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Supplementary Information

Synthesis and anion recognition characteristics of a Trapezoidal benzene cage

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Materials, methods, and abbreviations

Materials

All commercially available starting materials and reagents were used without further purification. Anhydrous solvents were obtained from commercial sources. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck 60F254) visualized with a UV lamp (254 nm). Column chromatography was performed with commercial glass columns using silica gel 200 - 300 mesh (particle size 0.045 - 0.075 mm).

Computational studies

All geometry optimizations were performed using Gaussian 16[1] at the m062x/def2svp level of theory. The SMD implicit solvation was used to simulate the solvation effect of THF used in experiments.

Mass spectrometry

High resolution electrospray ionization time-of-flight (HRESI-TOF) mass spectra were measured in the positive/negative ion mode on a Bruker Daltonic microTOF focus spectrometer.

NMR spectroscopy

^{1}H NMR spectra were recorded on a Bruker Avance III HD 400 or a Bruker Avance III HD 600 in $CDCl_3$, DMSO-d_6, or THF-d_8. Chemical shifts are reported in ppm relative to residual solvent signal of $CDCl_3$ (δ = 7.26 ppm), DMSO-d_6 (δ = 2.50 ppm), or THF-d_8 (δ = 1.73 ppm). Abbreviations used for signal multiplicity are: s = singlet, d = doublet, dd = doublet-doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances, br = broad. Coupling constants, *J*, are reported in Hertz (Hz). $^{13}C\{^{1}H\}$NMR spectra were recorded on a Bruker AVANCE III HD 400 or a Bruker Avance III HD 600 in $CDCl_3$, DMSO-d_6 or $CDCl_3$/DMSO-d_6 and the observed signals are reported in ppm relative to the residual solvent signal of $CDCl_3$ (δ = 77.16 ppm),

DMSO-d_6 (δ = 39.52 ppm) or to DMSO in $CDCl_3$/DMSO-d_6 (δ = 39.52 ppm). 2D NMR spectra were recorded on a Bruker AVANCE III HD 400 in THF-d_8 or 2%DMSO-d_6/$CDCl_3$.

2D NMR parameters

Spectra of nuclear overhauser effect spectroscopy (NOESY) and correlation spectroscopy (COSY) experiments were recorded on a Bruker Avance III HD 400 by means of a BBO (BB-H/F-D) probe. Data processing was performed with Topspin software. ^{1}H-^{1}H NOESY acquisitions were performed with a time domain size of 2048 (F2) × 256 (F1), 32 scans per increment, a pulse program of noesygpph, and a mixing time of 300 ms. ^{1}H-^{1}H COSY acquisitions were performed with a time domain size of 2048 (F2) × 256 (F1), 4 scans per increment, and a pulse program of cosygpppgf.

Fluorescence spectroscopy

Fluorescence spectra were recorded on an Edinburgh Instruments FLS 980 spectrometer with Xenon Xe1+400 nm lamp and visible PMT detector under following conditions: Dwell time = 0.1 s, step = 1 nm, number of scans = 1, without polarizer. The stock solutions of all anions and **1** were prepared with THF as the solvent at the concentrations of 0.5 mM (containing 10 μM **1**) and 10 μM, respectively. The detailed conditions for each sample are as follows: excitation wavelength (Ex.) = 306 nm, excitation bandwidth (ExBW.) = 2.4 nm and emission bandwidth (EmBW.) = 2.4 nm with a 330 nm filter for the emission spectra of Cl^-+**1**, Br^-+**1**, I^-+**1**, NO_3^-+**1**, HSO_4^-+**1**, $H_2PO_4^-$+**1** and ClO_4^-+**1**; Ex. = 304 nm, ExBW. = 2.4 nm and EmBW. = 2.3 nm with a 330 nm filter for the emission spectra of F^-+**1**, AcO^-+**1**, SO_4^{2-}+**1**, BF_4^-+**1**; Ex. = 304 nm, ExBW. = 2.5 nm and EmBW. = 2.4 nm with a 330 nm filter for the emission spectra of CF_3COO^-+**1**. Organic solvents for spectroscopic studies were of spectroscopic grade and used without further purification and all anions were prepared as tetrabutylammonium (TBA) salts. Cuvette specification: 10 mm × 10 mm.

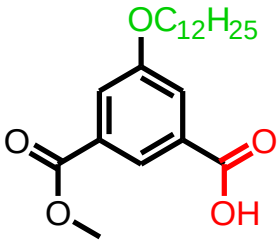
Abbreviations

HBTU = (2-(*1H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate; DIPEA = *N,N*-diisopropylethylamine; DMAP = 4-dimethylaminopyridine; DCM = dichloromethane; DMSO = dimethyl sulfoxide; THF = tetrahydrofuran; EDCL = N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride; Boc = *tert*-butyloxycarbonyl; DMF = N,N-dimethylformamide; PE = petroleum ether; EA = ethyl acetate; TBA = tetrabutylammonium; NBS = N-bromosuccinimide; AIBN = 2,2'-azobis(2-methylpropionitrile); TFA = trifluoroacetic acid; r.t. = room temperature.

Synthesis and characterization

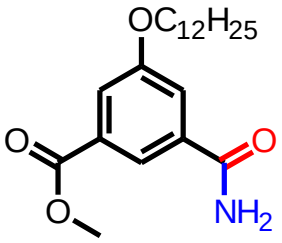
Compounds **2** and **5** are commercially available and were used without further purification. Compound **9** was prepared according to the previously reported protocol.[2]

Synthesis of 3-(dodecyloxy)-5-(methoxycarbonyl)benzoic acid (**3**)



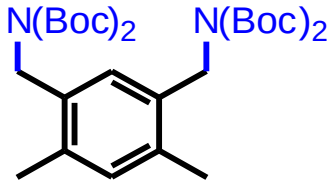
Dimethyl 5-hydroxyisophthalate (compound **2**, 20 g, 95 mmol, 1 equiv.) and K_2CO_3 (32.9 g, 238 mmol, 2.5 equiv.) were suspended in 500 mL DMF, followed by the addition of 1-bromododecane (34 mL, 143 mmol, 1.5 equiv.) at 80 ℃. The mixture was stirred at this temperature for 12 hours and cooled to room temperature. The reaction mixture was concentrated under vacuum and the residue was treated with water to allow precipitation. The solid was filtered and dried, then was directly dissolved in 500 mL THF/H_2O (90/10, v/v%) and followed by the addition of 5 M NaOH aqueous solution (19 mL, 95 mmol, 1 equiv.). The mixture was stirred at room temperature for 5 hours and the solvent was removed under vacuum. The mixture was acidified by 1 M HCl (aqueous) under stirring to afford the crude which was further purified by column chromatography (eluent: DCM/MeOH = 97/3, v/v%) to yield the title compound as a white solid (19 g, 54%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ (ppm) = 13.35 (s, 1H), 8.05 (t, J =1.2 Hz, 1H), 7.64 (dd, J_1 = 3.0, J_2 = 1.8 Hz, 1H), 7.61 (dd, J_1 = 2.4, J_2 = 1.2 Hz, 1H), 4.05 (t, J = 6.6 Hz, 2H), 3.87 (s, 3H), 1.71 (m, 2H), 1.40 (m, 2H), 1.31-1.21 (m, 16H), 0.08 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ (ppm) = 166.2, 165.3, 158.9, 132.7, 131.3, 121.9, 119.3, 118.8, 68.1, 52.5, 39.9, 31.3, 29.04, 29.03, 29.0, 28.73, 28.70, 28.5, 25.4, 22.1, 14.0. **HRMS** (ESI): m/z calcd for $C_{21}H_{32}O_5Na^+$ $[M+Na]^+$ = 387.2142 found: 387.2145.

Synthesis of methyl 3-carbamoyl-5-(dodecyloxy)benzoate (**4**)



Compound **3** (10 g, 27.4 mmol, 1 equiv.) was dissolved in 68 mL DCM followed by the addition of oxalyl chloride (4.64 mL, 54.8 mmol, 2 equiv.) under N_2. The solution was stirred at room temperature for four hours. The solvent and extra oxalyl chloride were removed under vacuum and re-dissolved in 137 mL anhydrous THF. Subsequently, 10.5 mL NH_3 H_2O was added and the mixture was stirred at room temperature for two hours. Solvents were evaporated under vacuum. The residue was washed with water then methanol to yield the title compound as a white powder (5.1 g, 51%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ (ppm) = 8.16 (s, 1H), 8.05 (s, 1H), 7.68 (s, 1H), 7.54 (br, 2H), 4.06 (br, 2H), 3.87 (s, 3H), 1.74 (m, 2H), 1.44 (m, 2H), 1.36-1.24 (m, 16H), 0.85 (br, 3H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ (ppm) = 166.6, 165.7, 158.7, 136.2, 131.0, 120.5, 118.2, 117.1, 68.1, 52.4, 31.3, 29.08, 29.05, 29.02, 29.01, 28.8, 28.7 28.5, 25.4, 22.1, 14.0. **HRMS** (ESI): m/z calcd for $C_{21}H_{33}NO_4H^+$ $[M+H]^+$ = 364.2482 found: 364.2486.

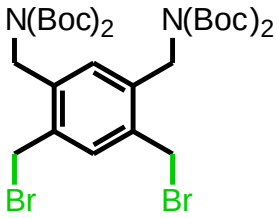
Synthesis of compound **6**



1,2,4,5-tetramethylbenzene (10 g, 75 mmol, 1 equiv.), N-bromosuccinimide (28 g, 157 mmol, 2.1 equiv.) and azobisisobutyronitrile (1.4 g, 5% of N-bromosuccinimide) were dissolved in 250 mL benzene. The mixture was stirred at 80 ^{o}C for 1 h. After cooling to room temperature, the filtrate was collected by filtration. The solvent was then evaporated under vacuum. The residue was mixed with N-Boc-tert-butylcarbamate (33 g, 150 mmol, 2 equiv.) and Cs_2CO_3 (49 g, 150 mmol, 2 equiv.) in 300 mL CH_3CN. The mixture was stirred at 80 ^{o}C for 2 hours. Solvent was evaporated under vacuum. The residue was then diluted with EA and extracted with water three times. The organic layer was dried with Na_2SO_4 and condensed under vacuum to give a yellow solid. The solid was then purified by column chromatography (eluent: PE/EA = 20/1, v/v) to yield the title compound as a white solid (4.5 g, 10%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.92 (s, 1H), 6.88 (s,

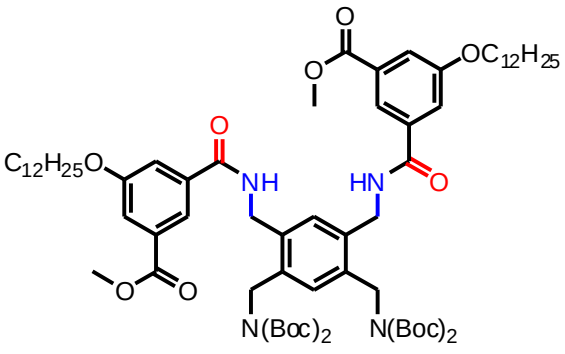
1H), 4.71 (s, 4H), 2.24 (s, 6H), 1.42 (s, 36H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ (ppm) = 152.6, 133.9, 133.4, 132.2, 124.0, 82.3, 47.1, 28.1, 18.8. **HRMS** (ESI): m/z calcd for $C_{30}H_{48}N_2O_8Na^+$ $[M+Na]^+$ = 587.3303, found:587.3306.

Synthesis of compound **7**



Compound **6** (4 g, 7 mmol, 1 equiv.), N-bromosuccinimide (3.2 g, 18 mmol, 2.5 equiv.), Cs_2CO_3 (5.8 g, 18 mmol, 2.5 equiv.) and azobisisobutyronitrile (160 mg, 5% of N-bromosuccinimide) were suspended in 140 mL benzene. The mixture was stirred at 80 ^{o}C for 2 h. After cooling to room temperature, the filtrate was collected by filtration. The solvent was evaporated under vacuum and the solid was then purified by column chromatography (eluent: PE/EA = 18/1, v/v) to give a crude product. Subsequently, the crude was further purified by washing with petroleum ether to yield the title compound as a white solid (1 g, 20%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) = 7.25 (s, 1H), 7.16 (s, 1H), 4.89 (s, 4H), 4.58 (s, 4H), 1.44 (s, 36H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ (ppm) = 152.5, 138.4, 134.0, 132.2, 126.2, 82.9, 46.1, 30.7, 28.2. **HRMS** (ESI): m/z calcd for $C_{30}H_{46}Br_2N_2O_8Na^+$ $[M+Na]^+$ = 743.1513, found: 743.1520.

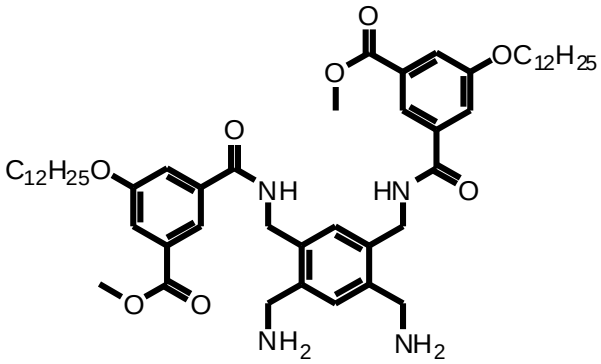
Synthesis of monomer compound **8**



Compound **4** (1 g, 2.8 mmol, 2.5 equiv.) and Cs_2CO_3 (1.8 g, 5.5 mmol, 5 equiv.) were suspended in 70 mL CH_3CN. Subsequently, compound **7** (800 mg, 1.1 mmol, 1 equiv.) was added and the mixture was stirred at 80 ^{o}C for 12 h. The solvent was evaporated under vacuum. The residue was diluted with DCM and extracted with water three times. The organic layer was dried with Na_2SO_4 and solvents were evaporated under vacuum. Column chromatography (eluent: PE/EA = 2/1, v/v) was performed to give a crude product. The crude was then washed with CH_3CN to

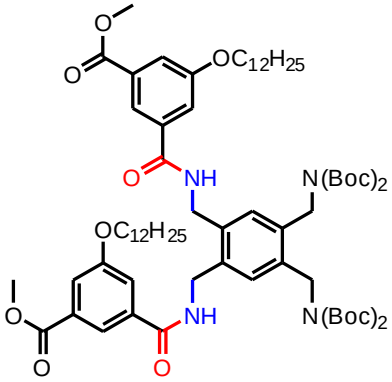
yield the title compound as a white solid (460 mg, 32%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.02 (br, 2H), 7.63 (br, 4H), 7.41 (t, J = 3.2 Hz, 2H), 7.36 (s, 1H), 7.21 (s, 1H), 4.84 (s, 4H), 4.66 (d, J =3.2 Hz, 4H), 4.01 (t, J = 4.4 Hz, 4H), 3.88 (s, 6H), 1.78-1.74 (m, 4H), 1.43 (s, 36H), 1.34-1.25 (m, 36H), 0.87 (t, J = 4.4 Hz, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ (ppm) = 166.5, 166.3, 159.5, 153.0, 137.1, 136.1, 134.3, 132.7, 131.7, 126.5, 120.2, 118.6, 118.1, 83.2, 68.7, 52.4, 46.4, 41.8, 32.0, 29.80, 29.76, 29.74, 29.71, 29.51, 29.48, 29.3, 28.2, 26.1, 22.8, 14.3. **HRMS** (ESI): m/z calcd for $C_{72}H_{110}N_4O_{16}Na^+$ $[M+Na]^+$ = 1309.7809, found: 1309.7796.

Preparation of **8**-NH_2



Compound **8** (400 mg, 0.31 mmol, 1 equiv.) was dissolved in 2.1 mL DCM. Then 0.9 mL TFA was slowly added into the DCM solution at room temperature. The mixture was stirred at room temperature for 12 h. Then, solvents were evaporated under vacuum as fast as possible and immediately precipitated in diethyl ether to get rid of remaining TFA and solvents. The resulting solid was then diluted with DCM and extracted with 5% K_2CO_3 twice. The organic layer was dried with Na_2SO_4 and condensed under vacuum to yield a white crude product (245 mg) which was used for the next reaction without further purification.

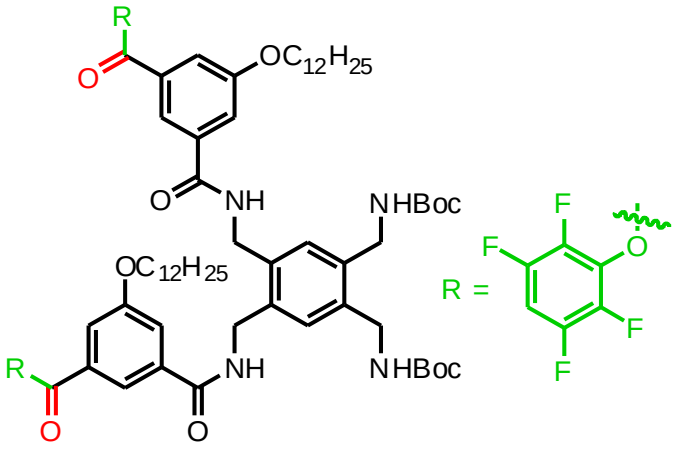
Synthesis of compound **10**



Compound **9** (467 mg, 0.65 mmol, 1 equiv.) and KN_3 (158 mg, 1.95 mmol, 3 equiv.) were suspended in 1 mL DMF. The suspension was stirred at 50 °C for 2 h. The reaction mixture was allowed to cool down to room temperature and precipitated in water. The solid was collected by filtration, followed by washing with

water. The resulting solid was then directly mixed with PPh_3 (511 mg, 1.95 mmol, 3 equiv.) in 3 mL THF, followed by the addition of a few drops of water. The mixture was allowed to stir at 50 ℃ for 3 h. After cooling down to room temperature, the resulting reaction mixture was then mixed with compound **3** (592 mg, 1.6 mmol, 2.5 equiv.) and HBTU (1.23 g, 3.25 mmol, 5 equiv.), followed by the addition of DIPEA (0.57 mL, 3.25 mmol, 5 equiv.). The reaction mixture was stirred at room temperature for 5 h under nitrogen atmosphere. Afterwards, solvent was evaporated under vacuum. The crude product was washed with methanol and further purified by column chromatography (eluent: PE/EA = 2/1, *v/v*) to yield the title compound as a white solid (592 mg, 71%). **^{1}H NMR** (600 MHz, $CDCl_3$):δ (ppm) = 7.99 (s, 2H), 7.79 (br, 2H), 7.62 (m, 4H), 7.19 (s, 2H), 4.80 (s, 4H), 4.67 (d, J = 4.8 Hz, 4H), 3.98 (t, J = 6.0 Hz, 4H), 3.87 (s, 6H), 1.74 (m, 4H), 1.37 (s, 36H), 1.25 (m, 36H), 0.87 (t, J = 6.0 Hz, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ (ppm) = 166.4, 166.3, 159.5, 152.6, 135.71, 135.69, 135.03, 131.6, 128.1, 120.0, 118.53, 118.47, 82.9, 68.7, 52.4, 46.6, 41.7, 32.1, 29.82, 29.77, 29.6, 29.53, 29.50, 29.3, 28.0, 26.1, 22.8, 14.3. **HRMS** (ESI): m/z calcd for $C_{72}H_{110}N_4O_{16}Na^+$ $[M+Na]^+$ = 1309.7809 found: 1309.7802.

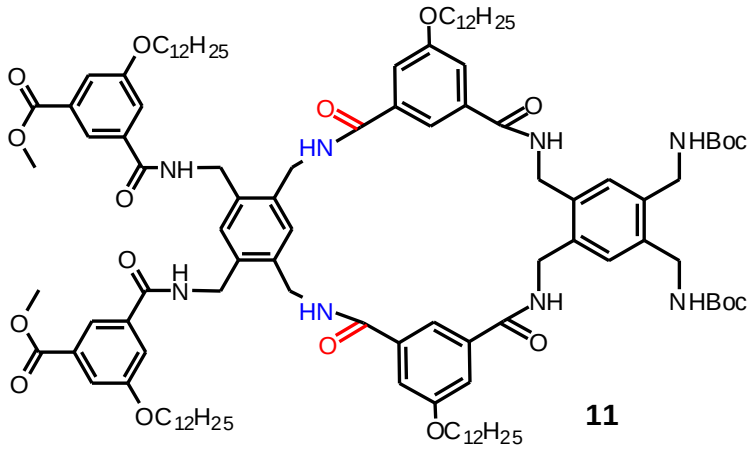
Preparation of **10**-F



Compound **10** (500 mg, 0.39 mmol, 1 equiv.) was dissolved in 20 mL MeOH/THF (10/90, v/v%) and 4 M NaOH aqueous solution (0.5 mL, 2 mmol, 5 equiv.) was slowly added into the solution at room temperature. The mixture was stirred at room temperature for 6 h. Solvents were evaporated under vacuum and then acidified by slowly adding 10 mM HCl (aqueous) under stirring to give a white solid. The resulting solid was then directly mixed with 2, 3, 5, 6-tetrafluorophenol (195 mg, 1.17 mmol, 3 equiv.) and DMAP (24 mg, 0.195 mmol, 0.5 equiv) in 8 mL anhydrous

THF, followed by the addition of EDCL (449 mg, 2.34 mmol, 6 equiv.). The reaction mixture was stirred at room temperature for 6 h under nitrogen atmosphere. Then the solvent was evaporated under vacuum and the residue was diluted with DCM and extracted with 1 M HCl aqueous solution three times. The organic layer was dried with Na_2SO_4 and condensed under vacuum to yield a white crude product (618 mg).

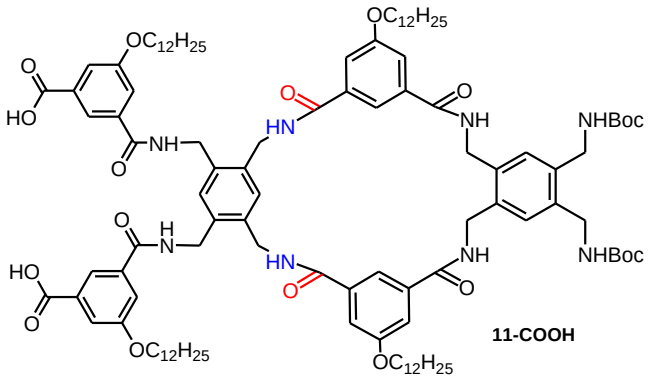
Synthesis of compound **11**



11

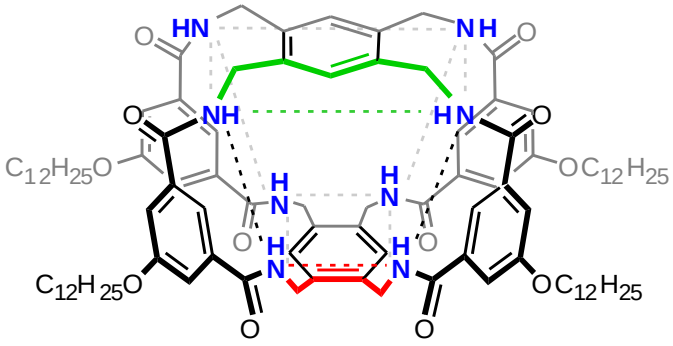
Compound **8**-NH_2 (245 mg, 0.31 mmol, 1 equiv.) and compound **10**-F (618 mg, 0.39 mmol, 1.25 equiv.) were suspended in 310 mL anhydrous THF, followed by the addition of DIPEA (162 µL, 0.93 mmol, 3 equiv.). The reaction mixture was stirred at room temperature for 12 hours under nitrogen atmosphere. The solvent was removed under vacuum and the crude was purified by column chromatography (eluent: DCM/MeOH = 97.5/2.5, v/v%) and then washed with methanol to yield the title compound as a white solid (207 mg, 35%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 9.14 (t, J = 3.2 Hz, 2H), 8.95 (br, 2H), 8.61 (br, 2H), 7.96 (s, 2H), 7.79 (s, 2H), 7.57 (s, 2H), 7.44 (s, 2H), 7.39 (s, 4H), 7.34 (t, J = 6.0 Hz, 2H), 7.24 (s, 2H), 7.19 (s, 1H), 7.12 (s, 1H), 4.50 (br, 8H), 4.44 (d, J = 2.0 Hz, 4H), 4.14 (d, J = 5.6 Hz, 4H), 3.91 (br, 8H), 3.84 (s, 6H), 1.65 - 1.75 (m, 8H), 1.35 (s, 18H), 1.23 (br, 72H), 0.84 (t, J = 6.0 Hz, 12H). **^{13}C{^{1}H} NMR** (151 MHz, 30% $CDCl_3$ /DMSO-d_6): δ (ppm) = 165.9, 165.5, 165.2, 158.64, 158.57, 155.5, 136.1, 136.0, 135.82, 135.78, 135.71, 134.8, 130.9, 129.7, 127.9, 124.0, 120.2, 120.1, 117.7, 117.2, 116.0, 115.7, 77.6, 67.9, 67.8, 52.1, 40.6, 40.24, 40.17, 40.1, 31.3, 29.8, 29.09, 29.06, 28.8, 28.76, 28.66, 28.60, 28.1, 25.53, 25.46, 22.1, 13.9. **HRMS** (ESI): m/z calcd for $C_{112}H_{164}N_8O_{18}Na^+$ $[M+Na]^+$ = 1932.2056 found: 1932.2075.

Preparation of compound **11**-COOH



Compound **11** (207 mg, 0.11 mmol, 1 equiv.) was dissolved in 6 mL MeOH/THF (10/90, v/v%), followed by the addition of 4 M NaOH aqueous solution (0.55 mL, 2.2 mmol, 20 equiv.) at room temperature. The suspension was stirred at room temperature for 5 h. Solvents were evaporated under vacuum and then acidified by slowly adding 10 mM HCl (aqueous) under stirring to give a white solid (210 mg). This crude product was directly used in the next step without further purification.

Synthesis of the cage **1**



Compound **11**-COOH (105 mg, 0.055 mmol, 1 equiv.) was then mixed with 2,3,5,6-tetrafluorophenol (28 mg, 0.17 mmol, 3 equiv.), EDCl (63 mg, 0.33 mmol, 6 equiv.) and DMAP (3 mg, 0.028 mmol, 0.5 equiv.) in 5 mL anhydrous THF. The mixture was stirred at room temperature for 6 h under nitrogen atmosphere. After solvents were evaporated under vacuum, the residue was then diluted with DCM and extracted with 10 mM HCl aqueous solution. The organic layer was dried with Na_2SO_4 and solvents were evaporated under vacuum. The resulting solid was then dissolved in 1.4 mL DCM and followed by the addition of 0.6 mL TFA at room temperature. The mixture was stirred at room temperature for 12 h, then solvents were evaporated under vacuum. The residue was washed with diethyl ether and dried under high vacuum. The resulting solid was then directly mixed with DIPEA (95 μL, 0.55 mmol, 10 equiv.) in 280 mL anhydrous THF. The mixture was stirred at room temperature for 12 h under nitrogen

atmosphere. The solvent was removed under vacuum and the resulting solid was washed with water and then methanol. The crude was further purified by column chromatography (eluent: DCM/MeOH = 97.5/2.5, v/v%) to yield the title compound as a white solid (23 mg, 25%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ (ppm) = 8.83 (t, J = 4.2 Hz, 8H), 7.36 (s, 4H), 7.35 (s, 8H), 6.97 (s, 4H), 4.56 (dd, J_1 = 14.4, J_2 = 3.6 Hz, 8H), 4.38 (dd, J_1 = 13.8, J_2 = 6.6 Hz, 8H), 4.04 (t, J = 6.0 Hz, 8H), 1.74 - 1.69 (m, 8H), 1.40 - 1.35 (m, 8H), 1.28 - 1.21 (m, 64 H), 0.85 (t, J = 6.6 Hz, 12H). **^{13}C{^{1}H} NMR** (101 MHz, 20% $CDCl_3$ /DMSO-d_6): δ (ppm) = 166.1, 158.2, 136.6, 135.8, 132.5, 118.1, 115.7, 67.9, 54.7, 31.3, 29.1, 29.06, 28.9, 28.8, 28.7, 25.5, 22.1, 13.9. **HRMS (ESI):** m/z calcd for $C_{100}H_{140}N_8O_{12}Na^+$ $[M+Na]^+$ = 1668.0483, found:1668.0497.

NMR, fluorescence, mass and computational studies

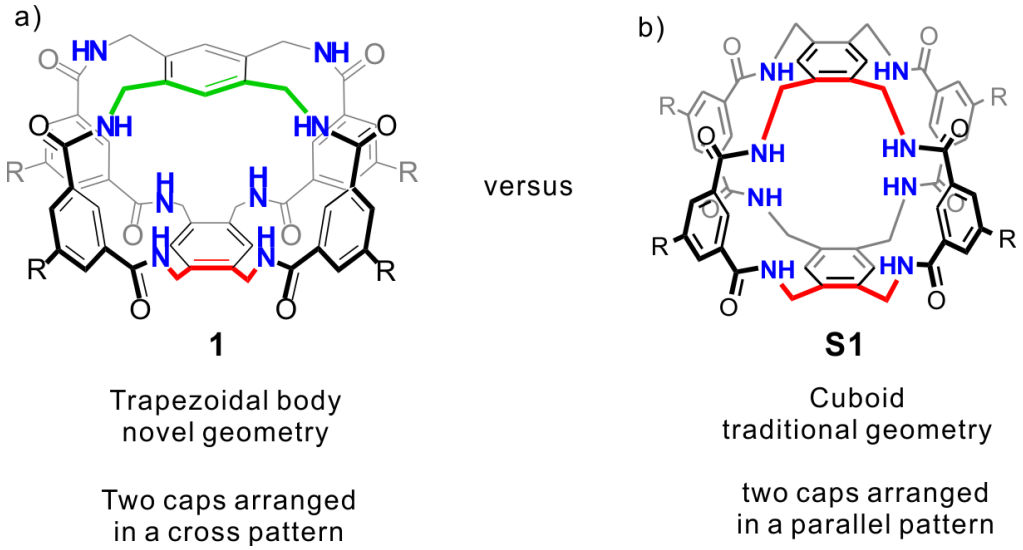


Figure S1. (a) Cage **1** with novel trapezoidal geometry. (b) Cage **S1** with traditional cuboid geometry.

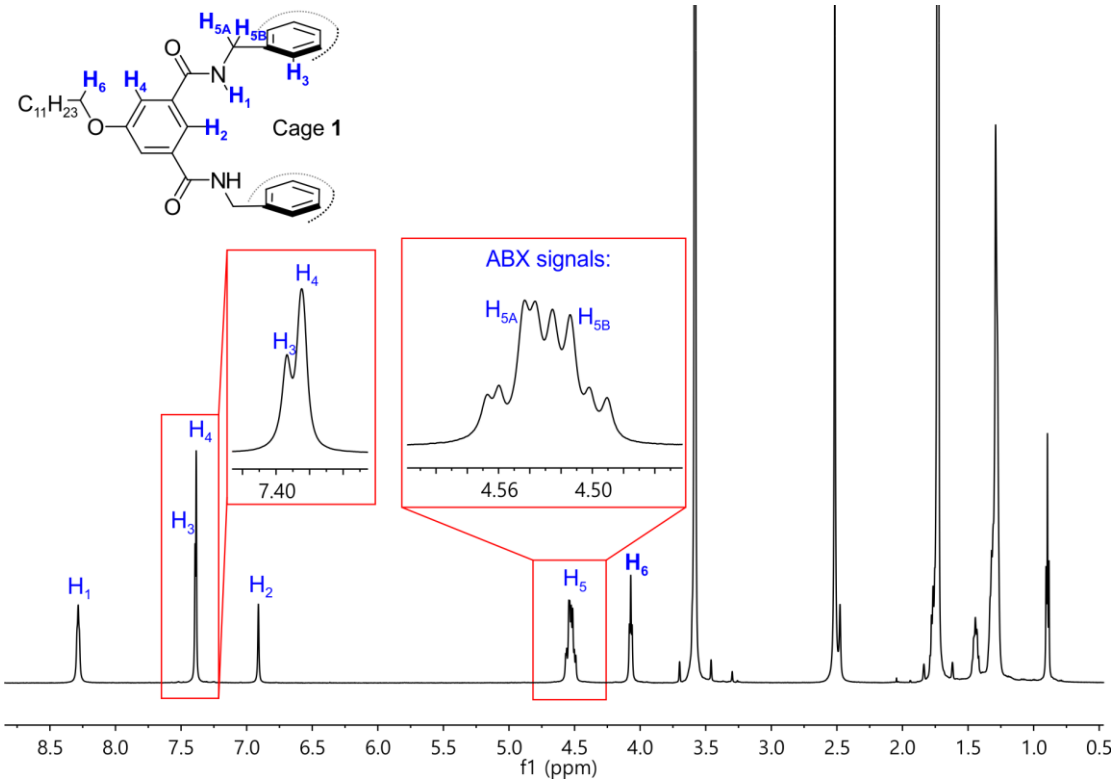


Figure S2. ^{1}H NMR spectrum (400 MHz) of **1** in THF-d_8 at 298 K.

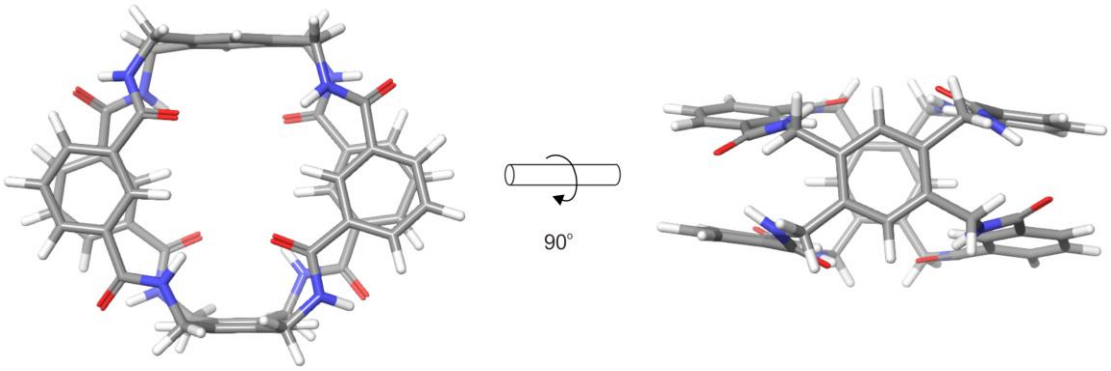


Figure S3. Molecular model (m062x/def2svp, SMD/THF) of **1**. Redundant side chains are omitted for clarity.

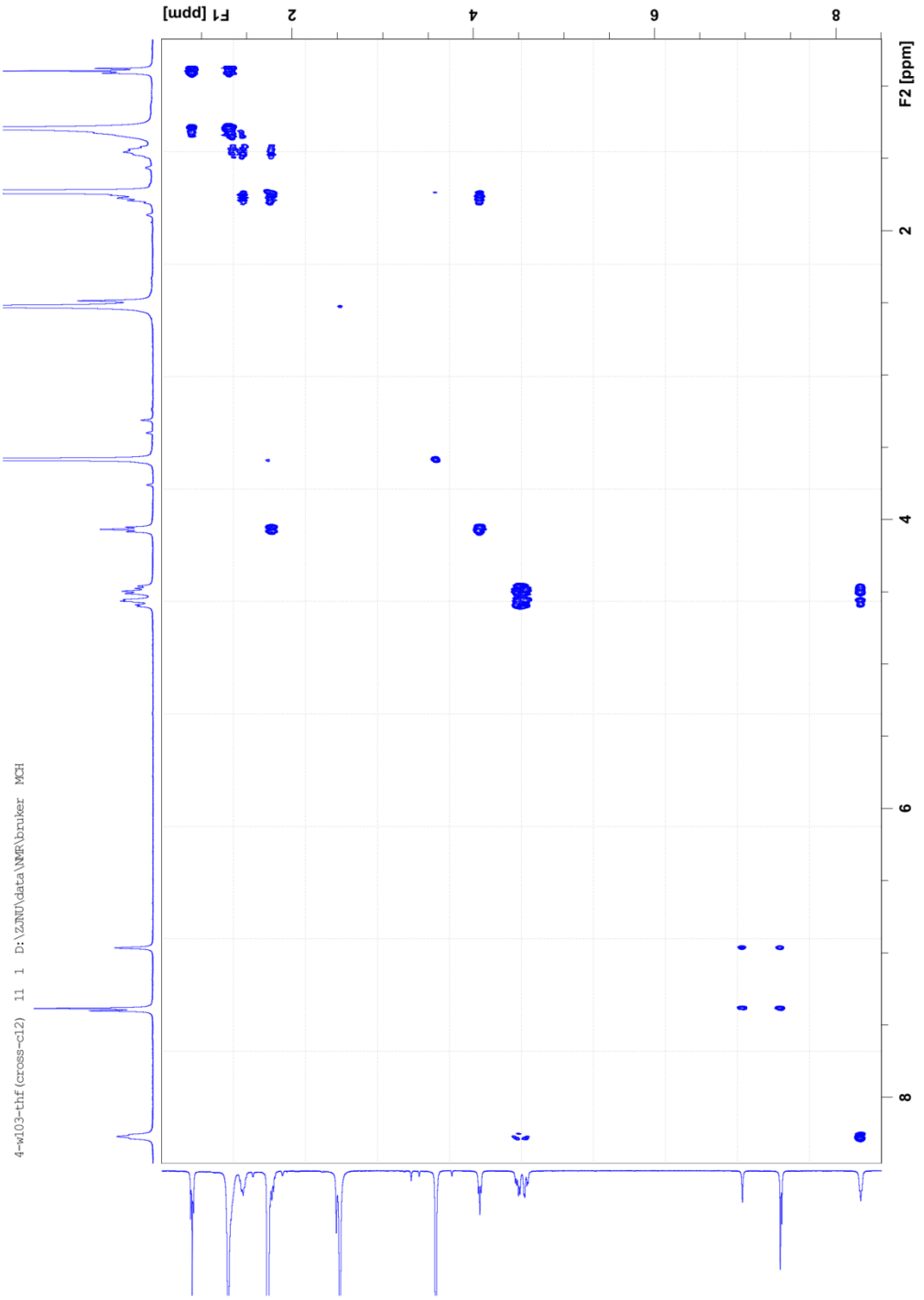


Figure S4. Full ^{1}H-^{1}H COSY (400 MHz) spectrum of **1** (1 mM) in THF-d_8 at 298 K.

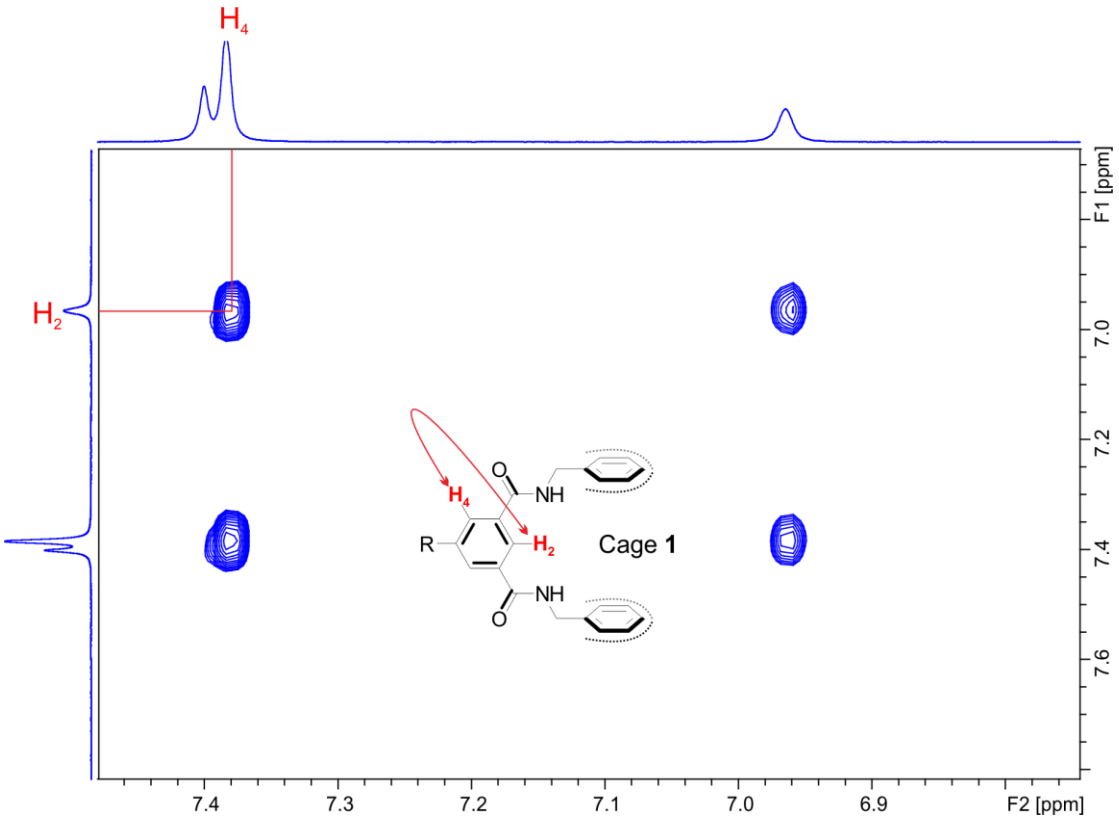


Figure S5. ^{1}H-^{1}H COSY (400 MHz) spectrum of **1** (1 mM) in THF-d_8 at 298 K, showing the COSY correlation of $H_2 \leftrightarrow H_4$.

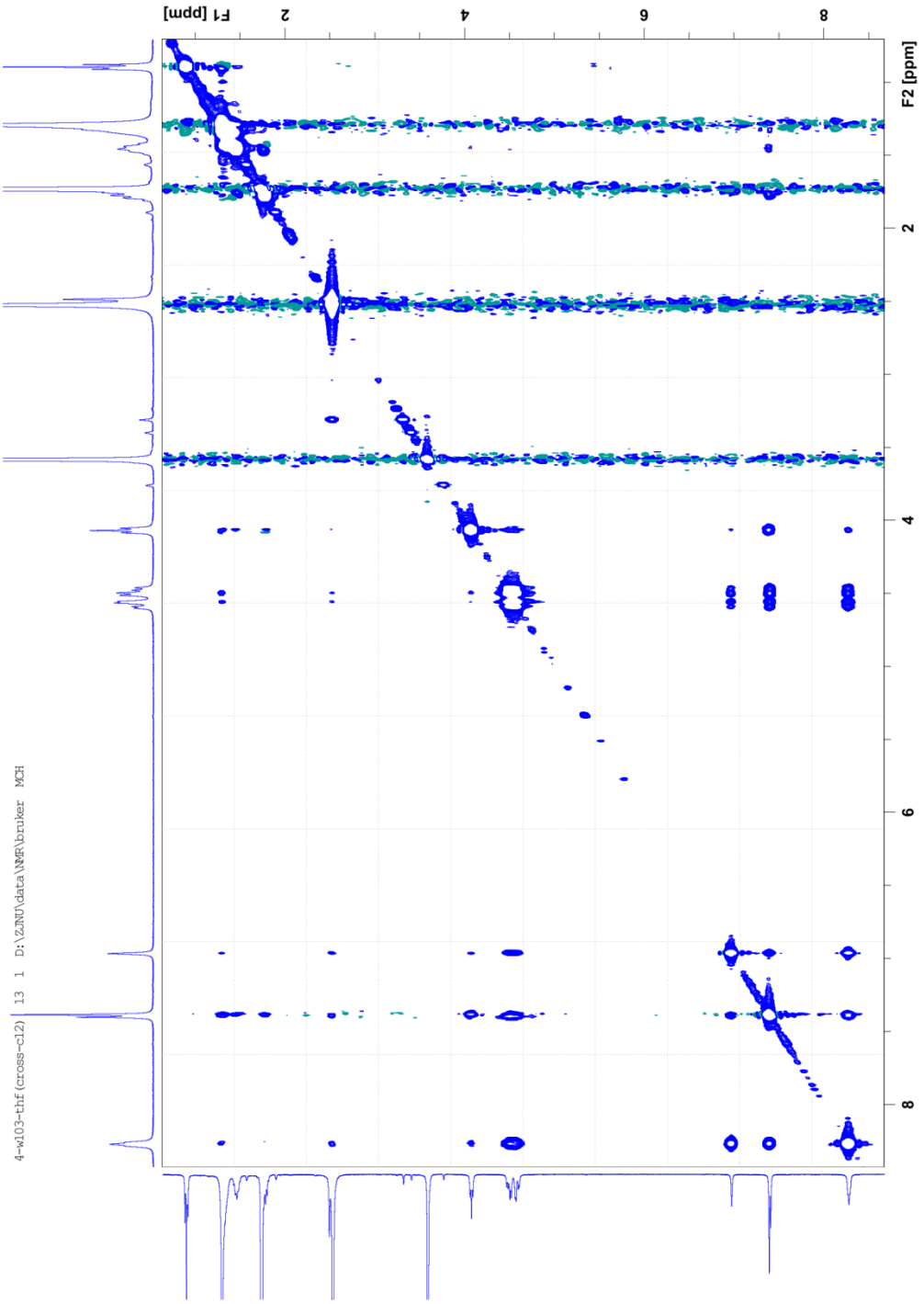


Figure S6. Full ^{1}H-^{1}H NOESY (400 MHz) spectrum of **1** (1 mM) in THF-d_8 at 298 K.

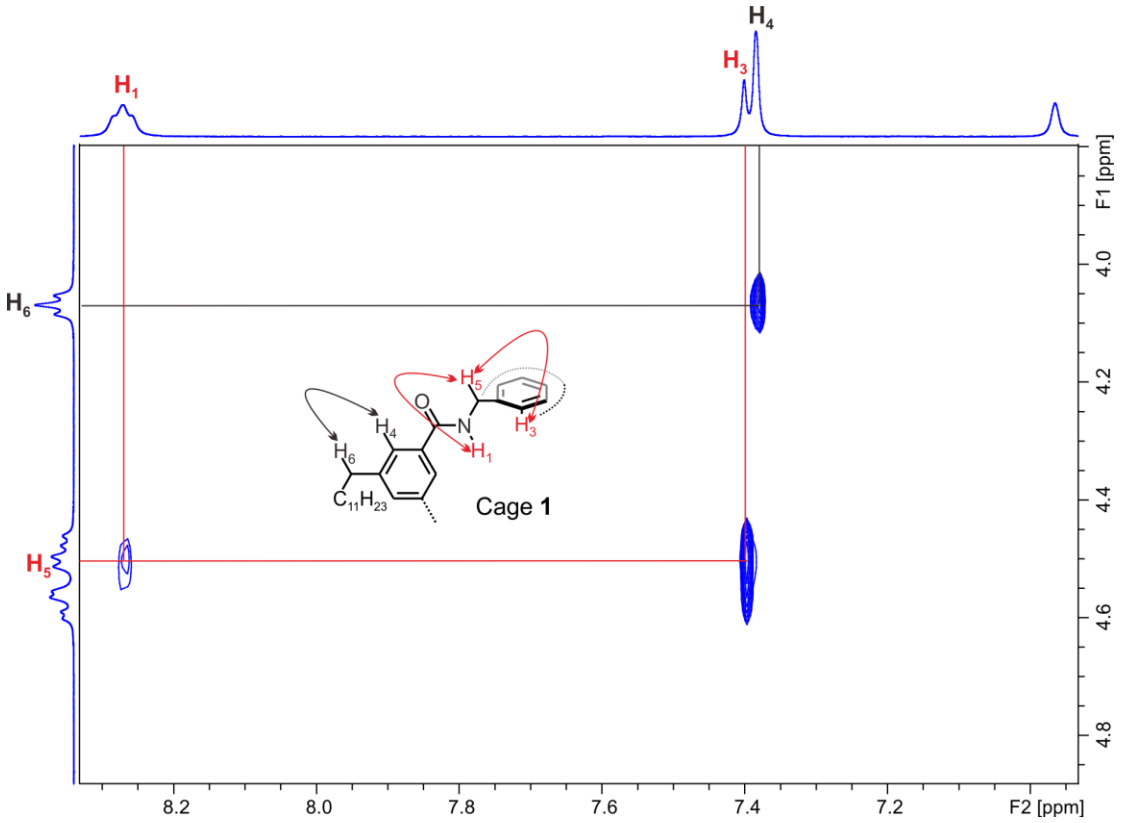


Figure S7. ^{1}H-^{1}H NOESY (400 MHz) spectrum of **1** (1 mM) in THF-d_8 at 298 K, showing the NOE correlations of $H_1 \leftrightarrow H_5$ (red), $H_3 \leftrightarrow H_5$ (red), and $H_4 \leftrightarrow H_6$ (black).

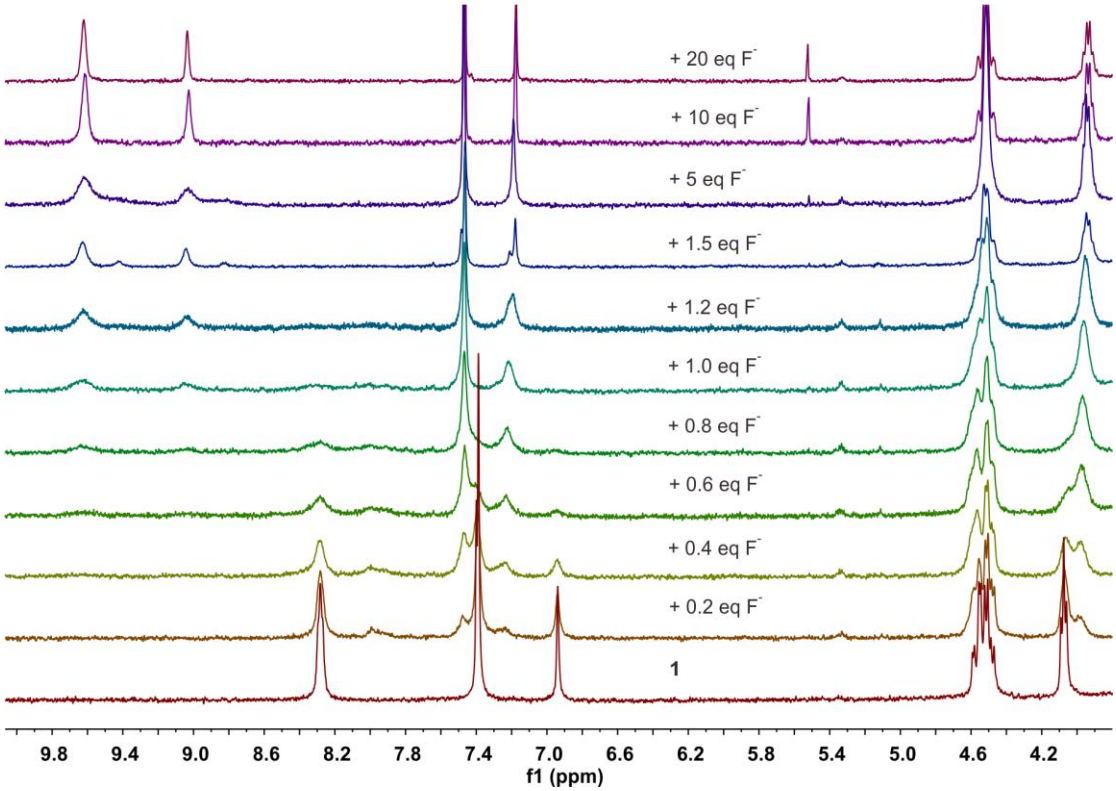


Figure S8. ^{1}H NMR (400 MHz) titration of **1** (0.5 mM) with F^- in THF-d_8.

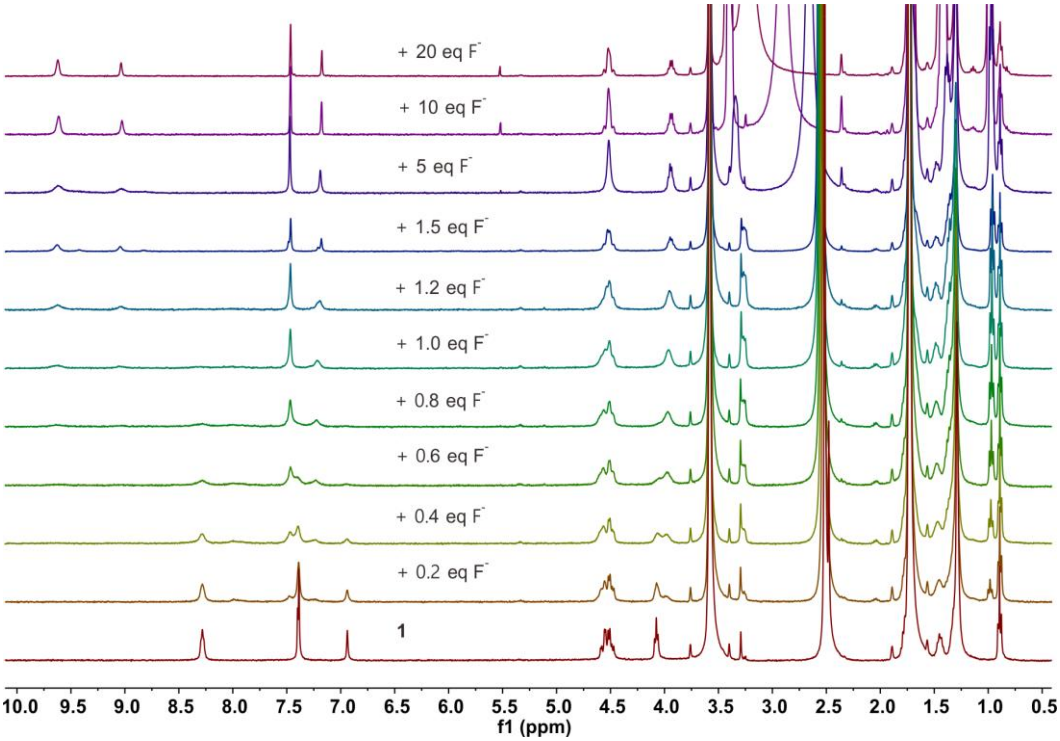


Figure S9. Full spectra of NMR titration study between **1** (0.5 mM) and F^- in THF-d_8.

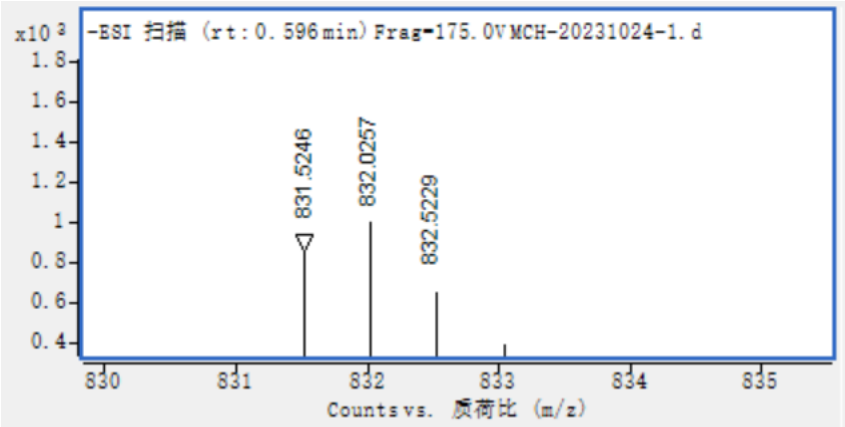


Figure S10. HRESI-TOF mass spectrum of **1**+1.2eqF^- (m/z calcd for $C_{100}H_{139}N_8O_{12}F^{2-}$ $[M+F-H]^{2-}$ = 831.5254, found 831.5246) indicating the existence of 1:1 host-guest complex(es). No other binding stoichiometry was observed under this condition.

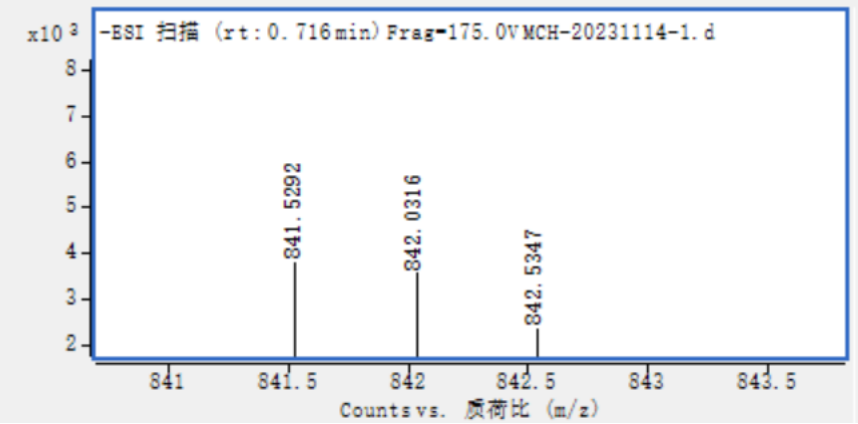


Figure S11. HRESI-TOF mass spectrum of **1**+10eqF^- (m/z calcd for $C_{100}H_{140}N_8O_{12}F_2^{2-}$ $[M+2F]^{2-}$ = 841.5285, found 841.5292) indicating the existence of 1:2 host-guest complex(es). No other binding stoichiometry was observed under this condition.

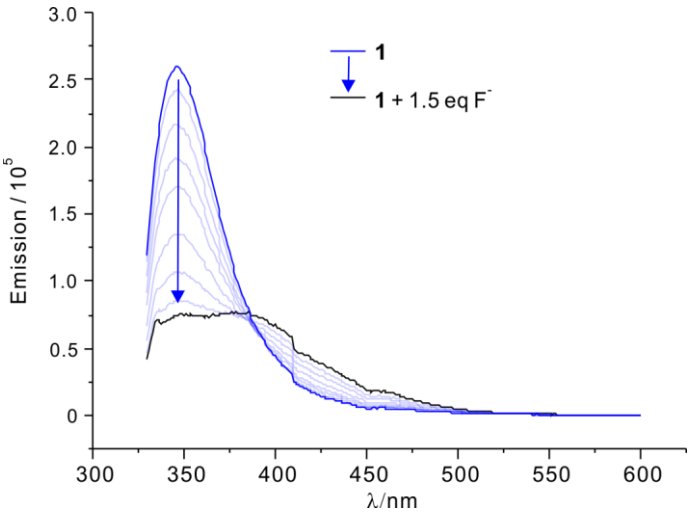


Figure S12. Fluorescence (λ_{ex} = 304 nm) titration of **1** (10 μM) with F^- in THF.

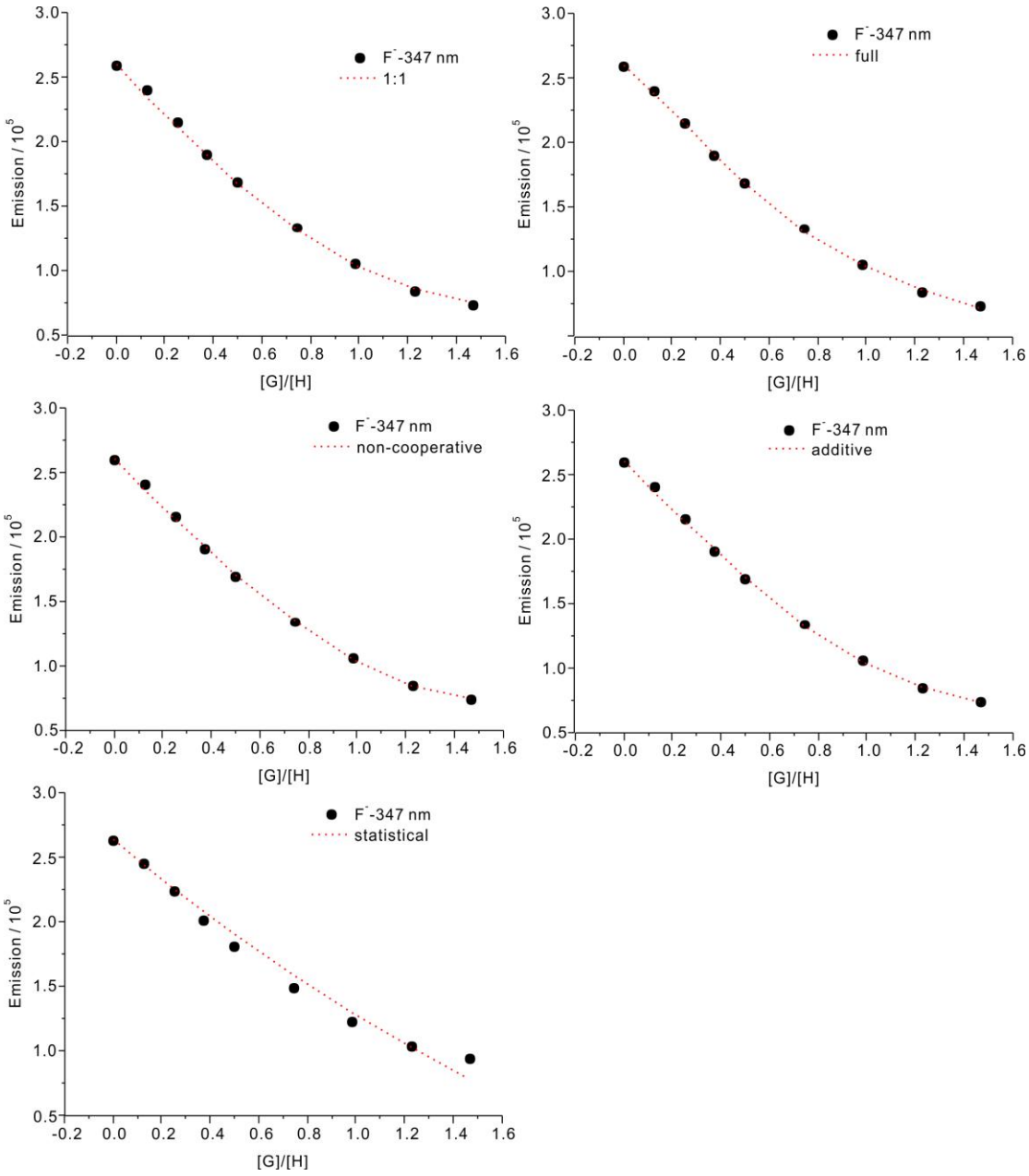


Figure S13. Binding analysis curves of the fluorescence titration between **1** (10 μM) and F^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S1. Summary of the binding analysis of the fluorescence titration between **1** and F^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$9.3(\pm13\%)\times10^5$	-	1.0×10^{-3}	√
Full (1:2)	$-5.2(\pm1.8\%)\times10^4$	$-2.3(\pm2.8\%)\times10^4$	2.7×10^{-4}	
Non-cooperative (1:2)	$-1.8(\pm2.5\%)\times10^4$	-4.6×10^3	8.4×10^{-4}	
Additive (1:2)	$1.6(\pm25.8\%)\times10^6$	$8.8(\pm111.5\%)\times10^3$	6.9×10^{-4}	
Statistical (1:2)	$2.1(\pm21.5\%)\times10^5$	5.2×10^4	1.8×10^{-2}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

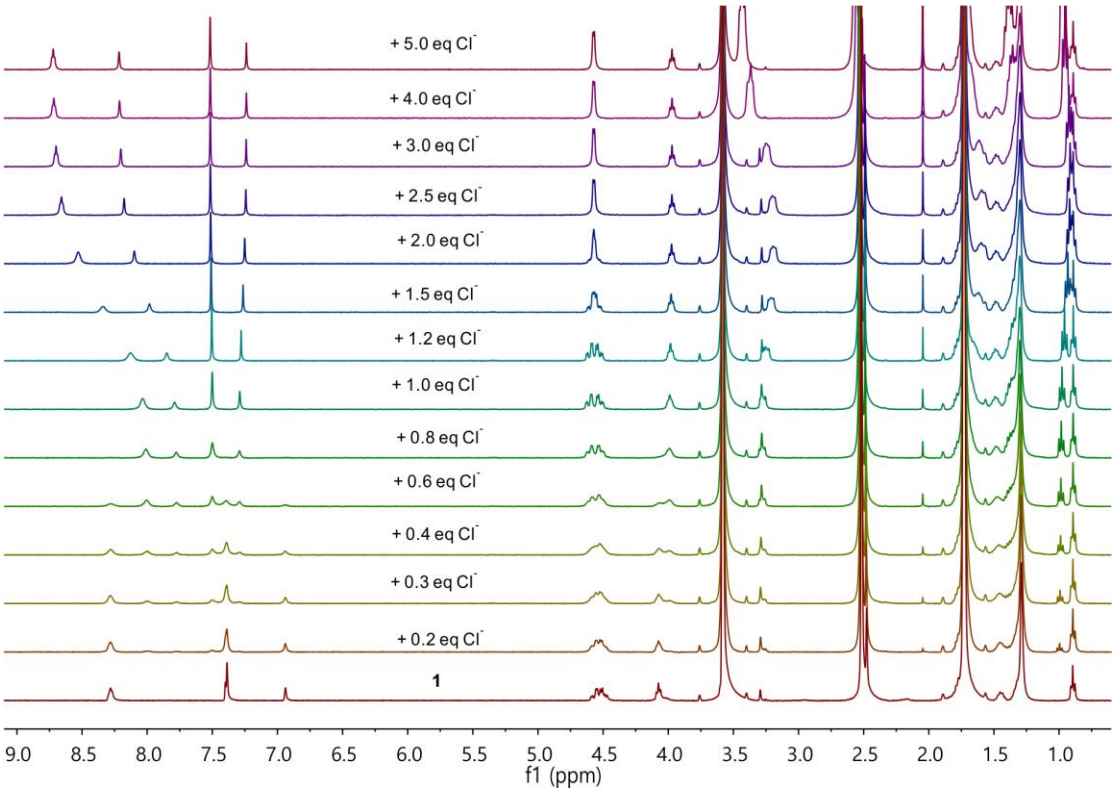


Figure S14. Full spectra of NMR titration study between **1** (0.5 mM) and Cl^- in THF-d_8.

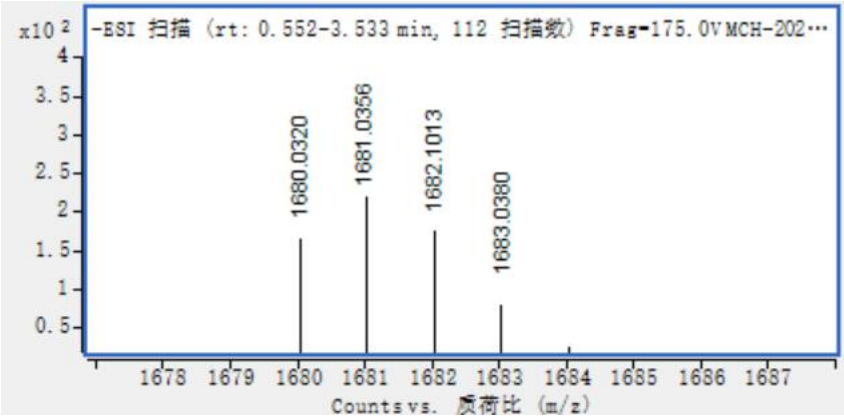


Figure S15. HRESI-TOF mass spectrum of **1**+1.2eqCl^- (m/z calcd for $C_{100}H_{140}N_8O_{12}Cl^-$ $[M+Cl]^-$ = 1680.0285, found 1680.0320) indicating the existence of 1:1 host-guest complex(es). No other binding stoichiometry was observed under this condition.

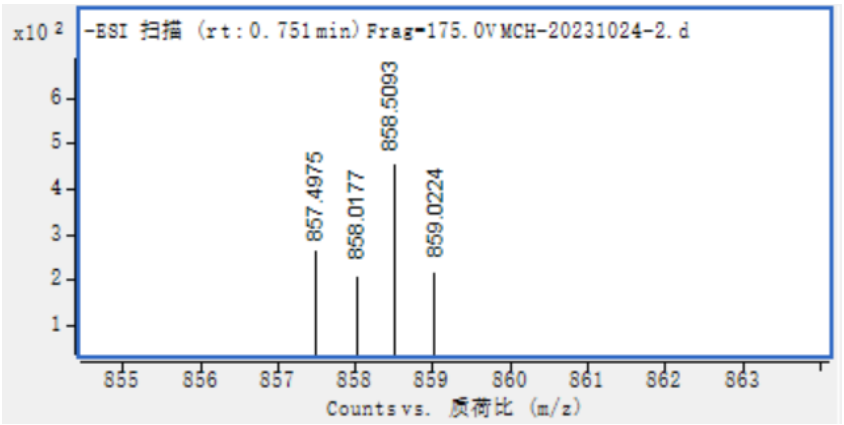


Figure S16. HRESI-TOF mass spectrum of **1**+10eqCl^- (m/z calcd for $C_{100}H_{140}N_8O_{12}Cl_2^{2-}$ $[M+2Cl]^{2-}$ = 857.4989, found 857.4975) indicating the existence of 1:2 host-guest complex(es). No other binding stoichiometry was observed under this condition.

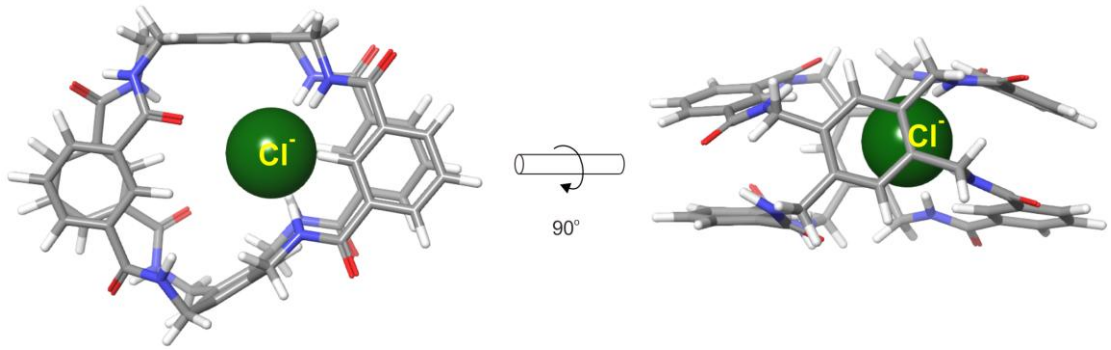


Figure S17. Molecular model (m062x/def2svp, SMD/THF) of [**1**-Cl^-**]**. Redundant side chains are omitted for clarity.

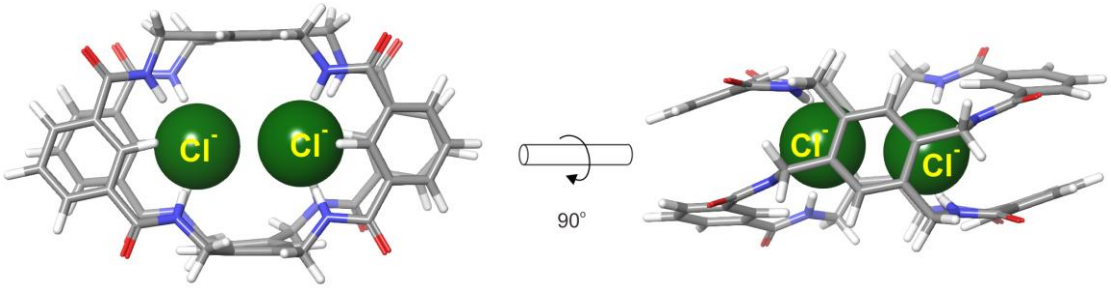


Figure S18. Molecular model (m062x/def2svp, SMD/THF) of [**1**-2Cl^-**]**. Redundant side chains are omitted for clarity.

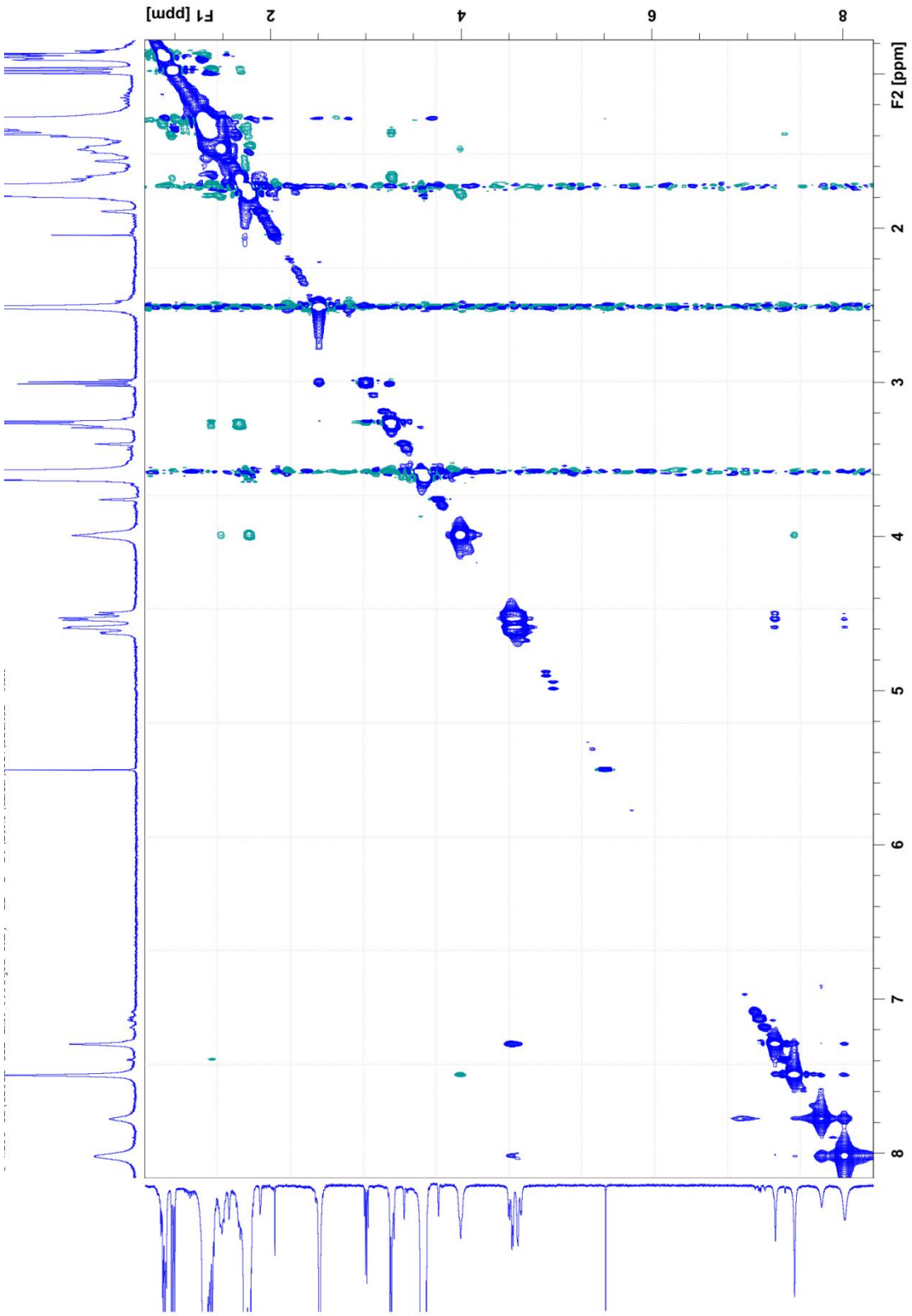


Figure S19. Full ^{1}H-^{1}H NOESY (400 MHz) spectrum of **1** (1 mM) + 1eq Cl^- in THF-d_8 at 298 K.

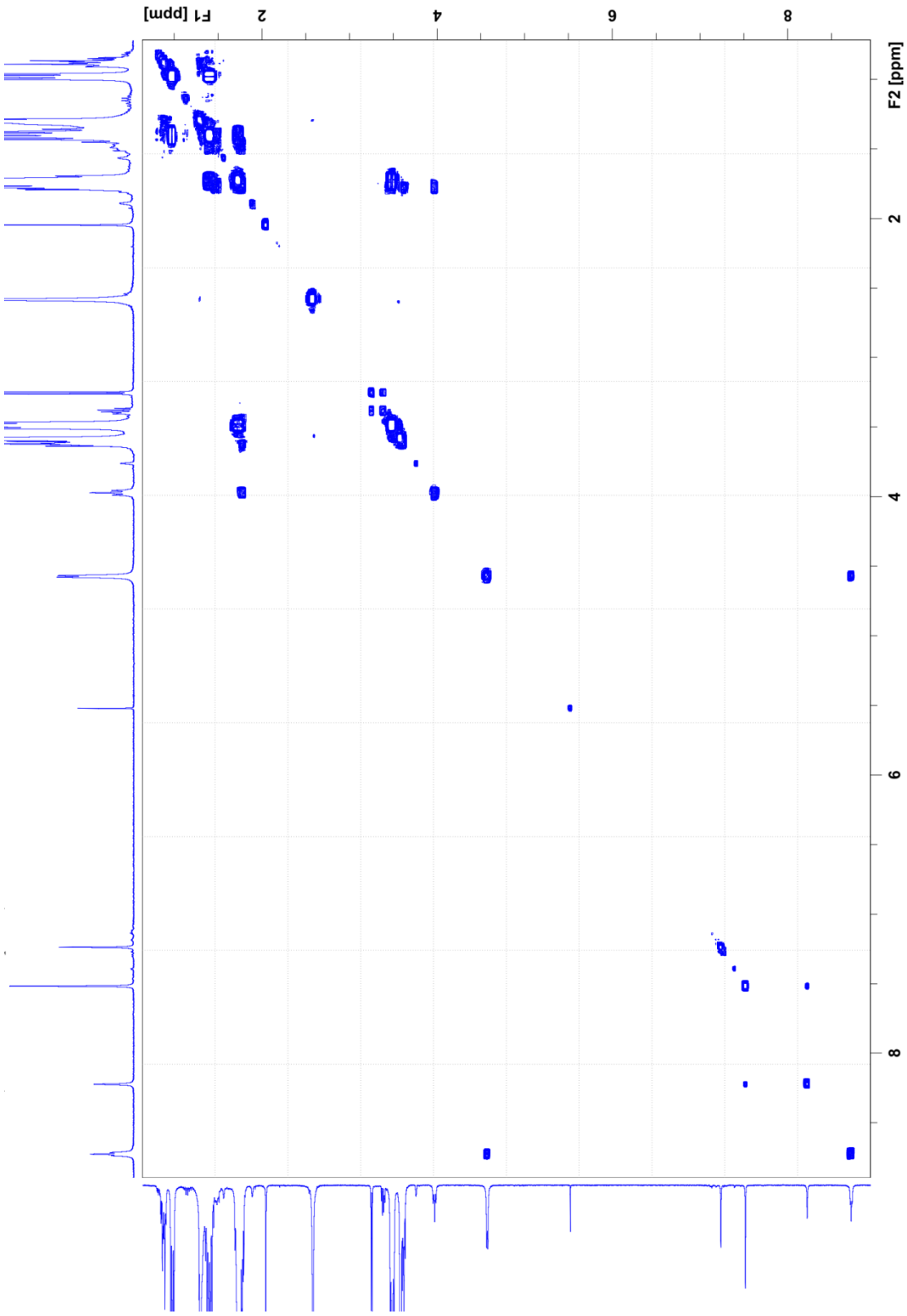


Figure S20. Full ^{1}H-^{1}H COSY (400 MHz) spectrum of **1** (1 mM) + 10 eq Cl^- in THF-d_8 at 298 K.

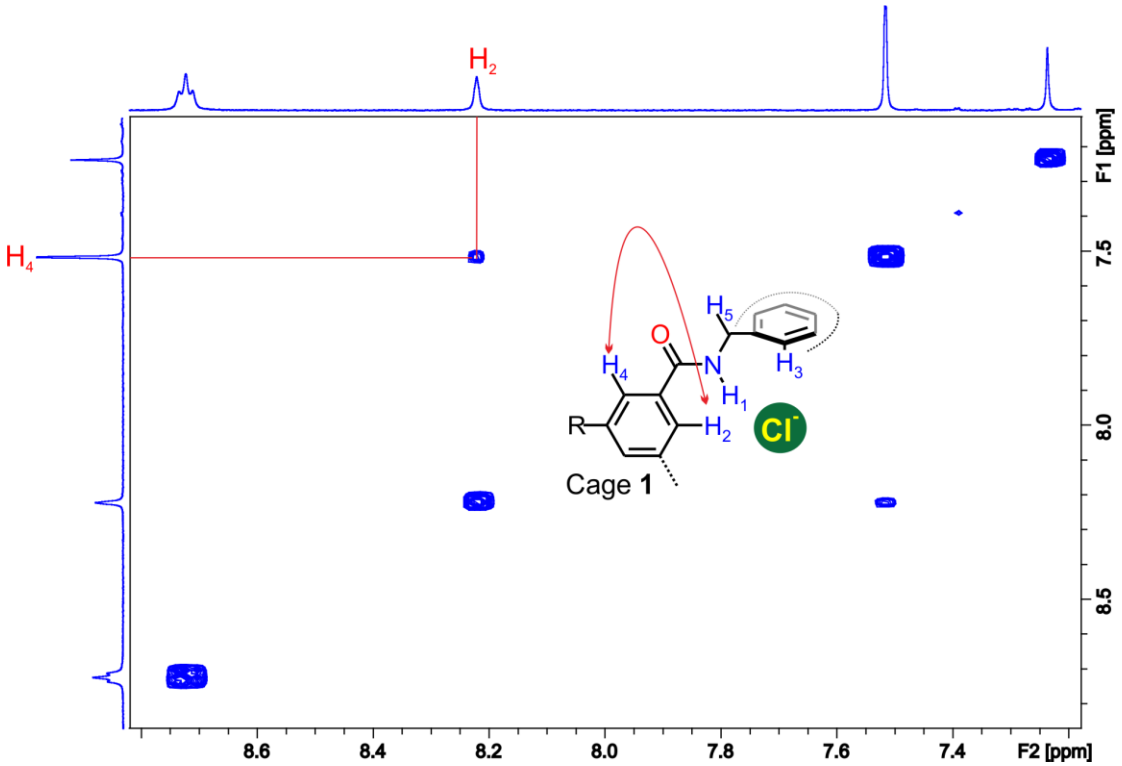


Figure S21. ^{1}H-^{1}H COSY (400 MHz) spectrum of **1** (1 mM) + 10 eq Cl^- in THF-d_8 at 298 K, showing the COSY correlation of $H_2 \leftrightarrow H_4$.

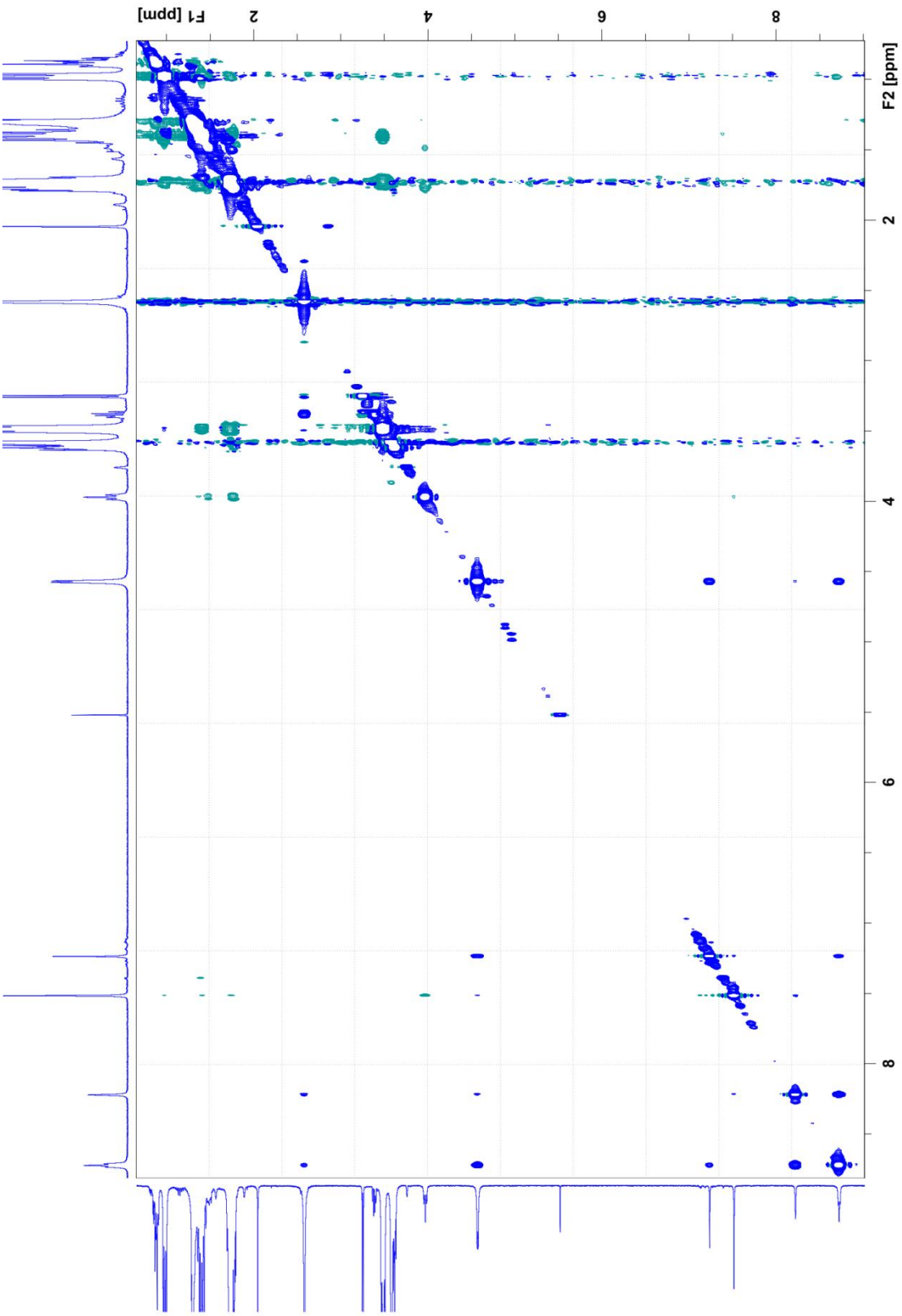


Figure S22. Full ^{1}H-^{1}H NOESY (400 MHz) spectrum of **1** (1 mM) + 10eq Cl^- in THF-d_8 at 298 K.

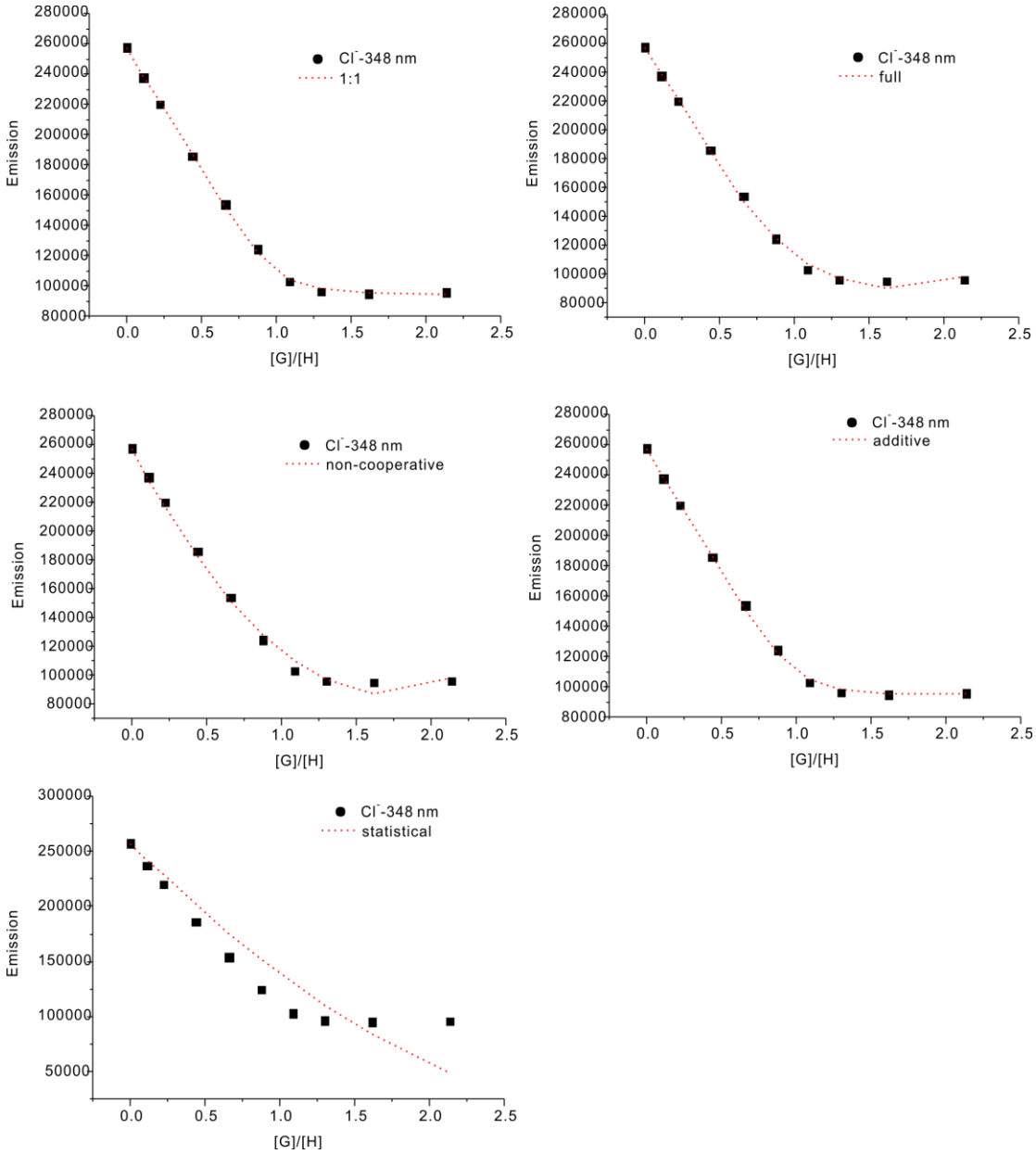


Figure S23. Binding analysis curves of the fluorescence titration between **1** (10 μM) and Cl^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S2. Summary of the binding analysis of the fluorescence titration between **1** and Cl^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$8.5(\pm33\%)\times10^{6}$	-	5.7×10^{-4}	√
Full (1:2)	$-4.3(\pm3.1\%)\times10^{4}$	$-1.8(\pm3.8\%)\times10^{4}$	1.7×10^{-3}	
Non-cooperative (1:2)	$-1.7(\pm5.7\%)\times10^{3}$	-4.4×10^{2}	4.2×10^{-3}	
Additive (1:2)	$6.2(\pm31\%)\times10^{6}$	$-1.4(\pm143\%)\times10^{3}$	5.4×10^{-4}	
Statistical (1:2)	$3.8(\pm68\%)\times10^{5}$	9.6×10^{4}	1.2×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

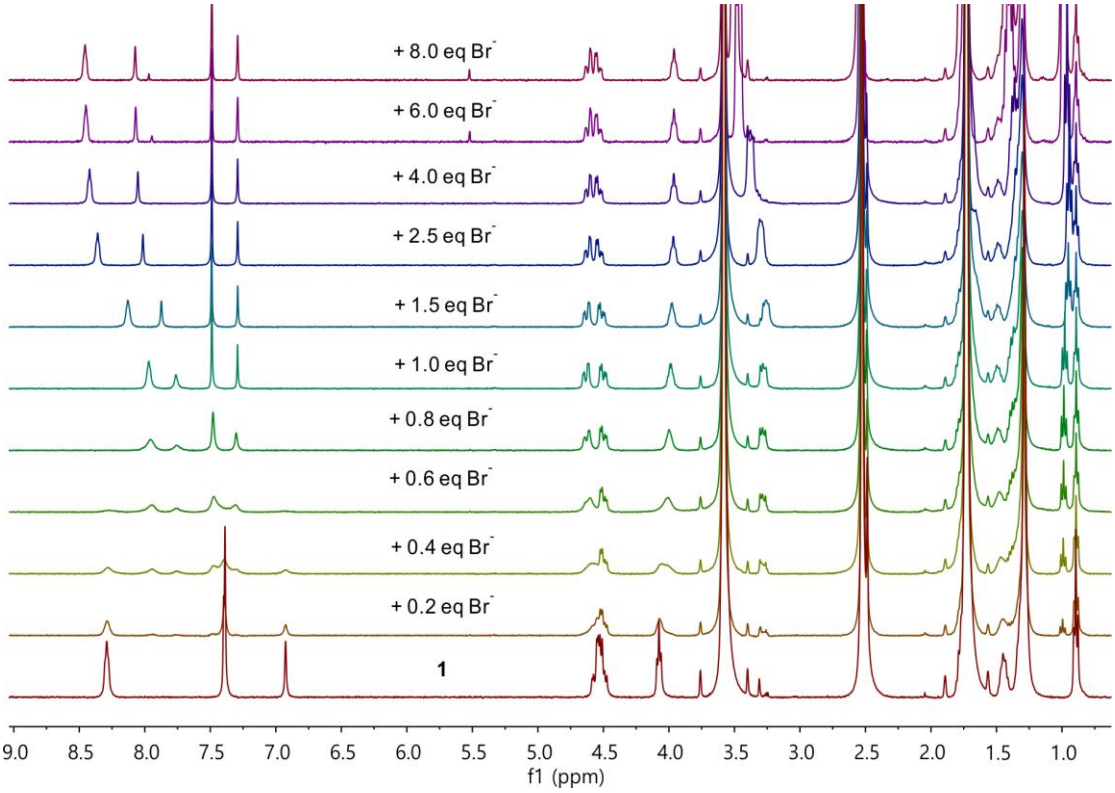


Figure S24. Full spectra of NMR titration study between **1** (0.5 mM) and Br^- in THF-d_8.

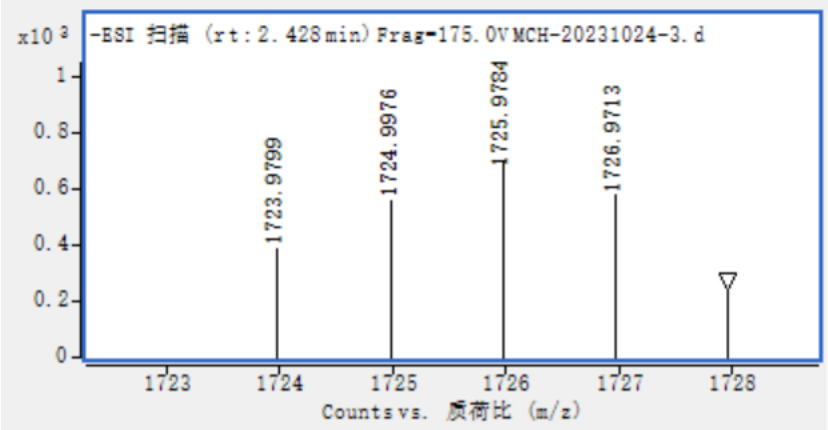


Figure S25. HRESI-TOF mass spectrum of **1**+1.2eqBr$^-$ (m/z calcd for $C_{100}H_{140}N_8O_{12}Br^-$ $[M+Br]^-$ = 1723.9780, found 1723.9799) indicating the existence of 1:1 host-guest complex(es). No other binding stoichiometry was observed under this condition.

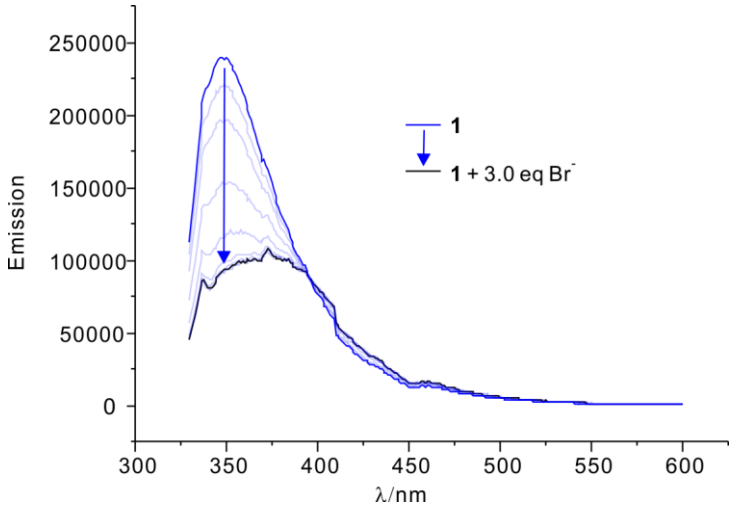


Figure S26. Fluorescence titration of **1** (10 μM) with Br$^-$ in THF.

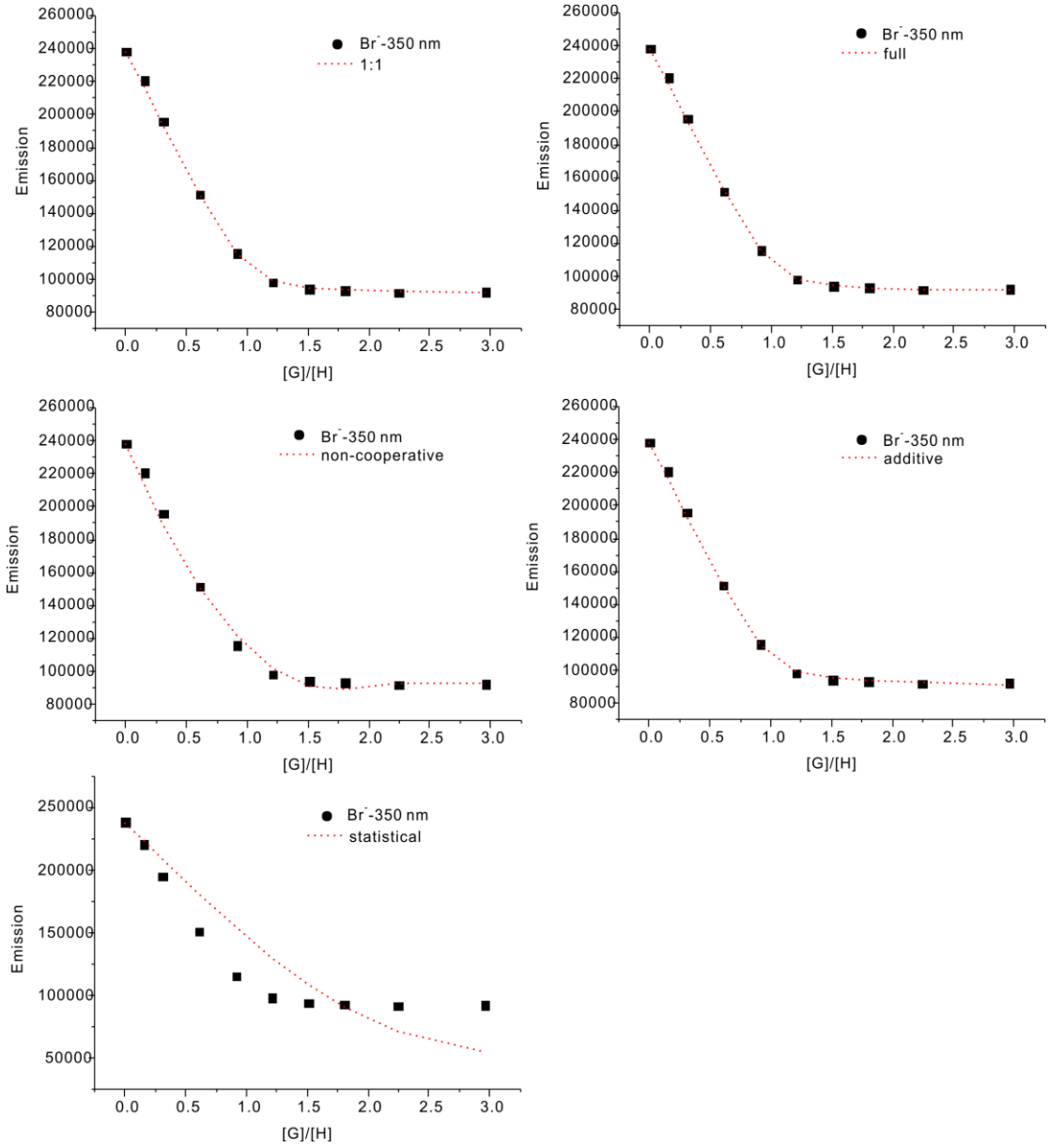


Figure S27. Binding analysis curves of the fluorescence titration between **1** (10 μM) and Br^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S3. Summary of the binding analysis of the fluorescence titration between **1** and Br^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$6.3(\pm37\%)\times10^{6}$	-	7.4×10^{-4}	√
Full (1:2)	$7.4(\pm1608\%)\times10^{8}$	$7.1(\pm1651\%)\times10^{6}$	5.9×10^{-4}	
Non-cooperative (1:2)	$2.0(\pm2.5\times10^{10}\%)\times10^{19}$	5.0×10^{18}	5.3×10^{-3}	
Additive (1:2)	$7.6(\pm50\%)\times10^{6}$	$5.8(\pm244\%)\times10^{2}$	7.4×10^{-4}	
Statistical (1:2)	$1.5(\pm169\%)\times10^{6}$	3.8×10^{5}	1.7×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

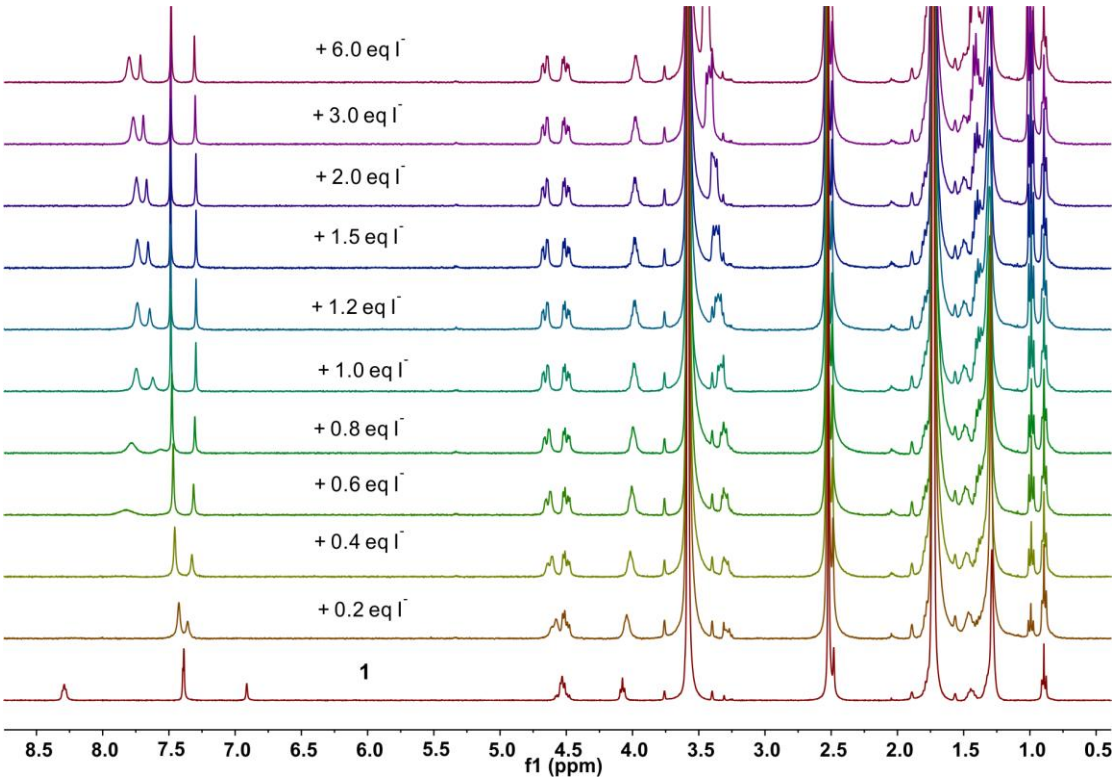


Figure S28. Full spectra of NMR titration study between **1** (0.5 mM) and I^- in THF-d_8.

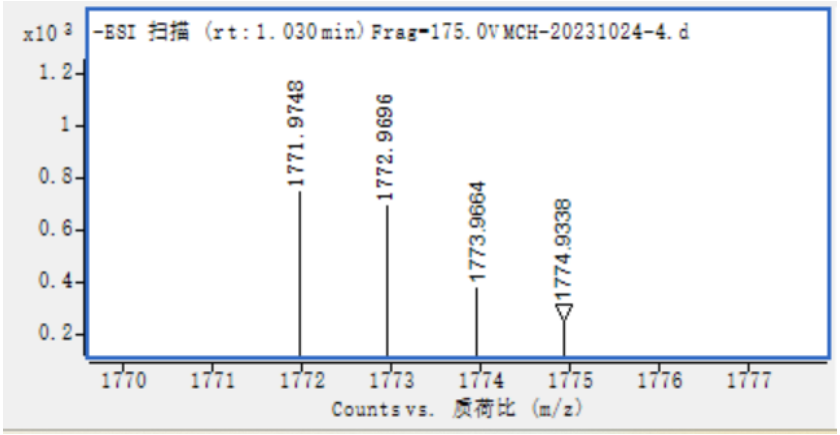


Figure S29. HRESI-TOF mass spectrum of **1**+1.2eqI^- (m/z calcd for $C_{100}H_{140}N_8O_{12}I^-$ $[M+I]^-$ = 1771.9641, found 1771.9748) indicating the existence of 1:1 host-guest complex(es). No other binding stoichiometry was observed under this condition.

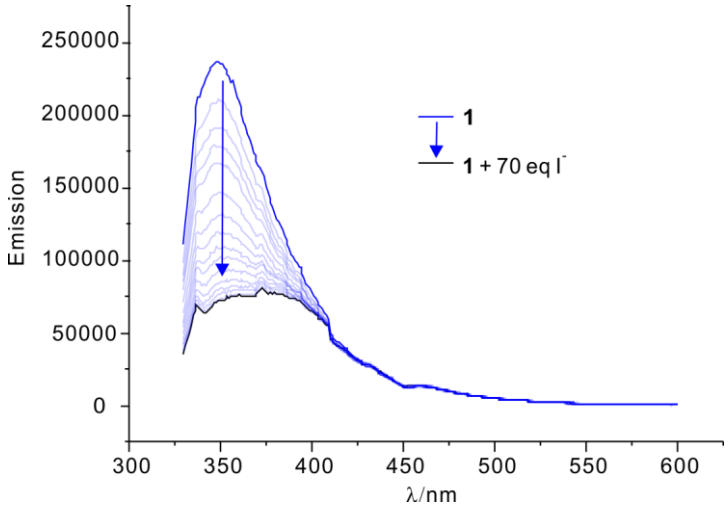


Figure S30. Fluorescence titration of **1** (10 μM) with I^- in THF.

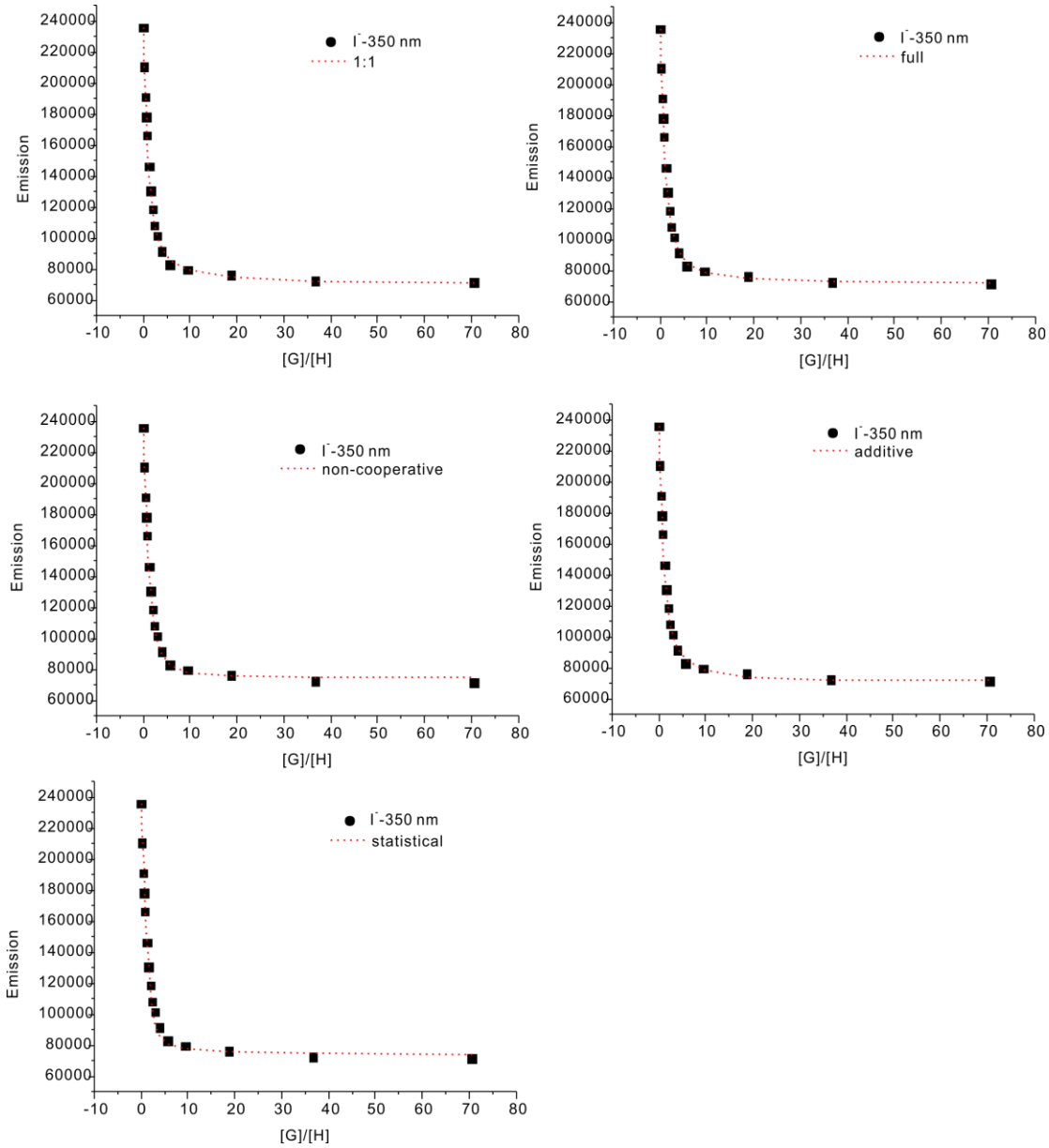


Figure S31. Binding analysis curves of the fluorescence titration between **1** (10 μM) and I^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S4. Summary of the binding analysis of the fluorescence titration between **1** and I^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$2.0(\pm7.0\%)\times10^5$	-	1.8×10^{-3}	√
Full (1:2)	$2.2(\pm10\%)\times10^5$	$1.1(\pm105\%)\times10^3$	1.7×10^{-3}	
Non-cooperative (1:2)	$2.5(\pm12\%)\times10^5$	6.2×10^4	3.0×10^{-3}	
Additive (1:2)	$2.0(\pm7.3\%)\times10^5$	$-1.5(\pm272\%)\times10^1$	1.8×10^{-3}	
Statistical (1:2)	$1.2(\pm48\%)\times10^6$	4.0×10^5	1.9×10^{-2}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

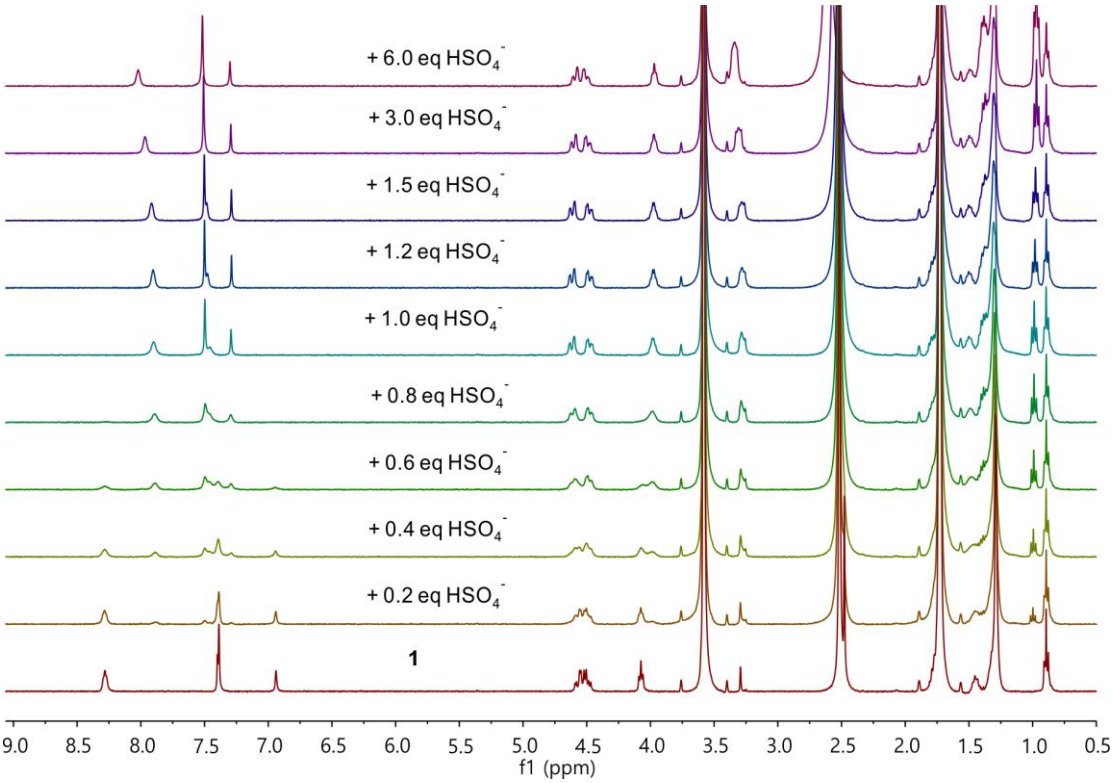


Figure S32. Full spectra of NMR titration study between **1** (0.5 mM) and HSO_4^- in THF-d_8.

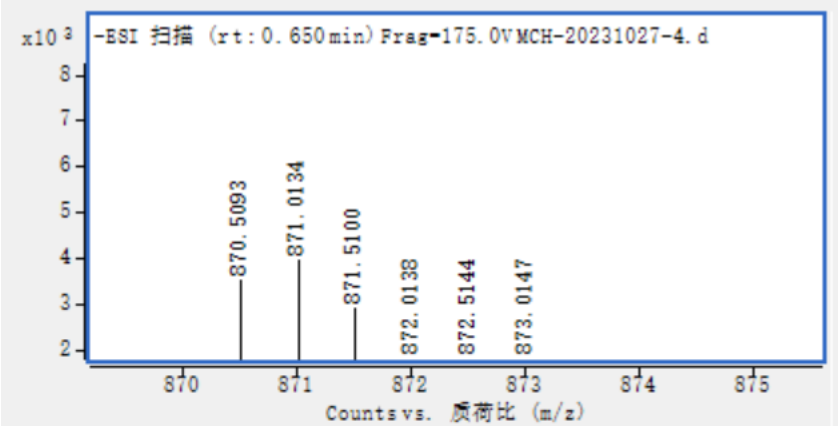


Figure S33. HRESI-TOF mass spectrum of **1**+1.2eqHSO_4^- (m/z calcd for $C_{100}H_{140}N_8O_{16}S^{2-}$ $[M+HSO_4\text{-}H]^{2-}$ = 870.5060, found 870.5093) indicating the existence of 1:1 host-guest complex(es). No other binding stoichiometry was observed under this condition.

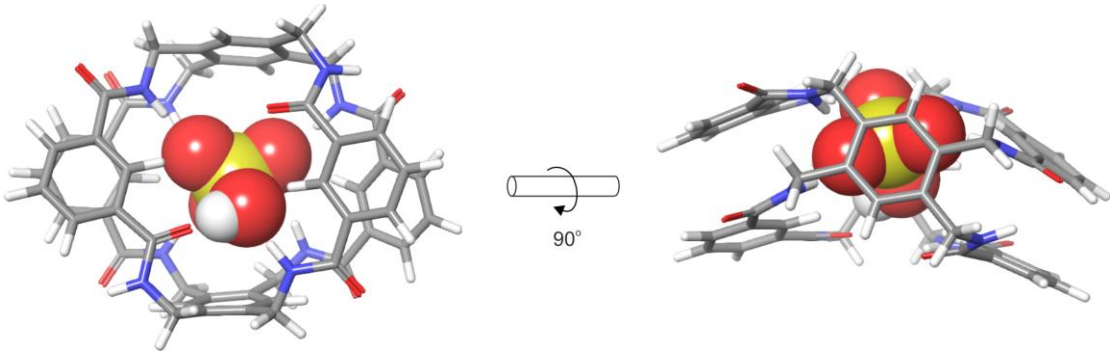


Figure S34. Molecular model (m062x/def2svp, SMD/THF) of [**1**-HSO_4^-]. Redundant side chains are omitted for clarity.

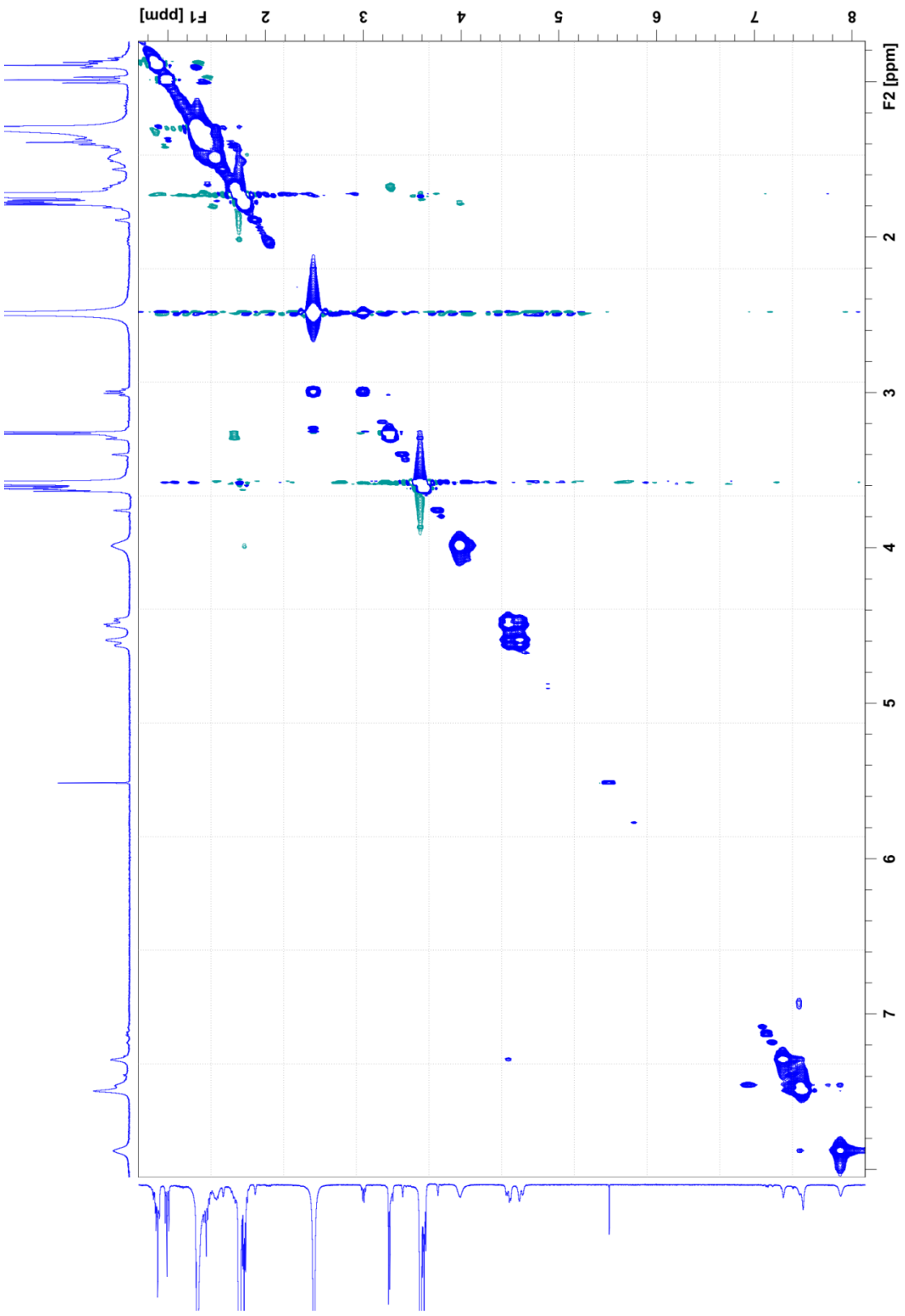


Figure S35. Full ^{1}H-^{1}H NOESY (400 MHz) spectrum of **1** (1 mM) + 1eq HSO_4^- in THF-d_8 at 298 K.

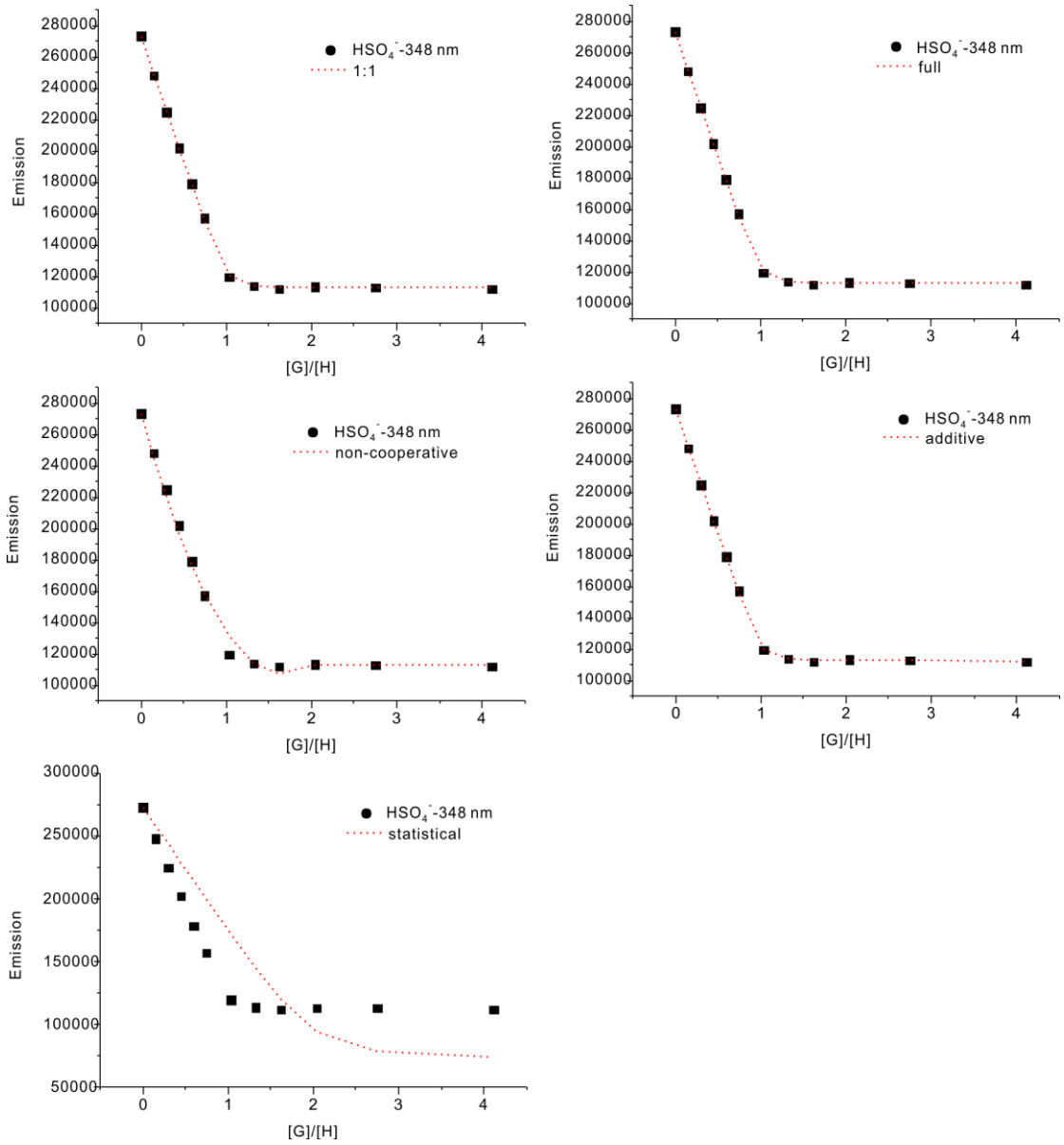


Figure S36. Binding analysis curves of the fluorescence titration between **1** (10 μM) and HSO_4^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S5. Summary of the binding analysis of the fluorescence titration between **1** and HSO_4^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$2.2(\pm34\%)\times10^{7}$	-	1.8×10^{-4}	√
Full (1:2)	$1.7(\pm2916\%)\times10^{9}$	$7.0(\pm2978\%)\times10^{6}$	1.4×10^{-4}	
Non-cooperative (1:2)	$7.0(\pm9.8\times10^{9}\%)\times10^{20}$	1.74×10^{19}	6.0×10^{-3}	
Additive (1:2)	$2.4(\pm39\%)\times10^{7}$	$7.0(\pm506\%)\times10^{1}$	1.8×10^{-4}	
Statistical (1:2)	$5.4(\pm421\%)\times10^{6}$	1.3×10^{5}	2.4×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

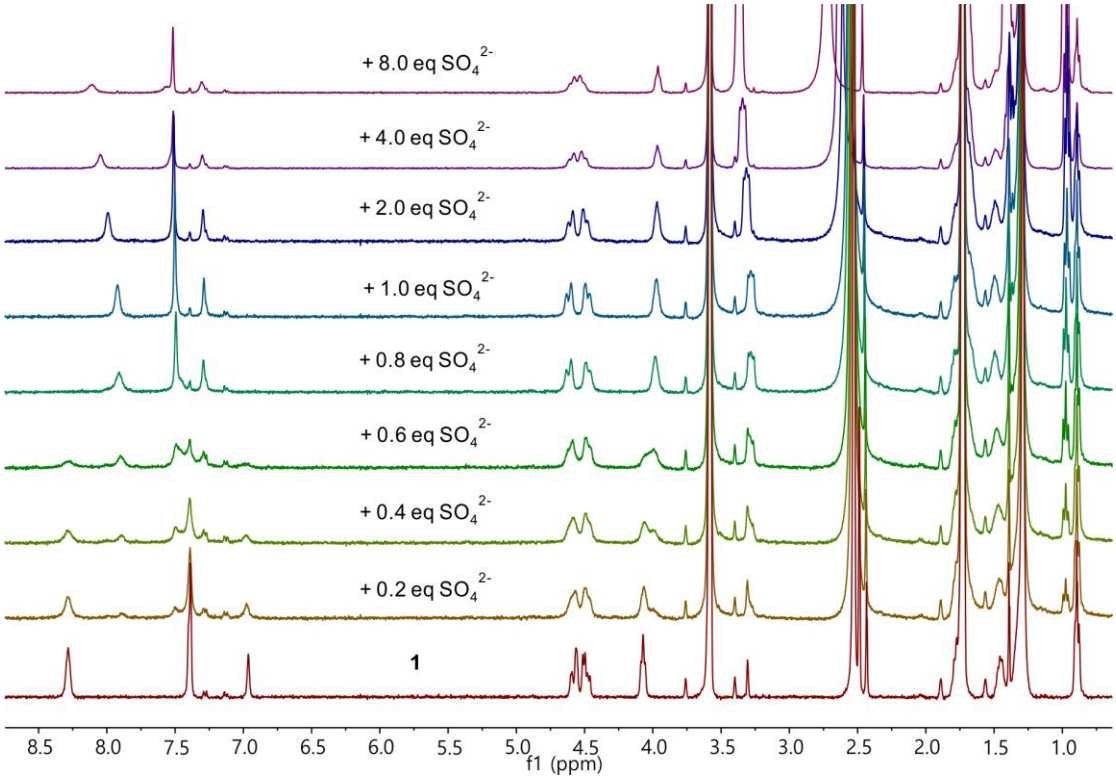


Figure S37. Full spectra of NMR titration study between **1** (0.5 mM) and SO_4^{2-} in THF-d_8.

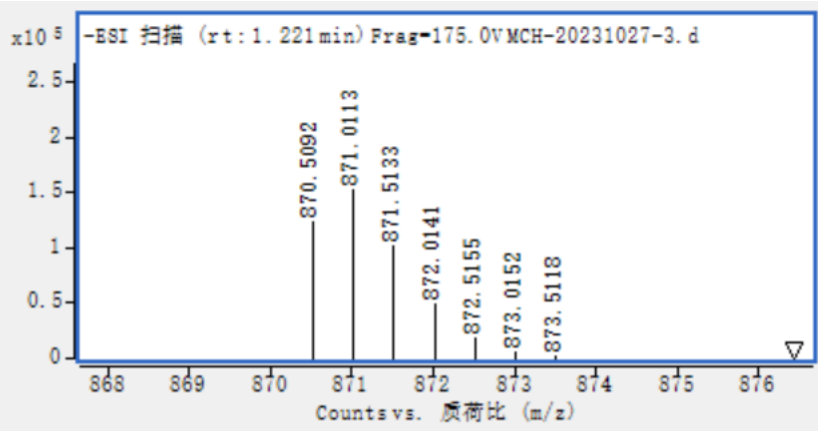


Figure S38. HRESI-TOF mass spectrum of **1**+1.2eqSO_4^{2-} (m/z calcd for $C_{100}H_{140}N_8O_{16}S^{2-}$ $[M+SO_4]^{2-}$ = 870.5060, found 870.5092) indicating the existence of 1:1 host-guest complex(es). No other binding stoichiometry was observed under this condition.

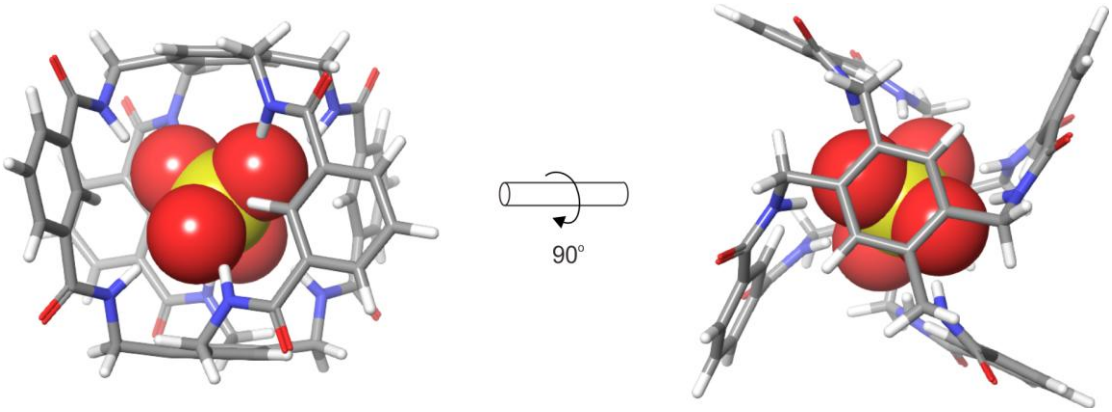


Figure S39. Molecular model (m062x/def2svp, SMD/THF) of [**1**-SO_4^{2-}]. Redundant side chains are omitted for clarity.

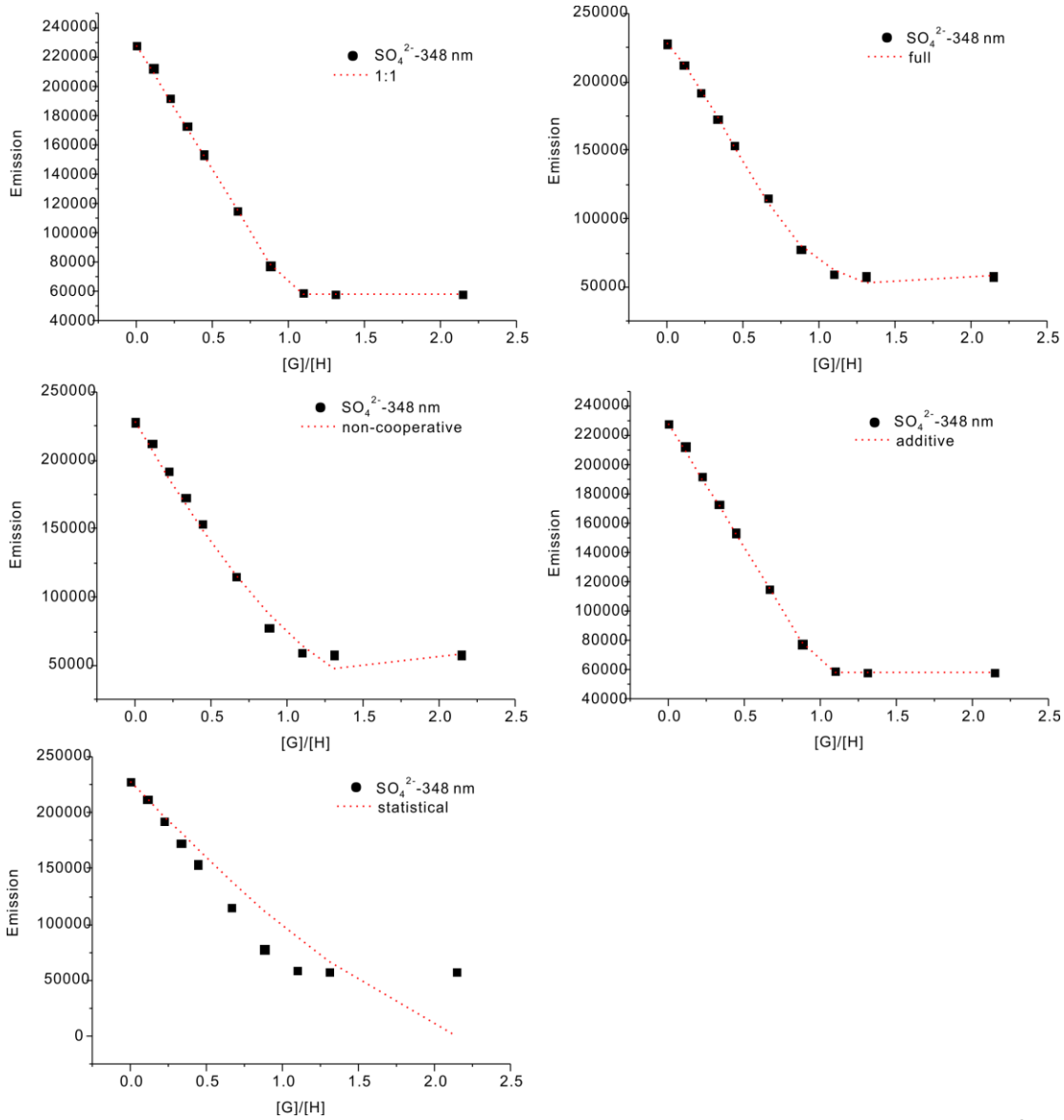


Figure S40. Binding analysis curves of the fluorescence titration between **1** (10 μM) and SO_4^{2-} in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S6. Summary of the binding analysis of the fluorescence titration between **1** and SO_4^{2-} in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	~10^9 2.9(±4842%)×10^9	-	4.0×10^{-4}	√
Full (1:2)	-4.7(±2.4%)×10^4	-1.7(±3.0%)×10^4	1.6×10^{-3}	
Non-cooperative (1:2)	-1.4(±4.7%)×10^4	3.5×10^3	8.0×10^{-3}	
Additive (1:2)	7.4(±1.2×10^9%)×10^{14}	4.9(±428%)×10^2	4.0×10^{-4}	
Statistical (1:2)	4.1(±83%)×10^5	1.0×10^5	1.4×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

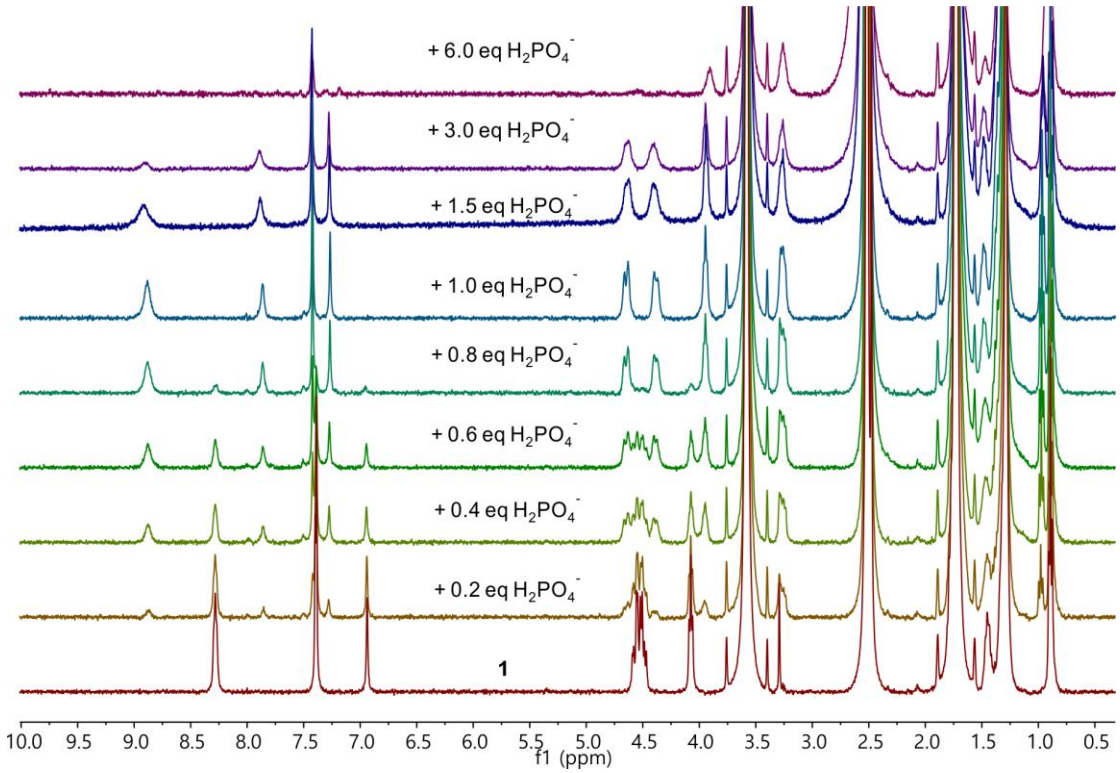


Figure S41. Full spectra of NMR titration study between **1** (0.5 mM) and $H_2PO_4^-$ in THF-d_8.

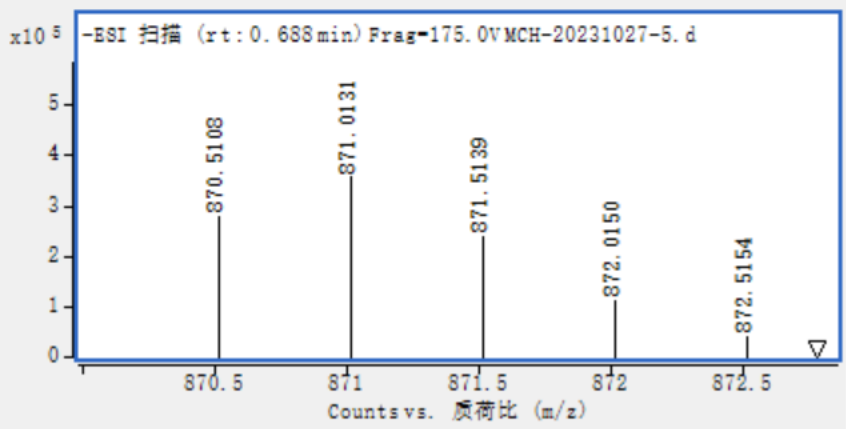


Figure S42. HRESI-TOF mass spectrum of **1**+1.2eq$H_2PO_4^-$ (m/z calcd for $C_{100}H_{141}N_8O_{16}P^{2-}$ $[M+H_2PO_4\text{-}H]^{2-}$ = 870.5107, found 870.5108) indicating the existence of 1:1 host-guest complex(es). No other binding stoichiometry was observed under this condition.

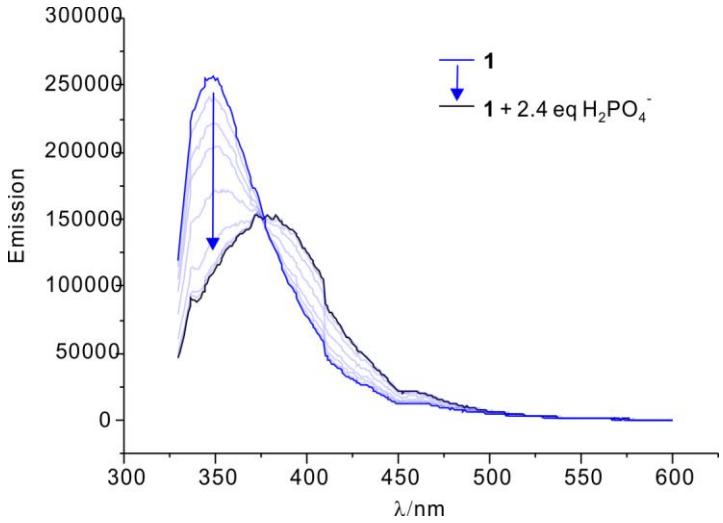


Figure S43. Fluorescence titration of **1** (10 μM) with $H_2PO_4^-$ in THF.

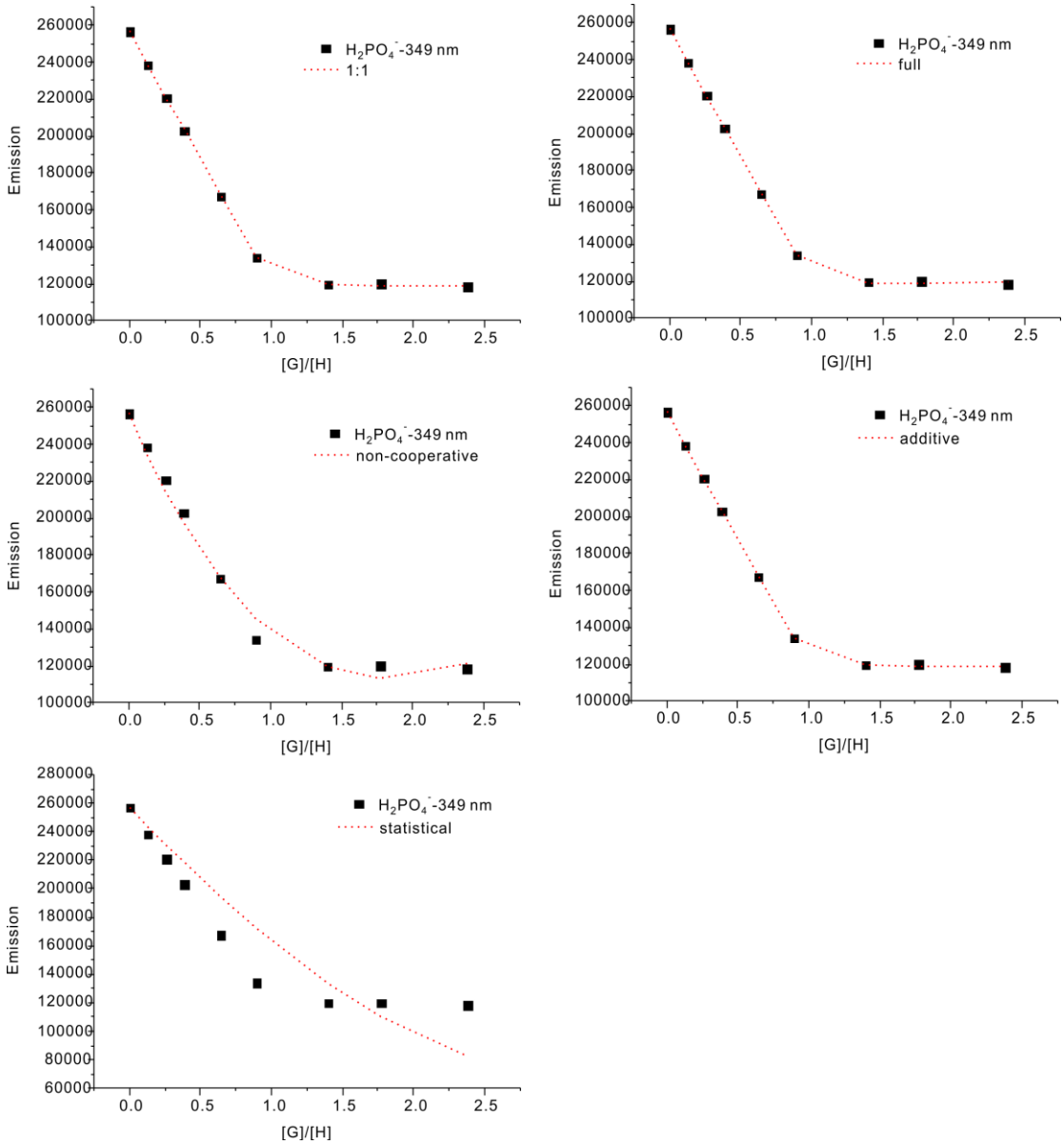


Figure S44. Binding analysis curves of the fluorescence titration between **1** (10 μM) and $H_2PO_4^-$ in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S7. Summary of the binding analysis of the fluorescence titration between **1** and $H_2PO_4^-$ in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	~10^8 1.1(±140%)×10^8	-	8.3×10^{-5}	√
Full (1:2)	1.6(±411%)×10^8	1.1(±751%)×10^5	8.2×10^{-5}	
Non-cooperative (1:2)	2.5(±16%)×10^4	6.2×10^3	1.1×10^{-2}	
Additive (1:2)	9.6(±140%)×10^7	-1.2(±625%)×10^2	8.4×10^{-5}	
Statistical (1:2)	4.7(±99%)×10^5	1.1×10^4	1.5×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

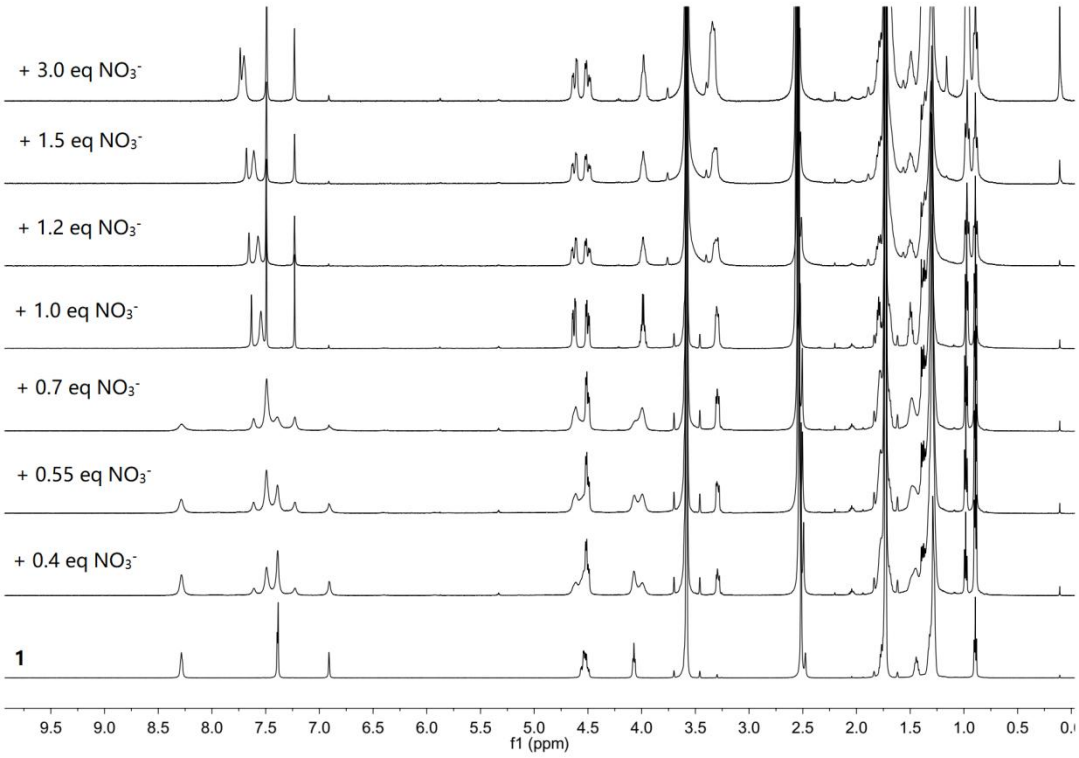


Figure S45. Full spectra of NMR titration study between **1** (0.5 mM) and NO_3^- in THF-d_8.

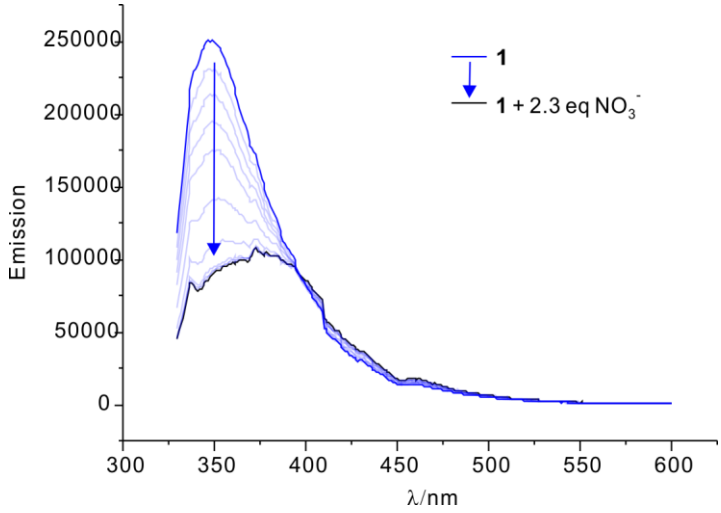


Figure S46. Fluorescence titration of **1** (10 μM) with NO_3^- in THF.

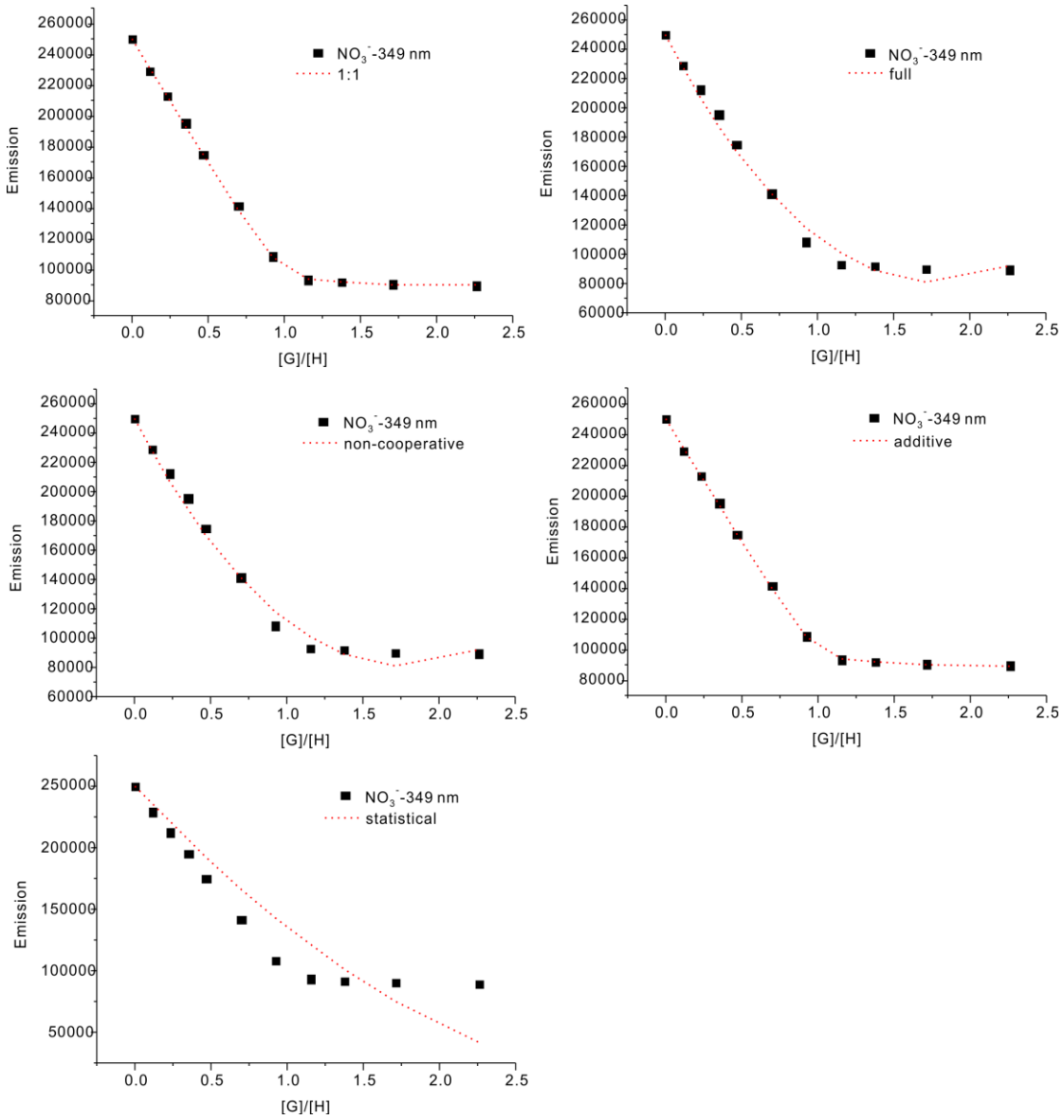


Figure S47. Binding analysis curves of the fluorescence titration between **1** (10 μM) and NO_3^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S8. Summary of the binding analysis of the fluorescence titration between **1** and NO_3^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$1.6(\pm34\%)\times10^{7}$	-	2.8×10^{-4}	√
Full (1:2)	$6.3(\pm9.0\%)\times10^{0}$	$1.9(\pm10\%)\times10^{7}$	8.7×10^{-3}	
Non-cooperative (1:2)	$3.8(\pm8.1\%)\times10^{3}$	9.5×10^{2}	8.9×10^{-3}	
Additive (1:2)	$1.9(\pm44\%)\times10^{7}$	$5.5(\pm230\%)\times10^{2}$	2.7×10^{-4}	
Statistical (1:2)	$4.2(\pm70\%)\times10^{5}$	1.1×10^{5}	1.4×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

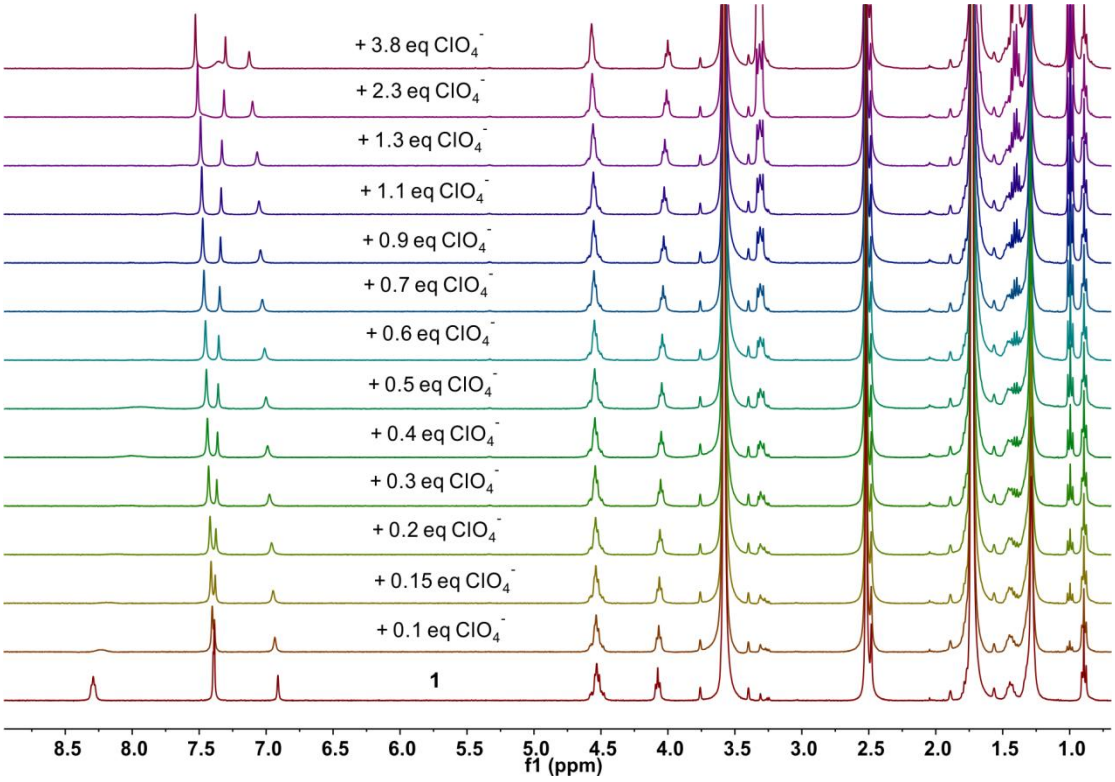


Figure S48. Full spectra of NMR titration study between **1** (0.5 mM) and ClO_4^- in THF-d_8.

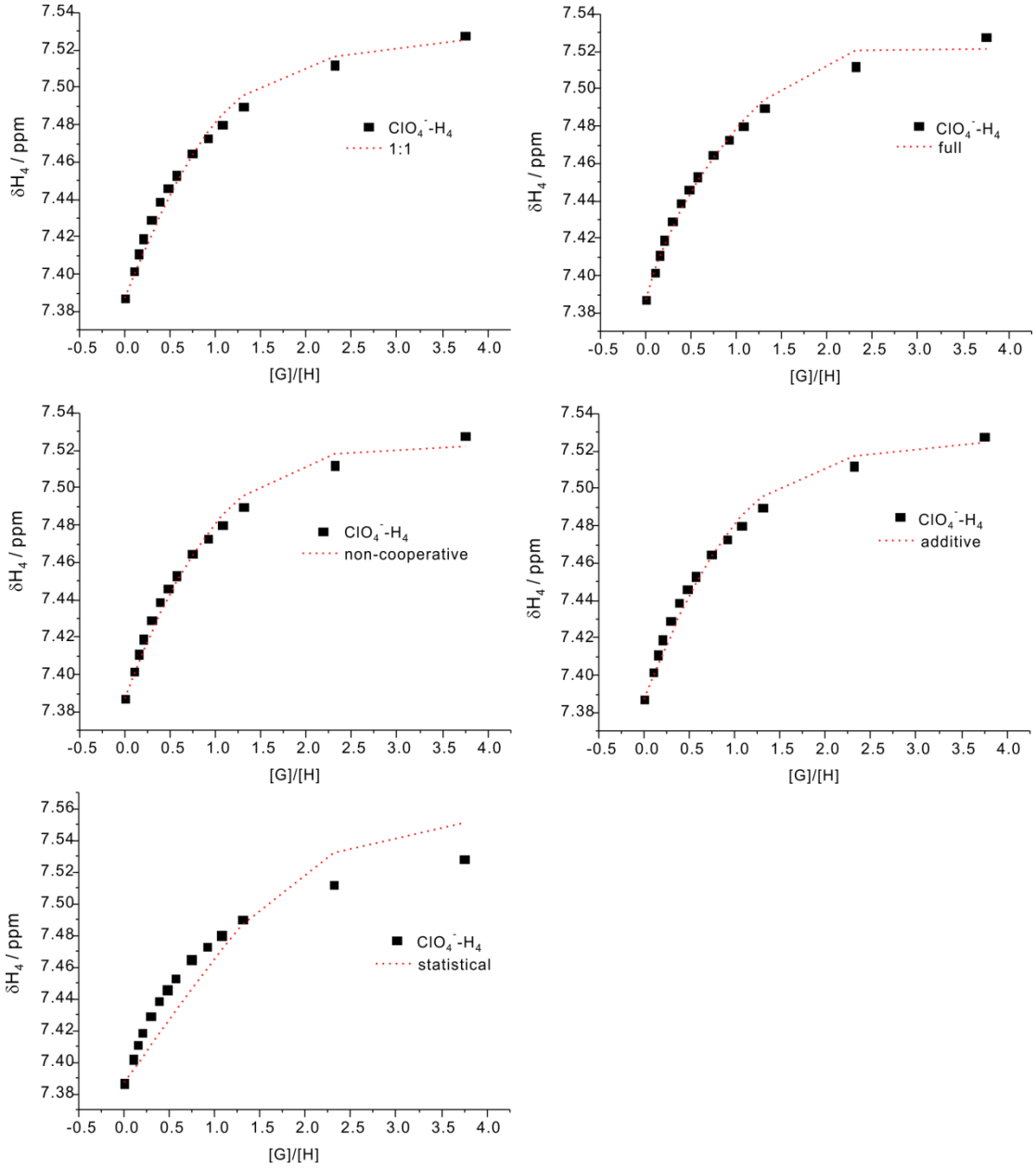


Figure S49. Binding analysis curves of the NMR titration between **1** (10 μM) and ClO_4^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S9. Summary of the binding analysis of the NMR titration between **1** and ClO_4^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$9.5(\pm26\%)\times10^{3}$	-	1.5×10^{-2}	√
Full (1:2)	$1.1(\pm21\%)\times10^{0}$	$6.9(\pm41\%)\times10^{6}$	8.7×10^{-3}	
Non-cooperative (1:2)	$4.7(\pm23\%)\times10^{3}$	1.2×10^{3}	1.3×10^{-2}	
Additive (1:2)	$7.0(\pm26\%)\times10^{3}$	$-37(\pm147\%)\times10^{1}$	1.5×10^{-2}	
Statistical (1:2)	$2.8(\pm144\%)\times10^{4}$	7.0×10^{3}	1.2×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

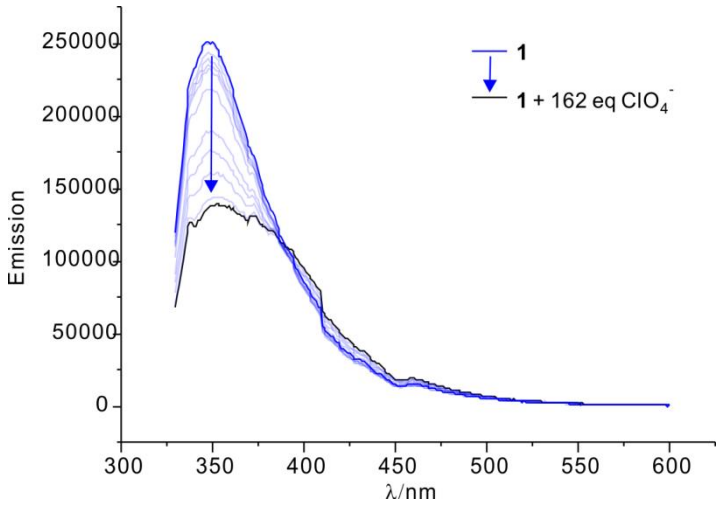


Figure S50. Fluorescence titration of **1** (10 μM) with ClO_4^- in THF.

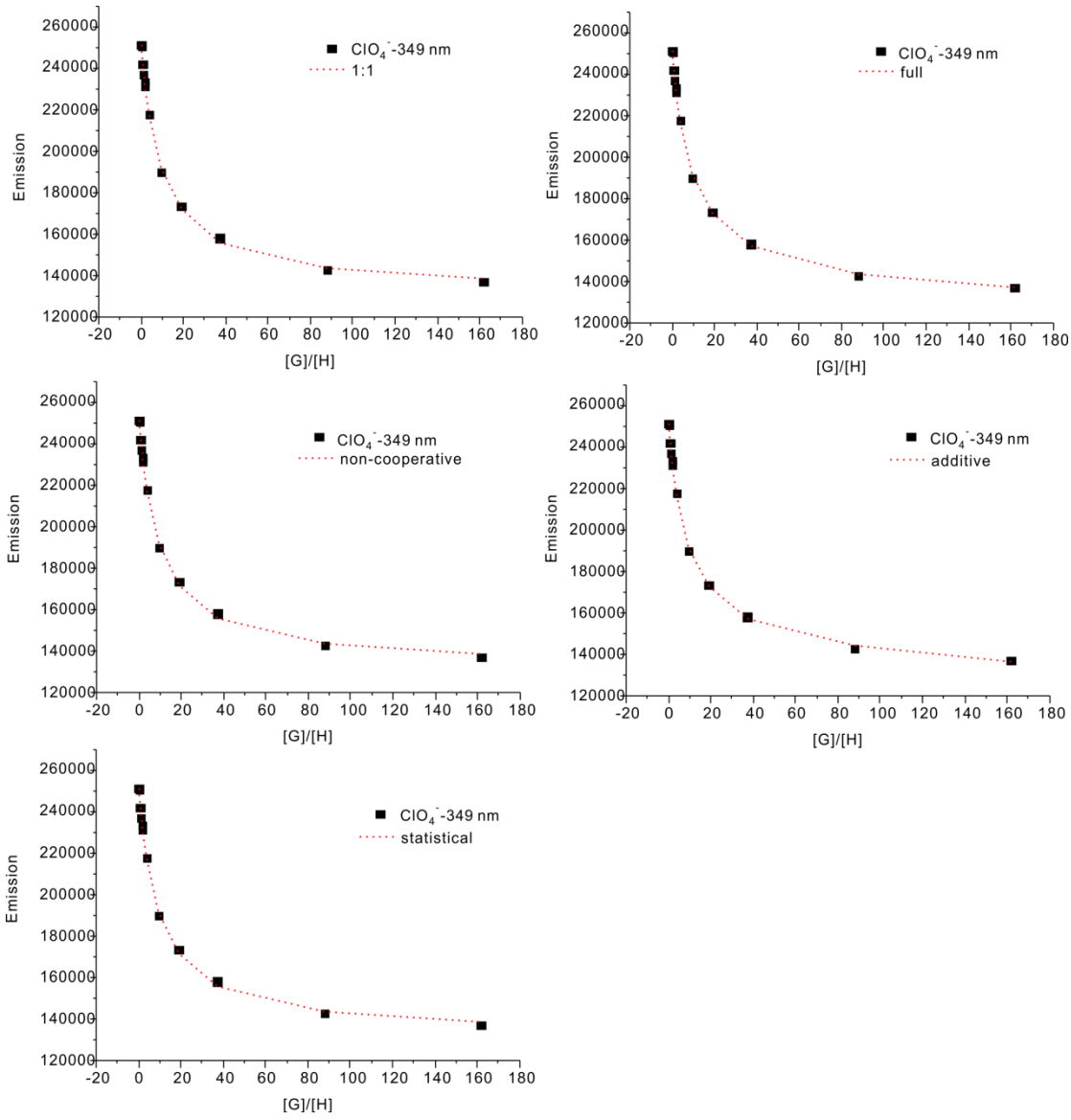


Figure S51. Binding analysis curves of the fluorescence titration between **1** (10 μM) and ClO_4^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S10. Summary of the binding analysis of the fluorescence titration between **1** and ClO_4^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$1.1(\pm 8.3\%)\times 10^4$	-	1.9×10^{-3}	√
Full (1:2)	$1.4(\pm 12\%)\times 10^4$	$9.6(\pm 39\%)\times 10^2$	1.5×10^{-3}	
Non-cooperative (1:2)	$2.1(\pm 10\%)\times 10^4$	5.3×10^3	2.2×10^{-3}	
Additive (1:2)	$1.2(\pm 8.9\%)\times 10^4$	$4.0(\pm 62\%)\times 10^1$	1.5×10^{-3}	
Statistical (1:2)	$2.4(\pm 9.4\%)\times 10^4$	5.9×10^3	2.2×10^{-3}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

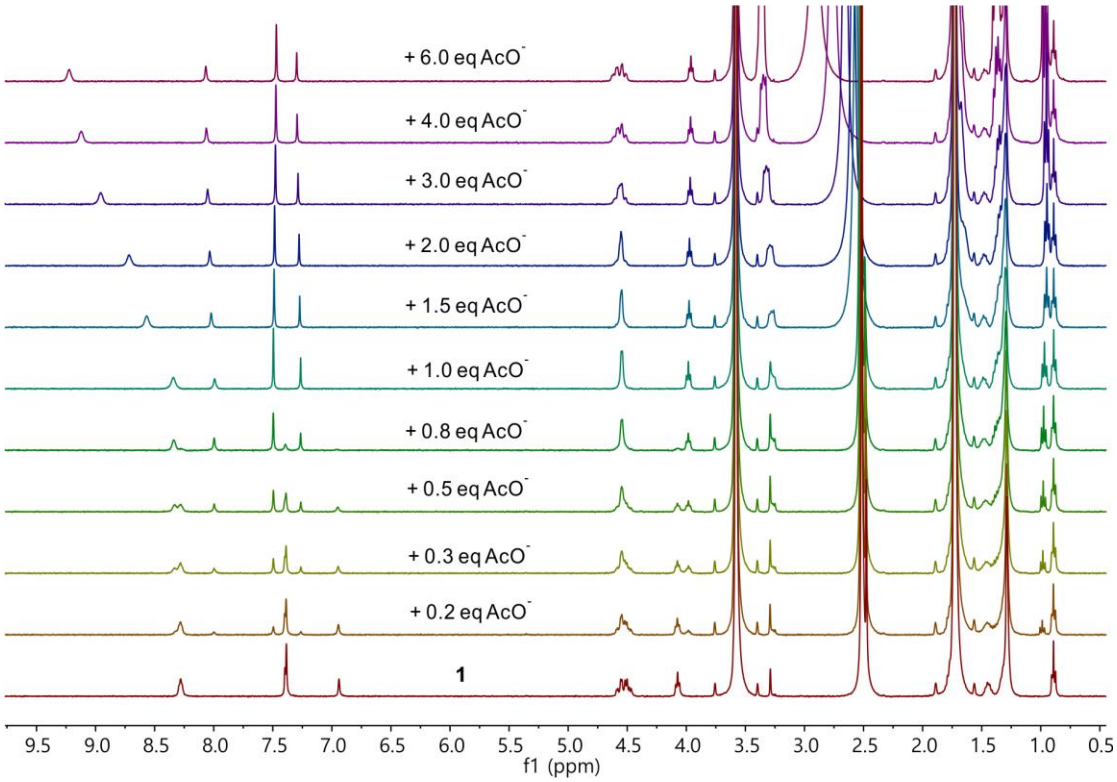


Figure S52. Full spectra of NMR titration study between **1** (0.5 mM) and AcO^- in THF-d_8.

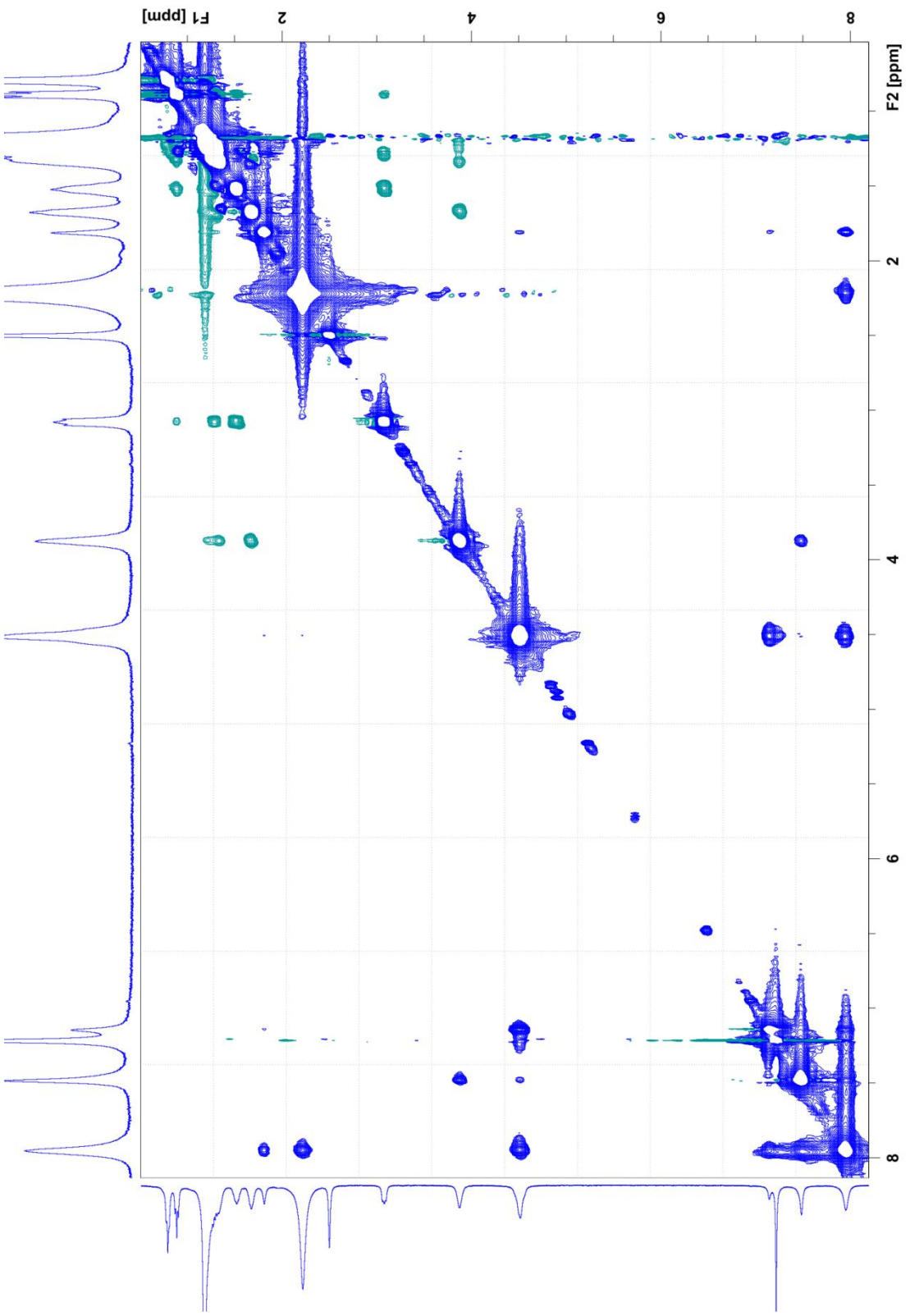


Figure S53. Full ^{1}H-^{1}H NOESY (400 MHz) spectrum of **1** (1 mM) + 1eq AcO^- in 2%DMSO-d_6/$CDCl_3$ at 298 K.

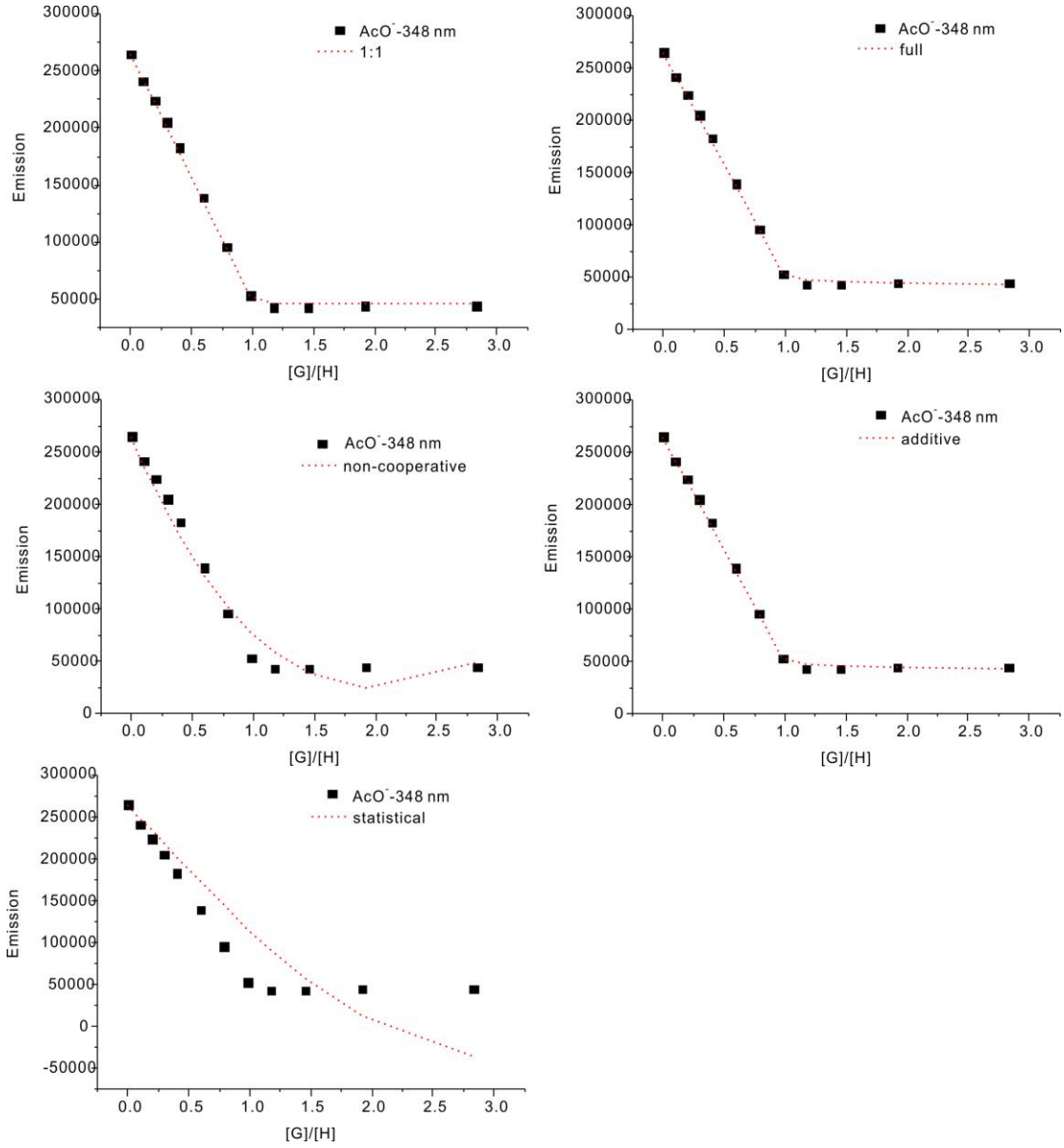


Figure S54. Binding analysis curves of the fluorescence titration between **1** (10 μM) and AcO^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S11. Summary of the binding analysis of the fluorescence titration between **1** and AcO^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	~10^8 2.2(±358%)×10^8	-	1.3×10^{-3}	√
Full (1:2)	2.6(±2139%)×10^{10}	1.2(±899%)×10^6	9.7×10^{-4}	
Non-cooperative (1:2)	2.7(±14%)×10^4	6.9×10^3	2.2×10^{-2}	
Additive (1:2)	1.6(±1476%)×10^9	1.4(±133%)×10^3	1.1×10^{-3}	
Statistical (1:2)	1.0(±138%)×10^6	2.5×10^5	1.9×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

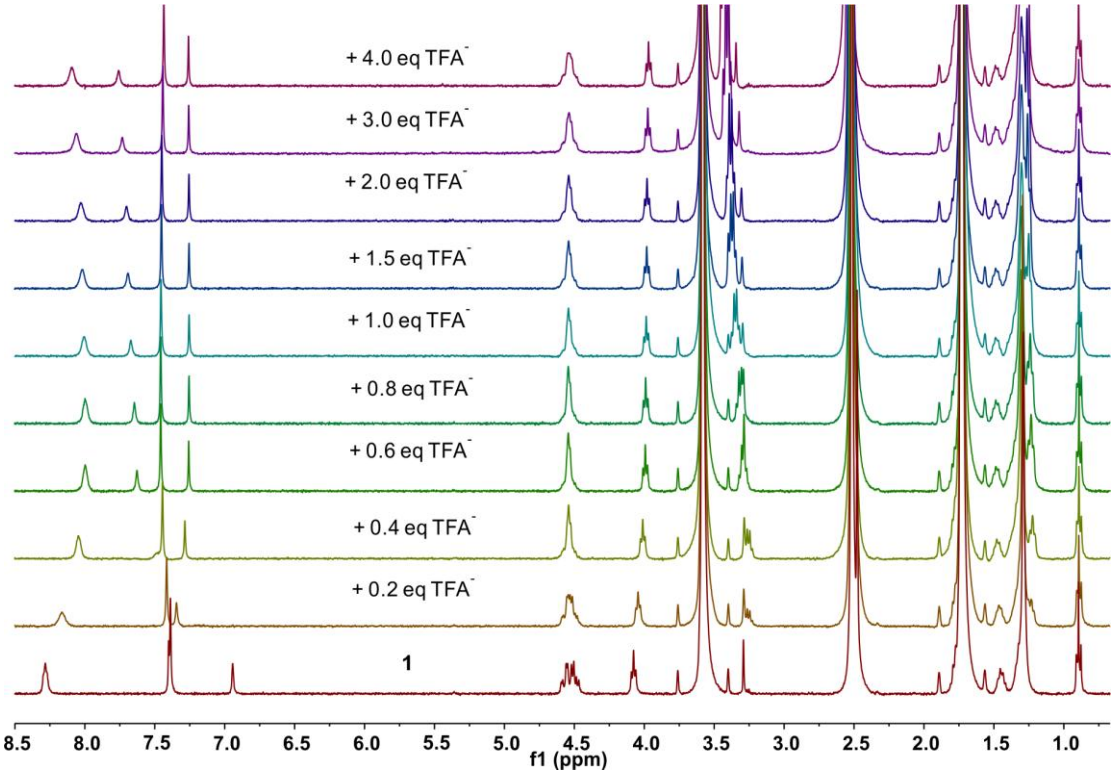


Figure S55. Full spectra of NMR titration study between **1** (0.5 mM) and TFA^- in THF-d_8.

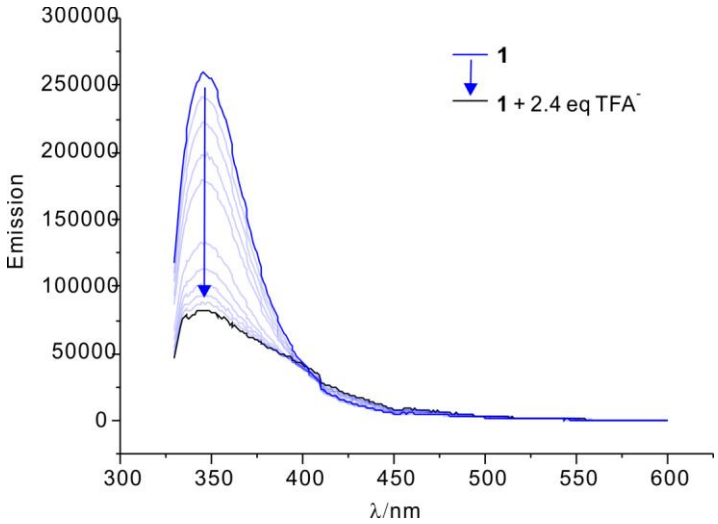


Figure S56. Fluorescence titration of **1** (10 μM) with TFA^- in THF.

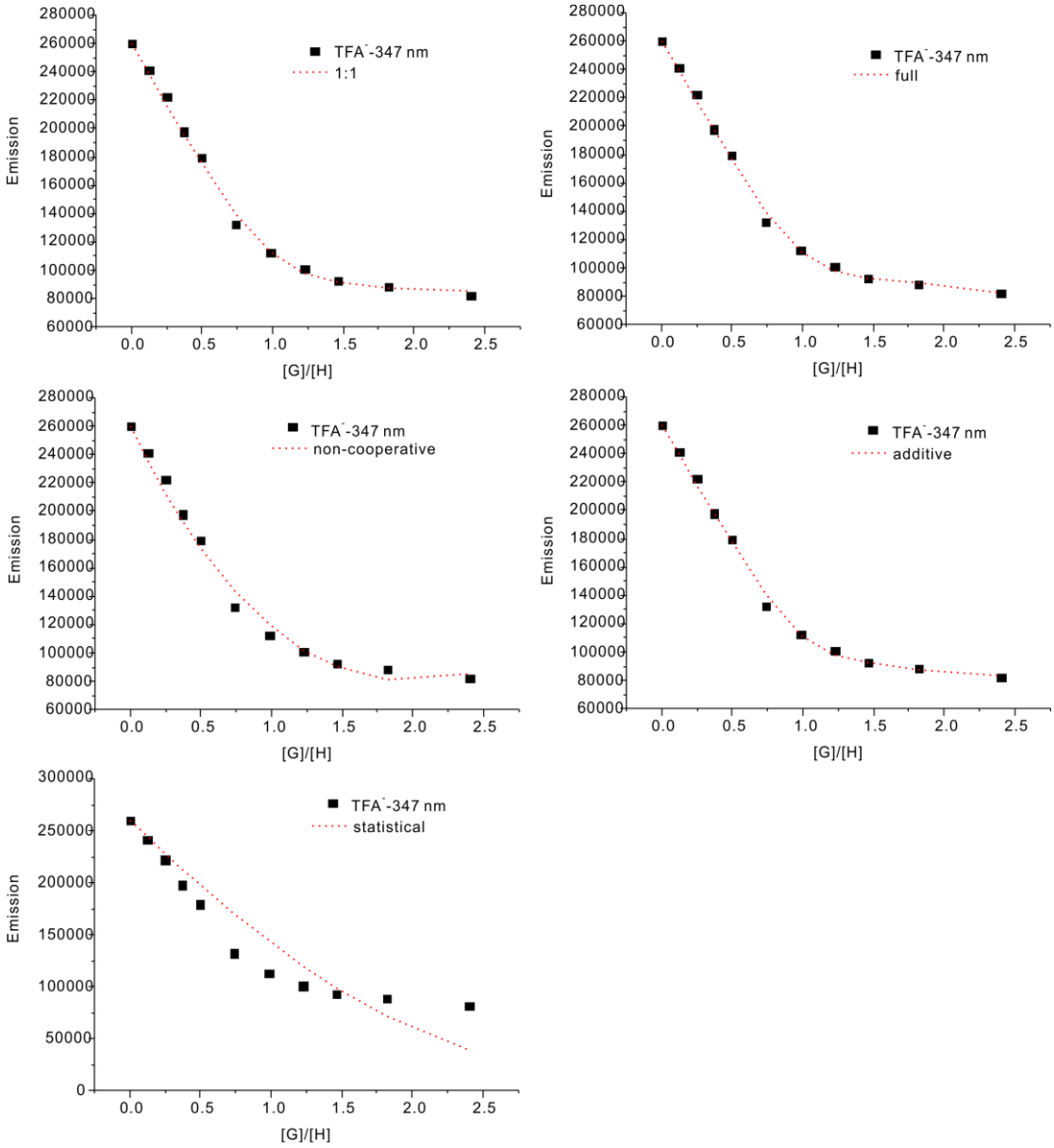


Figure S57. Binding analysis curves of the fluorescence titration between **1** (10 μM) and TFA^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S12. Summary of the binding analysis of the fluorescence titration between **1** and TFA^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$2.7(\pm35\%)\times10^6$	-	2.6×10^{-3}	√
Full (1:2)	$4.3(\pm55\%)\times10^6$	$-2.1(\pm12\%)\times10^4$	2.2×10^{-3}	
Non-cooperative (1:2)	$2.1(\pm11\%)\times10^4$	5.3×10^3	9.4×10^{-3}	
Additive (1:2)	$5.8(\pm63\%)\times10^6$	$3.8(\pm102\%)\times10^3$	2.3×10^{-3}	
Statistical (1:2)	$4.8(\pm69\%)\times10^5$	1.2×10^5	1.1×10^{-1}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

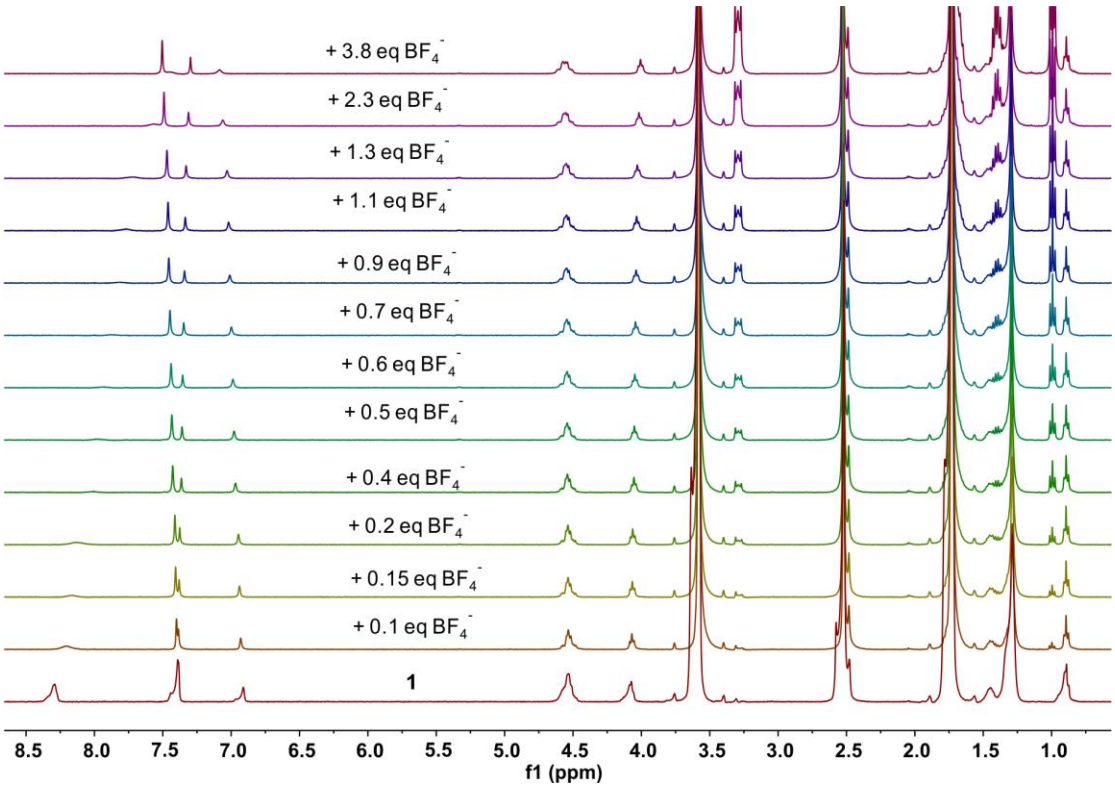


Figure S58. Full spectra of NMR titration study between **1** (0.5 mM) and BF_4^- in THF-d_8.

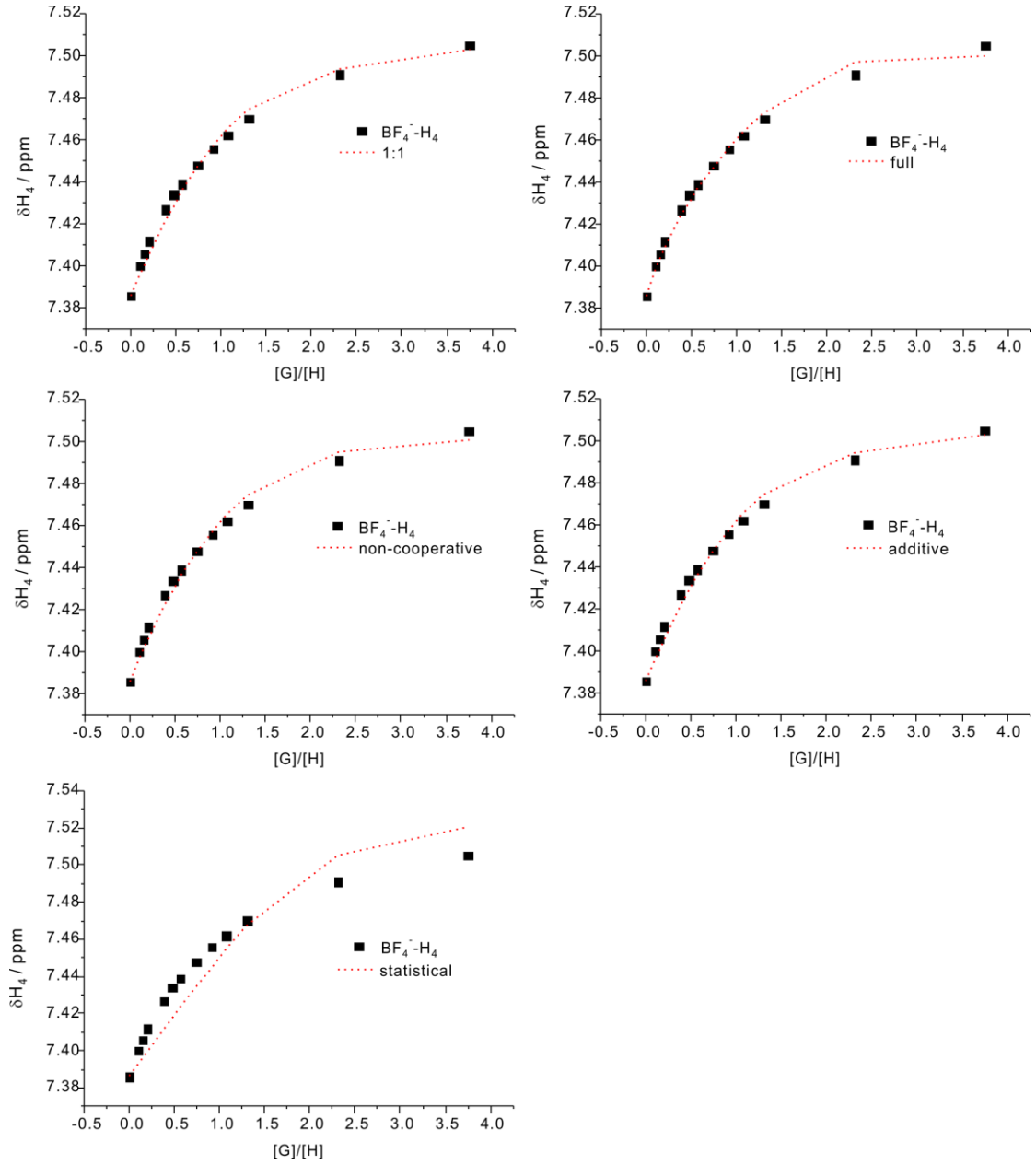


Figure S59. Binding analysis curves of the NMR titration between **1** (10 μM) and BF_4^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S13. Summary of the binding analysis of the NMR titration between **1** and BF_4^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$7.1(\pm21\%)\times10^{3}$	-	1.1×10^{-2}	√
Full (1:2)	$1.0(\pm22\%)\times10^{0}$	$7.4(\pm46\%)\times10^{6}$	7.1×10^{-3}	
Non-cooperative (1:2)	$4.0(\pm21\%)\times10^{3}$	1.0×10^{3}	1.0×10^{-2}	
Additive (1:2)	$6.1(\pm24\%)\times10^{3}$	$-2.1(\pm268\%)\times10^{1}$	1.2×10^{-2}	
Statistical (1:2)	$2.8(\pm134\%)\times10^{4}$	7.1×10^{3}	9.0×10^{-2}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

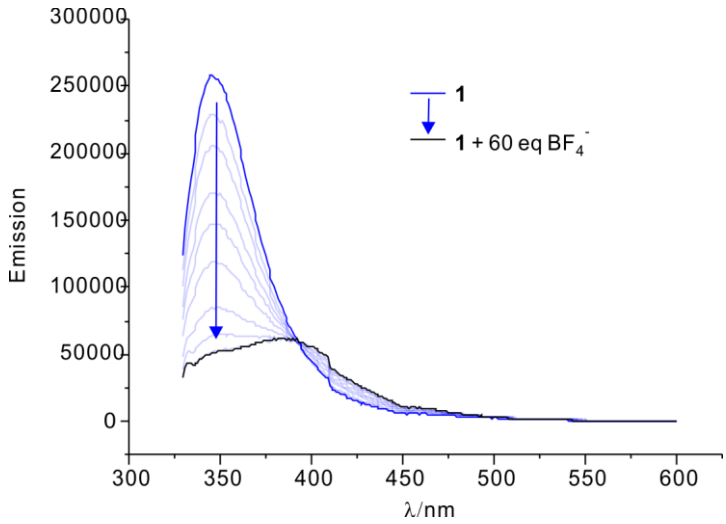


Figure S60. Fluorescence titration of **1** (10 μM) with BF_4^- in THF.

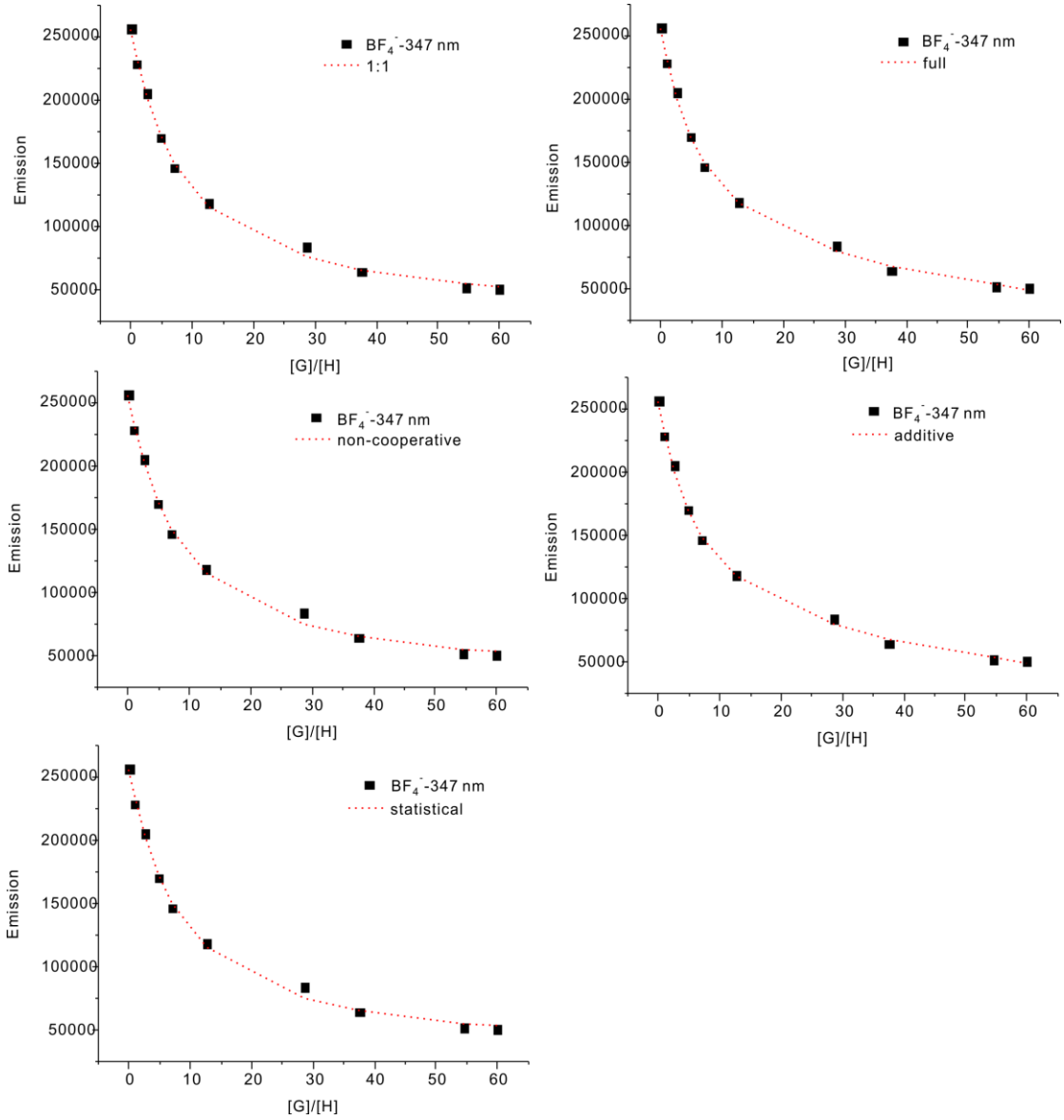


Figure S61. Binding analysis curves of the fluorescence titration between **1** (10 μM) and BF_4^- in THF. The 1:1, full (1:2), non-cooperative (1:2), additive (1:2), and statistical (1:2) binding models (receptor-substrate) are used for the analysis.[3,4]

Table S14. Summary of the binding analysis of the fluorescence titration between **1** and BF_4^- in THF.

Binding Model (host:guest)	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	Covariance	Conclusion[a]
1:1	$1.3(\pm 8.7\%)\times 10^4$	-	2.7×10^{-3}	√
Full (1:2)	$1.8(\pm 13\%)\times 10^4$	$7.2(\pm 26\%)\times 10^2$	1.7×10^{-3}	
Non-cooperative (1:2)	$2.5(\pm 11\%)\times 10^4$	6.2×10^3	3.0×10^{-3}	
Additive (1:2)	$1.7(\pm 11\%)\times 10^4$	$2.8(\pm 26\%)\times 10^2$	1.7×10^{-3}	
Statistical (1:2)	$2.9(\pm 10\%)\times 10^4$	7.2×10^3	3.1×10^{-3}	

[a] According to the covariance values (to select a more complex model, the value should be at least 3 times lower than a simpler one)[4] and the physical possibility, the 1:1 binding model should be more appropriate to describe the data.

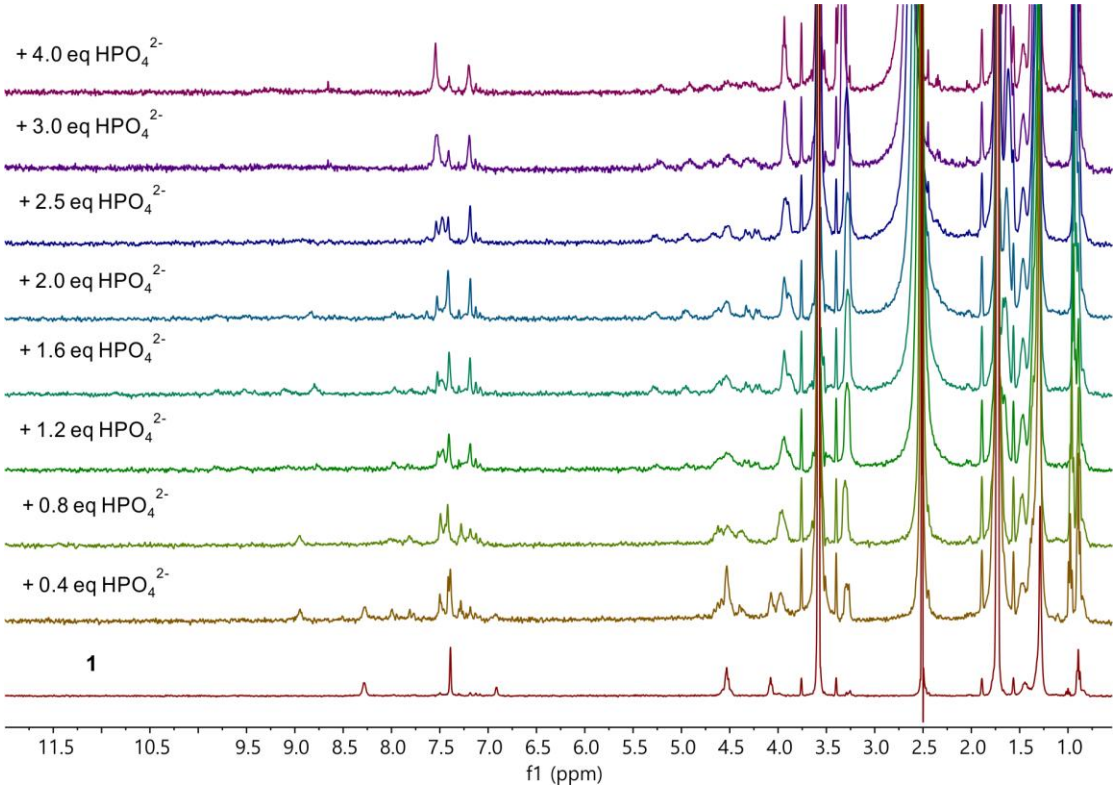


Figure S62. Full spectra of NMR titration study between **1** (0.5 mM) and HPO_4^{2-} in THF-d_8.

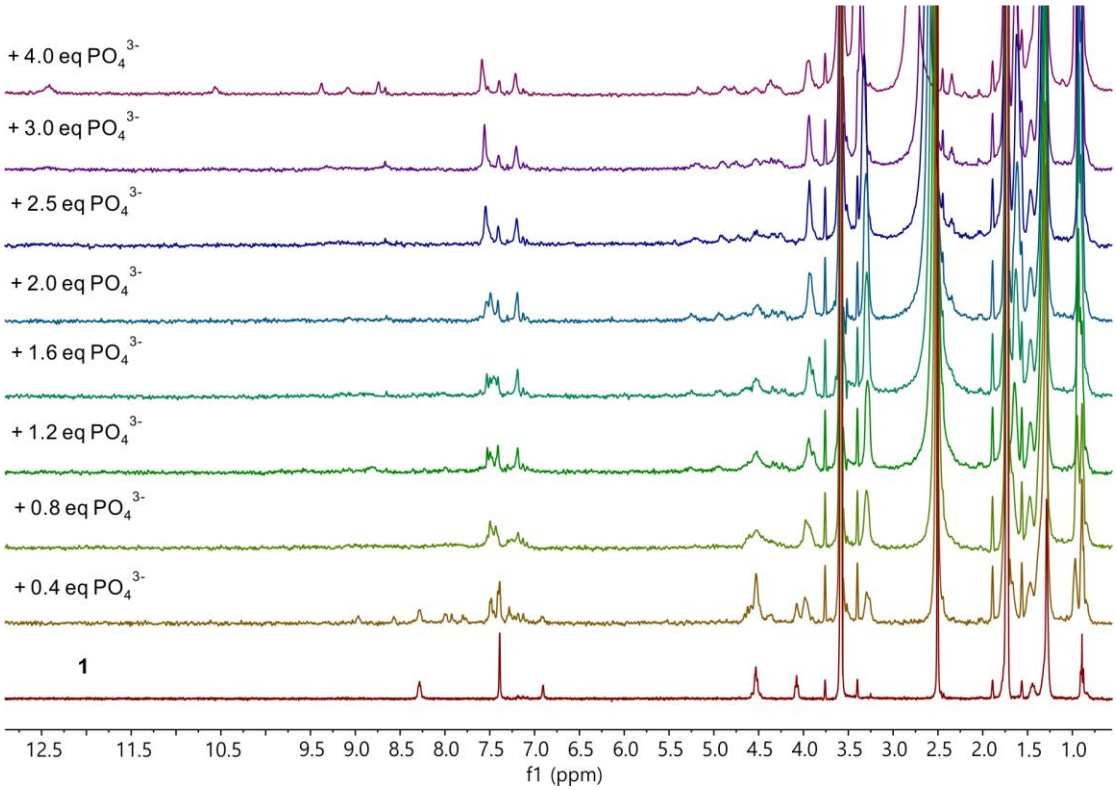
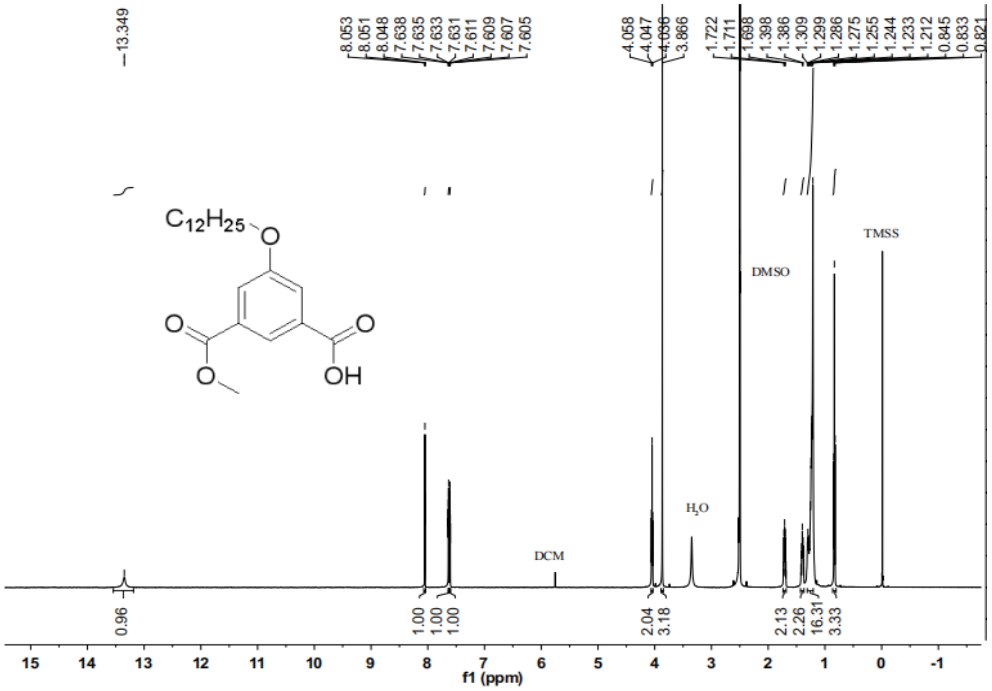


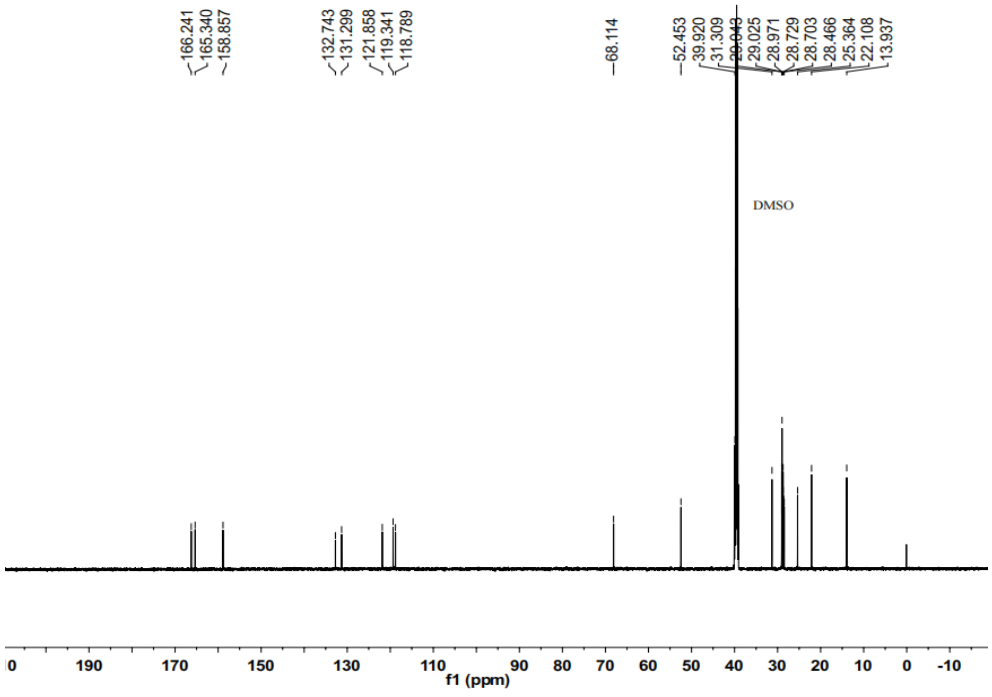
Figure S63. Full spectra of NMR titration study between **1** (0.5 mM) and PO_4^{3-} in THF-d_8.

1D NMR spectra

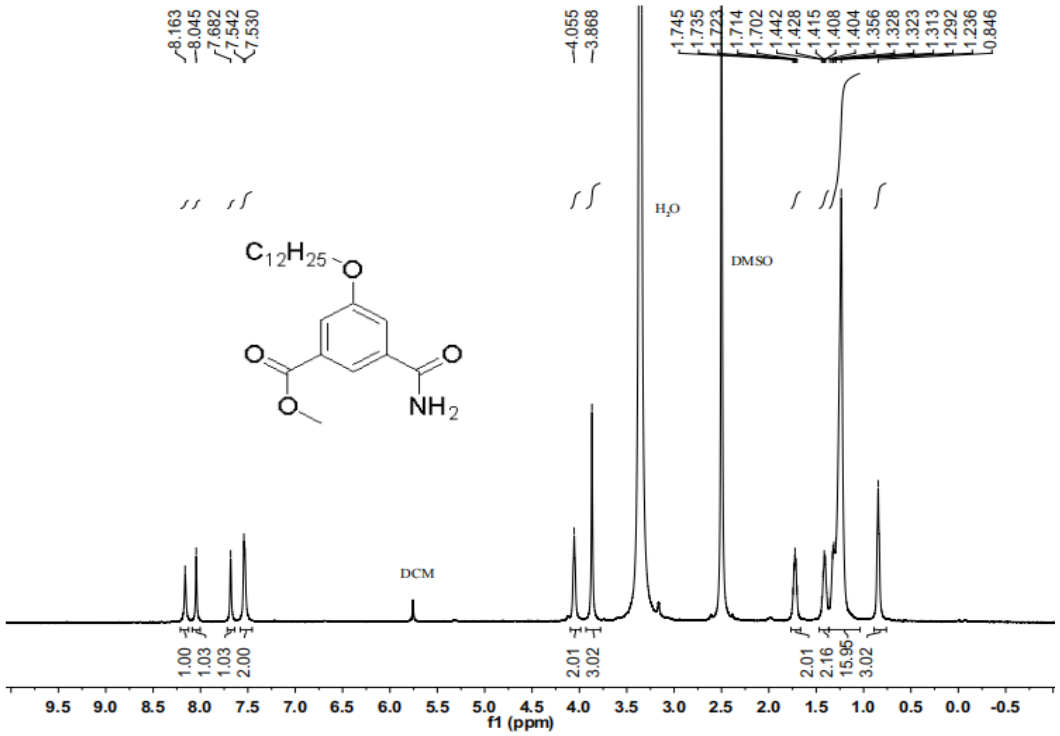
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of 3-(dodecyloxy)-5-(methoxycarbonyl)benzoic acid (**3**).



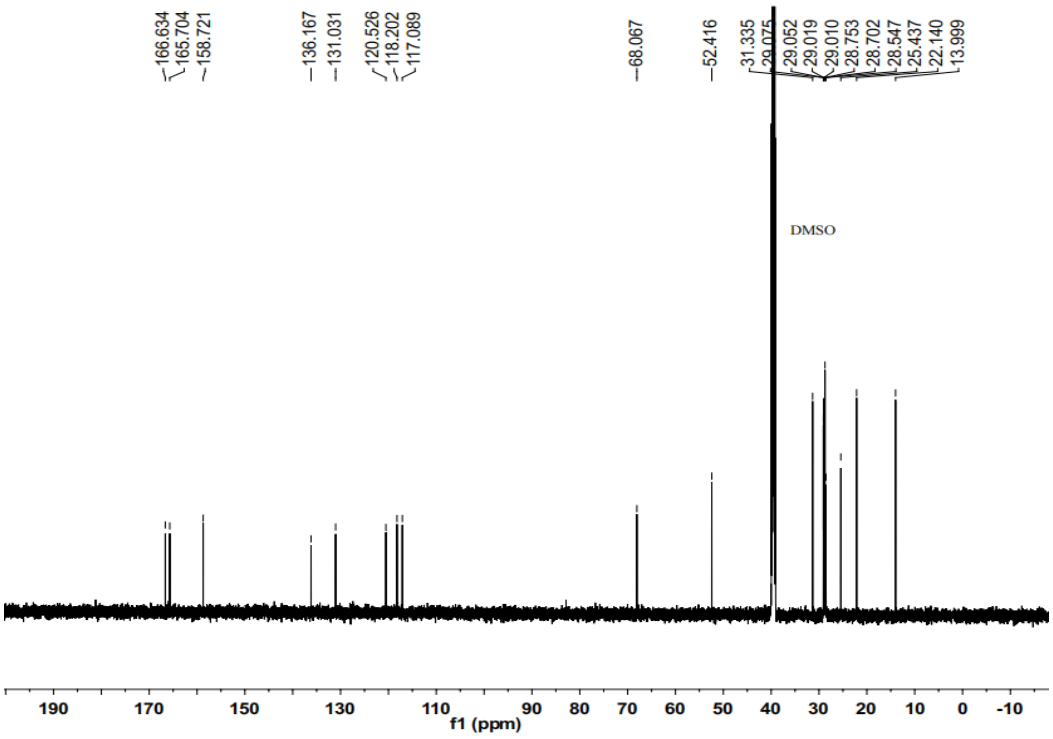
^{13}C {^{1}H} NMR (151 MHz, DMSO-d_6) spectrum of 3-(dodecyloxy)-5-(methoxycarbonyl)benzoic acid (**3**).



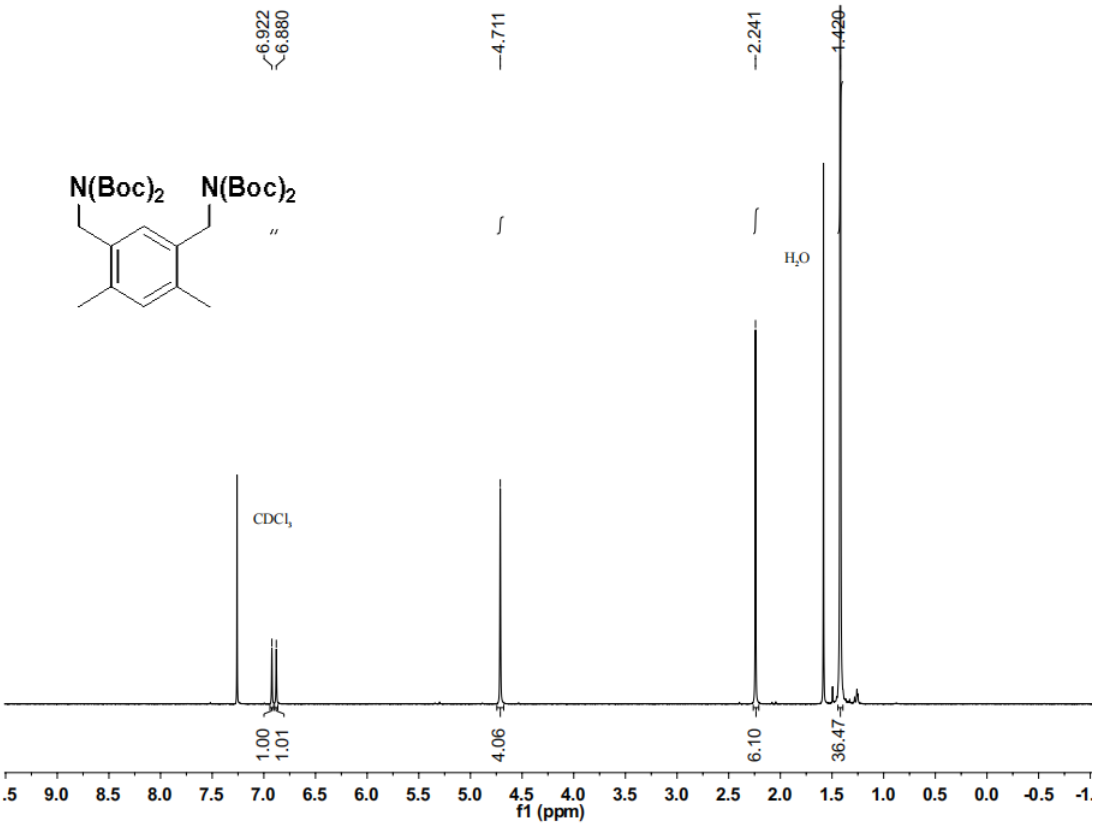
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of 3-carbamoyl-5-(dodecyloxy)benzoate (**4**).



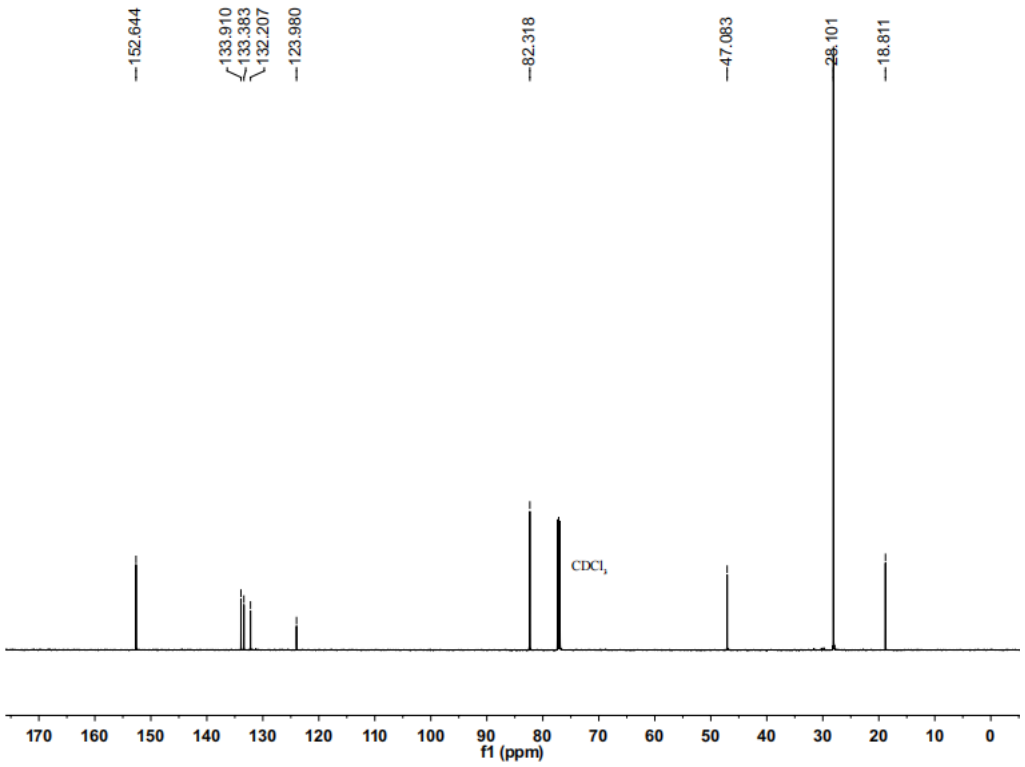
^{13}C {^{1}H} NMR (151 MHz, DMSO-d_6) spectrum of 3-carbamoyl-5-(dodecyloxy)benzoate (**4**).



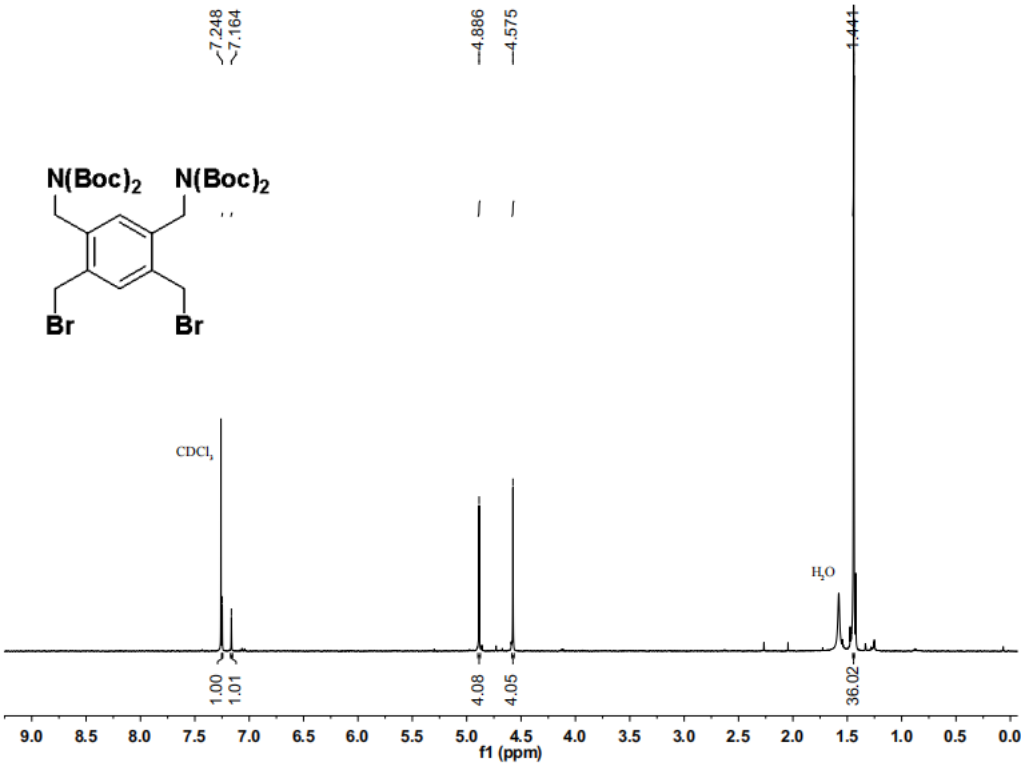
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**



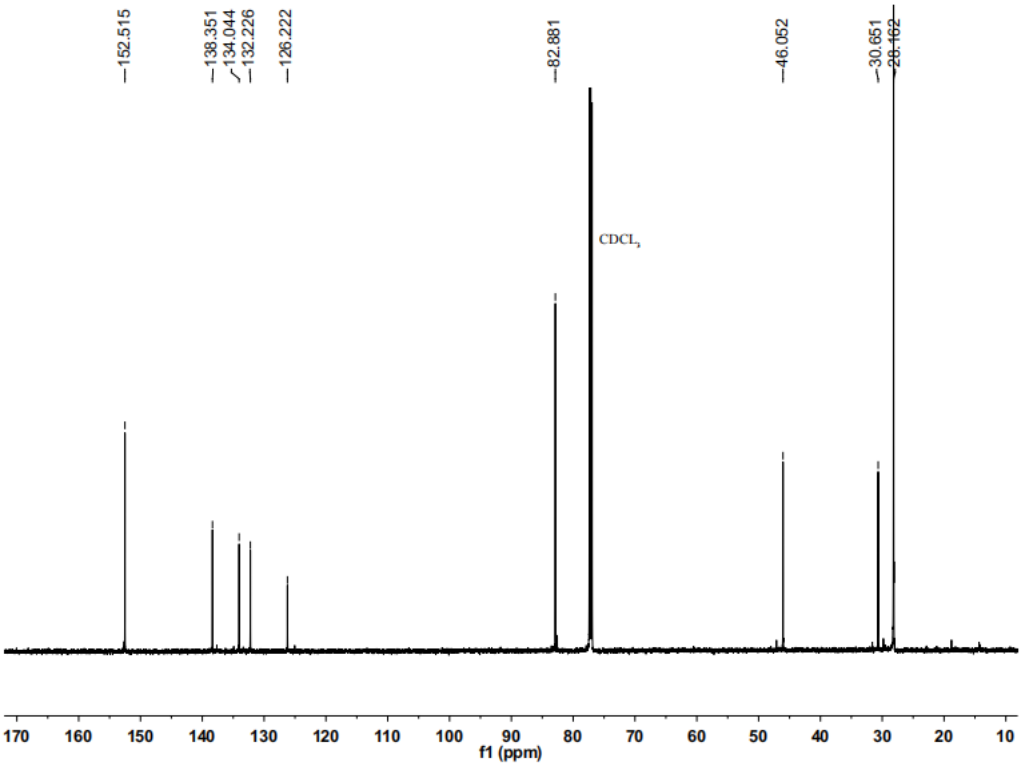
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **6**.



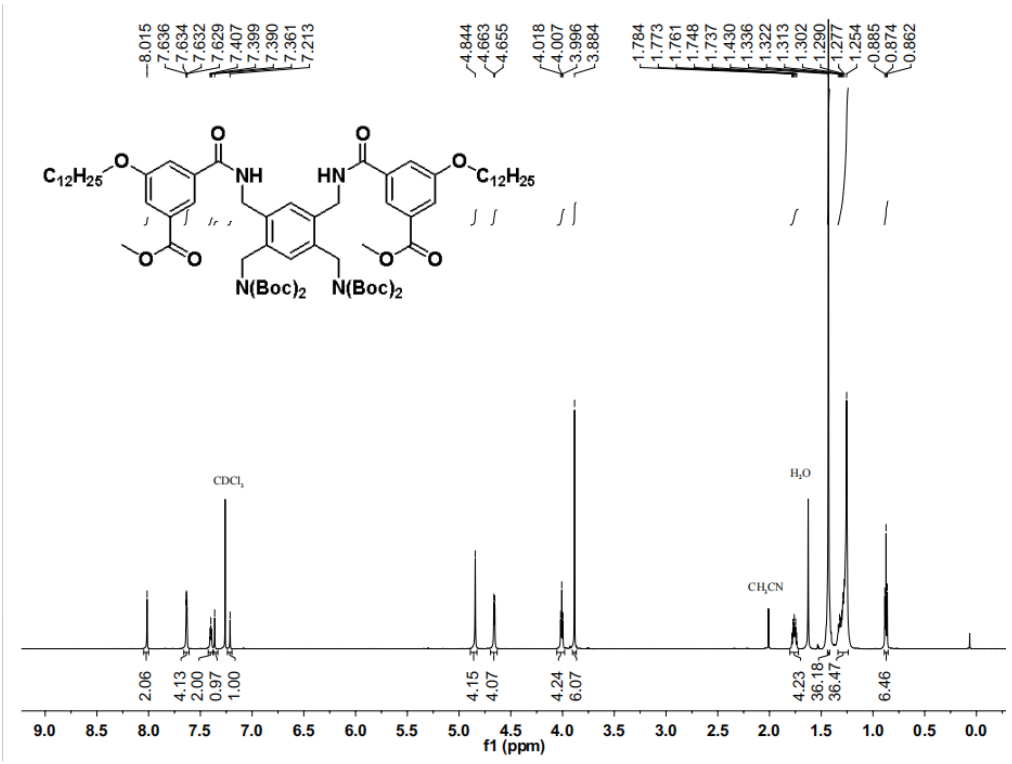
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **7**



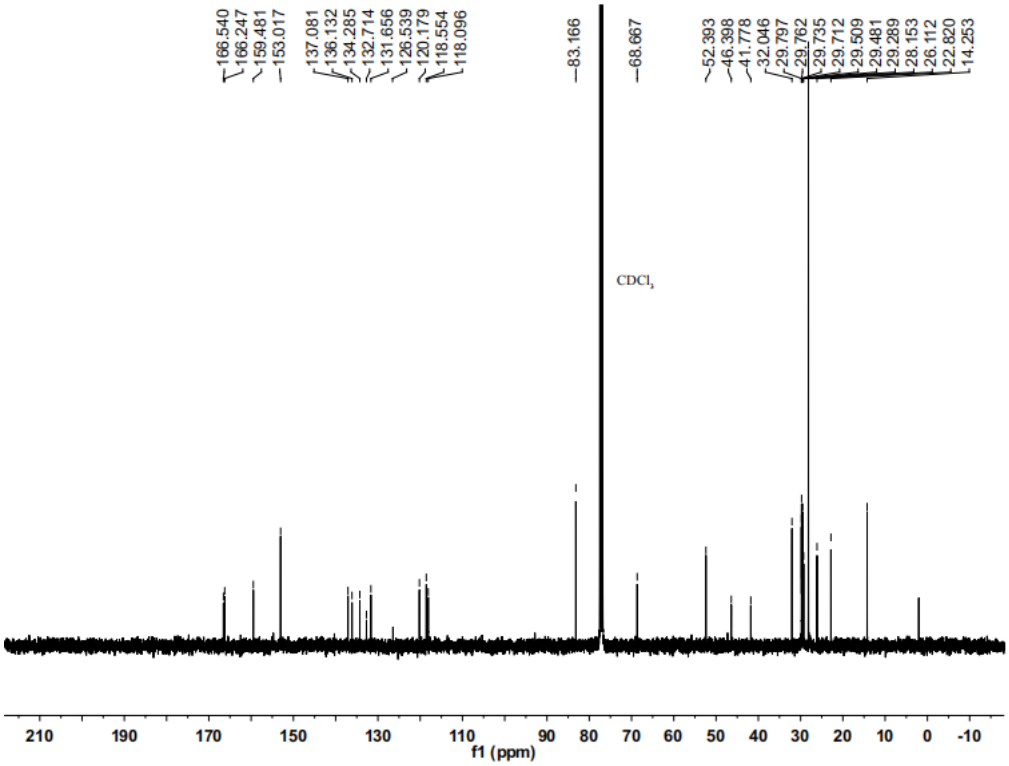
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of compound **7**



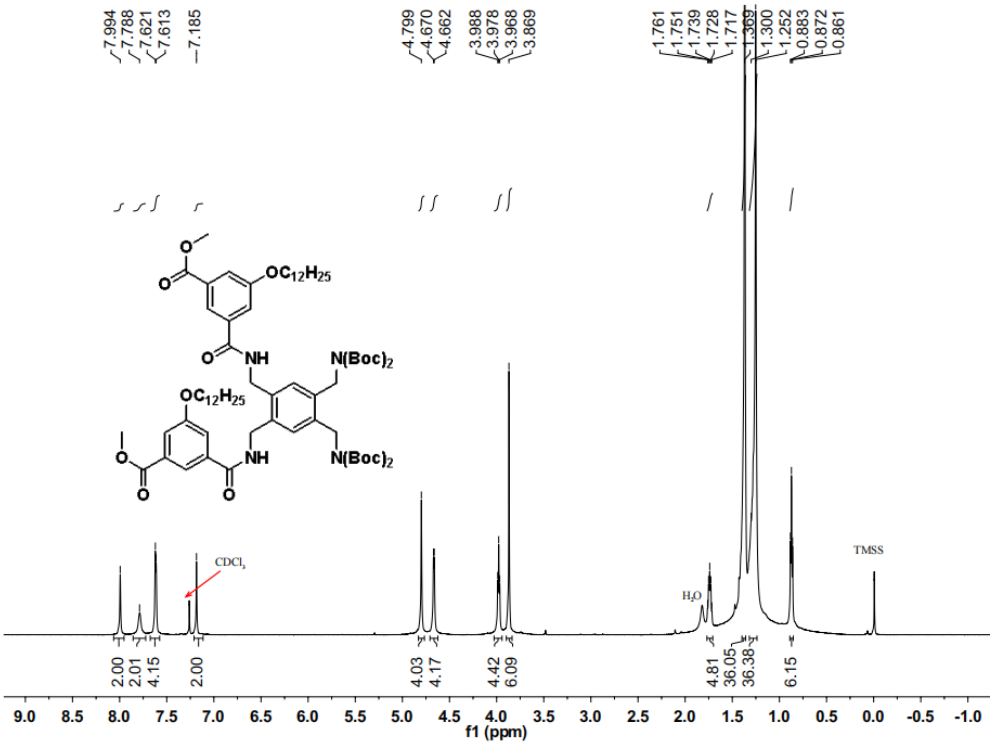
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**



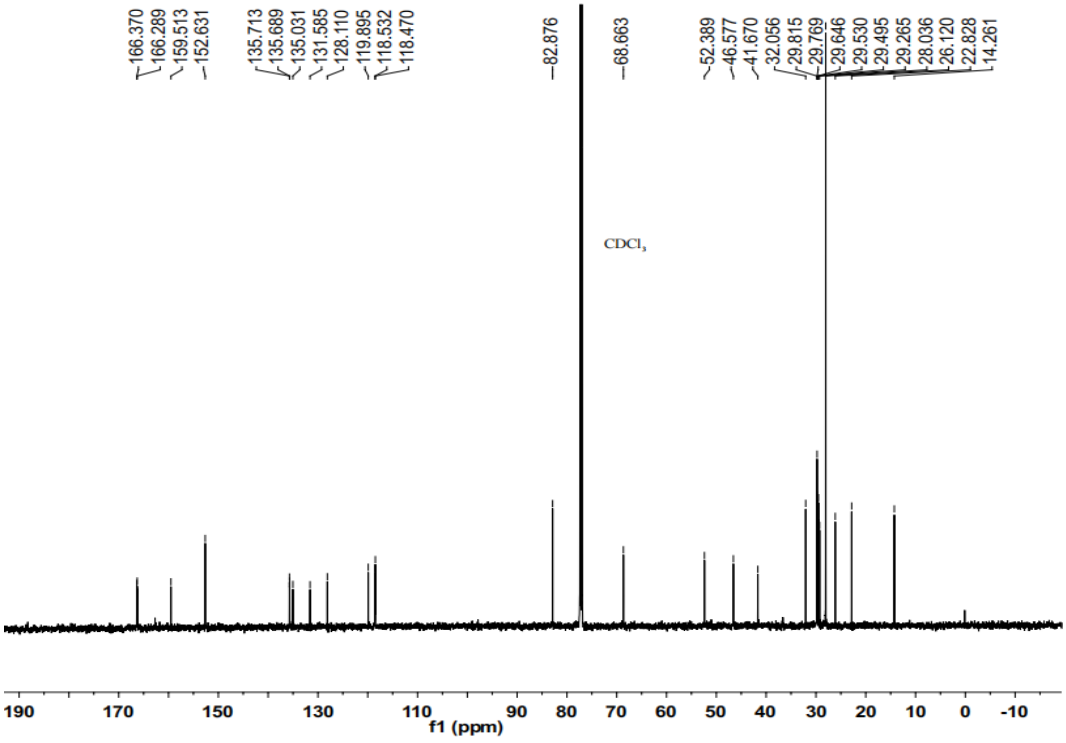
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **8**



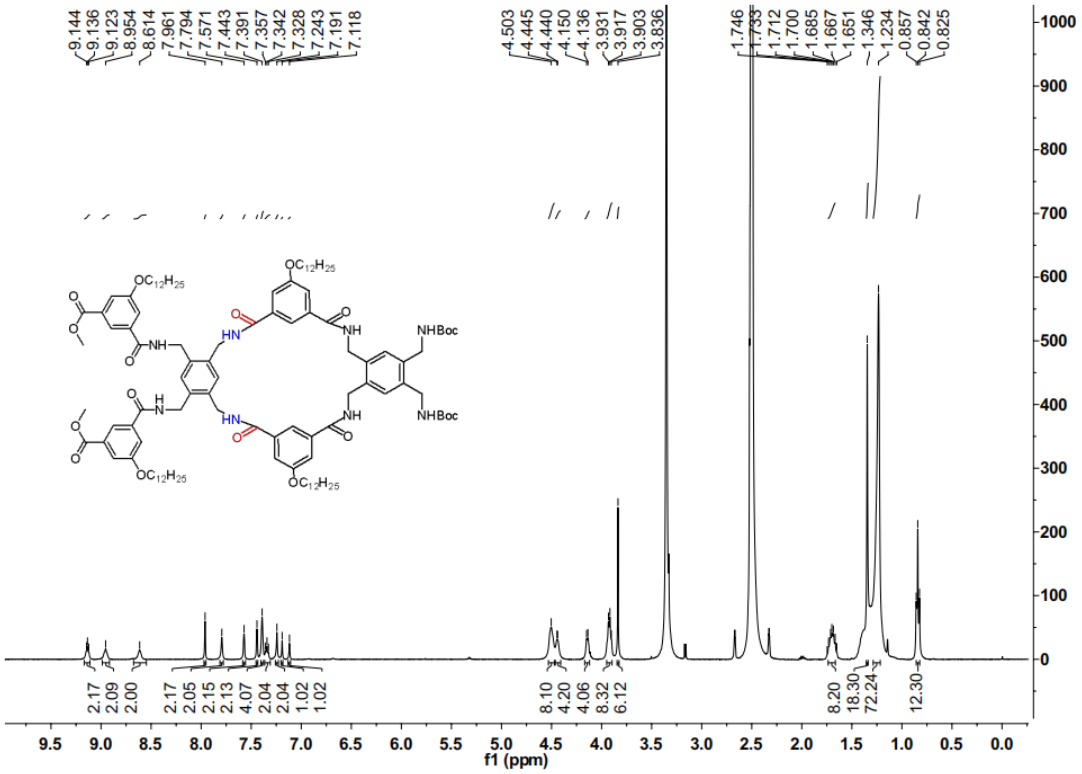
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **10**



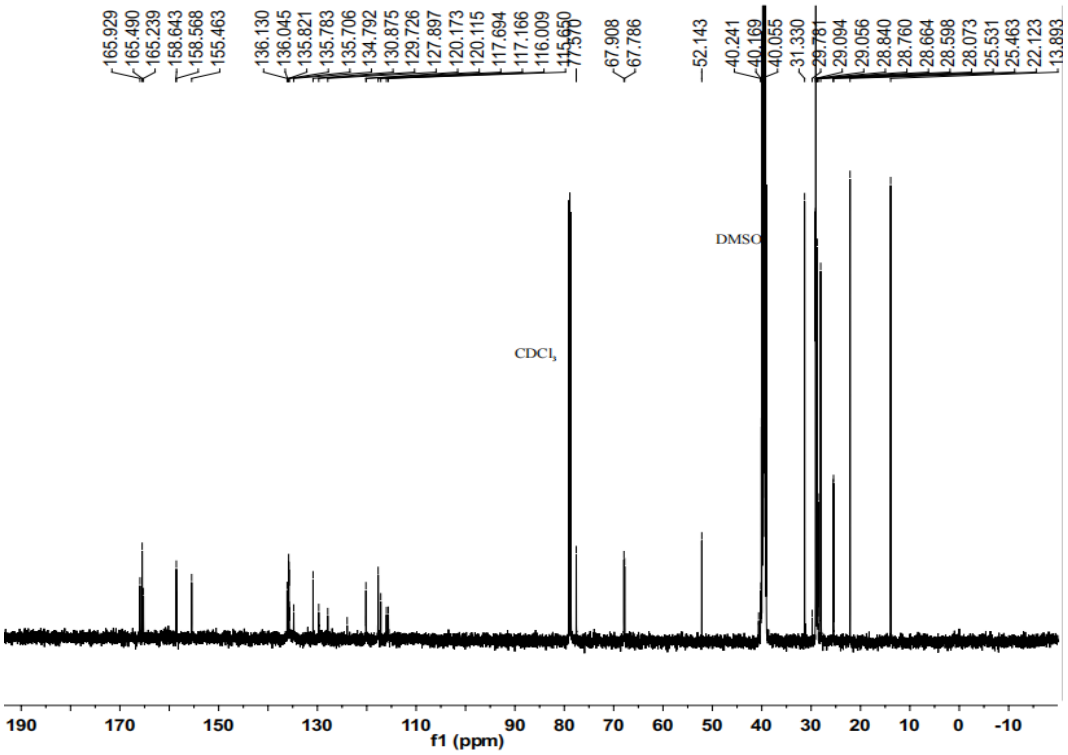
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of compound **10**



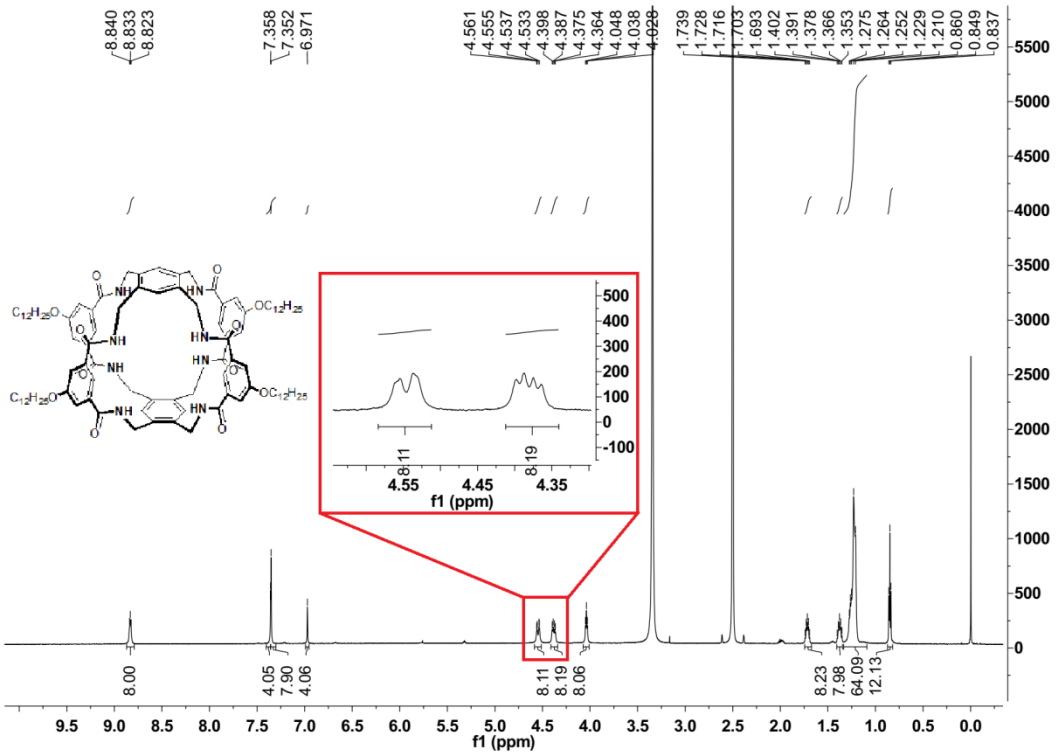
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **11**



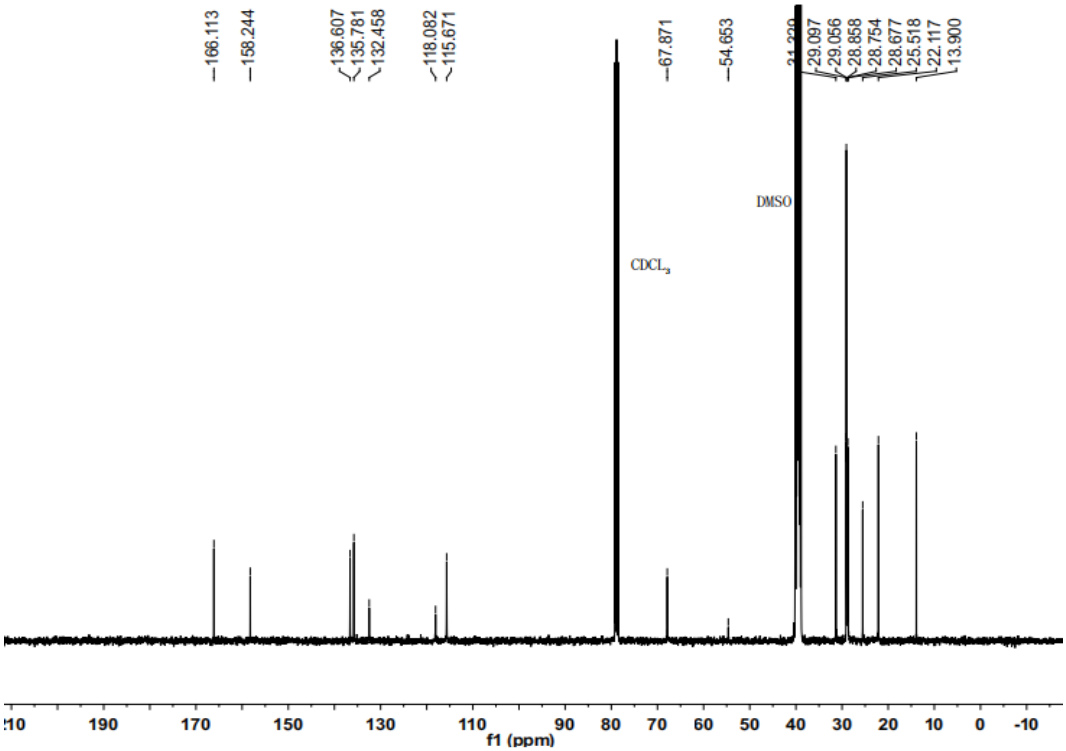
^{13}C{^{1}H} NMR (151 MHz, 30% $CDCl_3$/DMSO-d_6) spectrum of compound **11**



^{1}H NMR (600 MHz, DMSO-d_6) spectrum of cage **1**

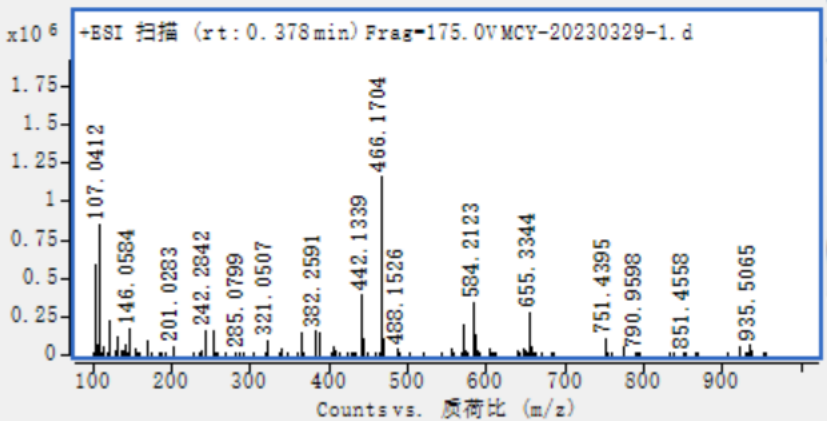


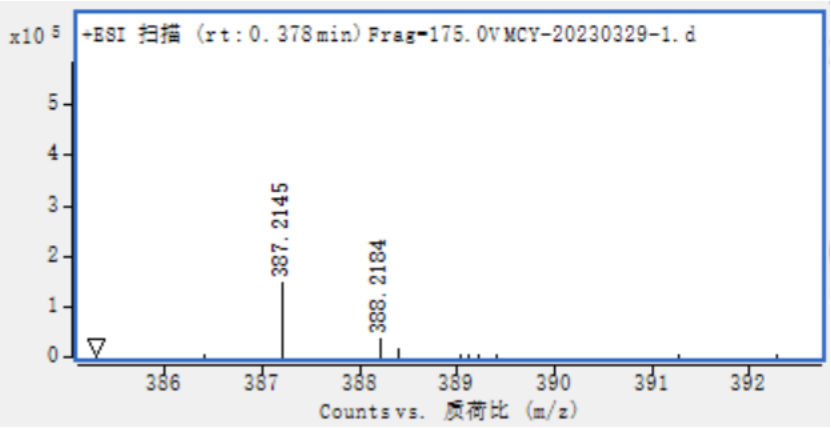
^{13}C{^{1}H} NMR (101 MHz, 20%$CDCl_3$/DMSO-d_6) spectrum of cage **1**



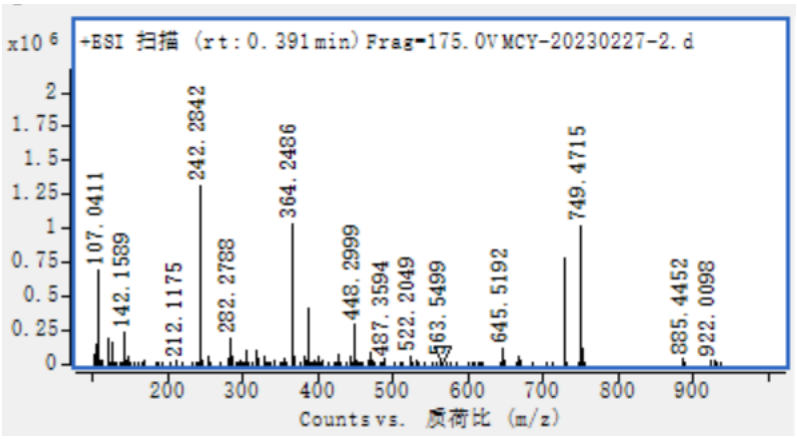
Mass spectra

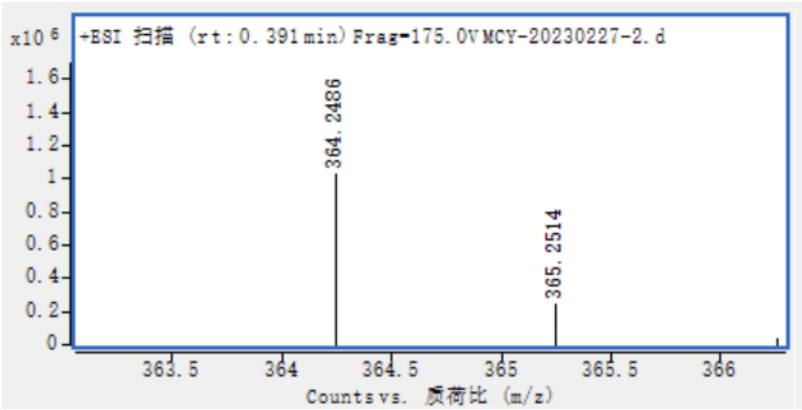
HRMS (ESI-TOF) of 3-(dodecyloxy)-5-(methoxycarbonyl)benzoic acid (**3**).



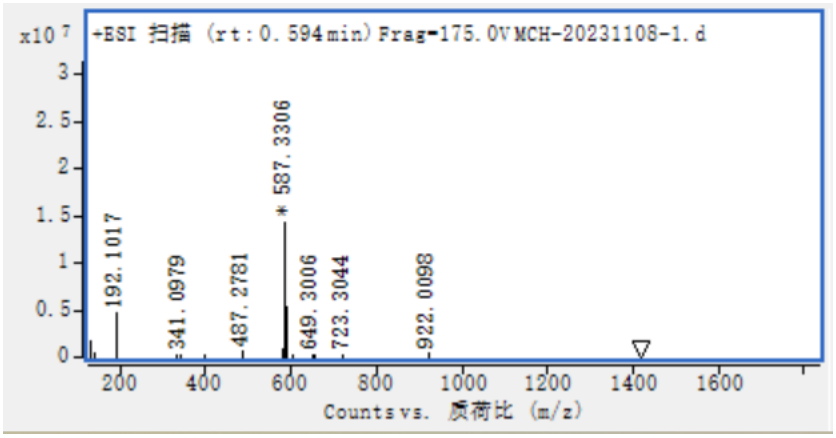


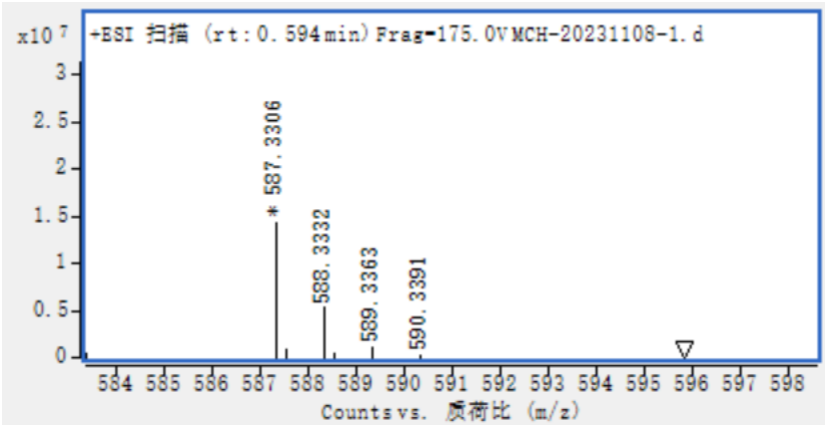
HRMS (ESI-TOF) of 3-carbamoyl-5-(dodecyloxy)benzoate (**4**)



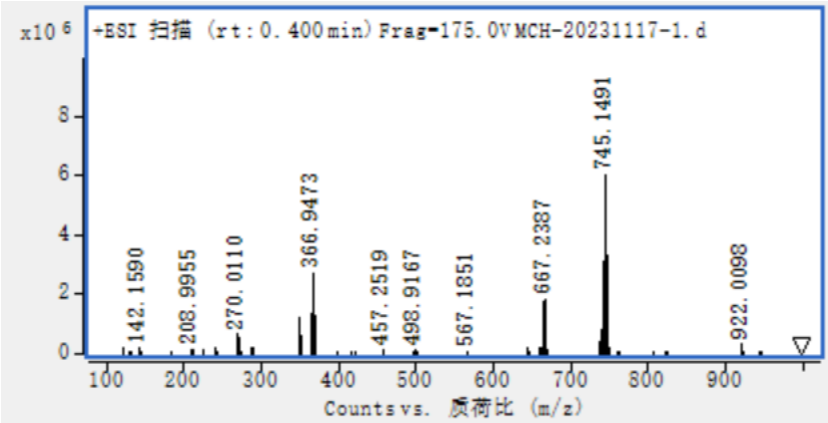


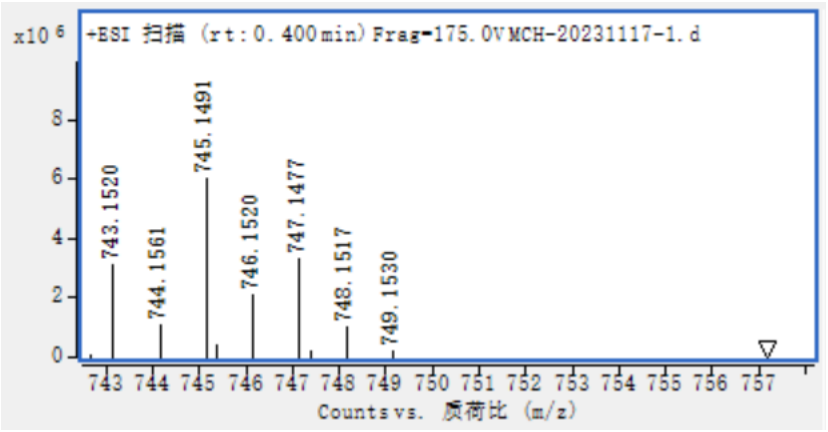
HRMS (ESI-TOF) of compound **6**



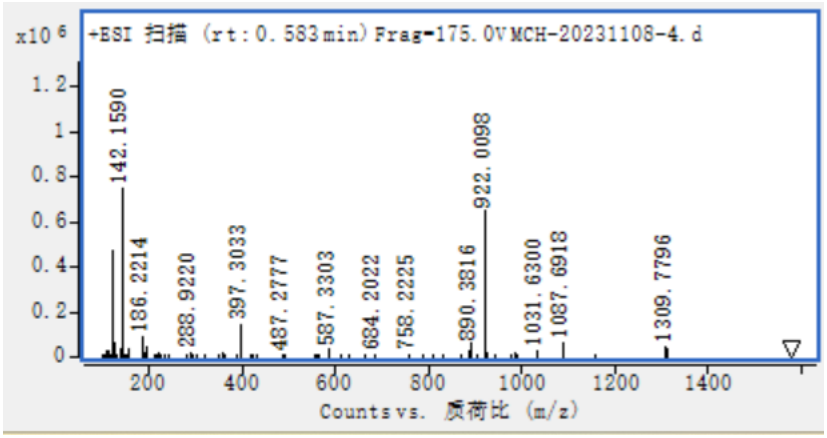


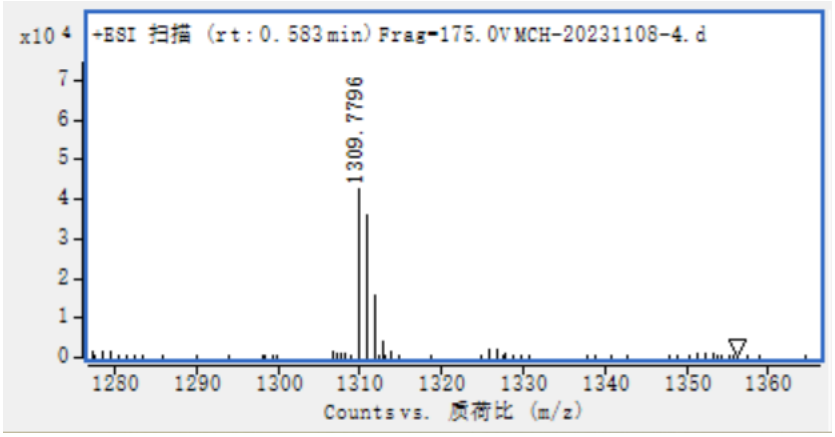
HRMS (ESI-TOF) of compound **7**



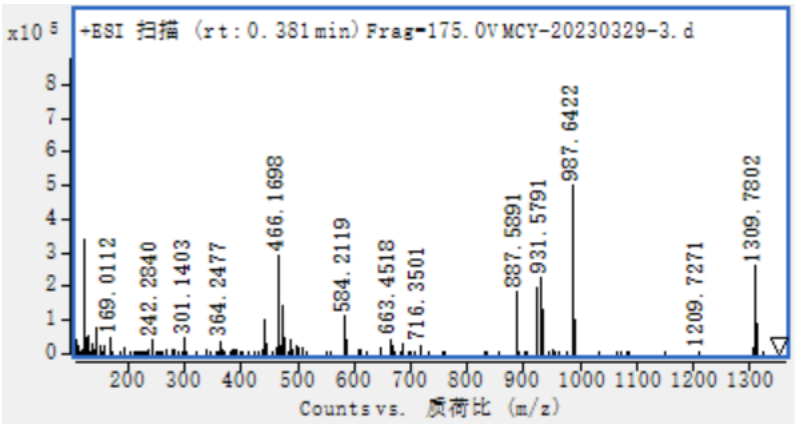


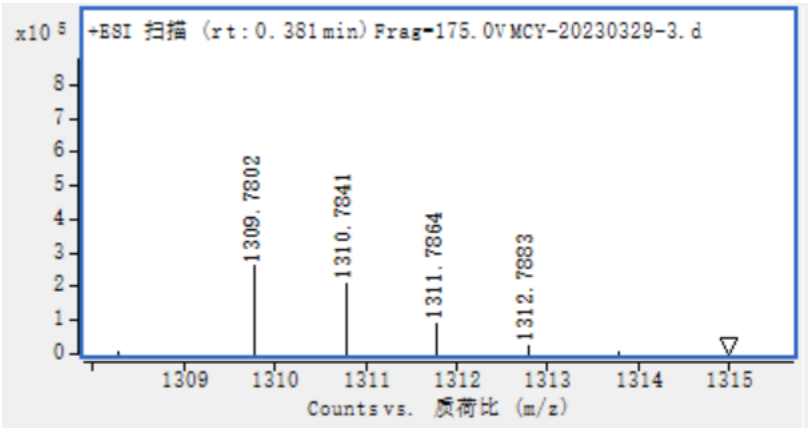
HRMS (ESI-TOF) of compound **8**



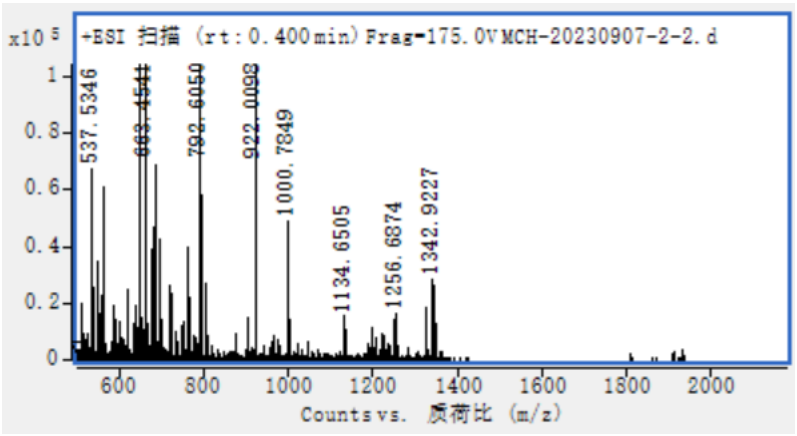


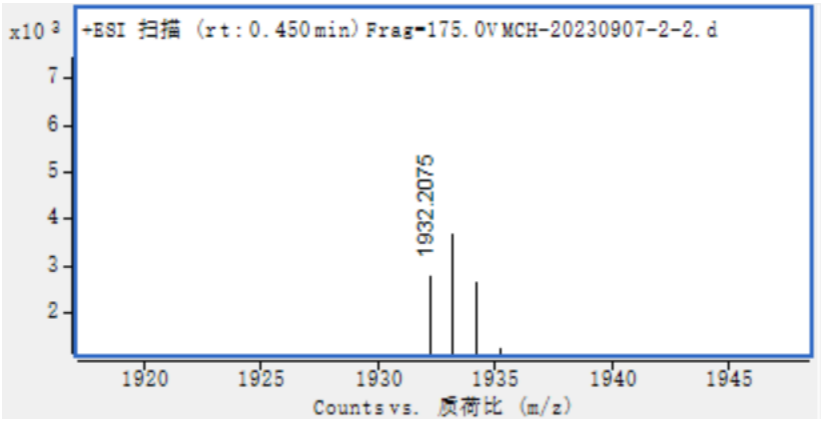
HRMS (ESI-TOF) of compound **10**



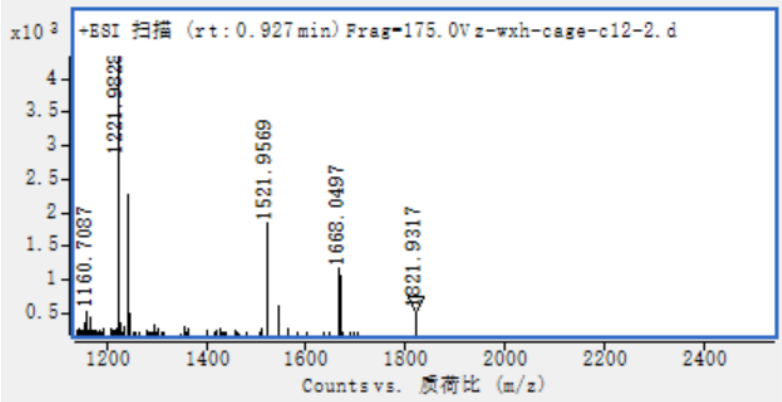


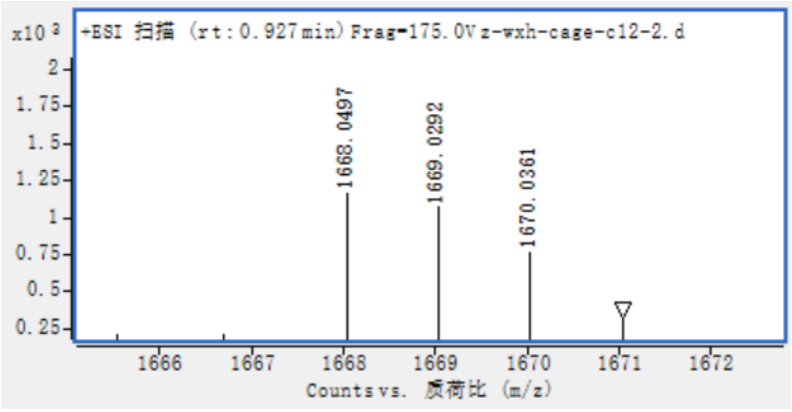
HRMS (ESI-TOF) of compound **11**





HRMS (ESI-TOF) of cage **1**





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[1] M. J. Frisch, et al. Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

[2] C. Mao, Y. He, X. Wang, Y. Cai and X. Hu, Synthesis and molecular recognition characteristics of a tetrapodal benzene cage, *Chin. Chem. Lett.*, 2023, 109362, doi.org/10.1016/j.cclet.2023.109362.

[3] P. Thordarson, Determining association constants from titration experiments in supramolecular chemistry, *Chem. Soc. Rev.*, 2011, **40**, 1305–1323.

[4] D. B. Hibbert and P. Thordarson, The death of the Job plot, transparency, open science and online tools, uncertainty estimation methods and other developments in supramolecular chemistry data analysis, *Chem. Commun.*, 2016, **52**, 12792–12805.