diffusion method. $\mathbf{L^3}$ (1.7 mg, 0.002 mmol) and $Zn(ClO_4)_2$ (1 mg, 0.0027 mmol) were dissolved in CH_3OH (1 mL), then $HCCl_3$ (1 mL) was added to the mixture slowly. The yellow crystals were obtained after standing the solution for several days at room temperature. Yield: 83%. ^{1}H NMR (500 MHz, CD_3CN) δ 13.25 (br, 8H), 9.02 (s, 8H), 8.62 – 8.26 (m, 40H), 7.82 (s, 8H), 7.35 – 7.05 (m, 16H), 4.27 (br, 8H), 4.07 (br, 8H), 3.78 – 3.17 (m, 64H). ^{13}C NMR (126 MHz, CD_3CN) δ 169.3, 153.9, 150.2, 146.2, 142.7, 132.3, 131.8, 129.1, 128.7, 128.3, 127.5, 127.1, 126.9, 125.1, 123.8, 120.3, 71.0, 70.0, 69.9, 69.2, 69.1. ESI-MS: m/z = 733.1217 [**3** - $8ClO_4^-$ - $3H^+$]$^{5+}$, 741.9145 [**3** - $8ClO_4^-$ - $5H^+$ + $2Na^+$]$^{5+}$, 750.7017 [**3** - $8ClO_4^-$ - $7H^+$ + $4Na^+$]$^{5+}$, 1254.8511 [**3** - $7ClO_4^-$ - $4H^+$]$^{3+}$. Elemental Analysis: Anal (%). Calcd for $C_{176}H_{160}Cl_8N_{24}O_{32}Zn_4(ClO_4)_8$: C, 47.35; H, 3.61; N, 7.53. Found: C, 47.20; H, 3.53; N, 7.48. FTIR (KBr, cm^{-1}): 3449 (br), 2921 (w), 1639 (s), 1592 (s), 1533 (s), 1487 (m), 1450 (w), 1345 (m), 1337 (s), 1286 (m), 1240 (m), 1190 (w), 1093 (s), 913 (w), 867 (w), 759 (m), 633 (s).

3. NMR and ESI-MS spectra of metallacycles 1-3

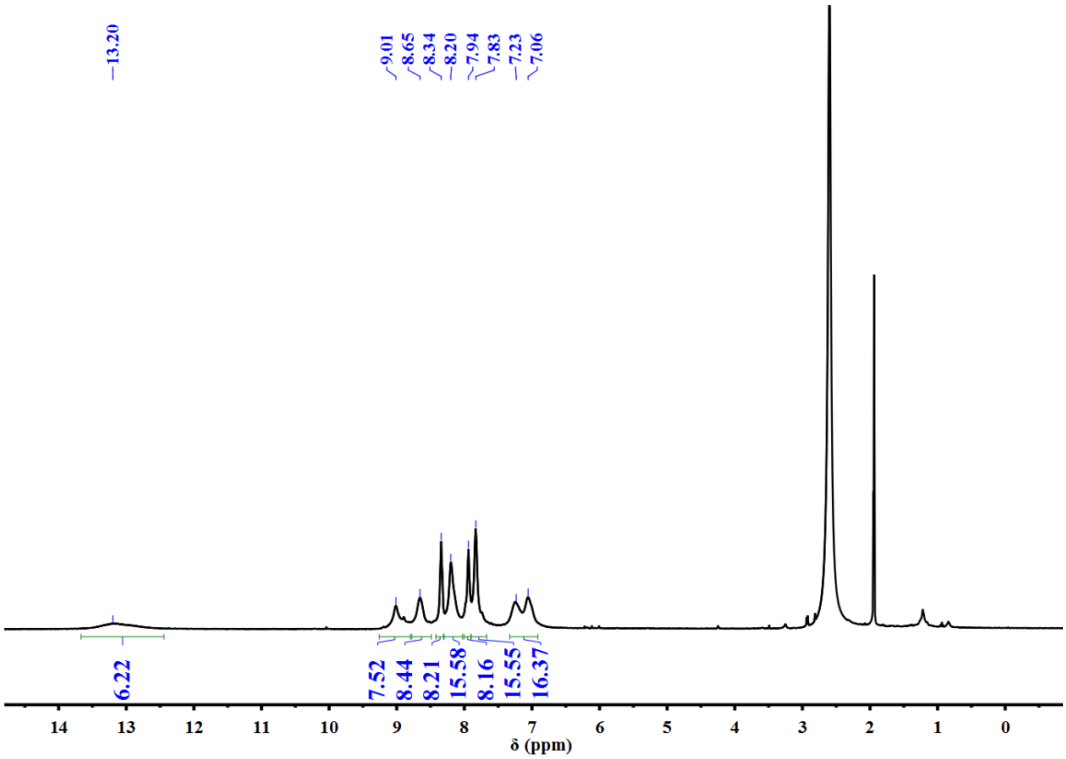


Figure S1. ^{1}H NMR spectrum (500 MHz, CD_3CN) of **1**.

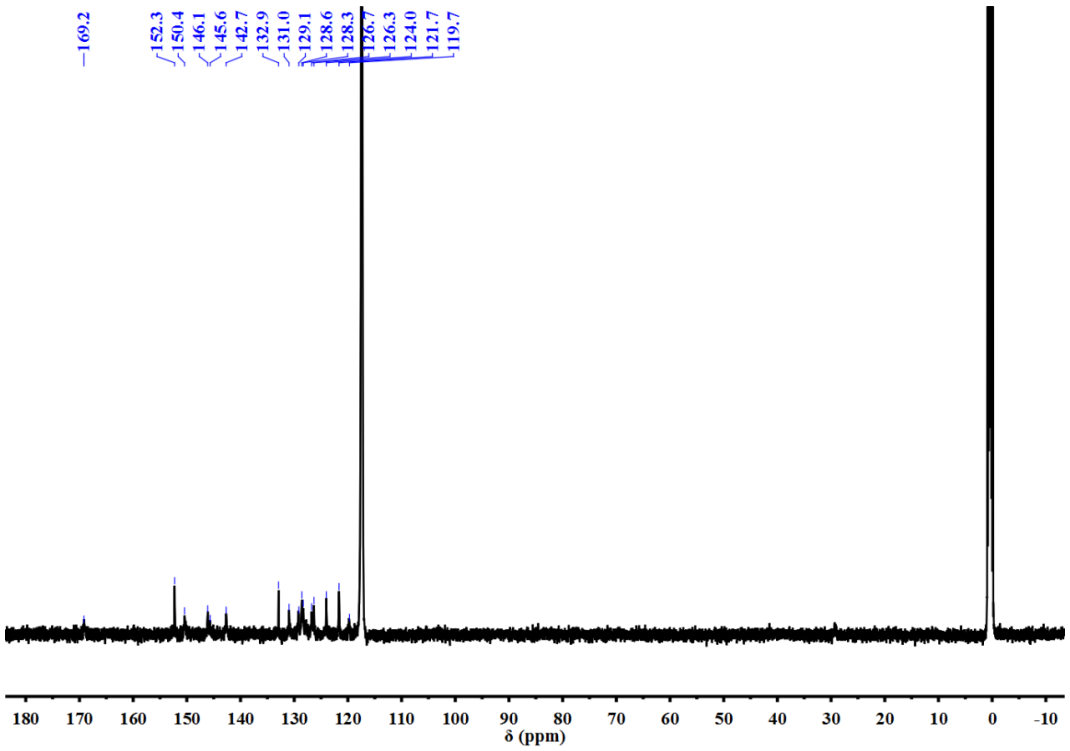


Figure S2. ^{13}C NMR spectrum (126 MHz, CD_3CN) of **1**.

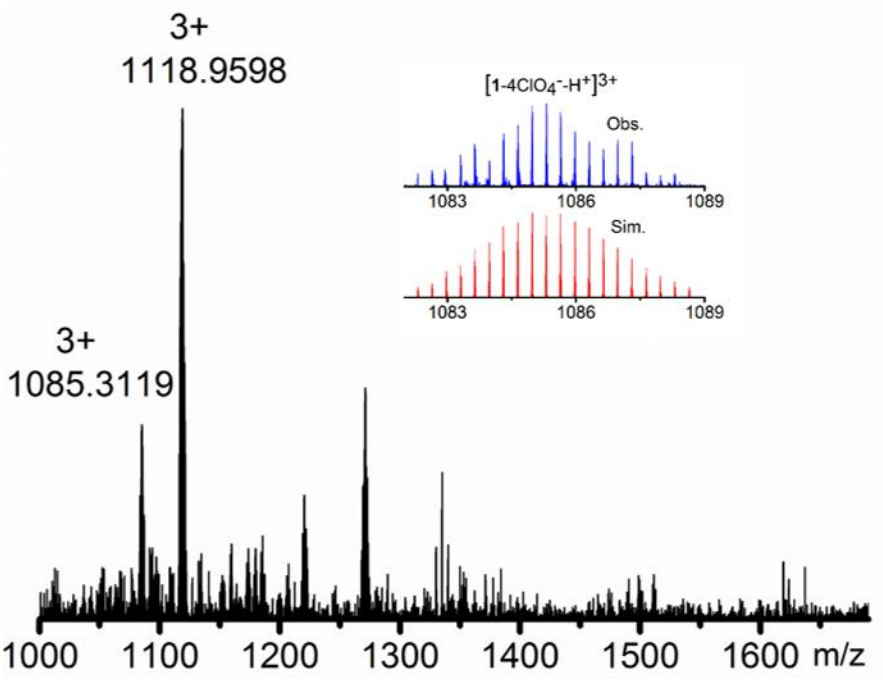


Figure S3. High-resolution ESI-MS spectrum of **1**.

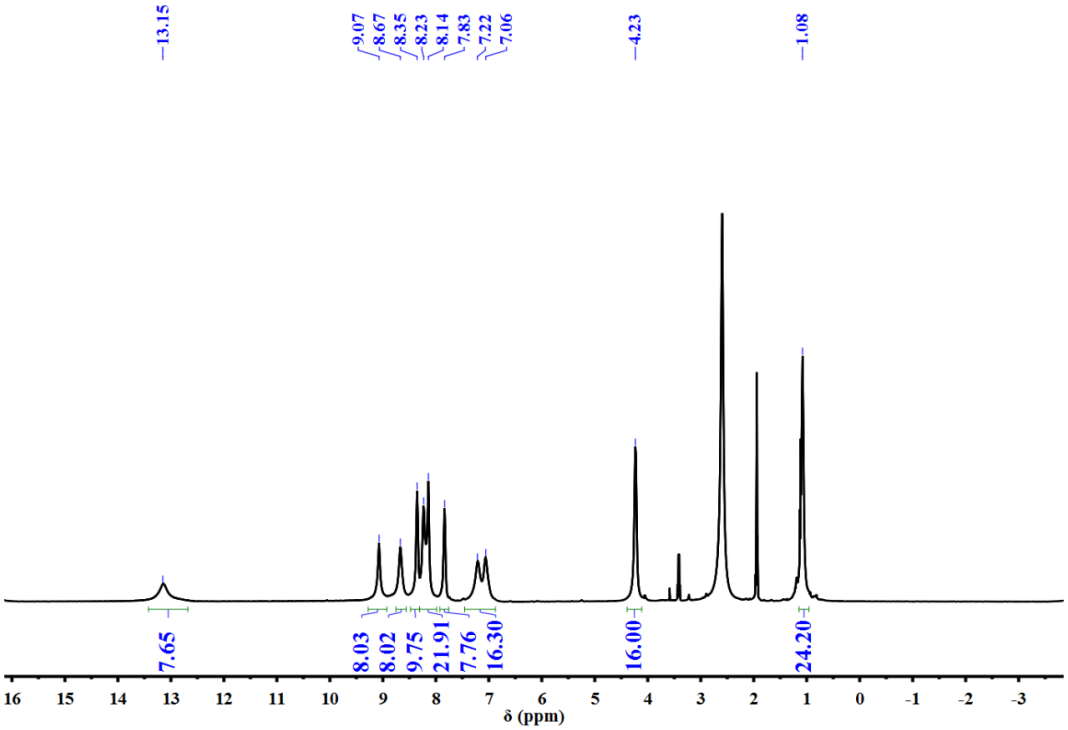


Figure S4. ^{1}H NMR spectrum (500 MHz, CD_3CN) of **2**.

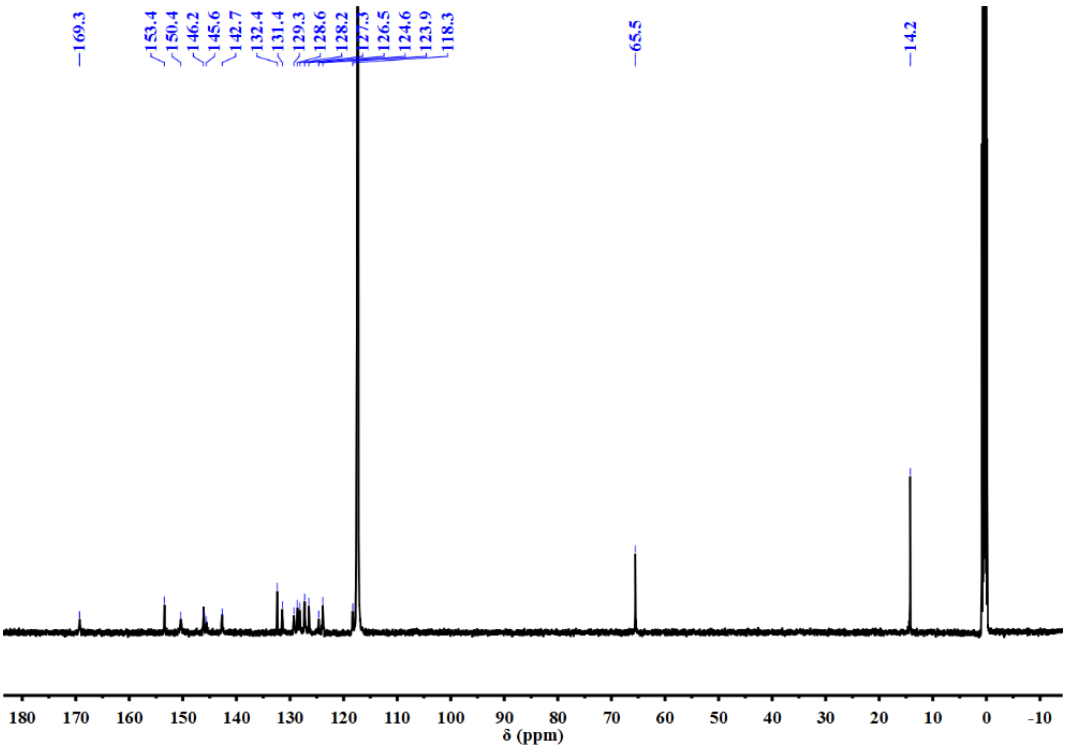


Figure S5. ^{13}C NMR spectrum (126 MHz, CD_3CN) of **2**.

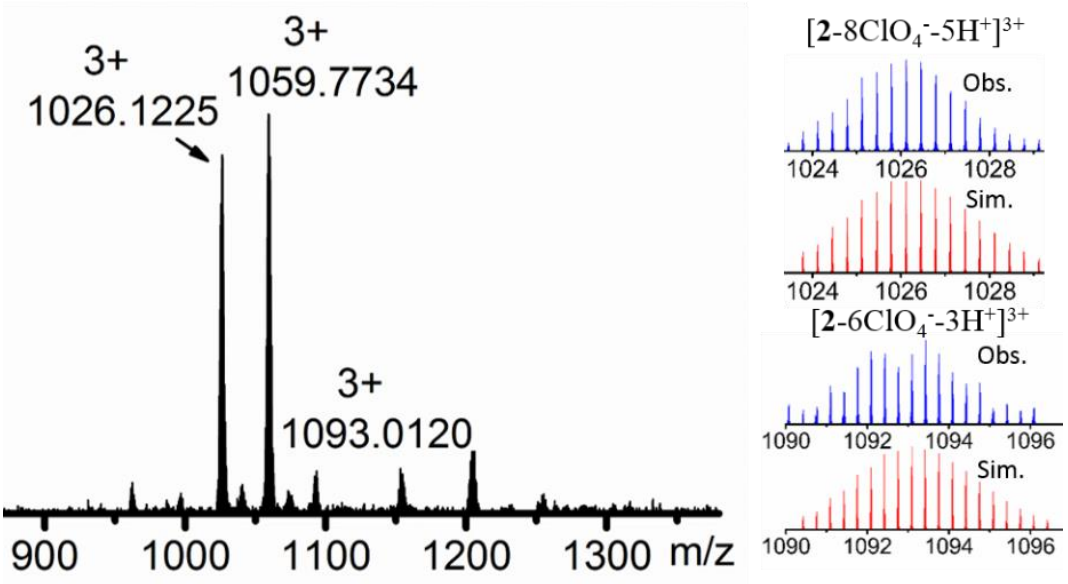


Figure S6. High-resolution ESI-MS spectrum of **2**.

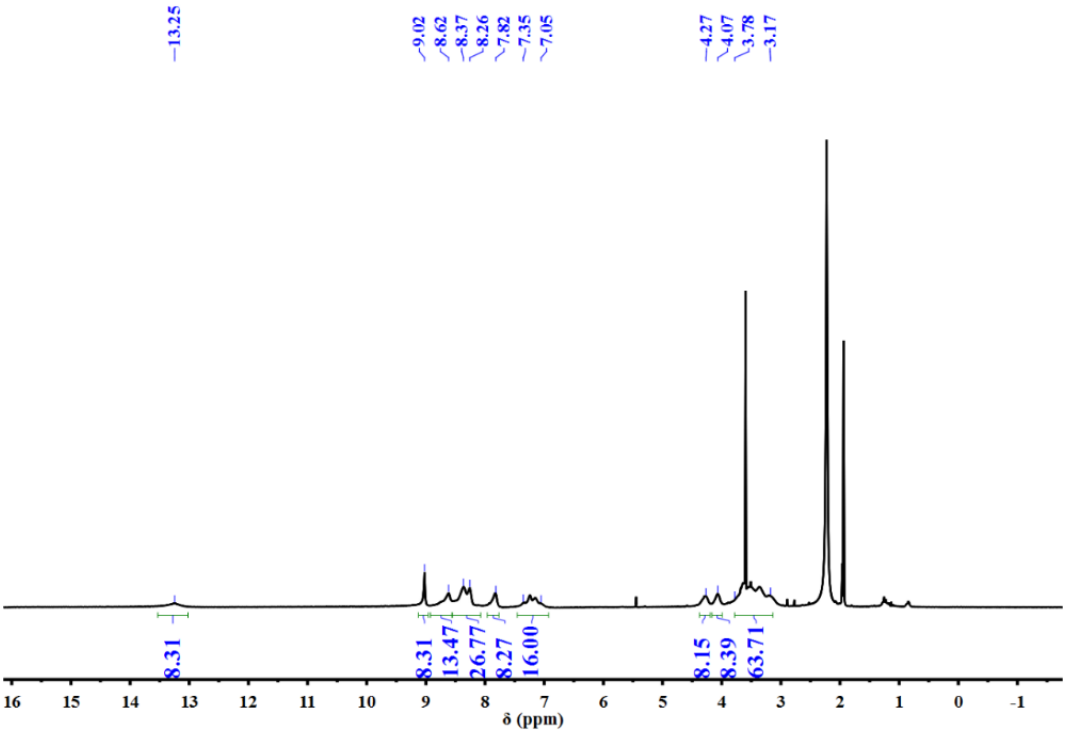


Figure S7. ^{1}H NMR spectrum (500 MHz, CD_3CN) of **3**.

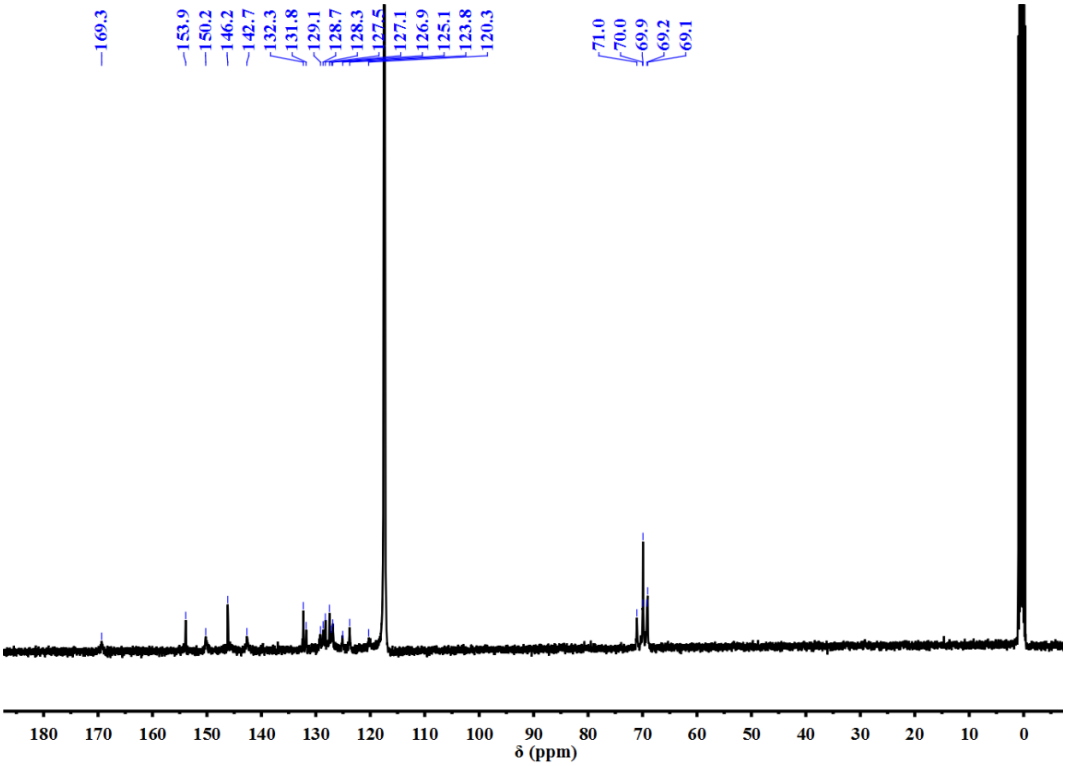


Figure S8. ^{13}C NMR spectrum (126 MHz, CD_3CN) of **3**.

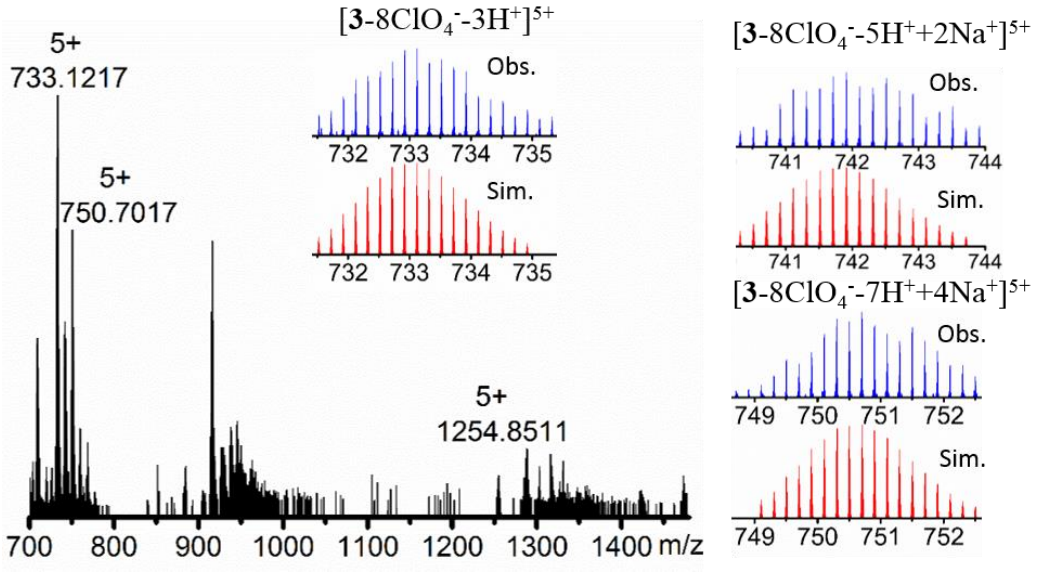


Figure S9. High-resolution ESI-MS spectrum of **3**.

4. CD spectra

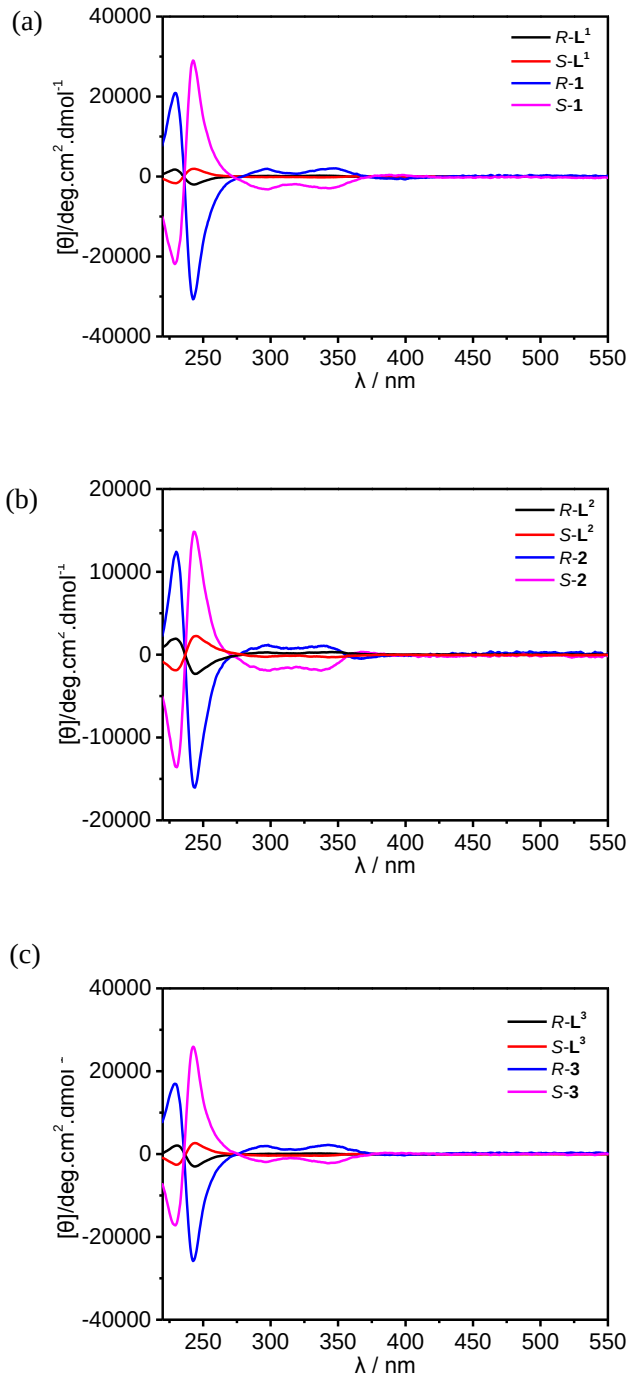


Figure S10. CD spectra of metallacycles and ligands. The ligands $\mathbf{L^{1\text{-}3}}$ were dissolved in CH_3OH (1.0 mM) and metallacycles **1-3** were dissolved in CH_3CN (0.25 mM). The cell length is 1.0 cm.

5. Table S1. Crystal data and structure refinement

Identification code	**2**
Empirical formula	$C_{152}\ H_{120}\ Cl_{14}\ N_{24}\ O_{40}\ Zn_4$
Formula weight	3680.49
Temperature (K)	173 (2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	*C*222
a (Å)	30.262(6)
b (Å)	36.517(7)
c (Å)	13.816(3)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$), Z	15268(5), 2
Density (calculated) (g / cm^3)	0.801
Absorption coefficient (mm^{-1})	0.478
F(000)	3756
Reflections collected / unique	3419/3419
Completeness to theta	19.782, 0.894
R_{int}	0.101
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3419 / 1464 / 479
Goodness of fit on F^2	1.088
Final R indices [I > 2sigma(I)]	$R_1 = 0.0711$, $wR_2 = 0.2146$
R indices (all data)	$R_1 = 0.0762$, $wR_2 = 0.2235$
Absolute structure parameter	0.02(4)
Residue peak / hole ($eÅ^{-3}$)	0.345 / -0.636

6. Table S2. Selected bond lengths and angles of 2

Zn(2)-N(2)	2.133(13)	N(5)-Zn(1)-N(6)	74.3(4)
Zn(2)-O(1)	2.243(10)	O(C(7)-O(4)-Zn(1)	111.6(11)
Zn(1)-N(6)	2.093(7)	C(1)-N(6)-Zn(1)	116.3(12)
Zn(2)-N(1)	2.122(8)	C(33)-N(2)-Zn(2)	151.5(2)
Zn(1)-O(4)	2.206(10)	N(4)-N(5)-Zn(1)	110.3(10)
Zn(1)-N(5)	2.065(12)	C(34)-N(1)-Zn(2)	124.5(6)
N(2)-Zn(2)-O(1)	75.1(5)	C(5)-N(6)-Zn(1)	114.5(5)
N(1)-Zn(2)-O(1)	96.6(4)	N(3)-N(2)-Zn(2)	114.3(9)
N(5)-Zn(1)-O(4)	73.8(5)	C(6)-N(5)-Zn(1)	122.5(10)
N(1)-Zn(2)-N(2)	121.5(4)	C(38)-N(1)-Zn(2)	115.5(6)
N(6)-Zn(1)-O(4)	147.2(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,-z+1 #2 -x+1,y,-z+1

7. Additional graphics of the structures

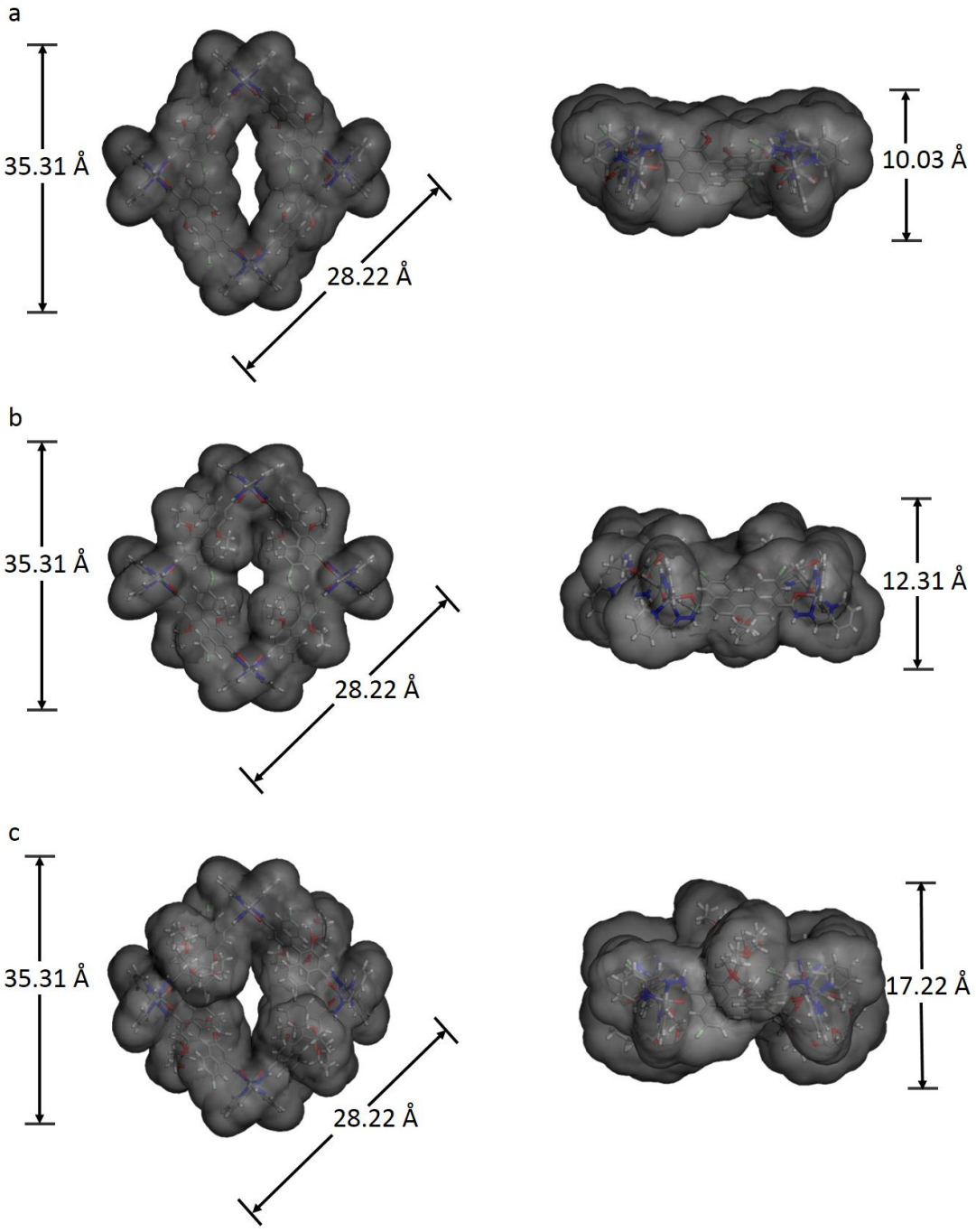


Figure S11. The size and height of **1** (a), **2** (b), and **3** (c).

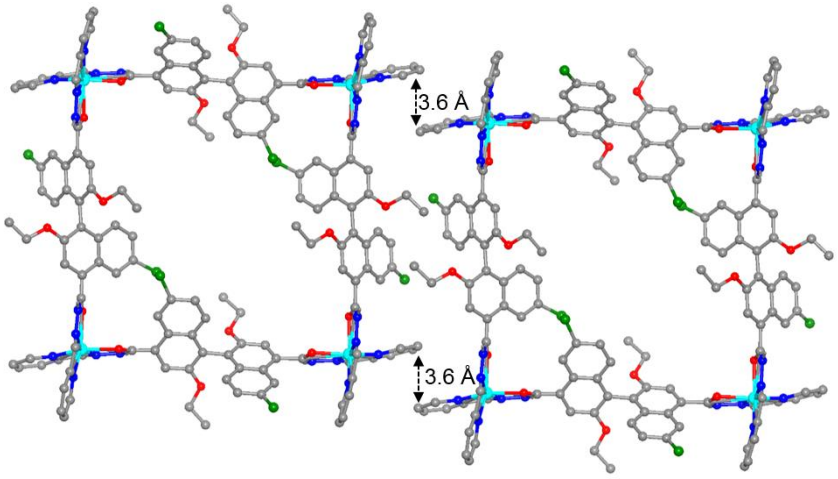


Figure S12. The π-π stacking in the vertices between two metallacycles.

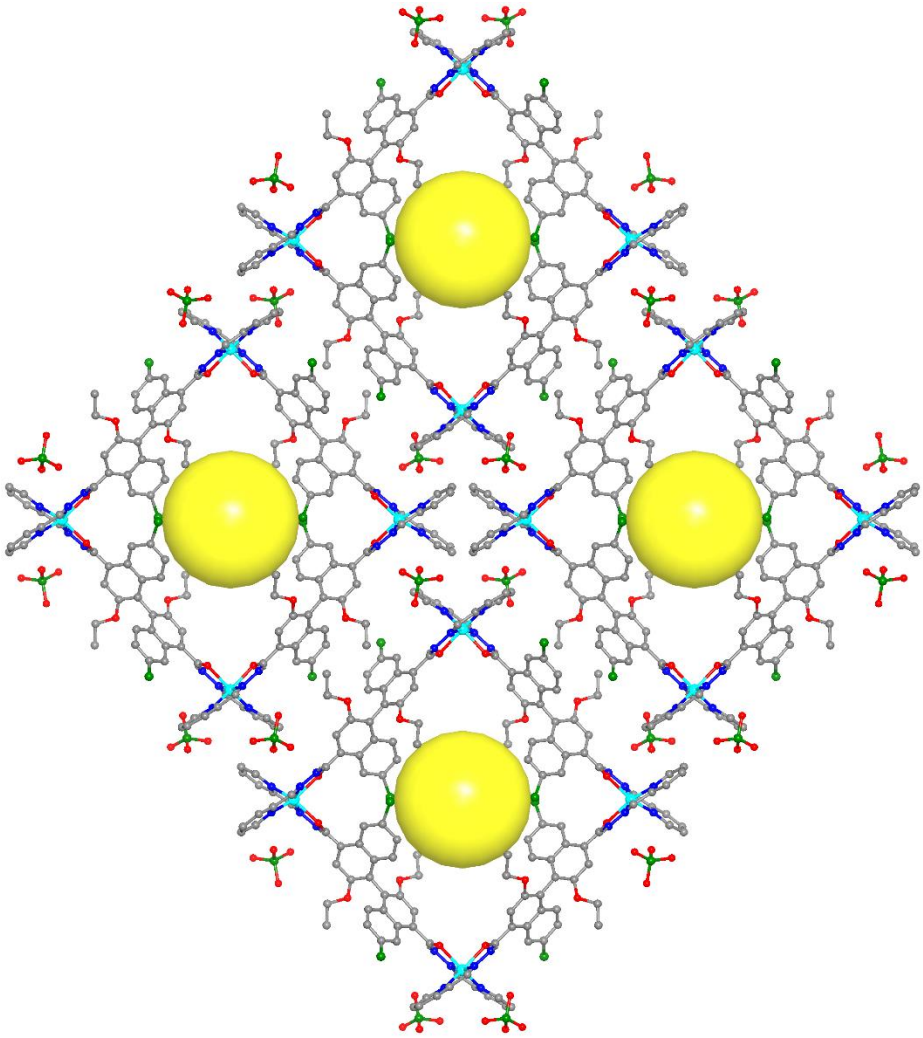
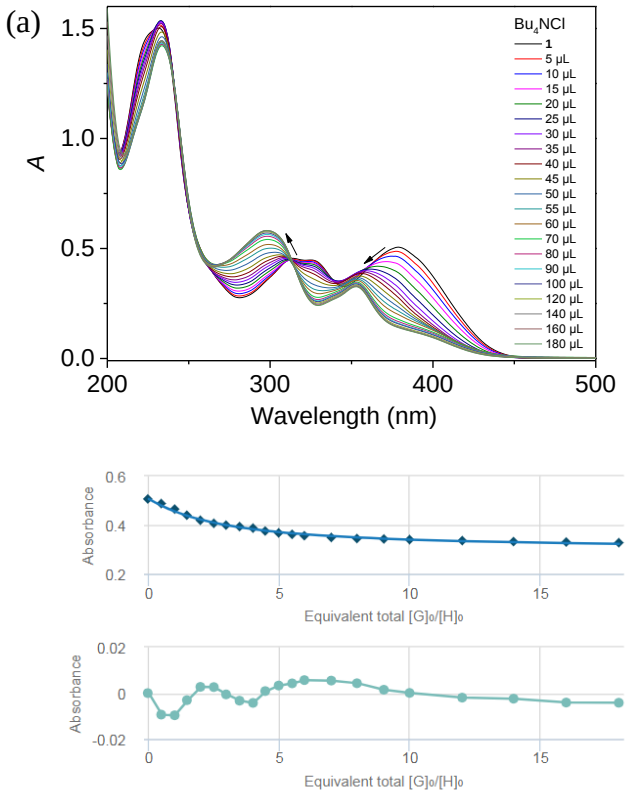
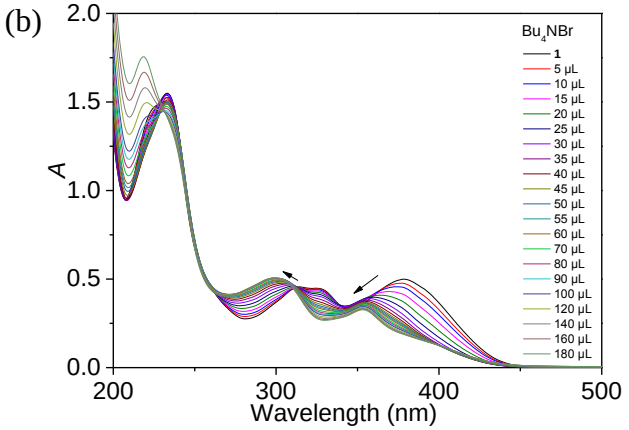


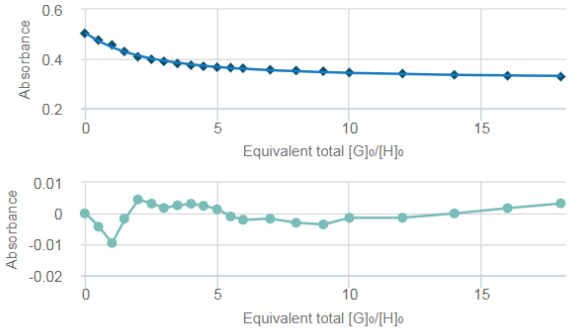
Figure S13. The packing model of **2** along *c*-aix.

8. UV-vis spectra of host-guest titration and the *BindFit* plots

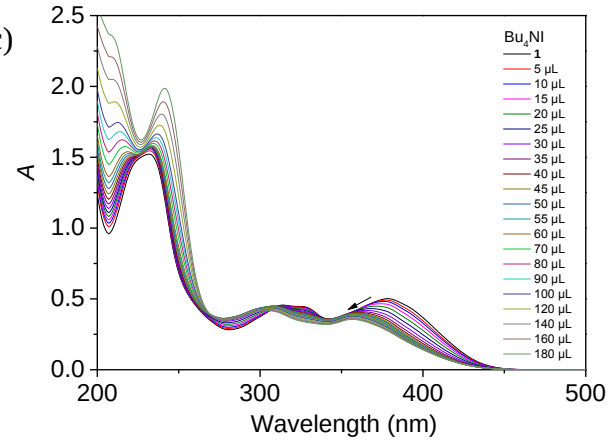
The titration experiments were carried out by adding 5/10 μL solution of ions (Bu_4NCl, Bu_4NBr, Bu_4NI, Bu_4NNO_3, Bu_4NClO_4, $LiBF_4$, $NaBF_4$, KBF_4 and $RbBF_4$, 1.0×10^{-3} mol L^{-1} in CH_3CN) to a solution of metallacycles **1-3** (5.0×10^{-6} mol L^{-1}) in 2.0 mL CH_3CN every 5 min. The absorption was measured at room temperature. The association constants *K* were calculated by fitting the change in absorbance at 377 nm (for anions) and 314 nm (for cations) using *Bindfit* (for this program, please see: http://app.supramolecular.org/bindfit/).

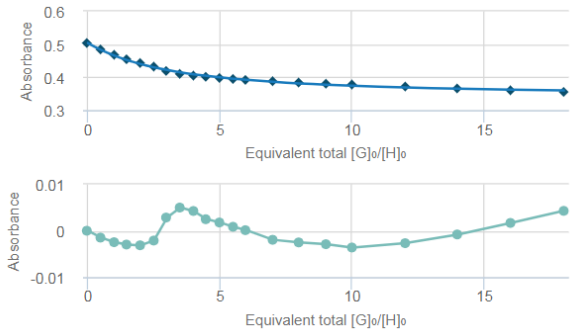




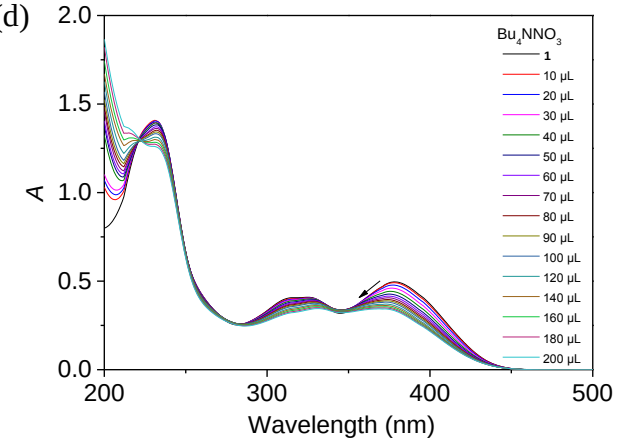

Absorbance
0.6
0.4
0.2
0
5
10
15
Equivalent total [G]₀/[H]₀
Absorbance
0.01
0
-0.01
-0.02
0
5
10
15
Equivalent total [G]₀/[H]₀

(c)


Bu4NI
1
5 μL
10 μL
15 μL
20 μL
25 μL
30 μL
35 μL
40 μL
45 μL
50 μL
55 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
A
2.5
2.0
1.5
1.0
0.5
0.0
200
300
400
500
Wavelength (nm)


Absorbance
0.6
0.5
0.4
0.3
0
5
10
15
Equivalent total [G]₀/[H]₀
Absorbance
0.01
0
-0.01
0
5
10
15
Equivalent total [G]₀/[H]₀

(d)


Bu4NNO3
1
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL
A
2.0
1.5
1.0
0.5
0.0
200
300
400
500
Wavelength (nm)

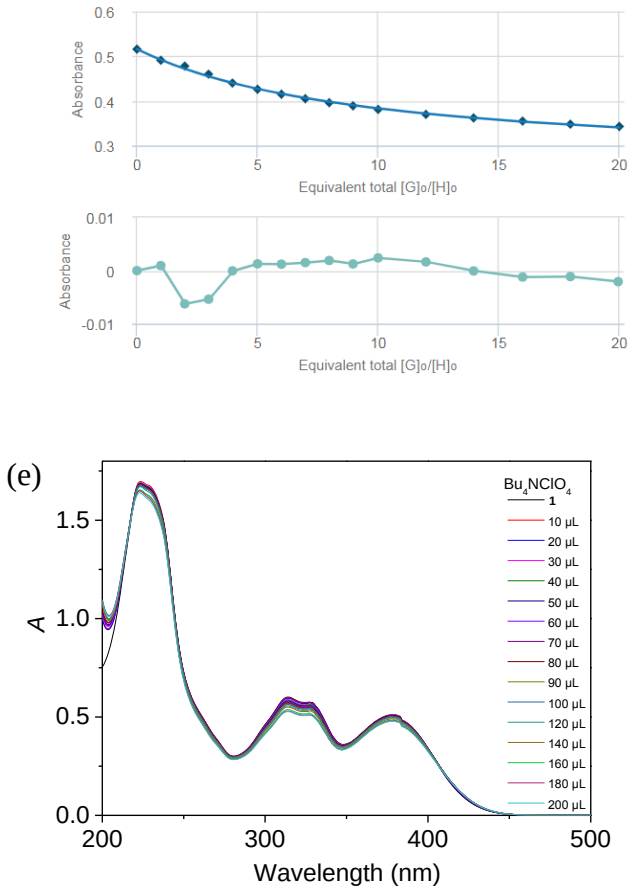
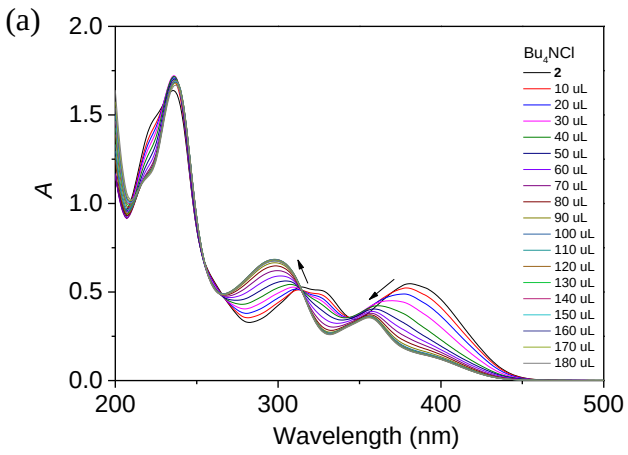
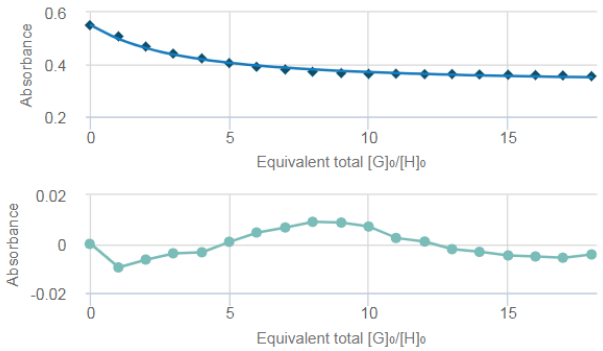
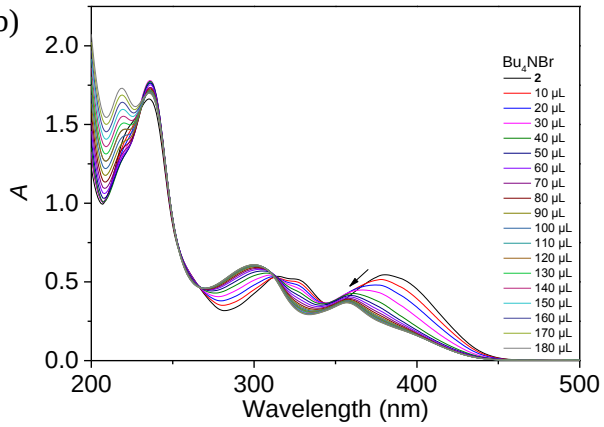


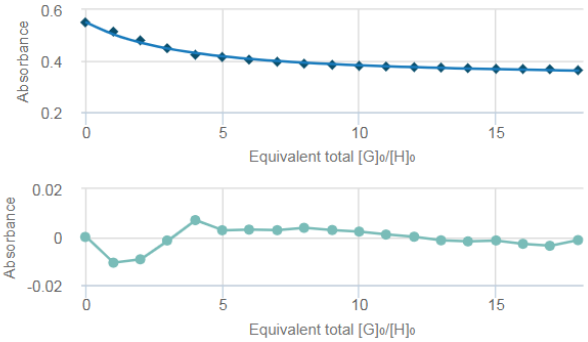
Figure S14. UV-vis spectra of **1** upon addition of different amounts of Bu_4NCl (a), Bu_4NBr (b), Bu_4NI (c), Bu_4NNO_3 (d), Bu_4NClO_4 (e) and the corresponding *BindFit* plots. Data were fitted to a normal 1:1 Nelder-Mead binding model.



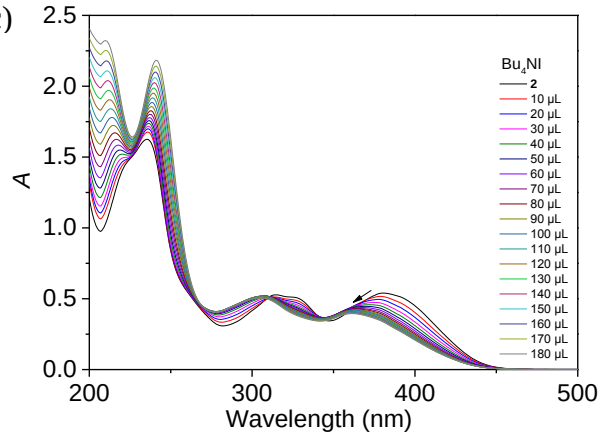

Absorbance
0.6
0.4
0.2
0
5
10
15
Equivalent total [G]0/[H]0
Absorbance
0.02
0
-0.02
0
5
10
15
Equivalent total [G]0/[H]0

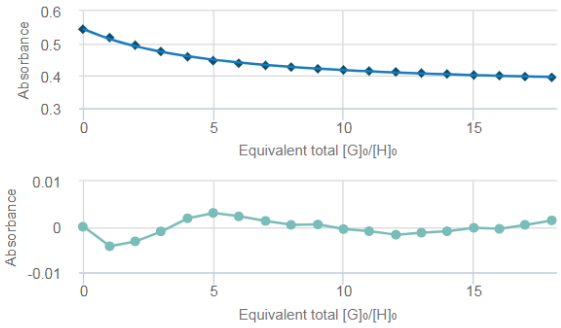
(b)

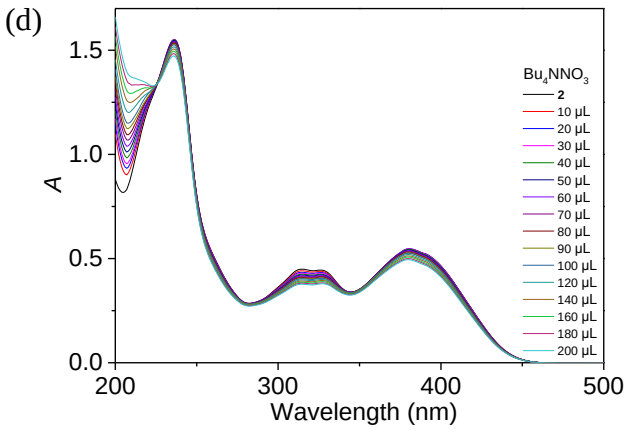

A
2.0
1.5
1.0
0.5
0.0
200
300
400
500
Wavelength (nm)
Bu4NBr
2
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
110 μL
120 μL
130 μL
140 μL
150 μL
160 μL
170 μL
180 μL


Absorbance
0.6
0.4
0.2
0
5
10
15
Equivalent total [G]0/[H]0
Absorbance
0.02
0
-0.02
0
5
10
15
Equivalent total [G]0/[H]0

(c)


A
2.5
2.0
1.5
1.0
0.5
0.0
200
300
400
500
Wavelength (nm)
Bu4NI
2
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
110 μL
120 μL
130 μL
140 μL
150 μL
160 μL
170 μL
180 μL





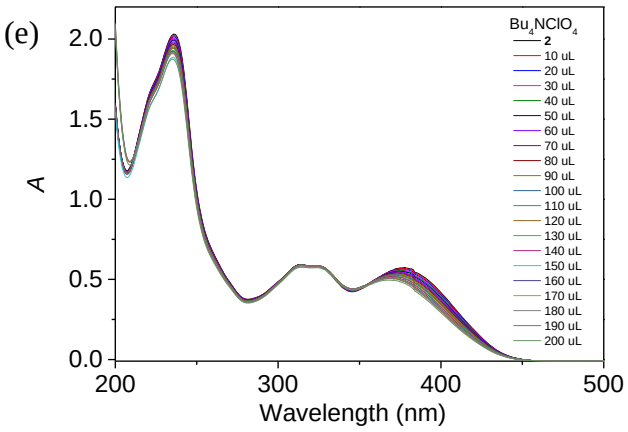
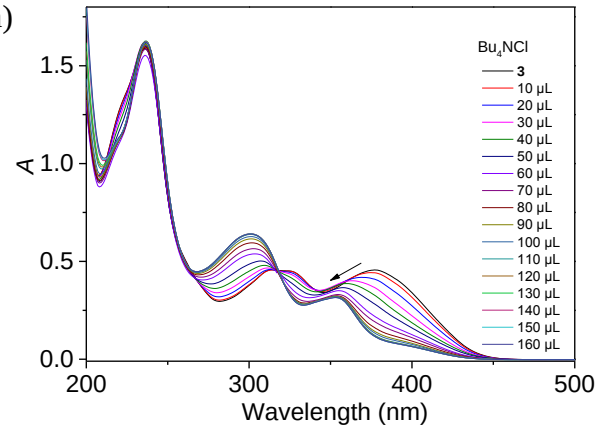
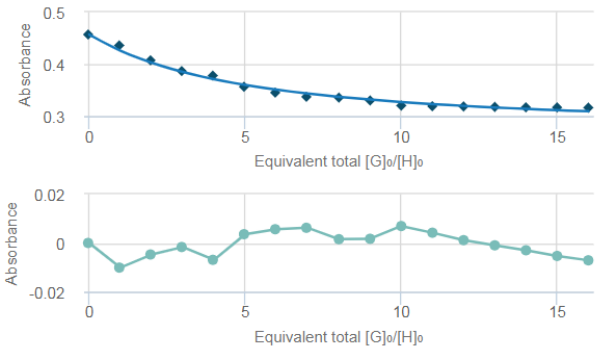


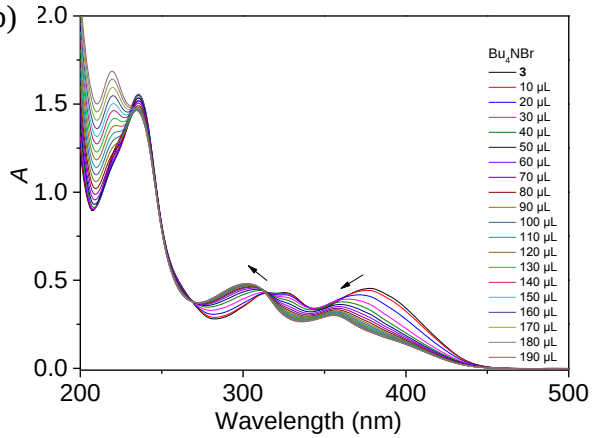
Figure S15. UV-vis spectra of **2** upon addition of different amounts of Bu_4NCl (a), Bu_4NBr (b), Bu_4NI (c), Bu_4NNO_3 (d), Bu_4NClO_4 (e) and the corresponding *BindFit* plots. Data were fitted to a normal 1:1 Nelder-Mead binding model.

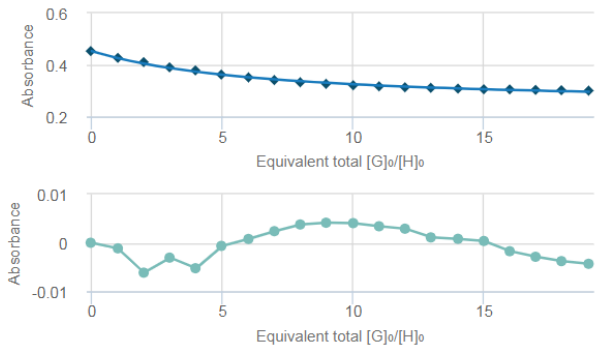
(a)


Bu4NCl
3
10 µL
20 µL
30 µL
40 µL
50 µL
60 µL
70 µL
80 µL
90 µL
100 µL
110 µL
120 µL
130 µL
140 µL
150 µL
160 µL
A
Wavelength (nm)

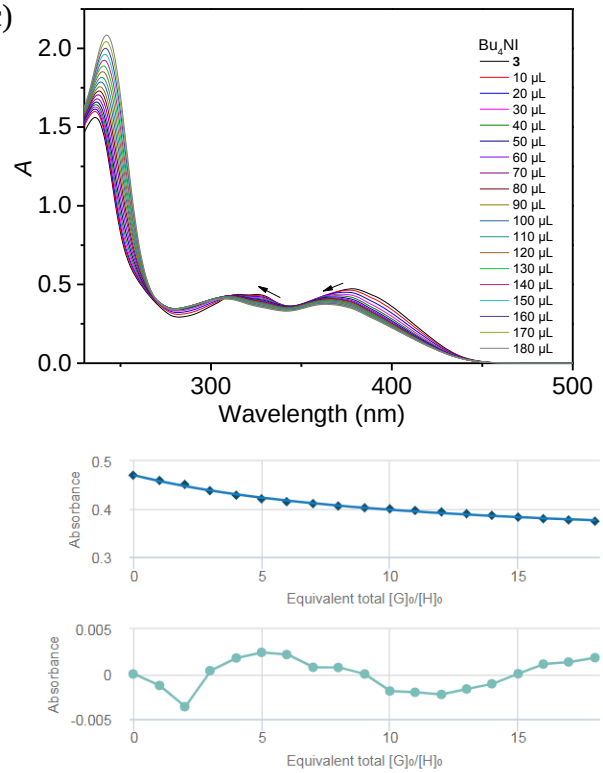

Absorbance
Equivalent total [G]0/[H]0
Absorbance
Equivalent total [G]0/[H]0

(b)

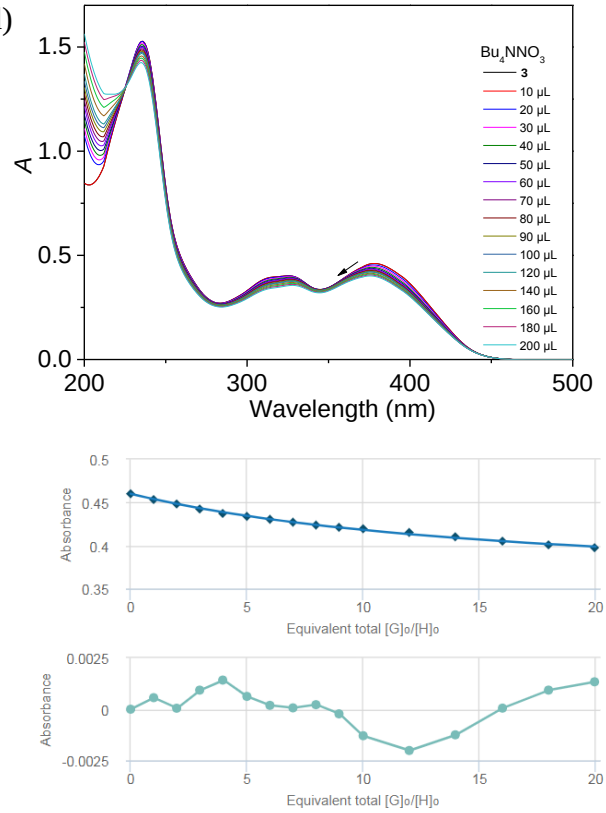

Bu4NBr
3
10 µL
20 µL
30 µL
40 µL
50 µL
60 µL
70 µL
80 µL
90 µL
100 µL
110 µL
120 µL
130 µL
140 µL
150 µL
160 µL
170 µL
180 µL
190 µL
A
Wavelength (nm)


Absorbance
Equivalent total [G]0/[H]0
Absorbance
Equivalent total [G]0/[H]0

(c)


Bu4NI
3
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
110 μL
120 μL
130 μL
140 μL
150 μL
160 μL
170 μL
180 μL
A
Wavelength (nm)
Absorbance
Equivalent total [G]0/[H]0
Absorbance
Equivalent total [G]0/[H]0

(d)


Bu4NNO3
3
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL
A
Wavelength (nm)
Absorbance
Equivalent total [G]0/[H]0
Absorbance
Equivalent total [G]0/[H]0

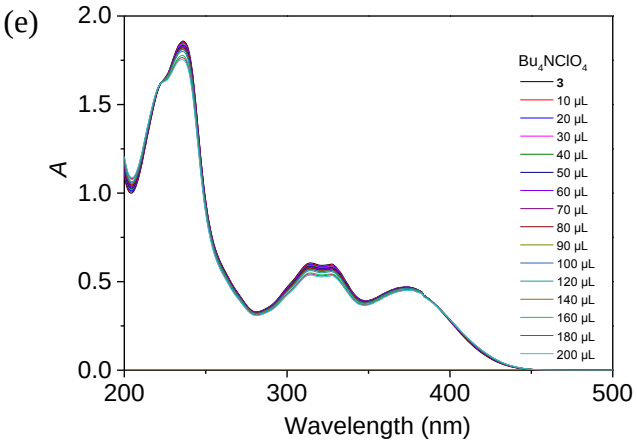
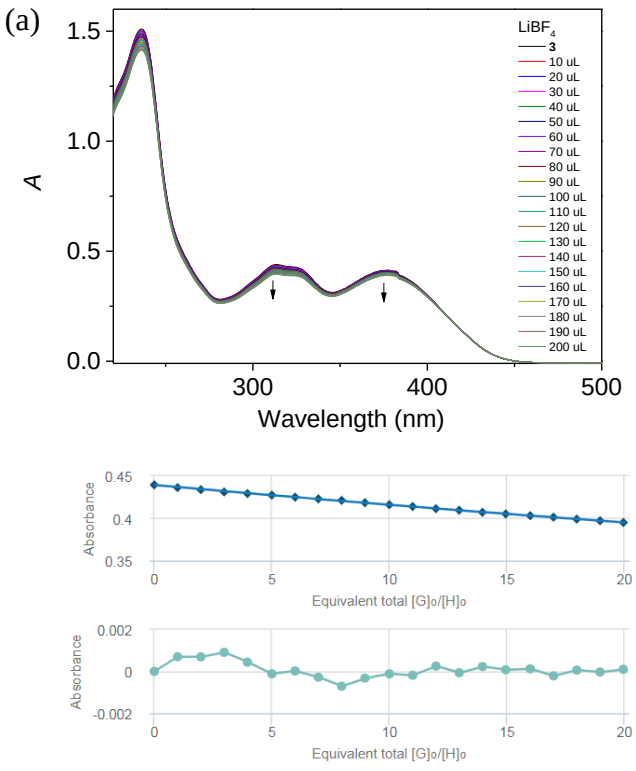
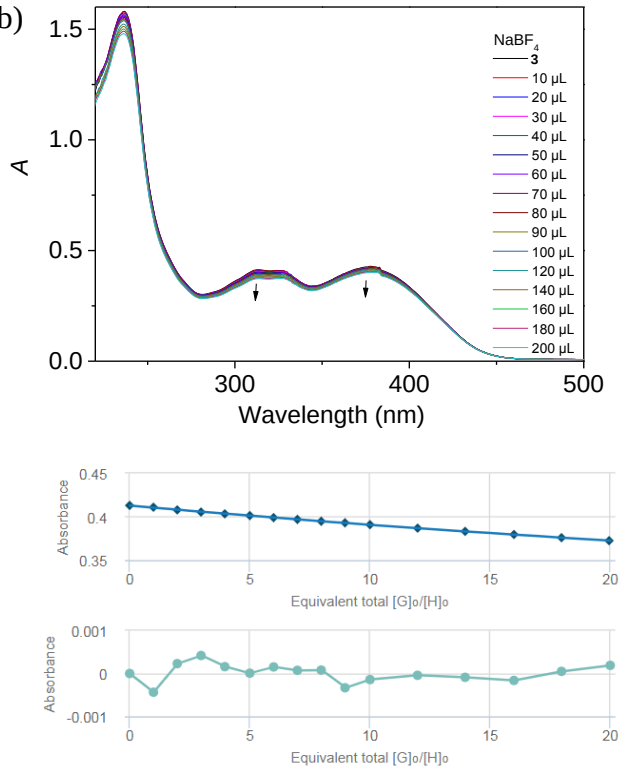


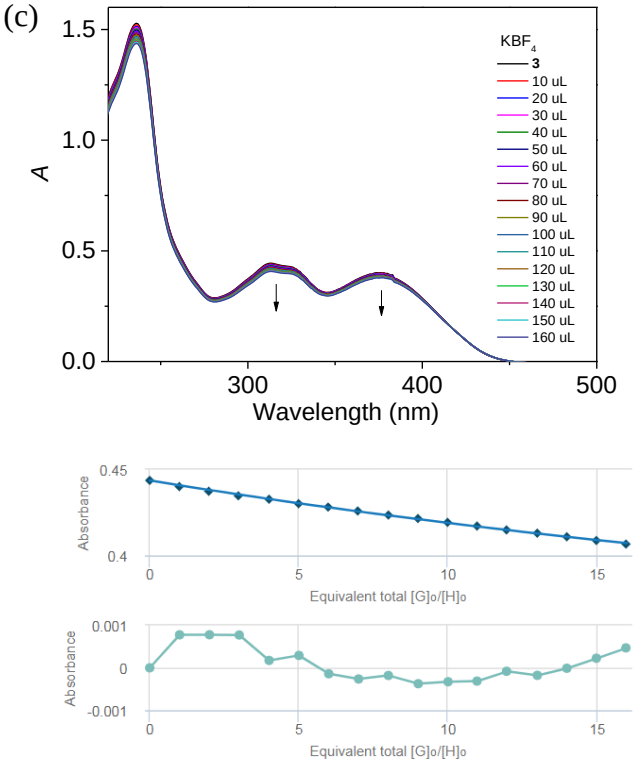
Figure S16. UV-vis spectra of **3** upon addition of different amounts of Bu_4NCl (a), Bu_4NBr (b), Bu_4NI (c), Bu_4NNO_3 (d), Bu_4NClO_4 (e) and the corresponding *BindFit* plots. Data was fitted to a normal 1:1 Nelder-Mead binding model.



(b)


NaBF4
3
10 µL
20 µL
30 µL
40 µL
50 µL
60 µL
70 µL
80 µL
90 µL
100 µL
120 µL
140 µL
160 µL
180 µL
200 µL
A
Wavelength (nm)
Absorbance
Equivalent total [G]0/[H]0

(c)


KBF4
3
10 uL
20 uL
30 uL
40 uL
50 uL
60 uL
70 uL
80 uL
90 uL
100 uL
110 uL
120 uL
130 uL
140 uL
150 uL
160 uL
A
Wavelength (nm)
Absorbance
Equivalent total [G]0/[H]0

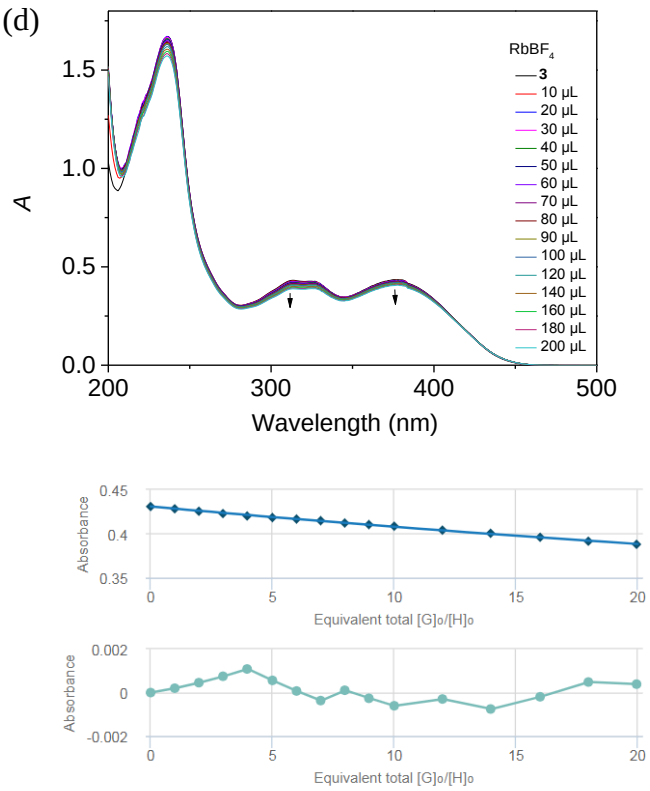


Figure S17. UV-vis spectra of **3** upon addition of different amounts of $LiBF_4$ (a), $NaBF_4$ (b), KBF_4 (c), $RbBF_4$ (d) and the corresponding *BindFit* plots. Data was fitted to a normal 1:1 Nelder-Mead binding model.

Table S3. Association constants *K* (M^{-1}) of metallacycles with the different ions.[a]

Titration	**Cl^-**	**Br^-**	**I^-**	**NO_3^-**	**ClO_4^-**
1	(11.9±0.6) ×10^4	(8.6±0.5) ×10^4	(6.6±0.2) ×10^4	(2.3±0.05) ×10^4	-[b]
2	(7.6±0.4) ×10^4	(6.8±0.3) ×10^4	(4.6±0.1) ×10^4	-[b]	-[b]
3	(3.8±0.3) ×10^4	(3.1±0.1) ×10^4	(1.9±0.06) ×10^4	(1.2±0.02) ×10^4	-[b]
	Li^+	**Na^+**	**K^+**	**Rb^+**	
3	1302±21	2293±40	3237±32	1856±24	

[a]The association constants are the average of three experiments. [b]The equilibrium constants are too small that can not be calculated exactly.

9. ESI-MS spectra of 1@Cl^-

Complex **1@Cl^-** was prepared by adding nBu_4NCl (1 mM in CH_3CN, 120 μL) to the solution of **1** (1 mM in CH_3CN, 100 μL) and the mixture was stirred overnight.

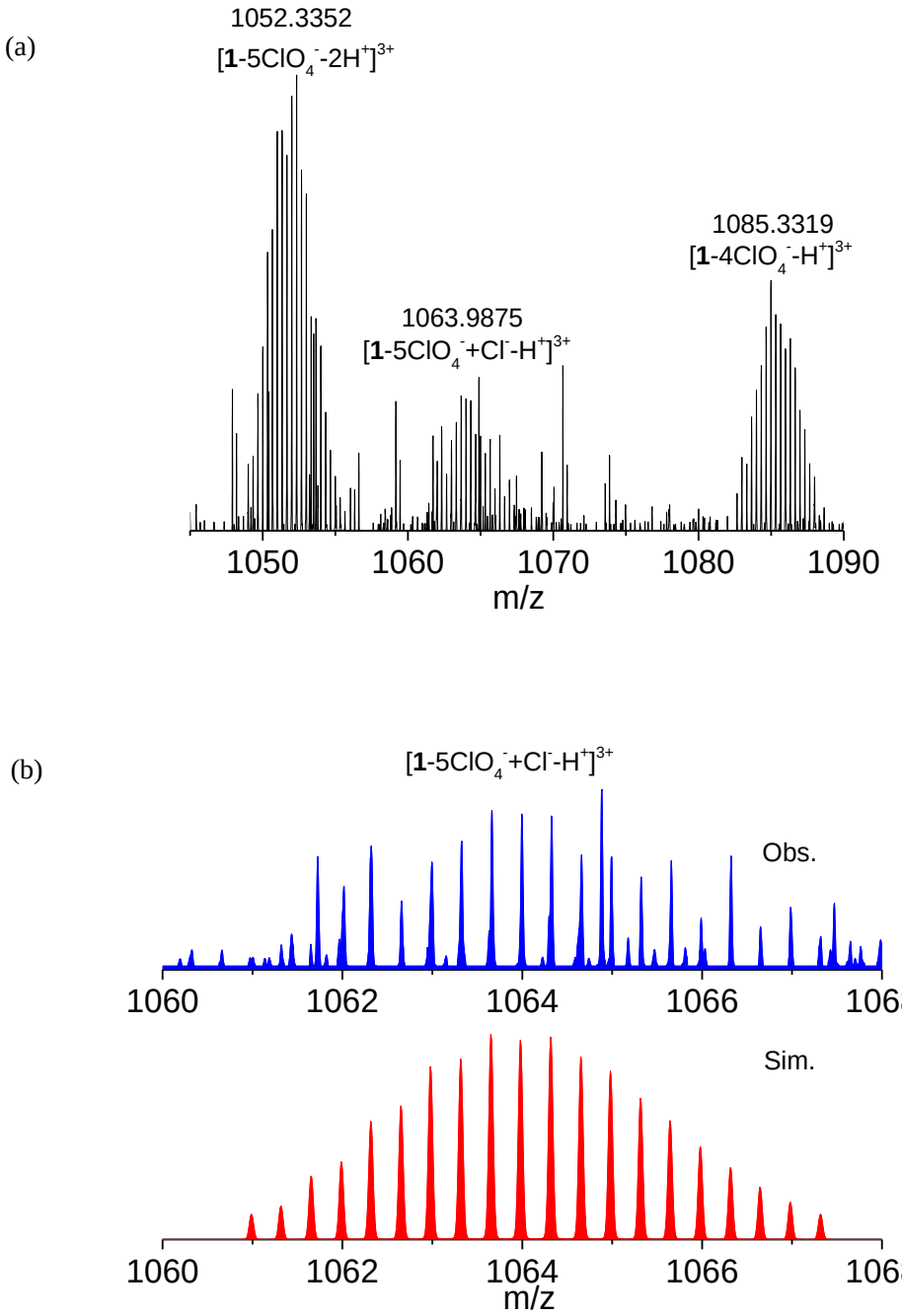


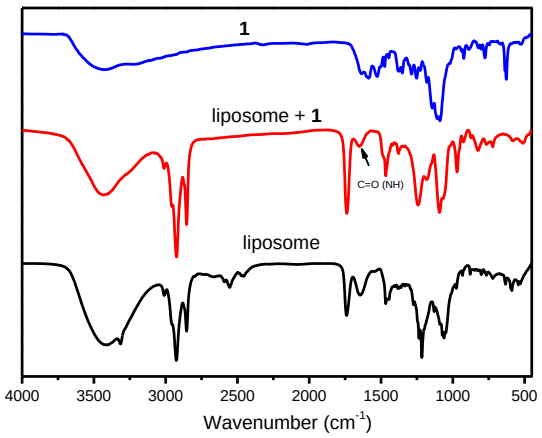
Figure S18. (a) ESI-MS spectrum of **1**@Cl^-. (b) Experimental ESI-MS and calculated isotope patterns of **1**@Cl^-.

10. IR experiments

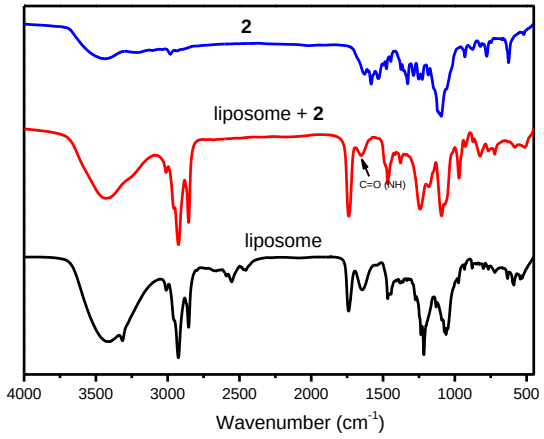
Preparation of the large unilamellar vesicles (LUVs): LUVs for IR experiments were prepared according to previously reported method.[2] Egg yolk L-α-phosphatidylcholine (EYPC) (100 mg) was dissolved in $CHCl_3$ (20 mL). The solution was evaporated under reduced pressure at 40 °C and the resulting thin film was dried under high vacuum overnight. The lipid film was hydrated with HEPES buffer solution (5.0 mL, HEPES = 10 mM, NaCl = 100 mM, pH = 7.0) at 40 °C for 2 h to give a milky suspension. Subsequently, the resulting suspension was subjected to 10 freeze/thaw cycles by using liquid N_2 to freeze and warm water bath to thaw, and extruded through the polycarbonate membrane (MILLIPORE Isopore, 0.2 μm) for 10 times to yield LUV suspension.

Preparation of the channel incorporated lipid membrane: A solution of **1**, **2** or **3** (1.0 mM, 130 μL) in CH_3CN was added to the prepared LUVs suspension (1 mL). The mixture was subjected to centrifugation (9600 r/min) for 1 h, and then the upper aqueous phase was removed. The centrifugation process was repeated for 3 times by using the same HEPES buffer. The resulting LUVs were dried under vacuum to generate **1**, **2** or **3** incorporated membrane.

(a)



(b)



(c)

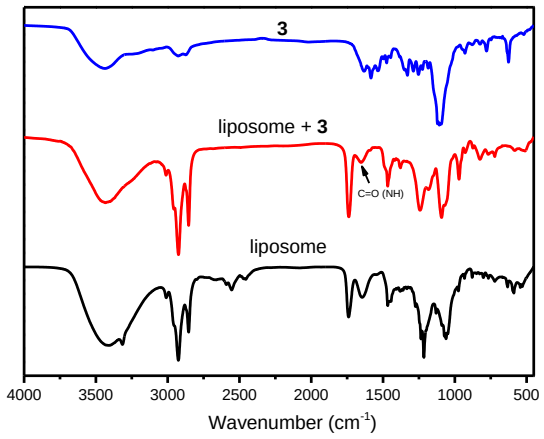


Figure S19. IR spectra of liposome, metallacycles and metallacycles@liposomes.

11. Confocal fluorescence microscopy

GUVs were prepared according to previously reported method.[3] 20 mg EYPC with 1.0 mg **1**, **2** or **3** was first dissolved in 10 ml $CHCl_3$. The solution was evaporated under reduced pressure at 40 ºC and the resulting thin film was dried under high vacuum overnight. Then the film was hydrated at 40 ºC overnight with 6 ml sucrose solution (0.2 M). Fluorescence imaging was performed on a Leica/TCS SP8 STED 3X microscope. The bright field images were taken in the monochromatic mode and fluorescence images were taken with sample excited at 405 nm. Blue circles indicate the presence of metallacycles in lipid bilayer.

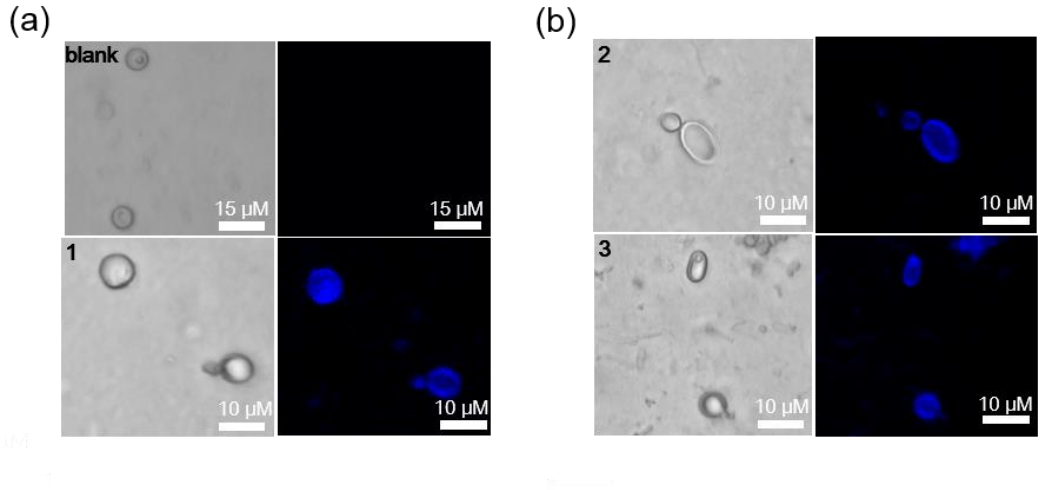


Figure S20. GUVs imaged in bright field (left) and fluorescence mode (right, excitation: 405 nm). (a) Images of pure GUV (up) and **1**•GUV (down); (b) Images of **2**•GUV (up) and **3**•GUV (down).

12. HPTS assays

Typical procedures for the preparation of the large unilamellar vesicles (LUVs): EYPC (200 mg) was dissolved in $CHCl_3$ (50 mL). The solution was evaporated under reduced pressure at 40 °C and the resulting thin film was dried under high vacuum overnight. The lipid film was hydrated with HEPES buffer solution (8.0 mL, [HPTS] = 1 mM, [HEPES] = 10 mM, [NaCl] = 100 mM) at 40 °C for 2 h to give a yellow milky suspension. Subsequently, the resulting suspension was subjected to 10 freeze/thaw cycles by using liquid N_2 to freeze and warm water bath to thaw, and extruded through the polycarbonate membrane (MILLIPORE Isopore, 0.2 μm) for 20 times to yield LUVs suspension.

The LUVs solution was placed in a dialysis tubing which has a molecular weight cut-off (MWCO) of 10000 to remove the HPTS that out of the LUVs. This dialysis procedure was repeated 12 times by using the HEPES buffer solution (200 mL, [HEPES] = 10 mM, [NaCl] = 100 mM) (12 times × 2 h/time) without HPTS. The resulting lipid suspension was diluted with HEPES buffer (without HPTS) to give a vesicle stock solution ([lipid] = 15 mM).

Procedure for HPTS assays

The vesicle stock solution (50 μL) was diluted with HEPES buffer (1950 μL), then the vesicle suspension was added to a fluorescence cuvette equipped with a stirred bar. Metallacycle (2 μL, 1 mM in CH_3CN, 0.26 mol% relative to total EYPC) was added into the mixture at 0 s, then the fluorescence emission at 510 nm was recorded, resulting from the simultaneous excitation at 405 nm and 460 nm (λ_{ex1} = 405 nm, λ_{em} = 510 nm, $I_{t(405)}$; λ_{ex2} = 460 nm, λ_{em} = 510 nm, $I_{t(460)}$; ratio fluorescence intensities $F_t = I_{t(460)} / I_{t(405)}$). A base pulse of 0.5 M NaOH (20 μL) was added at 60 s. Finally, Triton X-100 (10 μL, 20% v/v solution in water) was added at 360 s to lyse the vesicles. Fluorescence data was collected for a further 60 s to ensure the LUVs were completely lysed. Fluorescence time courses were normalized to fractional emission intensity I_{norm} using equation:

$$I_{norm} = (F_t - F_0)/(F_\infty - F_0) \qquad \textbf{equation S1}$$

F_0 is the ratio fluorescence intensity before addition of NaOH, and F_∞ is the ratio fluorescence intensity after addition of Triton X-100.

The concentration profile data were analyzed by Hill equation to get the effective concentration at half maximal activity (EC_{50}) and Hill coefficient (n).

$$Y = 1/(1+ (EC_{50}/c)^n) \qquad \textbf{equation S2}$$

Where Y is the I_{norm} value at 360 s and c is the concentration of metallacycle in the cuvette.

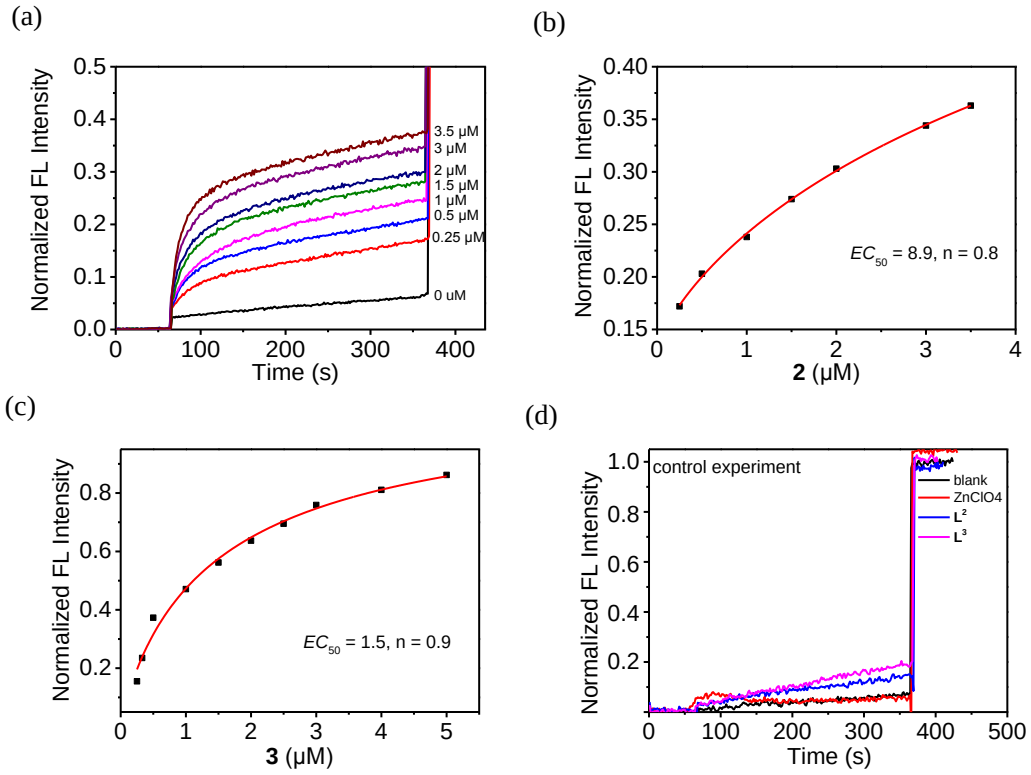


Figure S21. (a) Changes in fluorescence intensity of HPTS with the increasing of the concentration (0 – 3.5 μM) of **2**. (b, c) Determination of EC_{50} values for **2** and **3** using the ratiometric values of $I_{t(460)}/I_{t(405)}$ at different concentrations. (d) $\mathbf{L}^2$ (4 μM), $\mathbf{L}^3$ (4 μM) and $Zn(ClO_4)_2$ (4 μM) were used in the transport process as control experiments.

13. Fluorescence spectra of 2 and 3

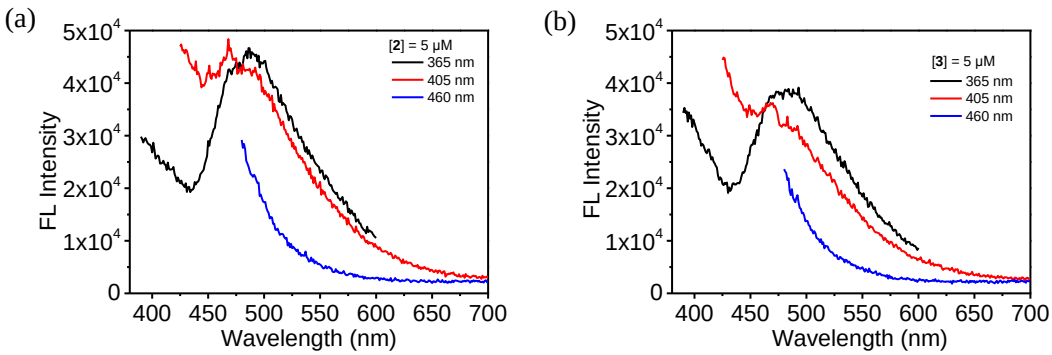


Figure S22. The fluorescence spectra of **2** (a) and **3** (b) at the different excitation wavelength. The quantum yield of **2** and **3** is 2.4% and 3.1% (λex=365 nm, λem=490 nm), respectively.

14. Ratio fluorescence assay of 2 and 3 without HPTS

EYPC (200 mg) was dissolved in $CHCl_3$ (50 mL). The solution was evaporated under reduced pressure at 40 °C and the resulting thin film was dried under high vacuum overnight. The lipid film was hydrated with HEPES buffer solution (8.0 mL, [HEPES] = 10 mM, [NaCl] = 100 mM) at 40 °C for 2 h to give a milky suspension. Subsequently, the resulting suspension was subjected to 10 freeze/thaw cycles by using liquid N_2 to freeze and warm water bath to thaw, and extruded through the polycarbonate membrane (MILLIPORE Isopore, 0.2 μm) for 20 times to yield LUVs suspension. The resulting lipid suspension was diluted with HEPES buffer to give a vesicle stock solution ([lipid] = 15 mM). And the test procedure is same as the HPTS assay.

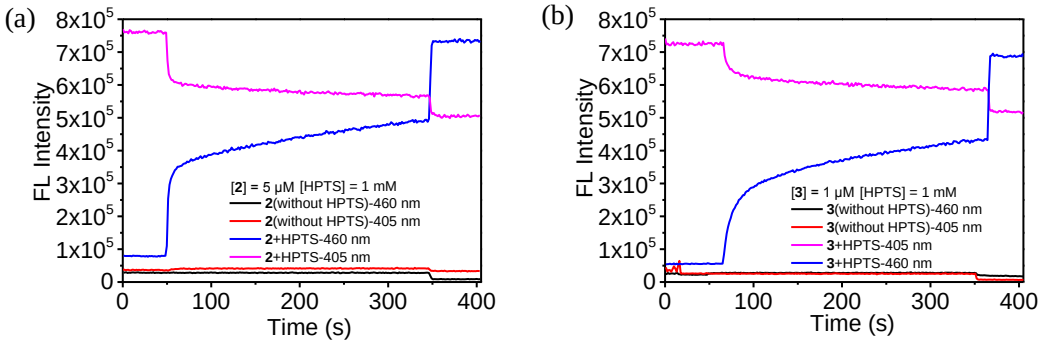


Figure S23. The fluorescence changes of **2@liposome** (a) and **3@liposome** (b) in the absence/presence of HPTS.

15. 5(6)-Carboxyfluorescein (CF) assay

Typical procedures for the preparation of the large unilamellar vesicles (LUVs): EYPC (200 mg) was dissolved in $CHCl_3$ (50 mL). The solution was evaporated under reduced pressure at 40 °C and the resulting thin film was dried under high vacuum overnight. The lipid film was hydrated with HEPES buffer solution (8.0 mL, [CF] = 50 mM, [HEPES] = 10 mM, [NaCl] = 100 mM, pH = 7.6) at 40 °C for 2 h to give a milky suspension. Subsequently, the resulting suspension was subjected to 10 freeze/thaw cycles by using liquid N_2 to freeze and warm water bath to thaw, and extruded through the polycarbonate membrane (MILLIPORE Isopore, 0.2 μm) for 20 times to yield LUVs suspension.

The LUVs solution was placed in a dialysis tubing which has a molecular weight cut-off (MWCO) of 10000 to remove the CF that out of the LUVs. This dialysis procedure was repeated 12 times by using the HEPES buffer solution (200 mL, [HEPES] = 10 mM, [NaCl] = 100 mM, pH = 7.6) (12 times × 2 h/time) without CF. The resulting lipid suspension was diluted with HEPES buffer (without CF) to give a vesicle stock solution ([lipid] = 15 mM).

Procedure for CF assays

The vesicle stock solution (50 μL) was diluted with HEPES buffer (1950 μL), the vesicle suspension was added to a fluorescence cuvette equipped with a stirred bar. Then the fluorescence emission at 517 nm was recorded, resulting from excitation at 492 nm. Metallacycle (5 μM) was added into the solution at 50 s. Finally, Triton X-100 (10 μL, 20% v/v solution in water) was added at 350 s to lyse the vesicles. Fluorescence data was collected for a further 50 s to ensure the LUVs were completely lysed. Fluorescence time courses were normalized to fractional emission intensity I_{norm} using equation:

$$I_{norm} = (I_t - I_0)/(I_\infty - I_0)$$

I_0 is the fluorescence intensity before addition of cage, and I_∞ is the fluorescence intensity after addition of Triton X-100.

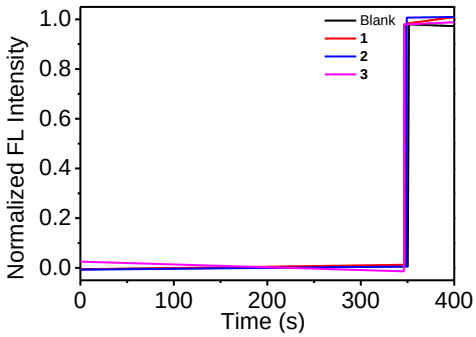


Figure S24. Schematic representation of CF dye leakage assay and fluorescence intensity changes in self quenching CF dye (λex = 492 nm, λem = 517 nm) after additions of metallacycles **1-3**. Inside LUVs: 10 mM HEPES, 100 mM NaCl, 50 mM CF, pH = 7.6; outside LUVs: 10 mM HEPES, 100 mM NaCl, pH = 7.6.

16. HPTS assay for cation selectivity

The HPTS-containing LUVs suspension (15.0 mM, 50 μL, [HPTS] = 1 mM, [HEPES] = 10 mM, [NaCl] = 100 mM) was added to a HEPES buffer solution (1950 μL, [HEPES] = 10 mM, [MCl] = 100 mM, M^+ = Li^+, Na^+, K^+, Rb^+ and Cs^+). Metallacycle (2 μL, 1 mM in CH_3CN, 0.26 mol% relative to total EYPC) was added into the solution at 0 s, then the fluorescence emission at 510 nm was recorded, resulting from the simultaneous excitation at 405 nm and 460 nm (λ_{ex1} = 405 nm, λ_{em} = 510 nm, $I_{t(405)}$; λ_{ex2} = 460 nm, λ_{em} = 510 nm, $I_{t(460)}$; ratio fluorescence intensities $F_t = I_{t(460)}/ I_{t(405)}$). A base pulse of 0.5 M MOH (20 μL, M^+ = Li^+, Na^+, K^+, Rb^+ and Cs^+) was added at 50 s. Finally, Triton X-100 (10 μL, 20% v/v solution in water) was added at 350 s to lyse the vesicles.

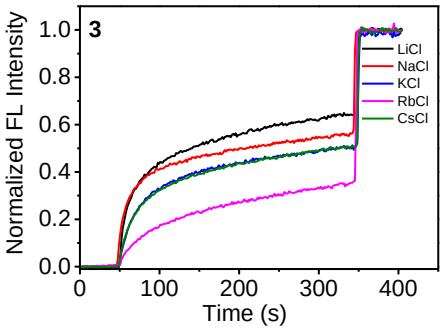


Figure S25. Transport activities toward Li^+, Na^+, K^+, Rb^+ and Cs^+ of **3** (1 μM).

17. Lucigenin assays

Typical procedures for the preparation of the large unilamellar vesicles (LUVs): EYPC (200 mg) was dissloved in $CHCl_3$ (50 mL). The solution was evaporated under reduced pressure at 40 °C and the resulting thin film was dried under high vacuum overnight. The lipid film was hydrated with HEPES buffer solution (8.0 mL, [lucigenin] = 1 mM, [HEPES] = 10 mM, [$NaNO_3$] = 100 mM) at 40 °C for 2 h to give a yellow milky suspension. Subsequently, the resulting suspension was subjected to 10 freeze/thaw cycles by using liquid N_2 to freeze and warm water bath to thaw, and extruded through the polycarbonate membrane (MILLIPORE Isopore, 0.2 μm) for 20 times to yield LUVs suspension.

The LUVs solution was placed in a dialysis tubing which has a molecular weight cut-off (MWCO) of 10000 to remove the lucigenin that out of the LUVs. This dialysis procedure was repeated 12 times by using the HEPES buffer solution (200 mL, [HEPES] = 10 mM, [$NaNO_3$] = 100 mM) (12 times × 2 h/time) without lucigenin. The resulting lipid suspension was diluted with HEPES buffer (without lucigenin) to give a vesicle stock solution ([lipid] = 15 mM).

Procedure for lucigenin assays

The vesicle stock solution (50 μL) was diluted with HEPES buffer (1950 μL), the vesicle suspension was added to a fluorescence cuvette equipped with a stirred bar. Metallacycle (8 μL, 1 mM in CH_3CN) was added into the solution at 0 s, then the fluorescence emission at 505 nm was recorded, resulting from excitation at 455 nm. A pulse of 1.0 M NaCl (20 μL) was added at 60 s. Finally, Triton X-100 (10 μL, 20% v/v solution in water) was added at 360 s to lyse the vesicles. Fluorescence data was collected for a further 60 s to ensure the LUVs were completely lysed. Fluorescence time courses were normalized to fractional emission intensity I_{norm} using equation:

$$I_{norm} = (I_t - I_\infty)/(I_0 - I_\infty) \qquad \textbf{equation S3}$$

I_0 is the fluorescence intensity before addition of NaCl, and I_∞ is the fluorescence intensity after addition of Triton X-100.

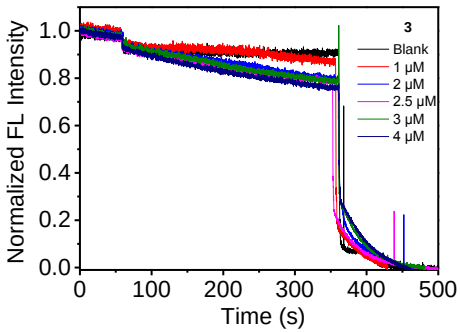


Figure S26. Lucigenin assay by nitrate/chloride exchange for confirming chloride as the transport species.

18. HPTS assay with FCCP and VA

HPTS assay in the presence of FCCP (carbonyl cyanide 4-(trifluoromethoxy)phenylhydrazone)

The HPTS-containing LUVs suspension (15.0 mM, 50 μL, [HPTS] = 1 mM, [HEPES] = 10 mM, [NaCl] = 100 mM) was added to a HEPES buffer solution (1950 μL, [HEPES] = 10 mM, [Na_2SO_4] = 75 mM). Metallacycle and FCCP were added into the mixture at 0 s, then the fluorescence emission at 510 nm was recorded, resulting from the simultaneous excitation at 405 nm and 460 nm (λ_{ex1} = 405 nm, λ_{em} = 510 nm, $I_{t(405)}$; λ_{ex2} = 460 nm, λ_{em} = 510 nm, $I_{t(460)}$; ratio fluorescence intensities $F_t = I_{t(460)}/ I_{t(405)}$). A base pulse of 0.5 M NaOH (20 μL) was added at 50 s. Finally, Triton X-100 (10 μL, 20% v/v solution in water) was added at 350 s to lyse the vesicles.

HPTS assay in the presence of VA (Valinomycin)

The HPTS-containing LUVs suspension (15.0 mM, 50 μL, [HPTS] = 1 mM, [HEPES] = 10 mM, [NaCl] = 100 mM) was added to a HEPES buffer solution (1950 μL, [HEPES] = 10 mM, [KCl] = 100 mM). Metallacycle and VA were added into the mixture at 0 s, then the fluorescence emission at 510 nm was recorded, resulting from the simultaneous excitation at 405 nm and 460 nm (λ_{ex1} = 405 nm, λ_{em} = 510 nm, $I_{t(405)}$; λ_{ex2} = 460 nm, λ_{em} = 510 nm, $I_{t(460)}$; ratio fluorescence intensities $F_t = I_{t(460)}/ I_{t(405)}$). A base pulse of 0.5 M NaOH (20 μL) was added at 50 s. Finally, Triton X-100 (10 μL, 20% v/v solution in water) was added at 350 s to lyse the vesicles.

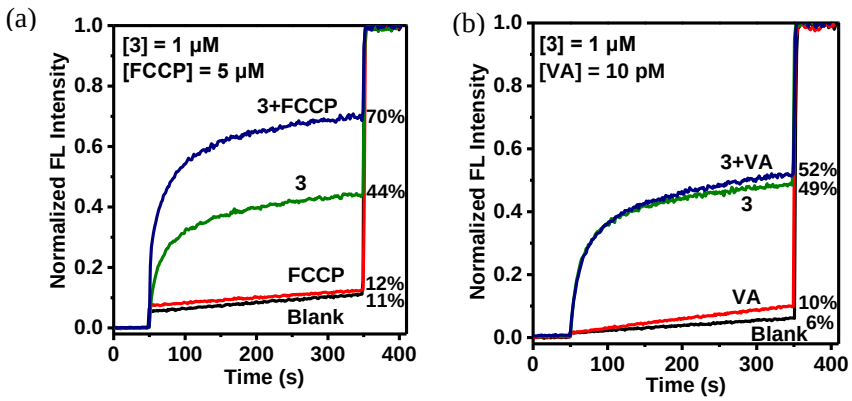


Figure S27. (a) Comparison of ion transport activity of **3** in the presence and the absence of FCCP. (b) Comparison of ion transport activity of **3** in the presence and the absence of VA.

19. Planar bilayer conductance studies

Details of preparing planar lipid bilayers is found elsewhere. Briefly, DPhPC (Avanti) lipid, dissolved in chloroform (10 mg ml^{-1}), was dried under a stream of nitrogen for a few minutes. The lipid was then dispersed in decane at 40 mg ml^{-1}. This mixture was used to precoat a 200 µm aperture on the outer side of a Delrin cup (Warner Instruments, Hamden, CT) on which a planar lipid bilayer membrane was formed at room temperature within a chamber having 1 mL KCl solution (1.0 M) on both sides. Formation of the membrane was monitored by microscopy and membrane capacitance. The test compound (**2**) in CH_3CN (1 mM) was added to both sides of the chamber to a final concentration of 5 ~ 20 µM. A holding potential of +100 mV was applied and the channel current was recorded. Channel activity was measured with respect to the trans (ground) side. Ag/AgCl electrodes were used to apply bias voltages and to record currents across the membrane. After observation of the channel activity, the voltages across the lipid bilayer were varied between –150 mV to +150 mV to determine the current (I)–voltage (V) relationship.

A Warner Instruments planar lipid bilayer workstation was used for all experiments. Data were amplified (BC-525D Bilayer Amplifier; Warner), digitized (NI PCI61 10; National Instruments, Austin, Texas, USA), filtered (LPF-8; Warner) and stored on a PC using the Signal Express (version 2.5; National Instruments). Data analysis was performed using the Origin 7.5. The data was sampled at 5 kHz and filtered by 1 kHz.

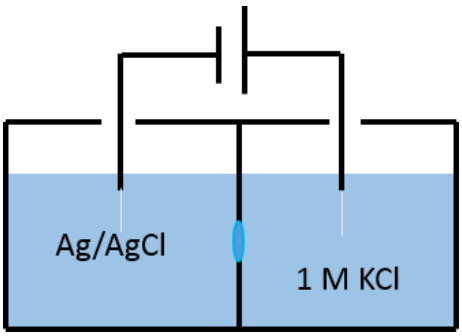


Figure S28. Schematic diagram for the planar lipid experiments. Experimental conditions: DPhPC in *n*-decane (40 mg mL^{-1}); *cis*/*trans* = 1.0 M/1.0 M KCl solution; applied voltages: 150 mV, 100 mV, 50 mV, 25 mV, 0 mV, -25 mV, -50 mV, -100 mV and -150 mV.

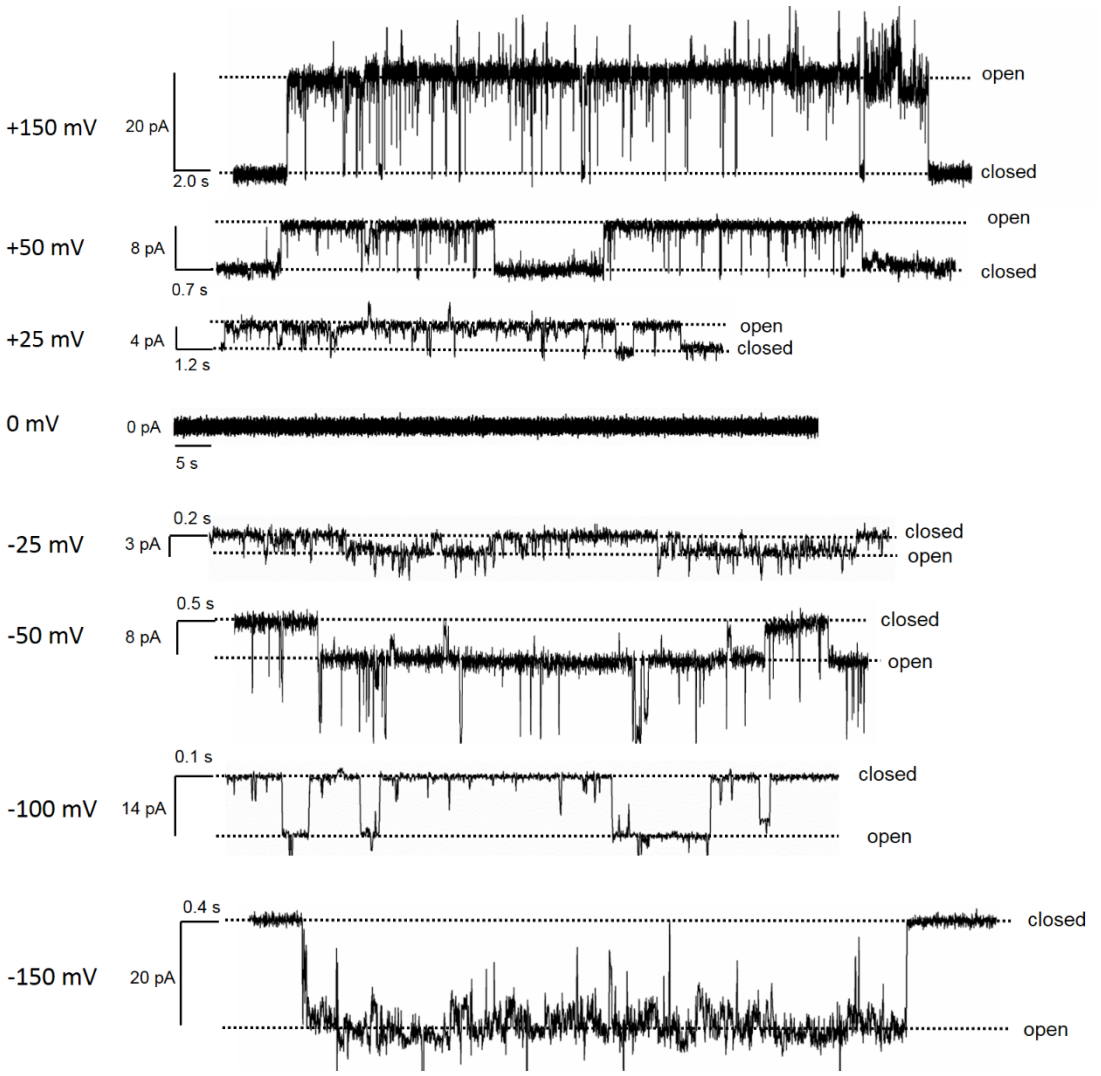


Figure S29. Representative single-channel planar bilayer current traces of ion channel **2** at different voltages in KCl solutions (*cis*/*trans* = 1.0 M/1.0 M).

Hille analysis

In studies of single channel formation in the literature, it is common to evaluate the pore size using the Hille equation,[4] which relates the conductance to the channel diameter and other experimental parameters. Sansom's correction factor of c = 4.6 was applied to the measured conductances.[5]

To calculate the channel size, the conductance of **2** (137 pS) was applied in the Hille **equation S4:**

$$\frac{1}{gc} = \frac{4l\rho}{\pi d^2} + \frac{\rho}{d} \qquad \textbf{equation S4}$$

Where g is the experiment conductance of **2** (137 pS), l is the length of bilayer (3.4 nm), ρ is the solution resistivity (0.08 Ω m for 1.0 M KCl).[6] Thus, 5.1 Å was obtained as the diameter (d) of the channel formed by **2**.

20. HPTS assay for anion selectivity

The HPTS-containing LUVs suspension (15.0 mM, 50 μL, [HPTS] = 1 mM, [HEPES] = 10 mM, [NaX] = 100 mM, X^- = Cl^-, Br^-, I^-, NO_3^- and ClO_4^-) was added to a HEPES buffer solution (1950 μL, [HEPES] = 10 mM, [NaX] = 100 mM, X^- = Cl^-, Br^-, I^-, NO_3^- and ClO_4^-). Metallacycle (2 μL, 1 mM in CH_3CN, 0.26 mol% relative to total EYPC) was added into the mixture at 0 s, then the fluorescence emission at 510 nm was recorded, resulting from the simultaneous excitation at 405 nm and 460 nm (λ_{ex1} = 405 nm, λ_{em} = 510 nm, $I_{t(405)}$; λ_{ex2} = 460 nm, λ_{em} = 510 nm, $I_{t(460)}$; ratio fluorescence intensities $F_t = I_{t(460)}/I_{t(405)}$). A base pulse of 0.5 M NaOH (20 μL) was added at 50 s. Finally, Triton X-100 (10 μL, 20% v/v solution in water) was added at 350 s to lyse the vesicles.

Fitting HPTS assay data to pseudo first order rate equations[7]

As the background rate of ClO_4^- and I^- transport is high, then the normalized fluorescence data (I_{norm}) was fitted to first order kinetics using an equation:

$$I_t = I_\infty - e^{((-k_{obs} \times t) + ln\,(I_\infty))} \qquad \textbf{equation S5}$$

I_t is the normalized fluorescence ratio at time t, I_∞ is the normalized fluorescence ratio at t = ∞, k_{obs} is the rate constant.

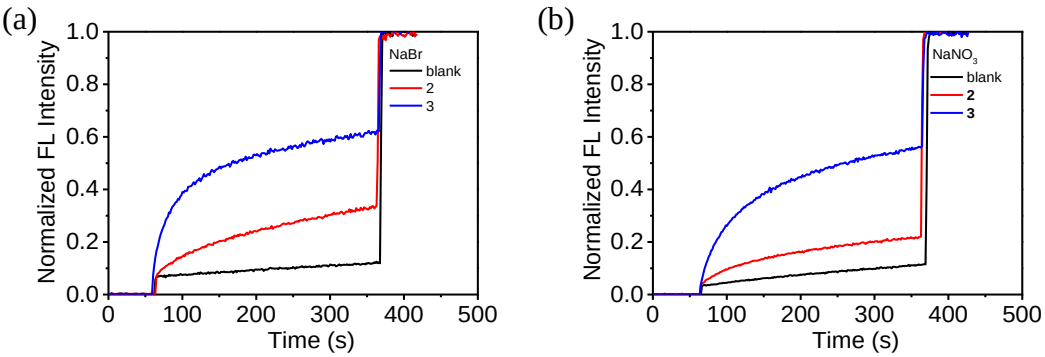


Figure S30. Changes in fluorescence intensity of HPTS encapsulated inside EYPC vesicles in the presence of varying intra- and extravesicular salts. HPTS assays toward (a) NaBr and (b) $NaNO_3$ of **2** and **3** (1 μM), respectively.

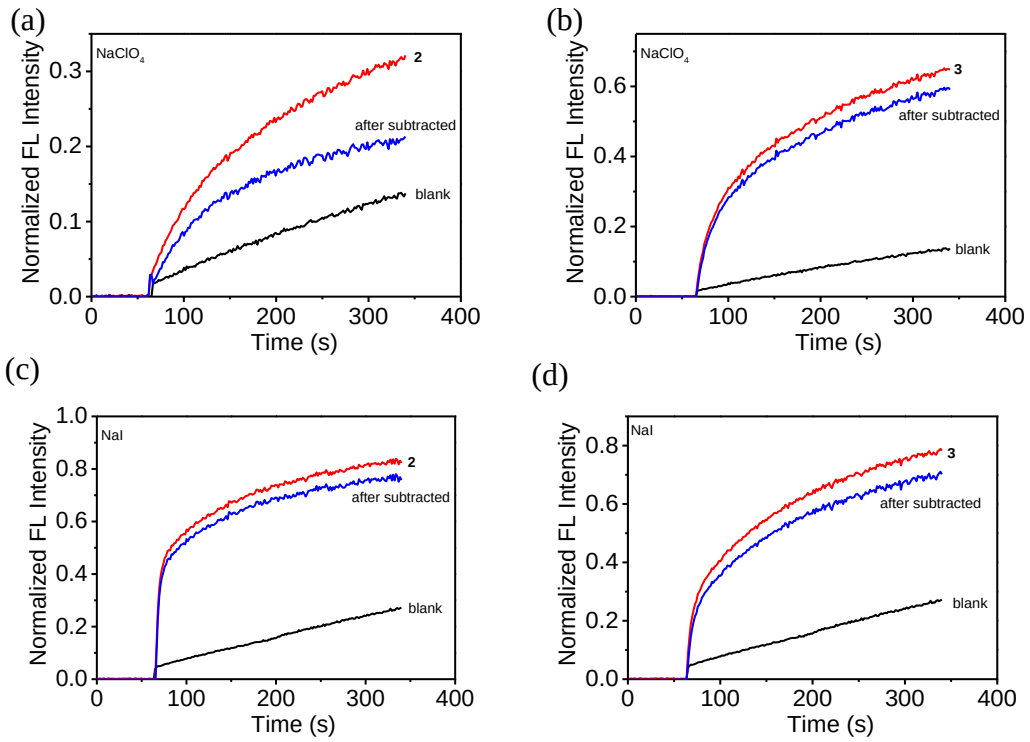


Figure S31. Changes in fluorescence intensity of HPTS encapsulated inside EYPC vesicles in the presence of varying intra- and extravesicular salts. And the background activities without metallacycles were subtracted after calibration. (a) HPTS assays toward $NaClO_4$ of **2**; (b) HPTS assays toward $NaClO_4$ of **3**; (c) HPTS assays toward NaI of **2**; (d) HPTS assays toward NaI of **3**.

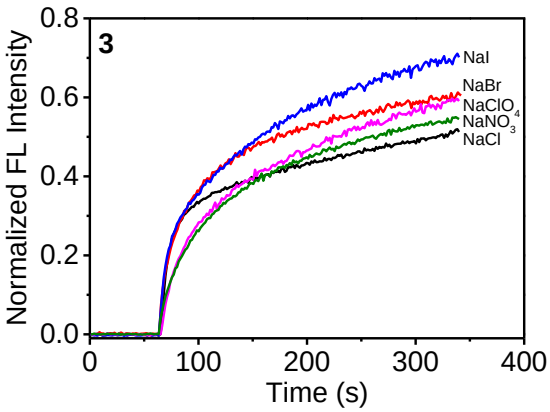


Figure S32. Transport activities toward Cl^-, Br^-, I^-, ClO_4^- and NO_3^- of **3** (1 μM). The background rate of I^- and ClO_4^- have been subtracted.

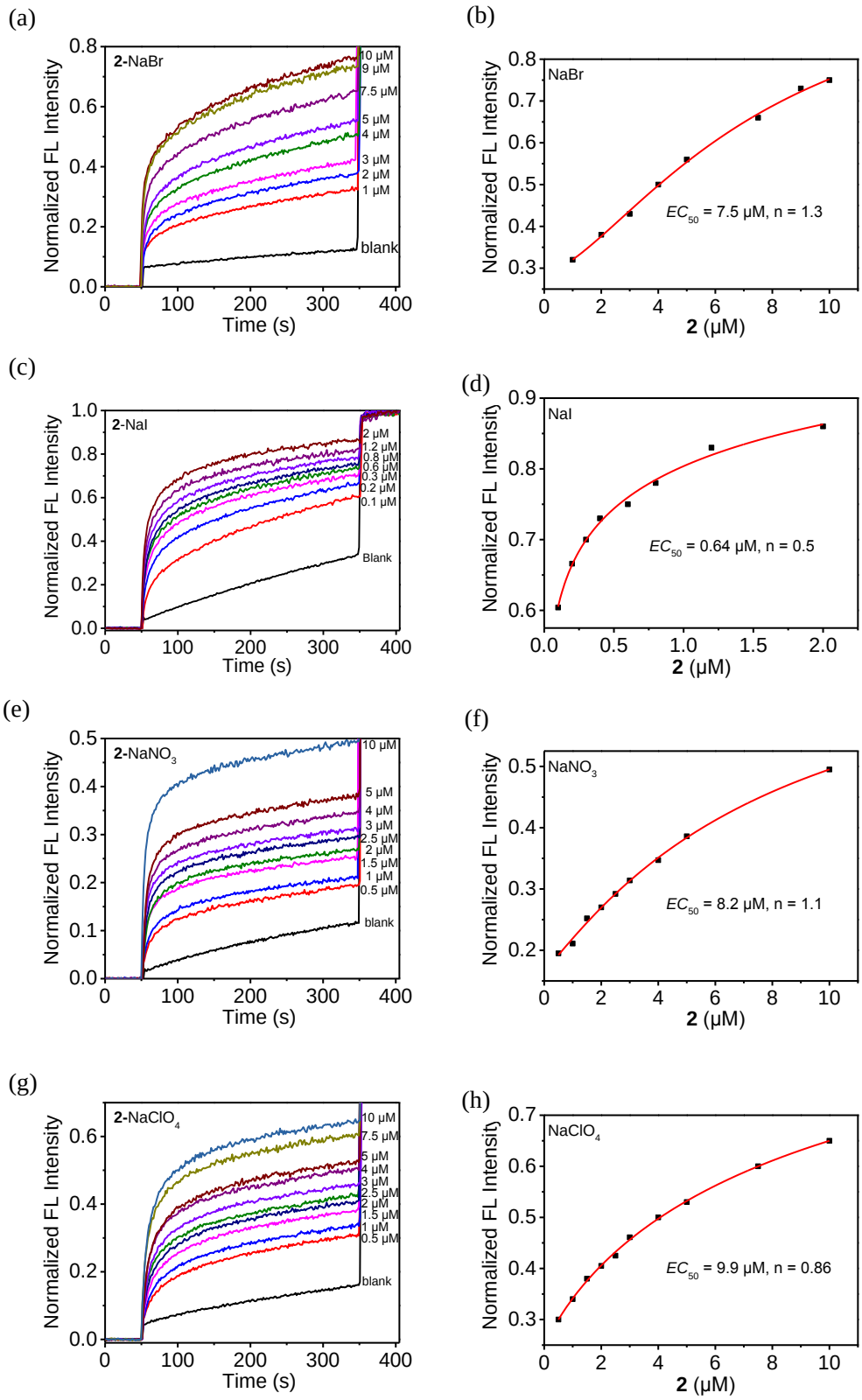


Figure S33. Changes in fluorescence intensity of HPTS with the increasing of the concentration of **2** for the different anions. Determination of EC_{50} values for **2** using the ratiometric values of $I_{t(460)}/I_{t(405)}$ at different concentrations.

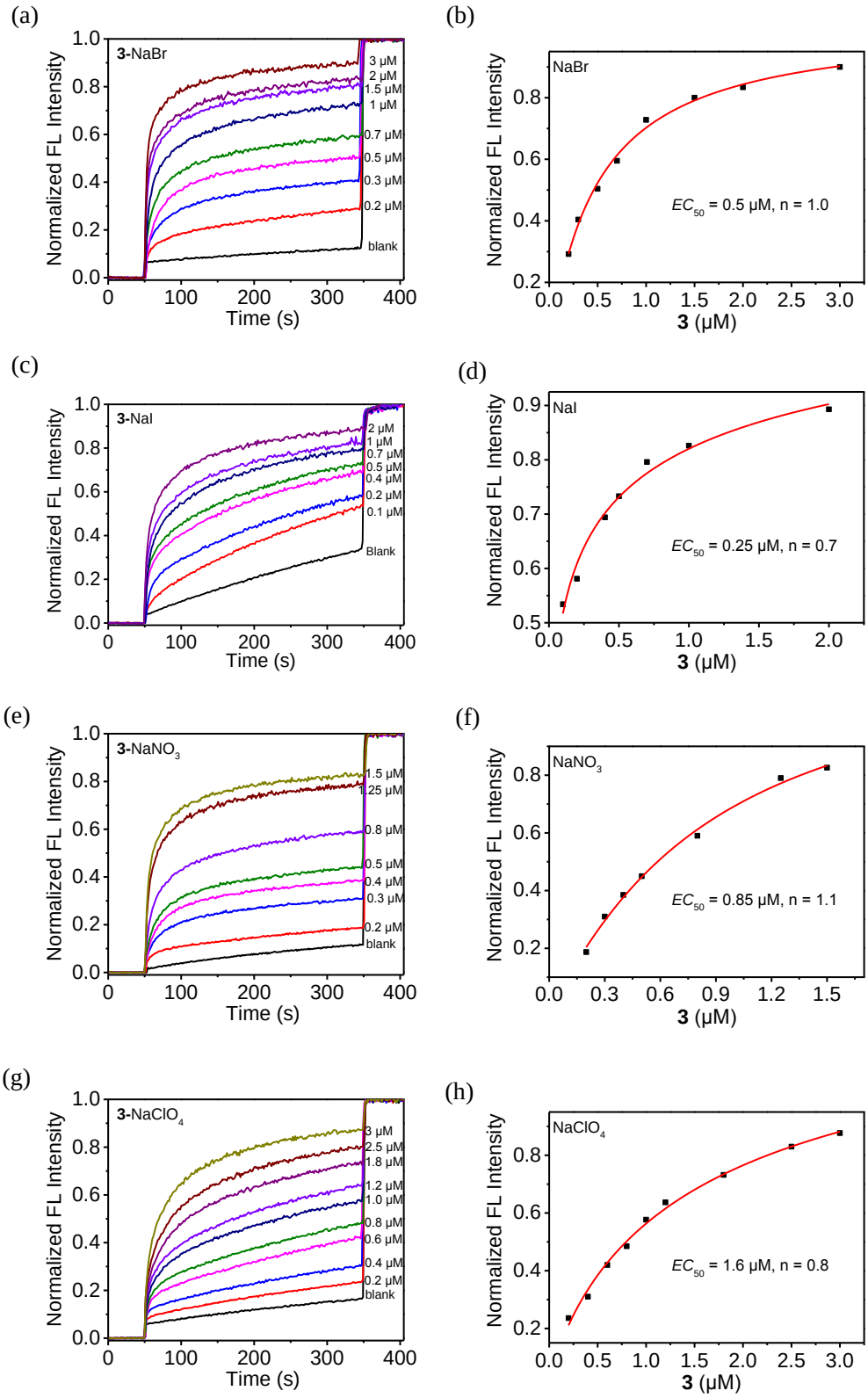


Figure S34. Changes in fluorescence intensity of HPTS with the increasing of the concentration of **3** for the different anions. Determination of EC_{50} values for **3** using the ratiometric values of $I_{t(460)}/I_{t(405)}$ at different concentrations.

21. Anion selectivity using the HPTS assay without salt[8,9]

Typical procedures for the preparation of the large unilamellar vesicles (LUVs): EYPC (200 mg) was dissloved in $CHCl_3$ (50 mL). The solution was evaporated under reduced pressure at 40 °C and the resulting thin film was dried under high vacuum overnight. The lipid film was hydrated with HEPES buffer solution (8.0 mL, [HPTS] = 1 mM, [HEPES] = 10 mM) at 40 °C for 2 h to give a milky suspension. Subsequently, the resulting suspension was subjected to 10 freeze/thaw cycles by using liquid N_2 to freeze and warm water bath to thaw, and extruded through the polycarbonate membrane (MILLIPORE Isopore, 0.2 μm) for 20 times to yield LUVs suspension.

The LUVs solution was placed in a dialysis tubing which has a molecular weight cut-off (MWCO) of 10000 to remove the HPTS that out of the LUVs. This dialysis procedure was repeated 12 times by using the HEPES buffer solution (200 mL, [HEPES] = 10 mM) (12 times × 2 h/time) without HPTS. The resulting lipid suspension was diluted with HEPES buffer (without HPTS) to give a vesicle stock solution ([lipid] = 15 mM).

Procedure for HPTS assays

The vesicle stock solution (50 μL) was diluted with HEPES buffer (1950 μL, [HEPES] = 10 mM), the vesicle suspension was added to a fluorescence cuvette equipped with a stirred bar. Metallacycle **2** (1 mM, 2 μL) was added into the mixture at 0 s, then the fluorescence emission at 510 nm was recorded, resulting from the simultaneous excitation at 405 nm and 460 nm (λ_{ex1} = 405 nm, λ_{em} = 510 nm, $I_{t(405)}$; λ_{ex2} = 460 nm, λ_{em} = 510 nm, $I_{t(460)}$; ratio fluorescence intensities $F_t = I_{t(460)}/I_{t(405)}$). A pulse of 1.0 M NaX (20 μL, X^- = Cl^-, Br^-, I^-, NO_3^- and ClO_4^-) was added at 50 s. Finally, Triton X-100 (10 μL, 20% v/v solution in water) was added at 350 s to lyse the vesicles. Fluorescence data was collected for a further 60 s to ensure the LUVs were completely lysed. Fluorescence time courses were normalized to fractional emission intensity I_{norm} using equation **S4**. The blank experiments were carried out for each anion in the absence of **2**. The background transport were subtracted to obtain the changes caused by only **2**.

Rate constant values were calculated by fitting the transport curves to a single exponential decay equation:

$$I = Ae^{-kt} \qquad \textbf{equation S6}$$

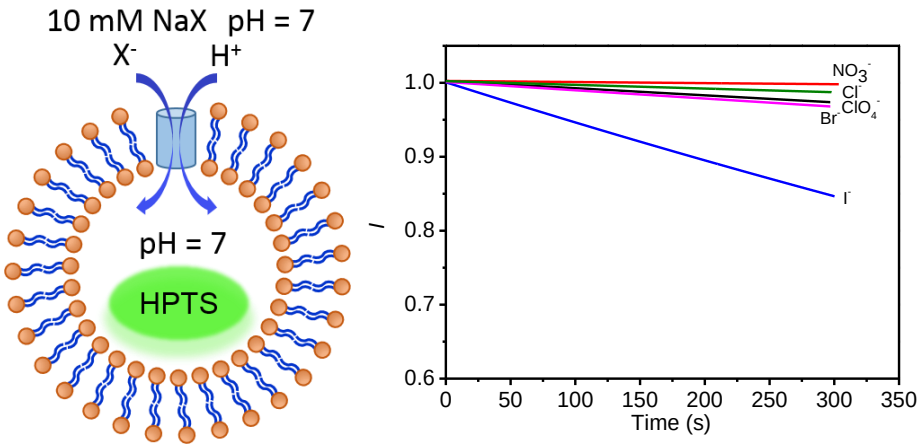


Figure S35. Fitted plots to calculate the initial rate constant (*k*) values of anions transport by **2** (1 μM).

Table S4. Rate constant (*k*) values of the different anions transport through **2**.

anion	*k* (s^{-1})
Cl^-	2.9×10^{-5}
Br^-	1.1×10^{-4}
I^-	5.7×10^{-4}
NO_3^-	1.5×10^{-5}
ClO_4^-	9.7×10^{-5}

Table S5. Reported results of iodide selectivity for other ion channels.

	I^-/Cl^-	I^-/Br^-	I^-/ClO_4^-	I^-/NO_3^-	reference
2	20	5	6	38	
Nanotube	42	25	5	14	[8]
Cage	60	6		1.8	[9]
Aminocyclodextrin	7.3	3.9			[10]
Star of David	2	1.3	2.1	4.7	[7]
Monopeptides	1	1.3	1.5	2	[11]
Calix[4]arene	1.6	1	5		[12]
Pentagonal Prism	2	1.6	4	4	[13]
Columnar Triazole	2	4.5		1	[14]

22. References

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