Electronic Supplementary Information For

Self-Assembled Cage-like Receptor that Binds Biologically Relevant Dicarboxylic Acids via Proton Coupled Anion Recognition

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b) Emission spectroscopic results: Fluorescence spectral titration results of host **7•7** titrated with fumaric acid, adipic acid, succinic acid, acetic acid, propionic acid, BPDSA, TPPTSA, TFA, PTSA, H_2SO_4, HCl, and TBACl, respectively, in THF at 298 K.

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f) X-ray structure and table of crystal data, structure refinement of the host–guest complex obtained between the supramolecular receptor **7•7** and sulfuric acid.

C. References

A. General Experimental Section

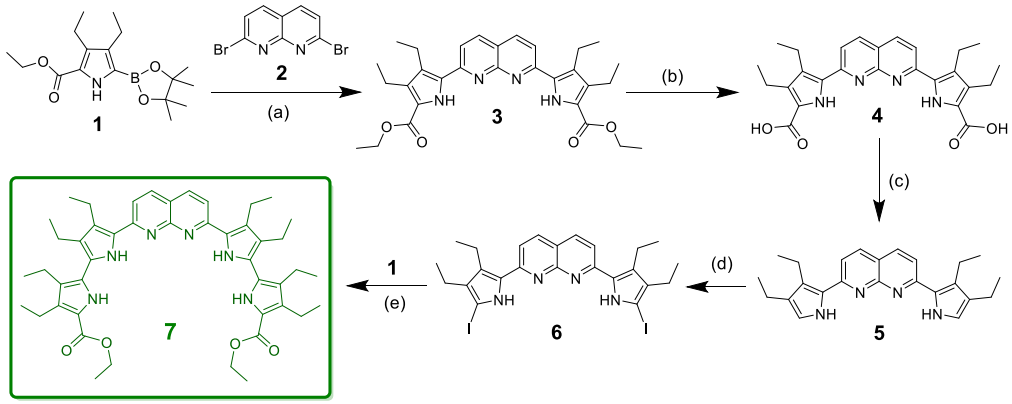
Materials. $Pd(OAc)_2$, $Pd(PPh_3)_4$, PPh_3, K_2CO_3, ethylene glycol, I_2, KI, $NaHCO_3$, $Na_2S_2O_3$, K_2CO_3 and all the carboxylic and sulfonic acids used under present studies were purchased from Aldrich Chemical Co., Acros, TCI, Energy Chemical and Adamas-beta® and used as received. All anhydrous solvents were acquired either from Aldrich Chemical Co. or Adamas-beta® and used as received. All reactions were carried out under an argon atmosphere unless noted otherwise. Chromatographic separations were performed by using 100–200 mesh silica gel obtained from Merck. All solvents used for column chromatography were purchased from local suppliers and dried prior to use. Thin-layer chromatographic (TLC) analyses were carried out using silica gel pre-coated on glass sheets. Column chromatography was performed on silica gel (mesh size 200–300). Final separations of the compounds were performed by using a recycling preparative GPC from Japan Analytical Industries (JAI) using THF as the mobile phase.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded using Bruker 600 MHz instruments in $CDCl_3$, THF-d_8, DMSO-d_6, respectively, at 298 K. Chemical shifts are reported in ppm using tetramethylsilane (TMS) or residual solvent signals as the internal reference standards. MALDI-TOF mass spectrometric measurements were made using a Bruker (Autoflex speed) matrix-assisted laser desorption ionization time-of-flight mass spectrometer. Some compounds were analyzed by means of a Bruker Microflex 2 LRF 20

spectrometer using dithranol (1,8,9-trihydroxyantharacene) as the matrix. UV–Vis spectra were recorded in THF at 298 K using a Varian Cary 50 spectrophotometer. The concentration of all the entities was maintained at 1×10^{-5} M in THF. Emission spectra were recorded using a Hitachi spectrophotometer in THF at 298 K.

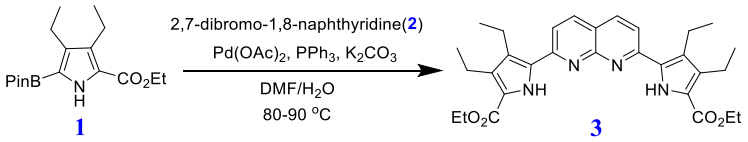
B. Synthesis and Characterization

I) Synthetic scheme for the 1,8-naphthyridine-based tetrapyrrolic receptor.



Scheme S1. Reagents, conditions, and range of yields: (a) $Pd(OAc)_2$, PPh_3, K_2CO_3, DMF/H_2O, N_2, reflux, 24 h, yields: 70%; (b) NaOH, $EtOH/H_2O$, 85 °C, heat 5 h, 95%; (c) ethylene glycol, 185 °C, 50 min, yields: 91%; (d) I_2/KI, $NaHCO_3$, CH_2Cl_2/H_2O, rt, 1 h, $Na_2S_2O_3$, yields: 75%; (e) $Pd(PPh_3)_4$, K_2CO_3, DMF/H_2O, reflux, 15 h, yields: 45%.

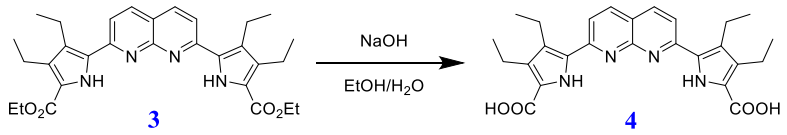
Synthesis of compound 3



To a 20 mL round-bottom flask was added **1**[S1] (1 mmol), $Pd(OAc)_2$ (0.1 mmol), PPh_3 (0.2 mmol), and K_2CO_3 (3.3 mmol) under an N_2 atmosphere. DMF (10 mL) and water (10 mL) were added through a syringe and the mixture was heated to 85 °C. **2** (1.2 mmol) was dissolved in 4 mL DMF and added via a syringe pump over the course of 1 h. The reaction was stirred at the same temperature for another 23 h. After the reaction mixture was cooled to r.t., the organic portion was extracted with CH_2Cl_2 and washed with water

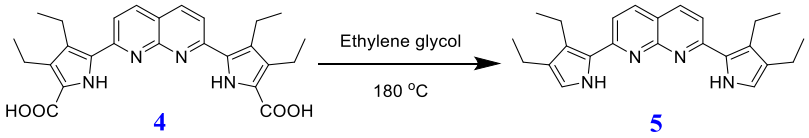
3 times. After removal of the solvents and other volatiles, the reaction mixture was purified by chromatography over silica gel (PE/EA, 10/1, v/v) to give **3** in the form of bright yellow crystals. Yield: 70%. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) δ: 10.26 (s, 2H, pyrrole NH), 8.15 (d, *J* = 8.1 Hz, 2H, naphthyridine CH), 7.78 (d, *J* = 8.4 Hz, 2H, naphthyridine CH), 4.51-4.22 (m, 4H, CH_2), 2.85 (t, *J* = 7.4 Hz, 8H, pyrrole CH_2), 1.41 (t, *J* = 7.3, 6.7 Hz, 6H, pyrrole CH_3), 1.28 (t, *J* = 7.5 Hz, 6H, pyrrole CH_3), 1.21 (t, *J* = 7.4 Hz, 6H, CH_3). ^{13}C NMR spectrum (150 MHz, $CDCl_3$) δ: 160.8, 155.7, 153.5, 137.5, 134.8, 129.5, 127.7, 120.4, 120.1, 119.0, 60.1, 18.2, 17.9, 15.9, 15.8, 14.6. MALDI-TOF MS Calcd for $C_{30}H_{36}N_4O_4$: 516.642; Found: 517.400 $[M + H]^+$.

Synthesis of compound 4



Compound **4** was synthesized by following the published literature method.[S2] Typically, this has been done by taking the mixture of **3** (1 mmol), sodium hydroxide (6 mmol), ethanol (25 ml), and water (12.5 ml) in a 250 mL two-necked round bottom flask, stirred at 85 °C under an N_2 atmosphere for 5 h. After cooling under N_2, HCl aqueous was added dropwise to the reaction mixture until it turned acidic (pH = 1). The white precipitates were filtered, washed with water, and then dried under vacuum. This gave the product **4** in the form of yellowish-brown solid. Yield: 95%. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ: 12.56 (s, 2H, -COOH), 11.48 (s, 2H, pyrrole NH), 8.36 (d, *J* = 8.5 Hz, 2H, naphthyridine CH), 8.11 (d, *J* = 8.5 Hz, 2H, naphthyridine CH), 2.98 (t, *J* = 7.1 Hz, 4H, pyrrole CH_2), 2.77 (t, *J* = 7.2 Hz, 4H, pyrrole CH_2), 1.24 (t, *J* = 7.3 Hz, 6H, pyrrole CH_3), 1.14 (t, *J* = 7.4 Hz, 6H, pyrrole CH_3). ^{13}C NMR spectrum (150 MHz, DMSO-*d*$_6$) δ: 162.6, 155.6, 154.3, 137.6, 133.6, 130.6, 128.7, 120.9, 119.9, 119.6, 18.3, 17.9, 16.6, 16.3. MALDI-TOF MS Calcd for $C_{26}H_{28}N_4O_4$: 460.534; Found: 461.148 $[M + H]^+$.

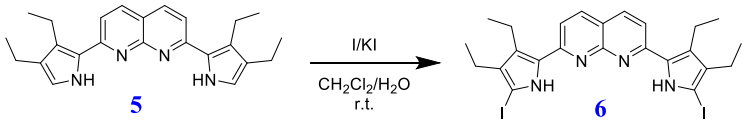
Synthesis of compound 5



4 5

The dicarboxylic acid **4** was suspended in ethylene glycol (30 ml) and then heated at 180 °C for 50 min with stirring under an N_2 atmosphere. After cooling under N_2, cold water was added to cause precipitation of the decarboxylated product. Filtration and then drying under vacuum afforded **5** as a green powder. Yield: 91%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.93 (s, 2H, pyrrole NH), 7.97 (d, J = 8.5 Hz, 2H, naphthyridine CH), 7.62 (d, J = 8.5 Hz, 2H, naphthyridine CH), 6.74 (s, 2H, pyrrole α-H), 2.85 (t, J = 7.6 Hz, 4H, pyrrole CH_2), 2.52 (t, J = 7.5 Hz, 4H, pyrrole CH_2), 1.28 (t, J = 7.6 Hz, 6H, pyrrole CH_3), 1.25 (t, J = 7.5 Hz, 6H, pyrrole CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.1, 153.9, 136.8, 127.3, 126.9, 126.4, 118.6, 117.9, 117.5, 18.6, 18.2, 15.5, 14.8. MALDI-TOF MS Calcd for $C_{24}H_{28}N_4$: 372.516; Found: 373.356 $[M + H]^+$.

Synthesis of compound 6

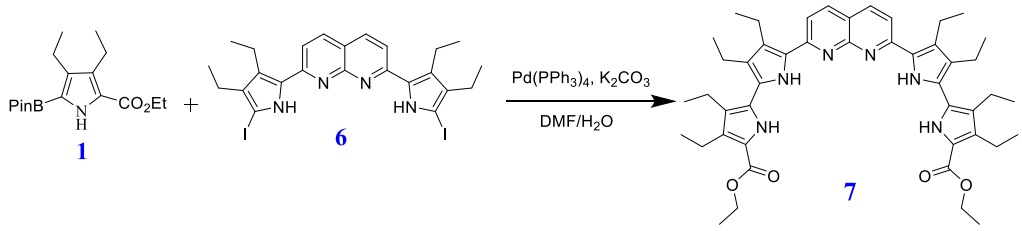


5 6

To a solution of **5** (1 mmol) in 10 mL CH_2Cl_2, was added $NaHCO_3$ (4.6 mmol in 10 mL H_2O). An aqueous mixture of I_2 (1.5 mmol) and KI (3 mmol) was then added dropwise to the reaction mixture at r.t. The contents of the reaction vessel were stirred for another 1 h before the reaction was quenched with $Na_2S_2O_3$. Column chromatographic separation of the crude product over silica gel using PE/CH_2Cl_2 (2/1, v/v) as eluent yielded the pure product **6**[S3] as brown crystalline material. Yield: 65%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.85 (s, 2H, pyrrole NH), 8.01 (d, J = 8.1 Hz, 2H, naphthyridine CH), 7.59 (d, J = 8.4 Hz, 2H, naphthyridine CH), 2.86 (t, J = 7.6 Hz, 4H, pyrrole CH_2), 2.45 (t, J = 7.5 Hz, 4H,

pyrrole CH_2), 1.27 (t, J = 7.6 Hz, 6H, pyrrole CH_3), 1.13 (t, J = 7.5 Hz, 6H, pyrrole CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 151.7, 136.1, 131.0, 130.1, 127.5, 127.4, 126.5, 118.1, 116.2, 28.7, 18.9, 18.2, 14.7, 14.7. MALDI-TOF MS Calcd for $C_{24}H_{26}I_2N_4$: 624.309; Found: 625.266 $[M + H]^+$.

Synthesis of receptor 7



A mixture of **6** (0.5 mmol), $Pd(PPh_3)_4$ (0.025 mmol), and K_2CO_3 (2.5 mmol) was suspended in 10 mL DMF and 5 mL water and the reaction was heated to 75 ℃ under an N_2 atmosphere. **1** (1.2 mmol) was dissolved in 4 mL DMF and added via a syringe pump over the course of 1 h. The reaction was stirred at the same temperature for another 14 h. After the reaction mixture was cooled to r.t., water was added. The organic layer was extracted with CH_2Cl_2 and washed with water 3 times. After removal of the solvent, the reaction mixture was purified by silica gel chromatography using PE/EA, 20:1 (v/v) as eluent yielded **7** as light yellow solid. Yield: 45%. ^1H NMR spectrum (600 MHz, $CDCl_3$) δ: 9.80 (s, 2H, pyrrole NH), 8.76 (s, 2H, pyrrole NH), 8.01 (d, J = 8.4 Hz, 2H, naphthyridine CH), 7.67 (d, J = 8.5 Hz, 2H, naphthyridine CH), 4.32 (t, J = 7.1 Hz, 4H, CH_2), 2.89 (t, J = 7.5 Hz, 4H, pyrrole CH_2), 2.80 (t, J = 7.4 Hz, 4H, pyrrole CH_2), 2.52 (t, J = 7.7 Hz, 8H, pyrrole CH_2), 1.36 (t, J = 7.2 Hz, 6H, pyrrole CH_3), 1.31 (t, J = 7.5 Hz, 6H, pyrrole CH_3), 1.21 (t, J = 7.4 Hz, 6H, pyrrole CH_3), 1.12 (t, J = 7.5 Hz, 6H, pyrrole CH_3), 1.08 (t, J = 7.5 Hz, 6H, CH_3). ^{13}C NMR spectrum (150 MHz, $CDCl_3$): δ: 161.3, 155.9, 153.4, 136.8, 133.6, 127.5, 127.1, 126.8, 125.9, 124.7, 122.9, 118.9, 118.3, 117.6, 59.8, 18.8, 18.4, 17.8, 17.7, 16.4, 16.1, 15.8, 15.7, 14.45. MALDI-TOF MS Calcd for $C_{26}H_{28}N_4O_4$: 759.008; Found: 759.384 $[M]^+$.

II) NMR and MALDI TOF MS analyses for the compounds

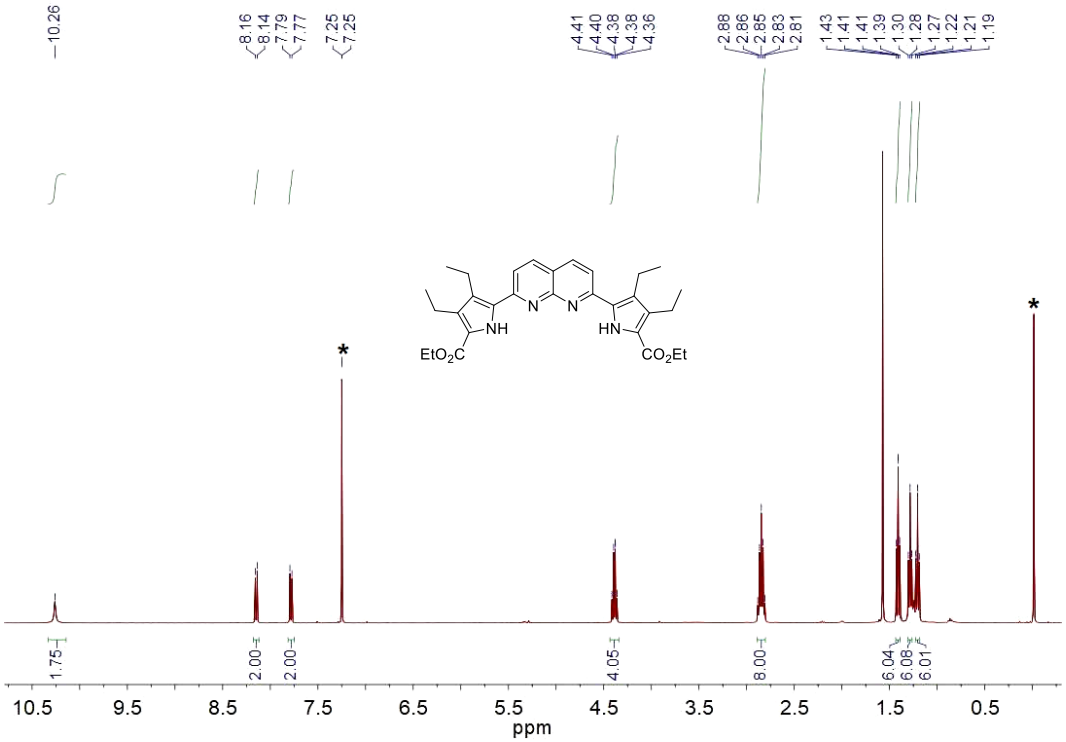


Figure S1. ^{1}H NMR (600 MHz, $CDCl_3$ at 298 K) spectrum of **3**.

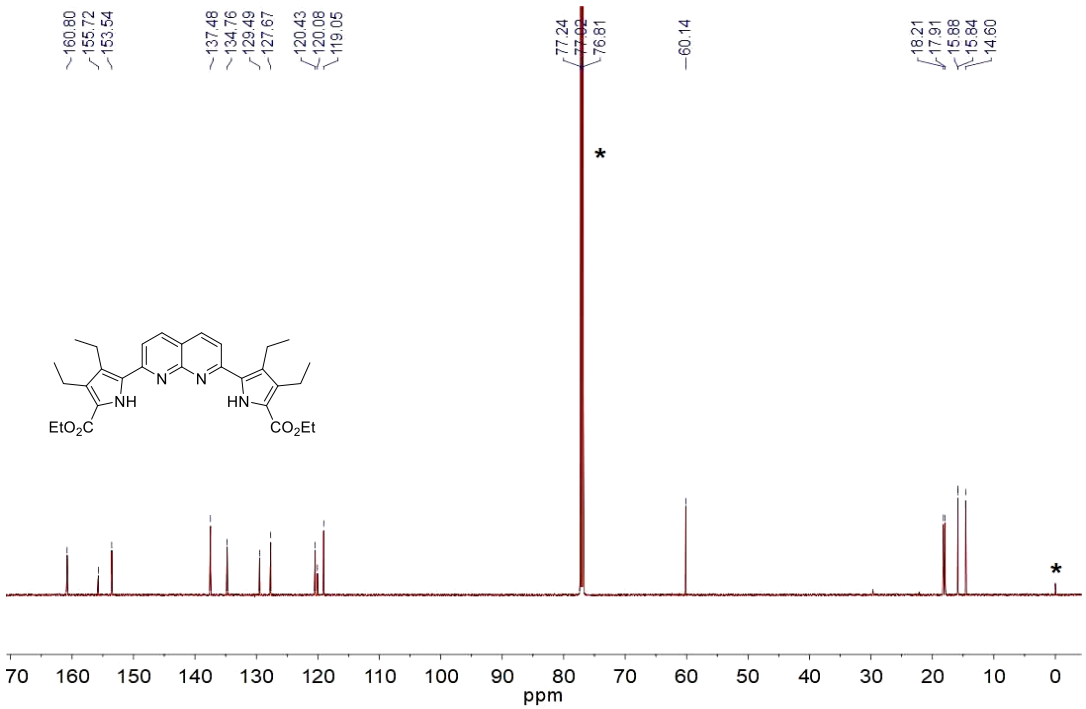


Figure S2. ^{13}C NMR (150 MHz, $CDCl_3$ at 298 K) spectrum of **3**.

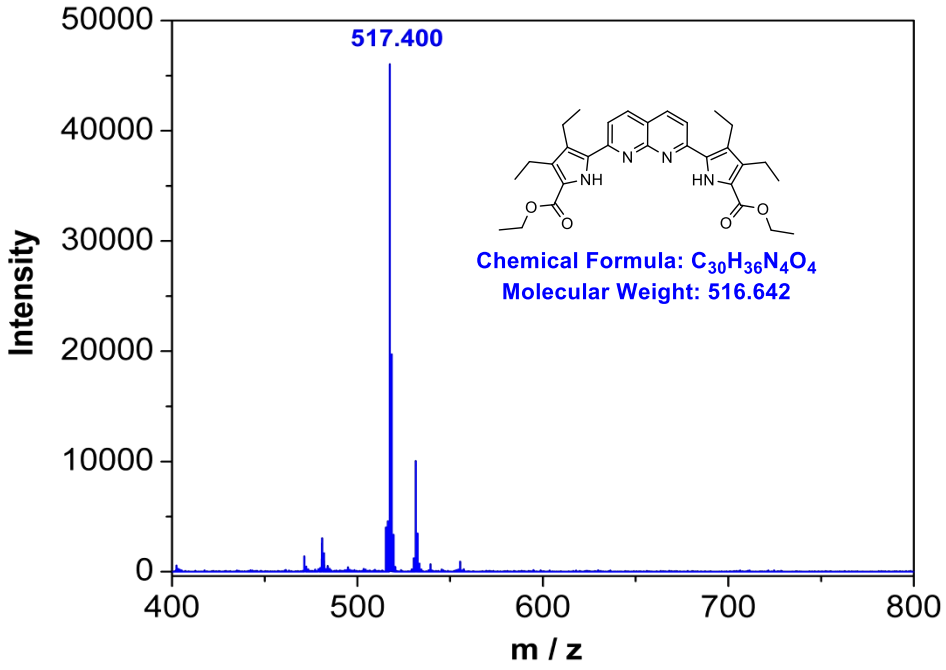


Figure S3. MALDI-TOF MS of compound **3**.

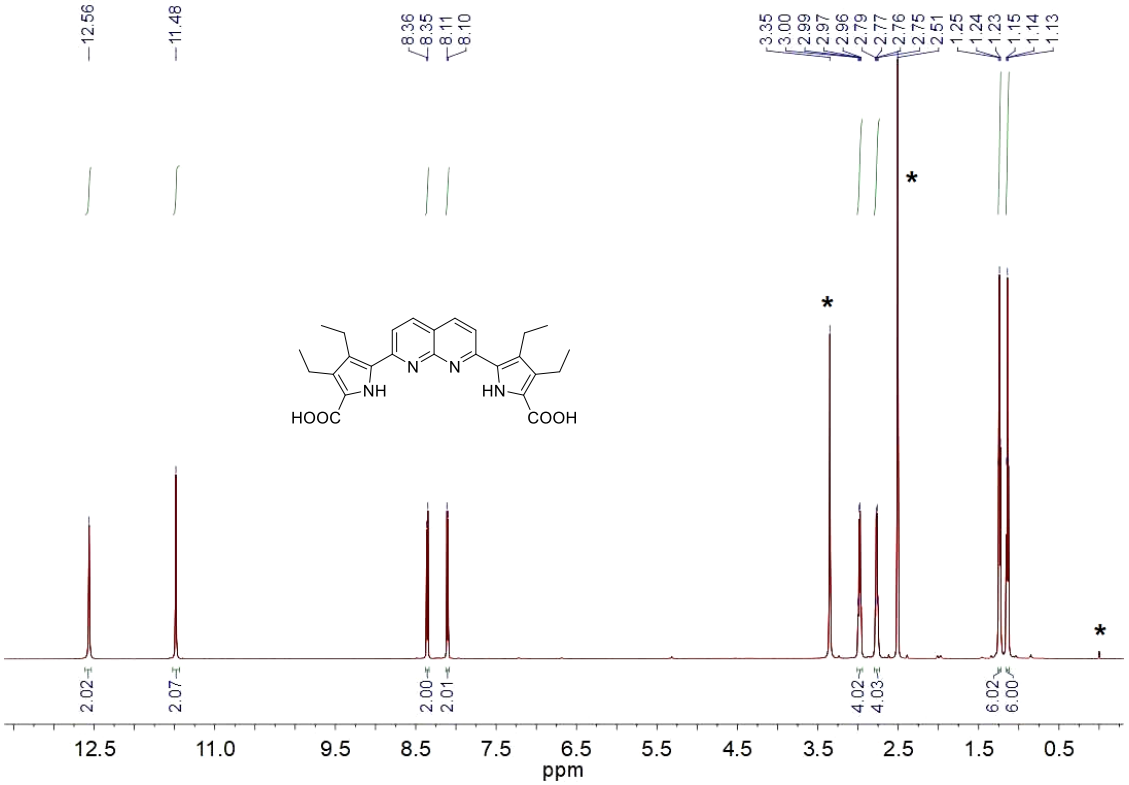


Figure S4. ^{1}H NMR (600 MHz, DMSO-d_6 at 298 K) spectrum of **4**.

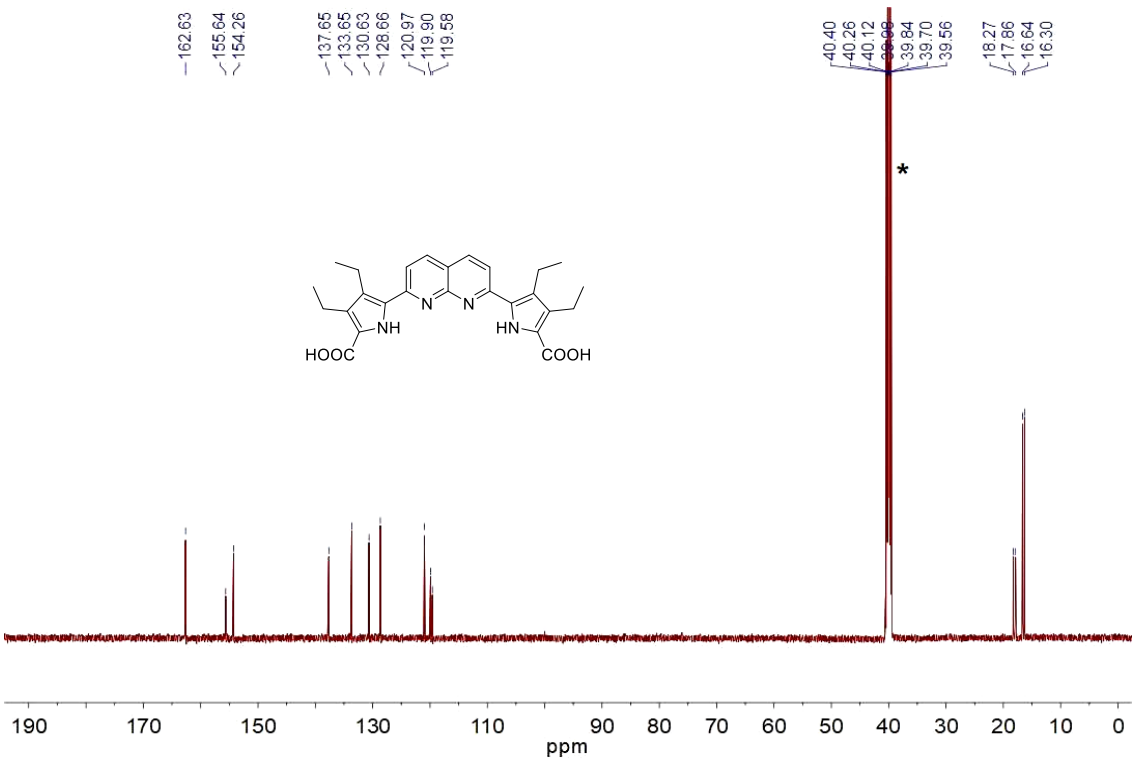


Figure S5. ^{13}C NMR (150 MHz, DMSO-d_6 at 298 K) spectrum of **4**.

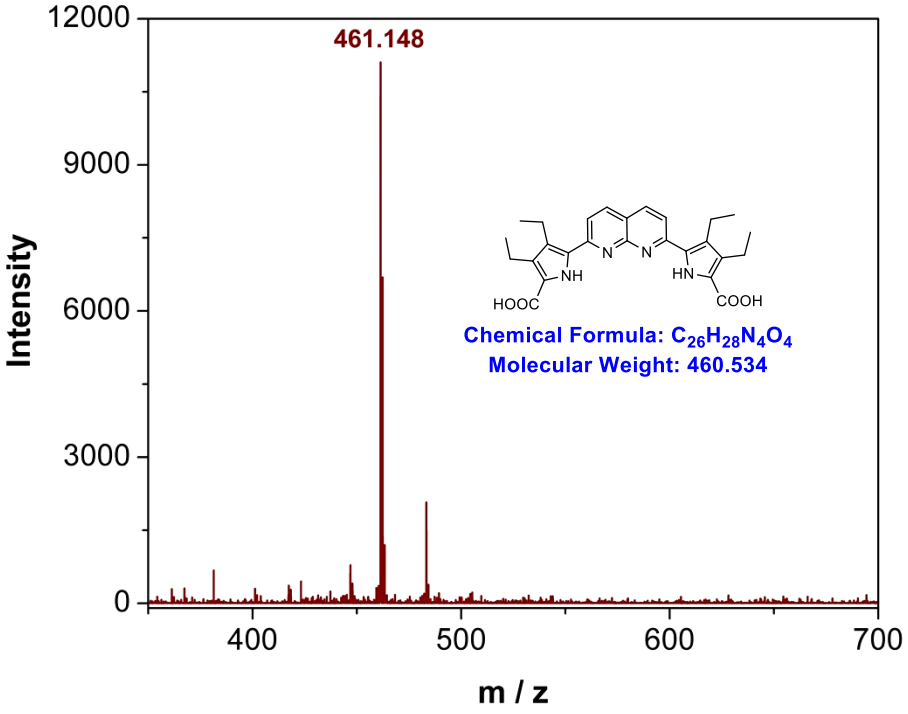


Figure S6. MALDI-TOF MS of compound **4**.

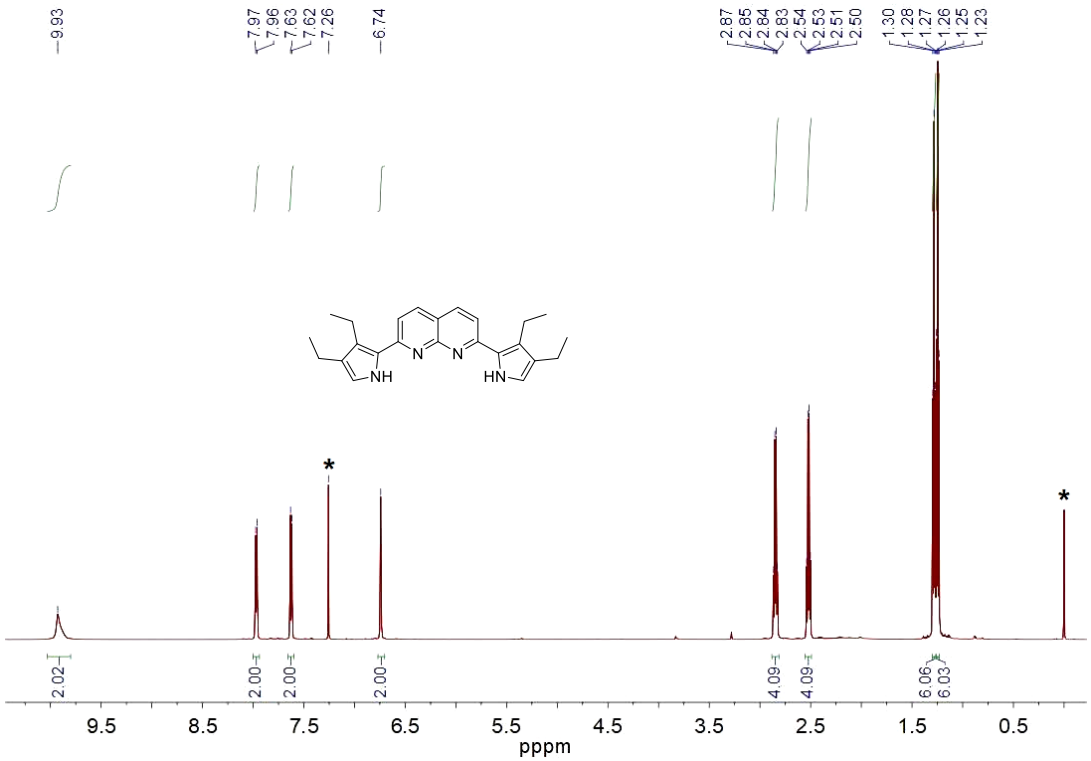


Figure S7. ^{1}H NMR (600 MHz, $CDCl_3$ at 298 K) spectrum of **5**.

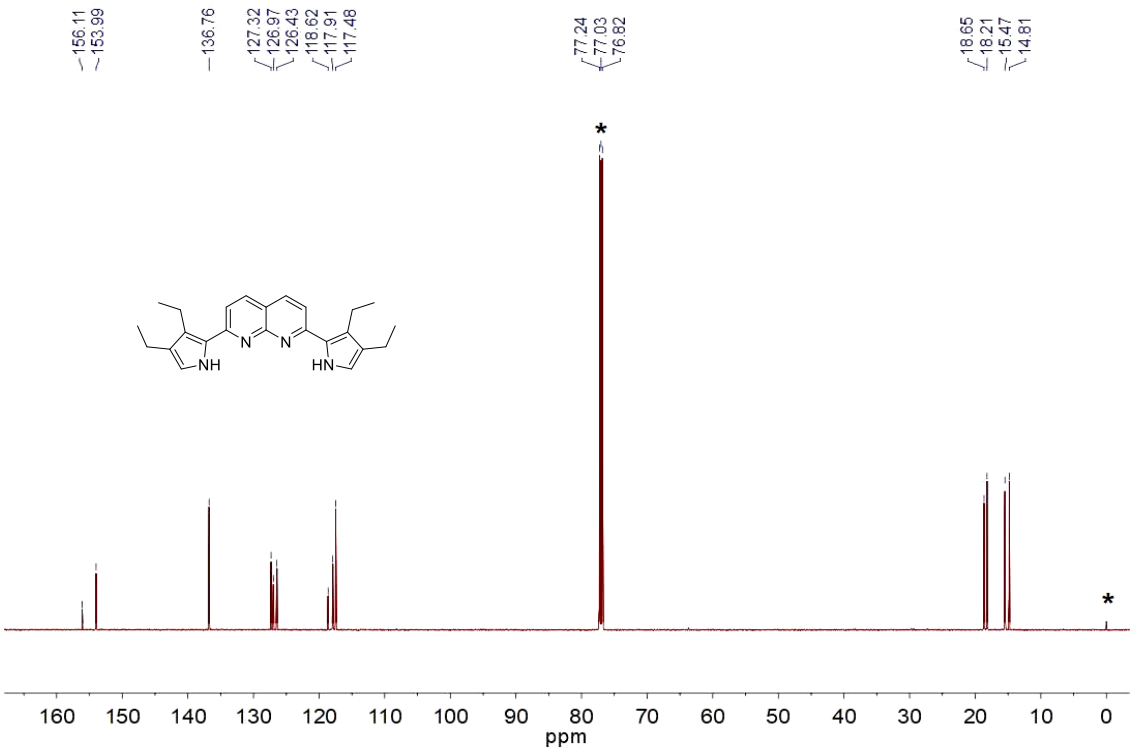


Figure S8. ^{13}C NMR (150 MHz, $CDCl_3$ at 298 K) spectrum of **5**.

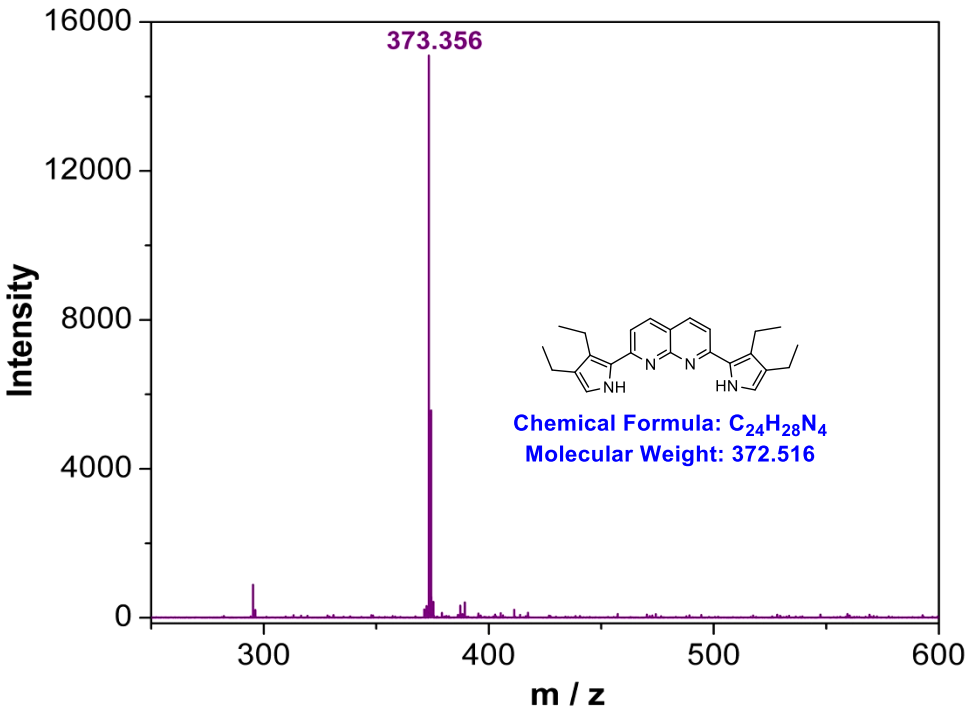


Figure S9. MALDI-TOF MS of compound **5**.

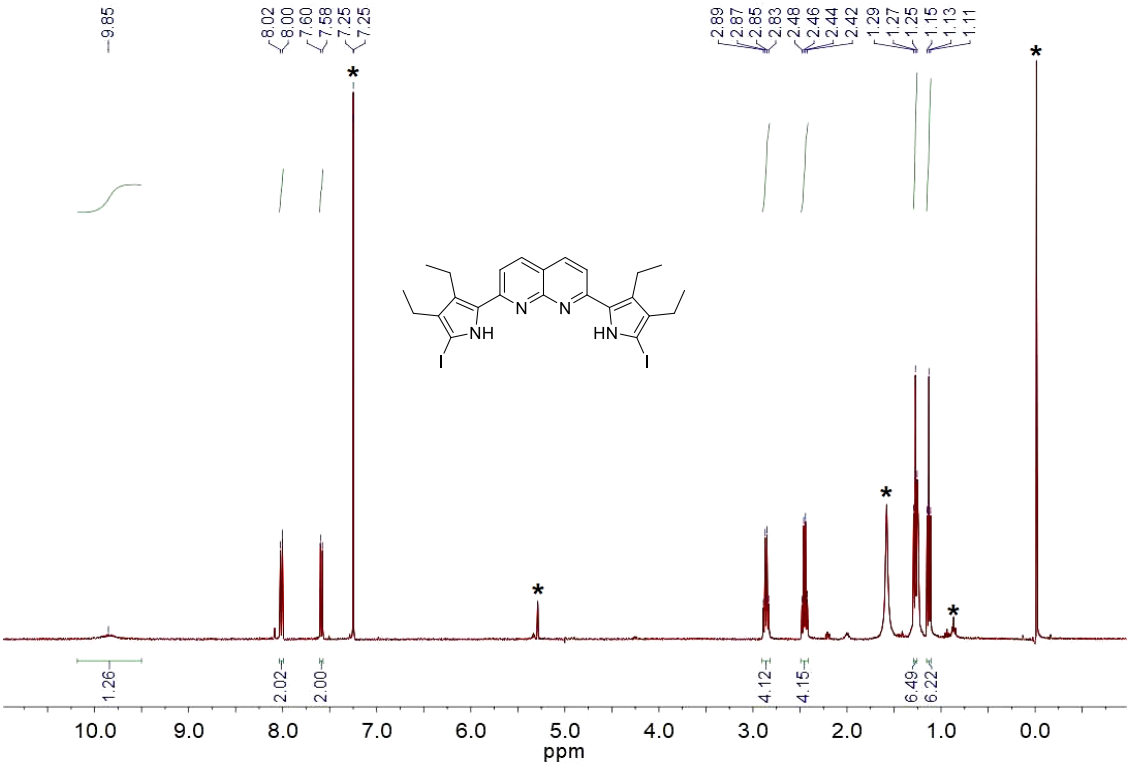


Figure S10. ^{1}H NMR (600 MHz, $CDCl_3$ at 298 K) spectrum of **6**.

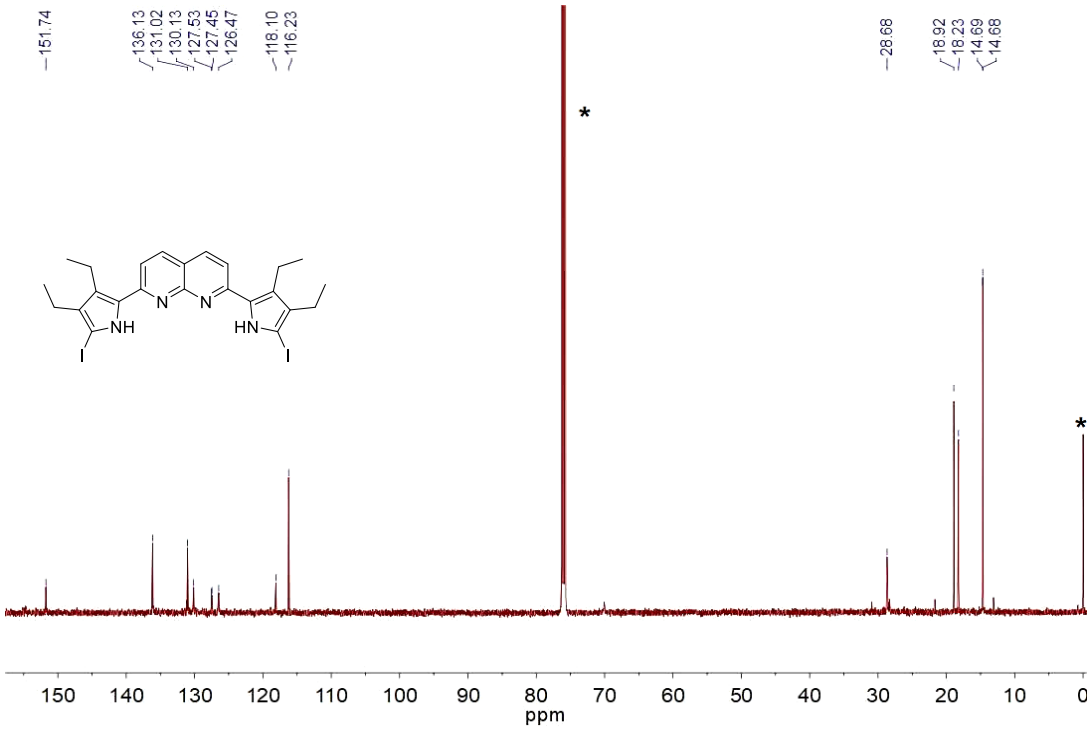


Figure S11. ^{13}C NMR (150 MHz, $CDCl_3$ at 298 K) spectrum of **6**.

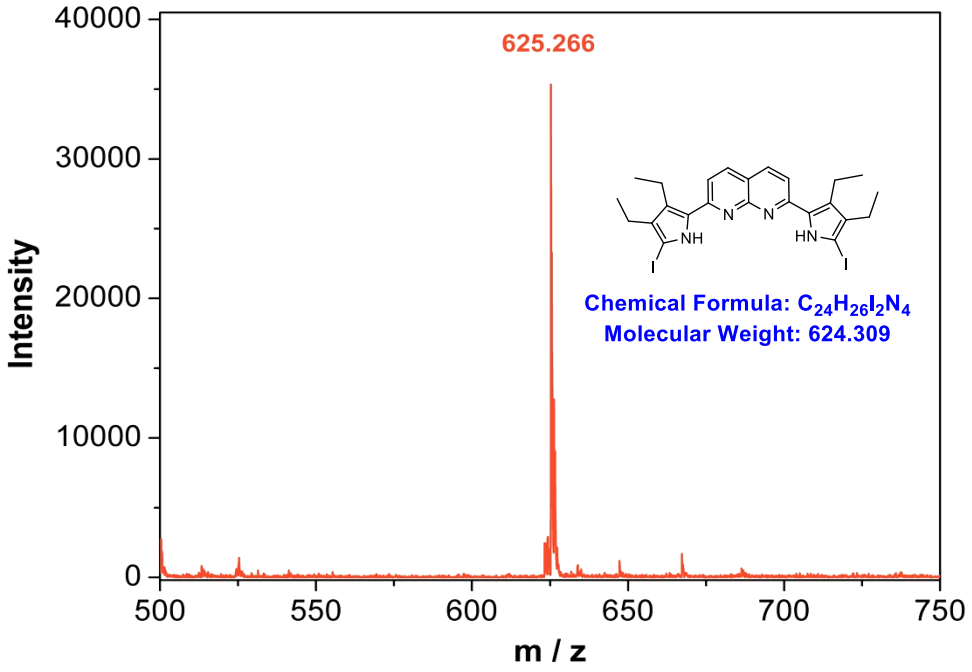


Figure S12. MALDI-TOF MS of compound **6**.

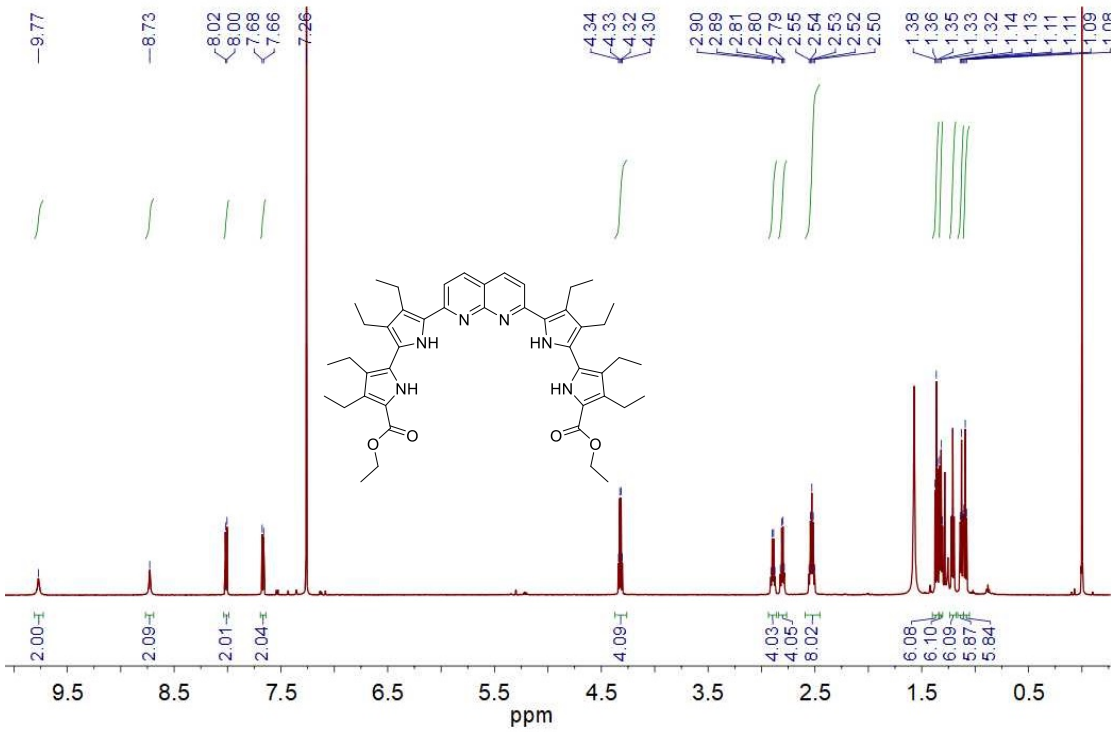


Figure S13. ^{1}H NMR (600 MHz, $CDCl_3$ at 298 K) spectrum of **7**.

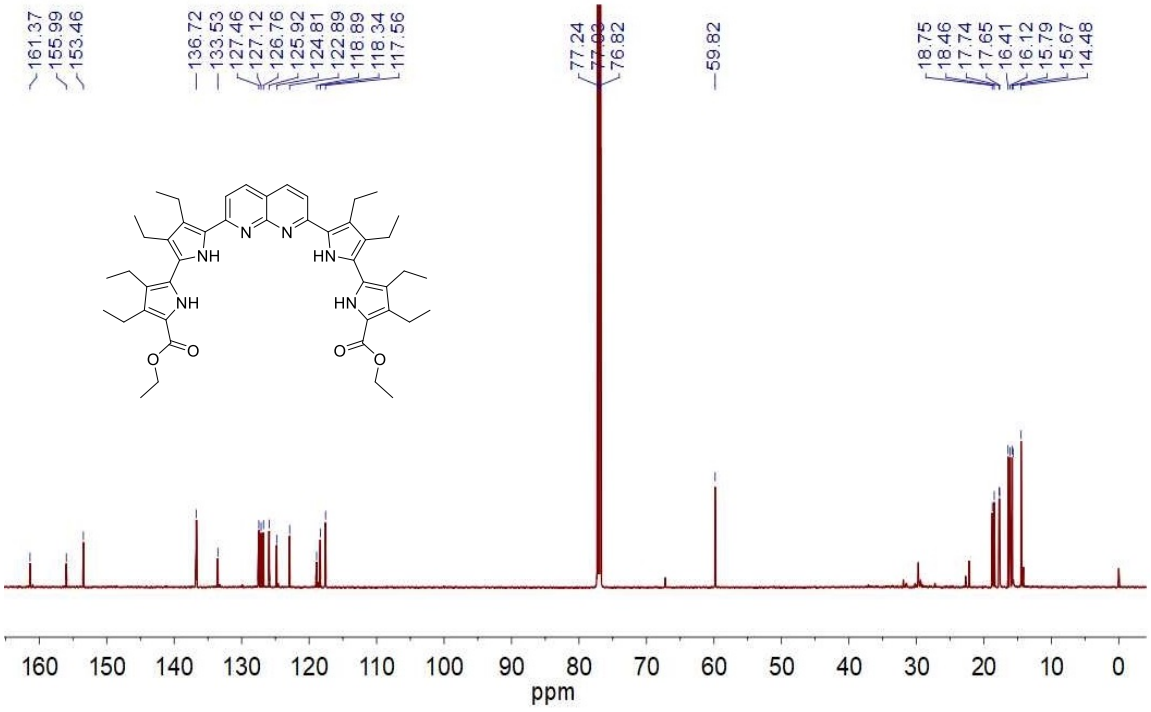


Figure S14. ^{13}C NMR (150 MHz, $CDCl_3$ at 298 K) spectrum of **7**.

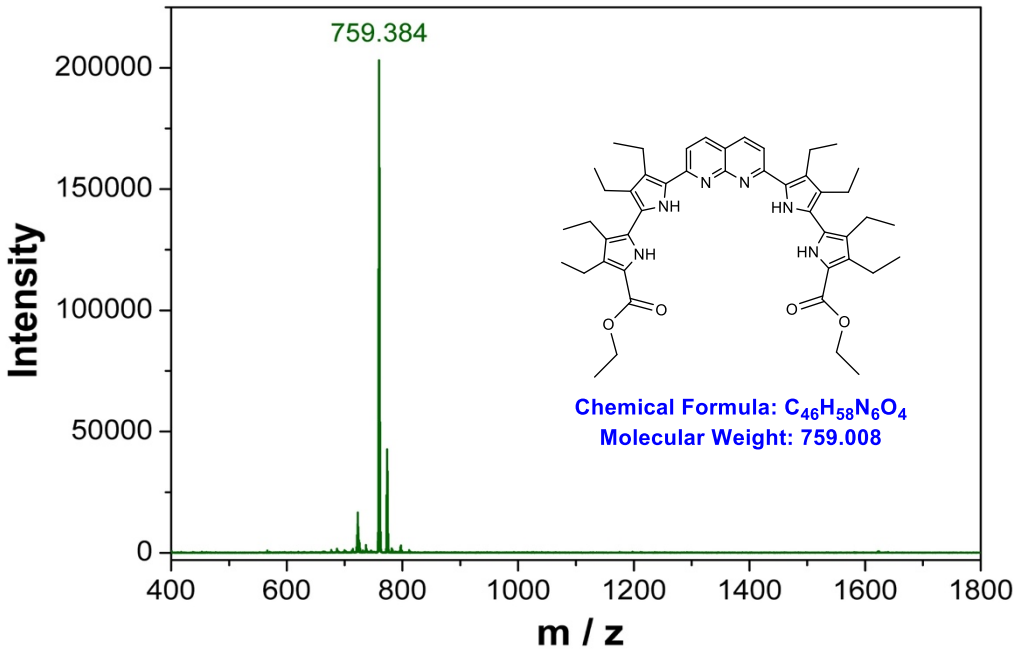


Figure S15. MALDI-TOF MS of final receptor unit **7**.

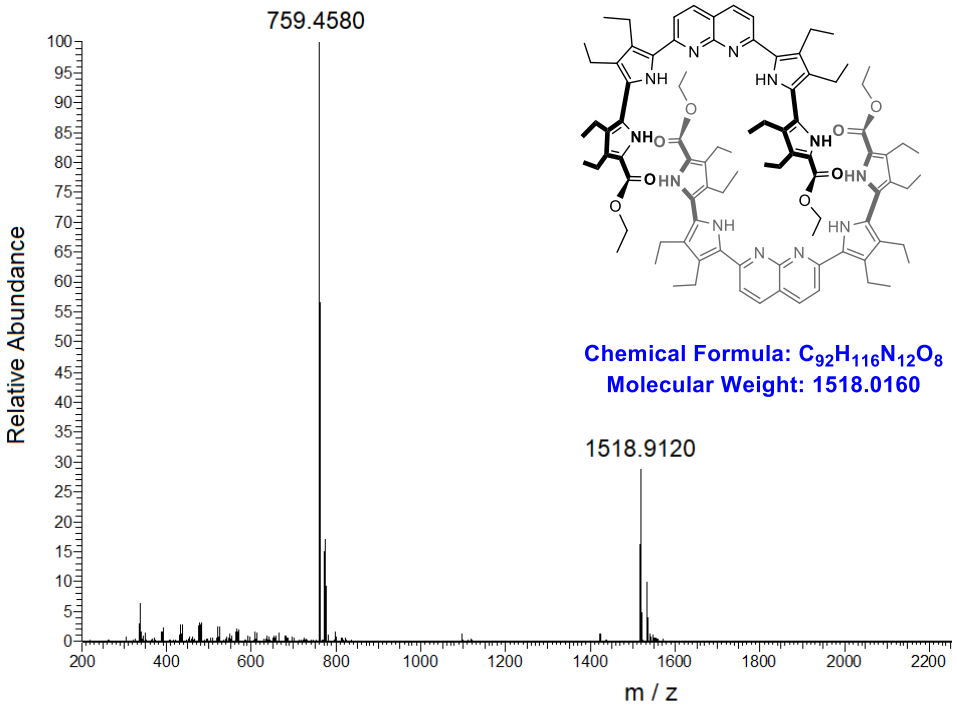


Figure S16. ESI-TOF MS of the receptor, showing 'm/z' corresponding to the hydrogen-bonded dimeric macrocyclic species **7•7**.

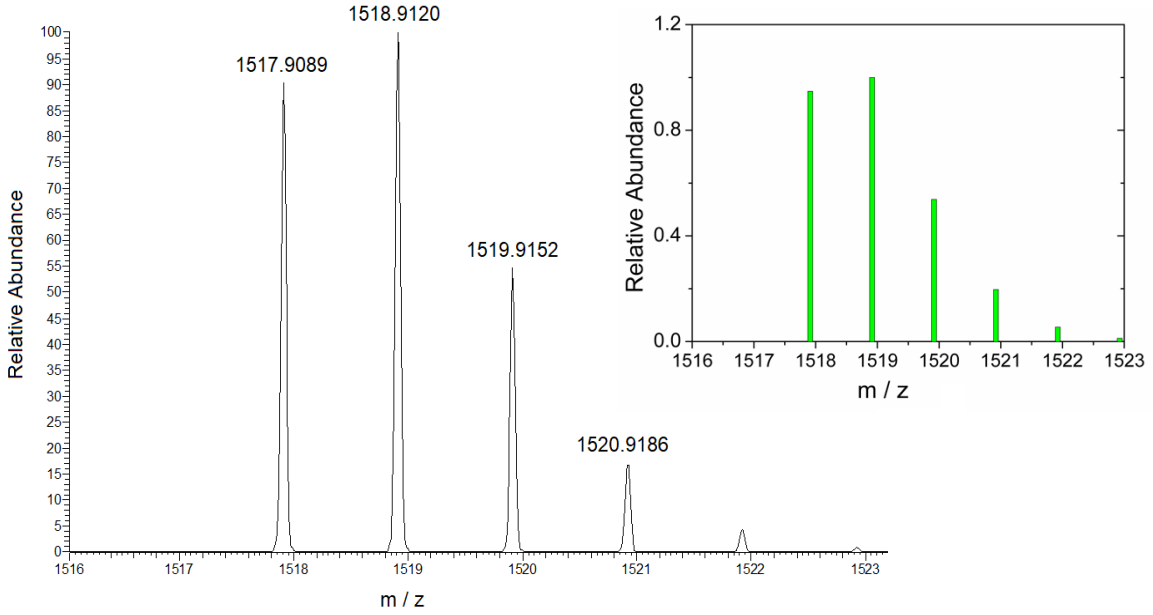


Figure S17. Isotopic distribution pattern of the dimeric macrocyclic receptor **7•7** predicted by ESI-TOF MS, considering $(M+1)^+$. **Inset**: Green bars represent the simulated version of isotopic distribution pattern of receptor **7•7**.

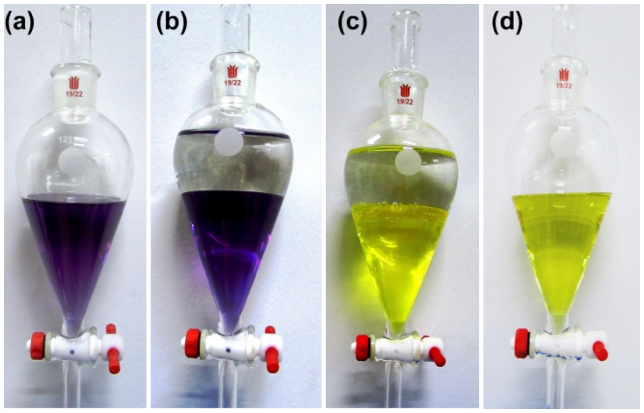


Figure S18. Pictorial demonstration of the aqueous extraction involving receptor **7•7** and oxalic acid. The organic (CH_2Cl_2) part containing supramolecular ensemble (a); the **undisturbed** organic and aqueous parts before aqueous wash up (b); **washed** organic part after aqueous extraction where the oxalic acid goes to the aqueous layer and the receptor goes to the CH_2Cl_2 phase (c); the organic phase with **pristine host** only (d).

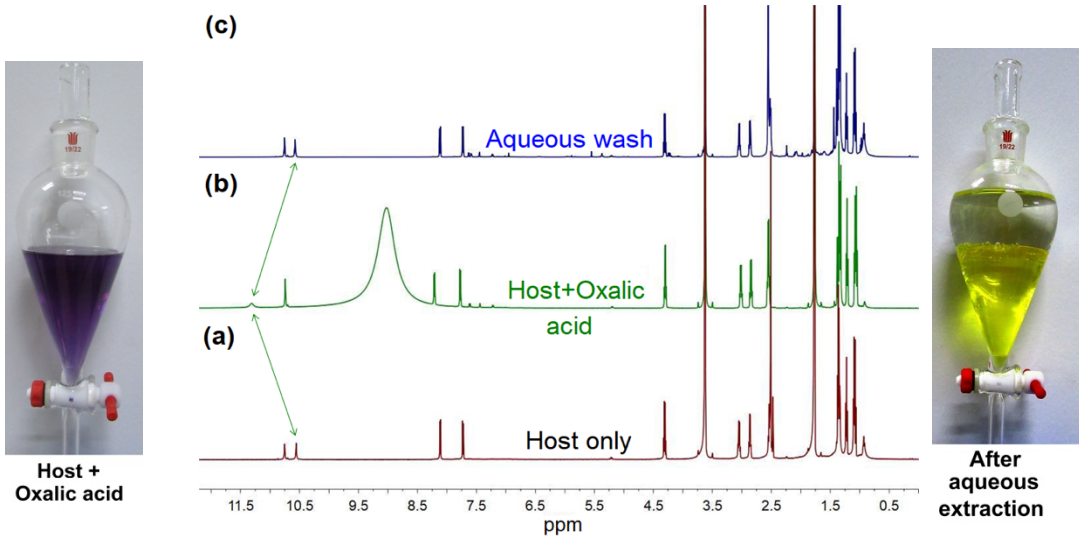


Figure S19. Comparative ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectra of pristine receptor **7•7** (a), with oxalic acid (b), and the organic phase after aqueous extraction (c). The spectrum (c) reveals that the guest removed from **7•7** upon aqueous extraction, which gives similar spectroscopic signature as pristine host, **7•7** (a).

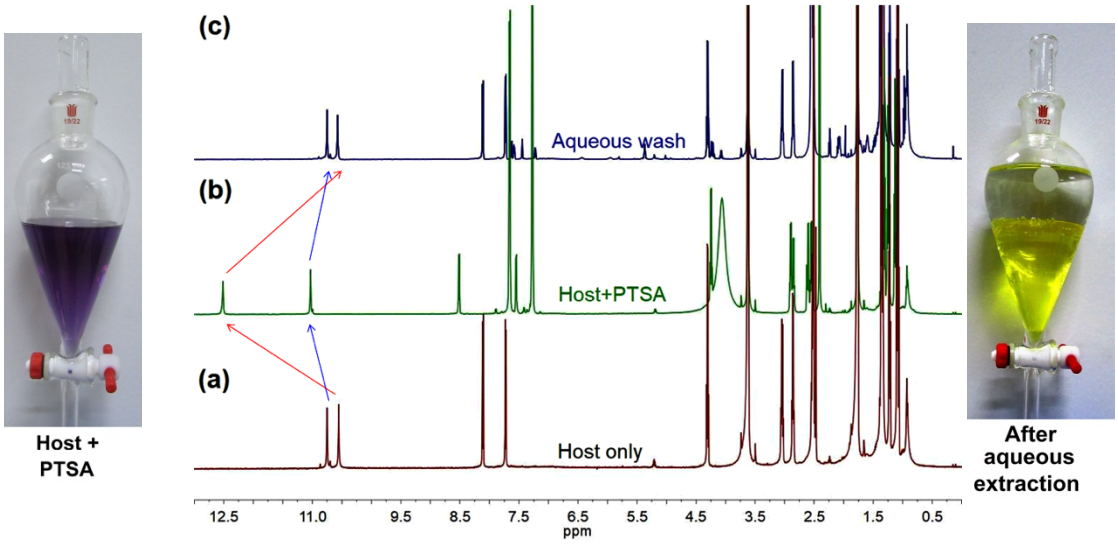


Figure S20. ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectra of pristine receptor **7•7** (a), with PTSA (b), and the organic phase after aqueous extraction (c). The spectrum (c) reveals that the supramolecular receptor releases PTSA upon aqueous wash.

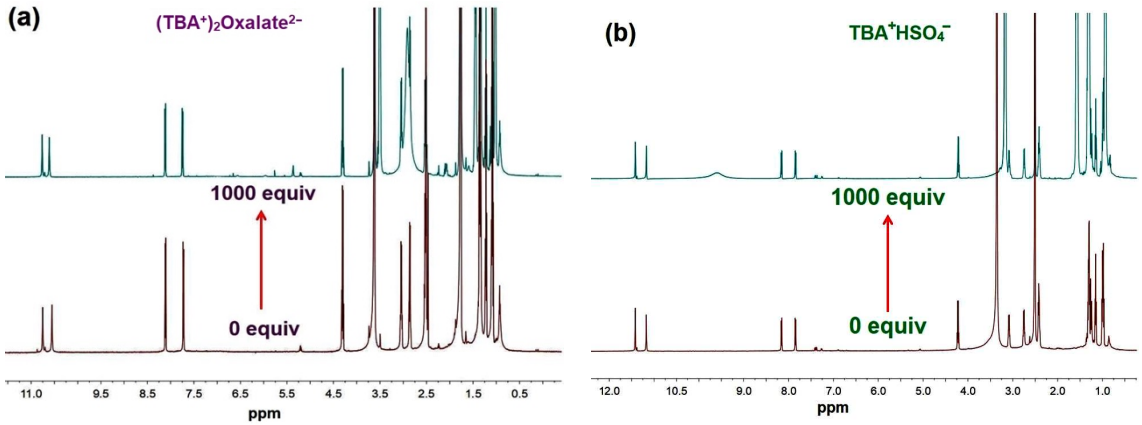


Figure S21. ^{1}H NMR (600 MHz at 298 K) spectra of receptor **7•7** recorded in the presence of 1000 equiv of tetrabutylammonium oxalate in THF-d_8 (a), and tetrabutylammonium hydrogen sulfate in DMSO-d_6 (b), respectively.

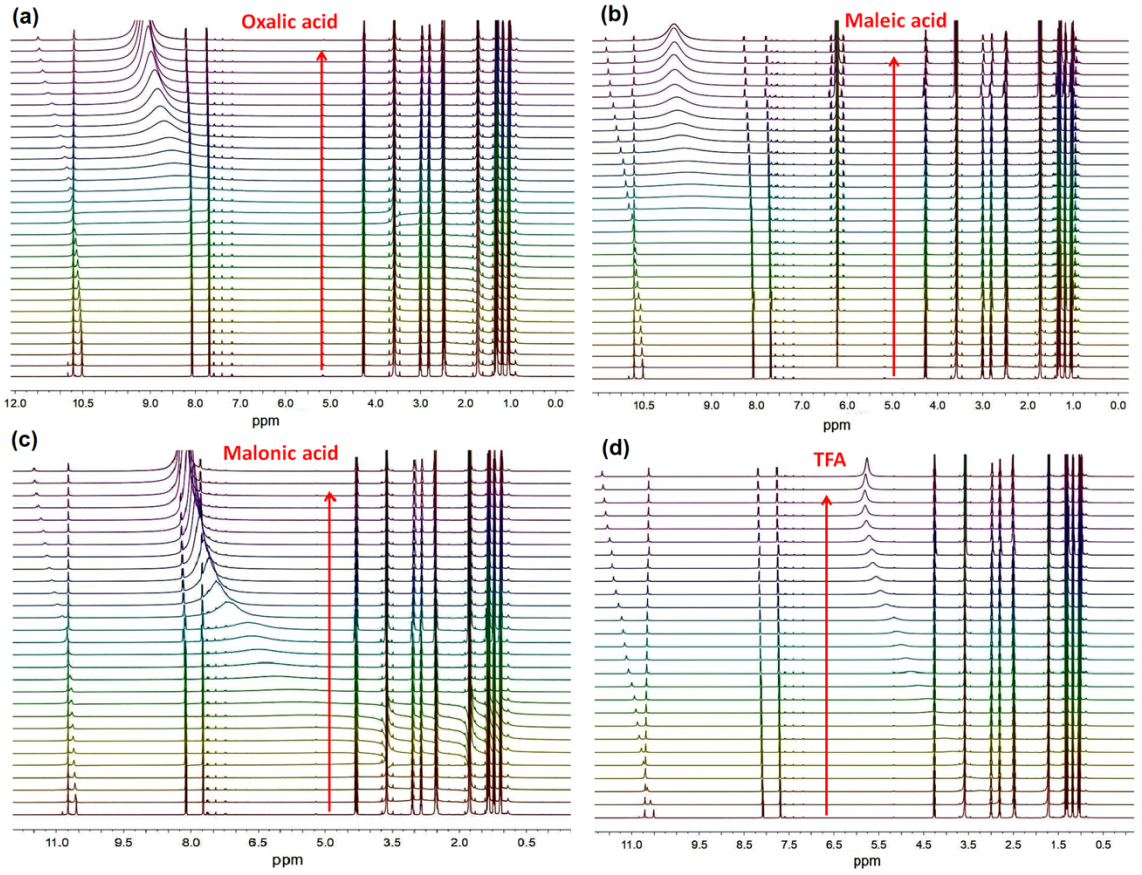


Figure S22. (a–d) ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectroscopic titration results of host **7•7** against 100 equiv of oxalic acid, maleic acid, malonic acid, and against 10 equiv of TFA, respectively.

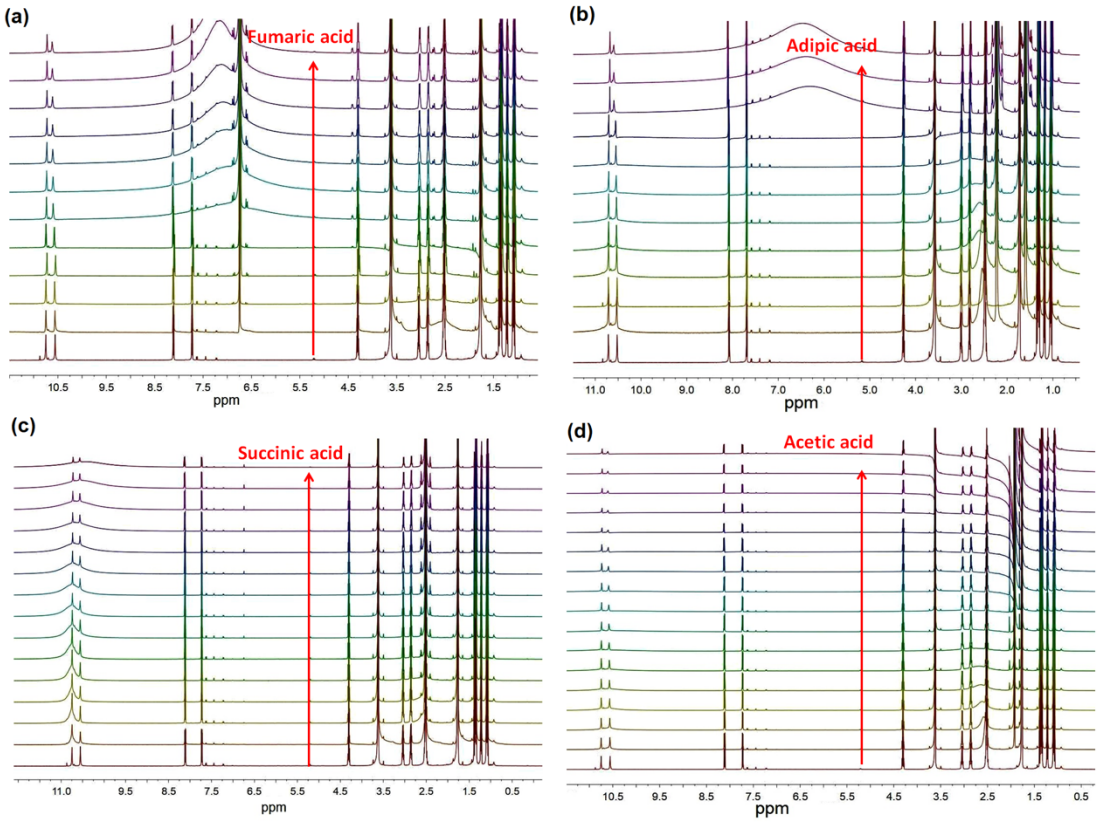


Figure S23. (a–d) ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectroscopic titration results of host **7•7** against 100 equiv fumaric acid, adipic acid, succinic acid, and acetic acid, respectively.

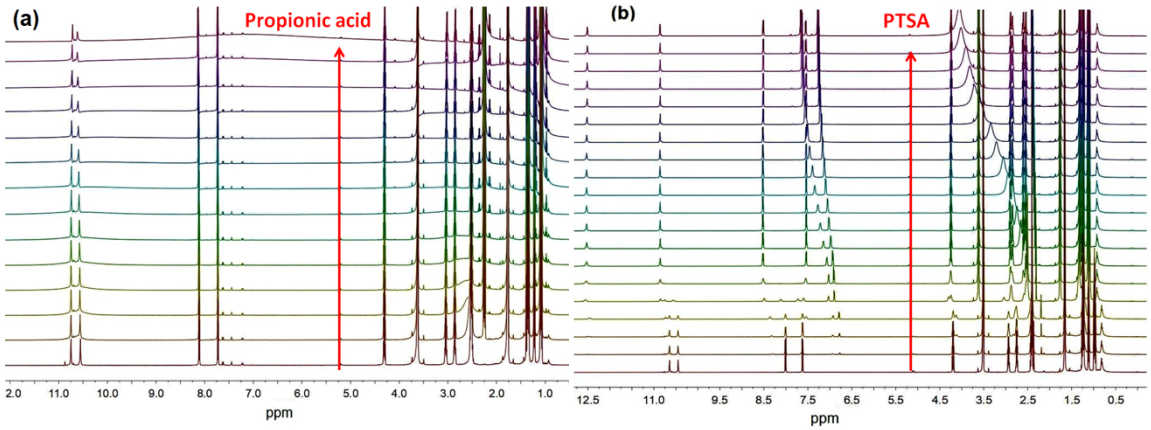


Figure S24. ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectroscopic titration results of host **7•7** against 100 equiv propionic acid (a), and vs 10 equiv PTSA (b), respectively.

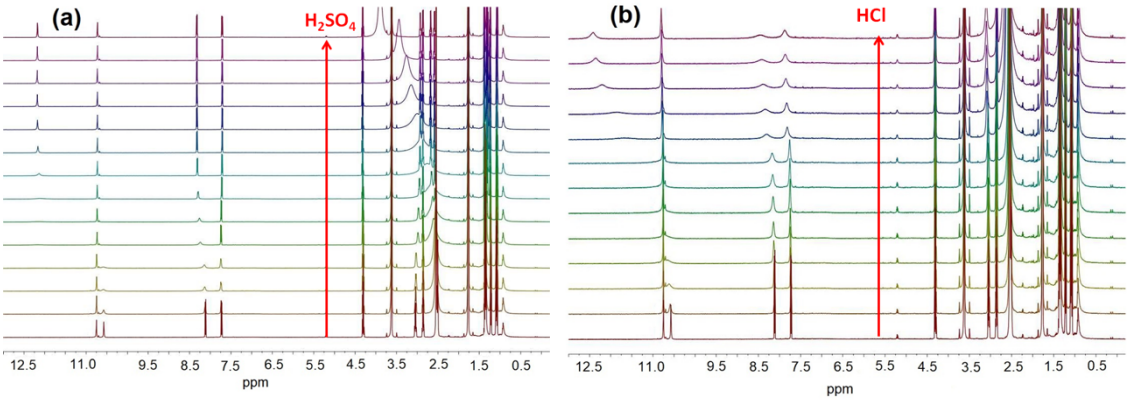


Figure S25. ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectroscopic titration results of host **7•7** against 10 equiv of sulfuric acid (a), and 10 equiv of HCl (b), respectively.

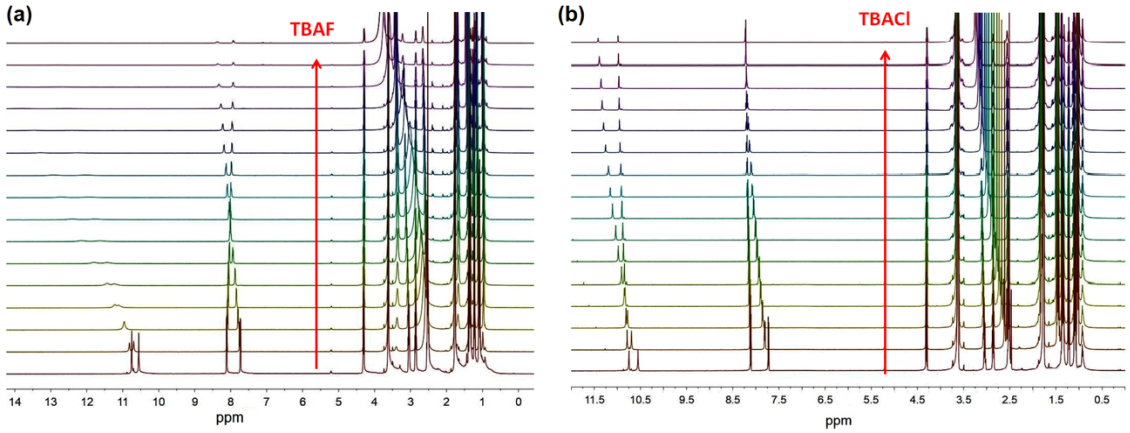


Figure S26. ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectroscopic titration results of host **7•7** against 20 equiv of TBAF (a), and 50 equiv of TBACl (b), respectively.

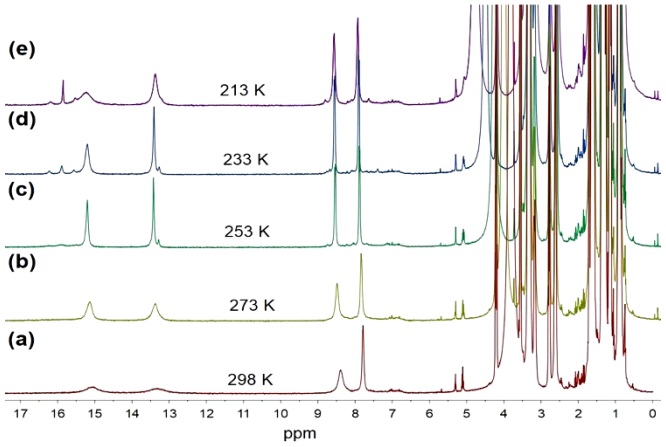


Figure S27. (a–e) Variable temperature ^{1}H NMR (400 MHz in THF-d_8) spectra of host 7•7 against TBAF. The signal at 15.85 ppm corresponds to the generation of HF_2^-, which is visible at 233 K (d), and 213 K (e), respectively.

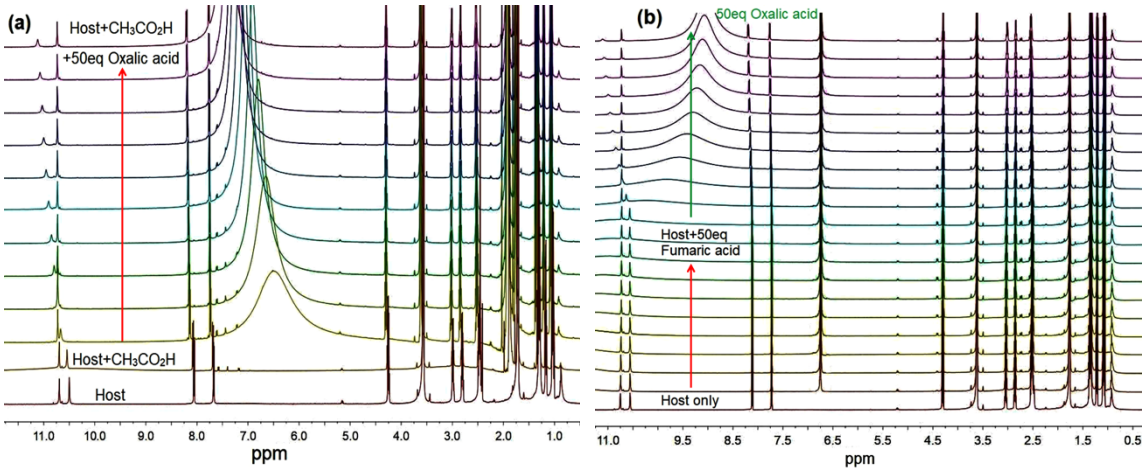


Figure S28. Competitive experiments in the presence of a large excess of one component: Representative acids from mono- (acetic acid) and di-acids (fumaric acid) were taken for this purpose. ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectroscopic titration results of host **7•7** against oxalic acid in the presence of 100 equiv of acetic acid (a), and the titration result of host **7•7** against oxalic acid in the presence of 100 equiv of fumaric acid (b), respectively.

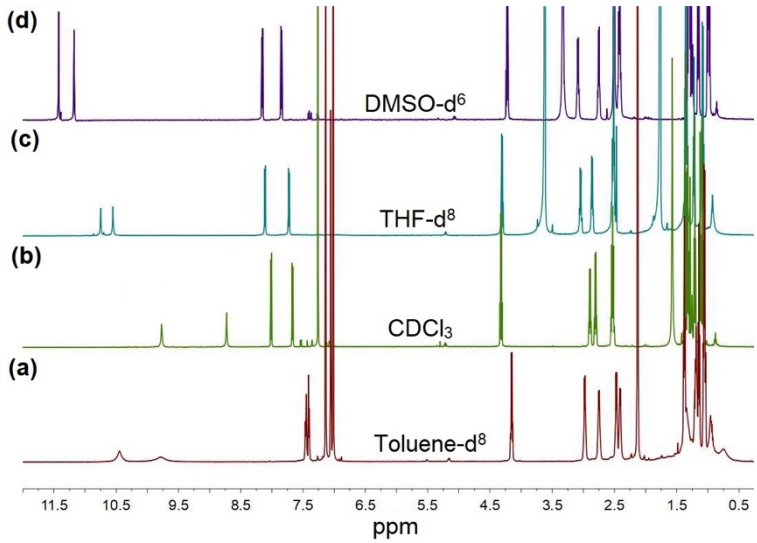


Figure S29. (a–d) Solvent dependent ^{1}H NMR (600 MHz at 298 K) spectra of host **7•7** in toluene-d_8 (a), $CDCl_3$ (b), THF-d_8 (c), and DMSO-d_8 (d), respectively, under identical experimental conditions.

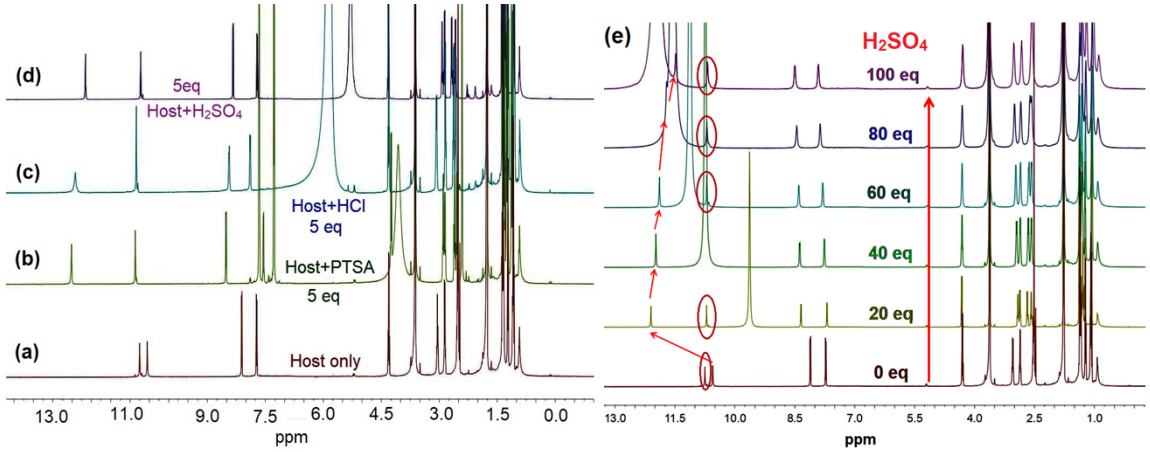


Figure S30. (a–d) ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectra of host **7•7** (a); in the presence of 5 equiv of PTSA (b) 5 equiv of HCl (c) and 5 equiv of H_2SO_4 (d), respectively. (e) ^{1}H NMR (600 MHz, THF-d_8 at 298 K) titration result with host **7•7** upon incremental addition of up to 100 equiv of H_2SO_4.

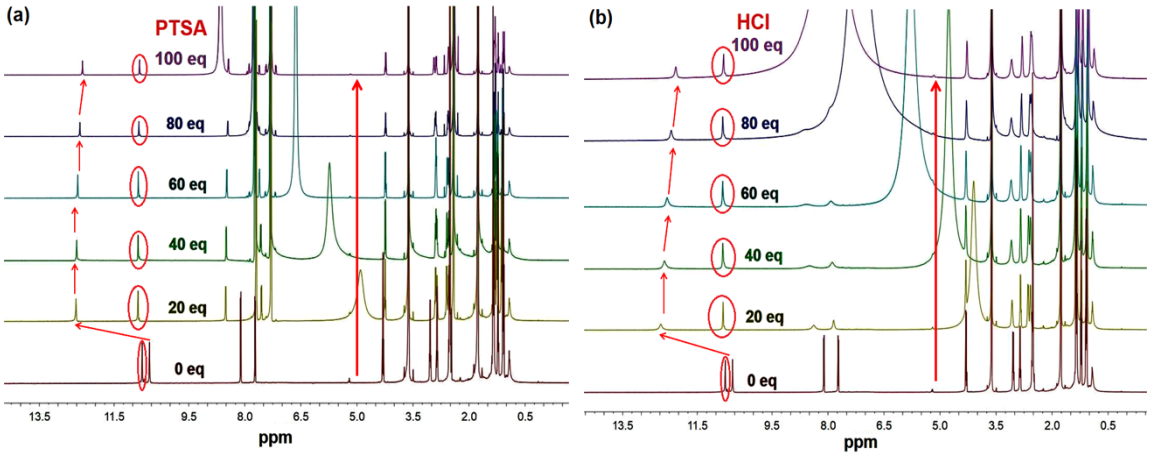


Figure S31. ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectroscopic titration results of host **7•7** with 100 equiv of PTSA (a) and 100 equiv of HCl (b), respectively.

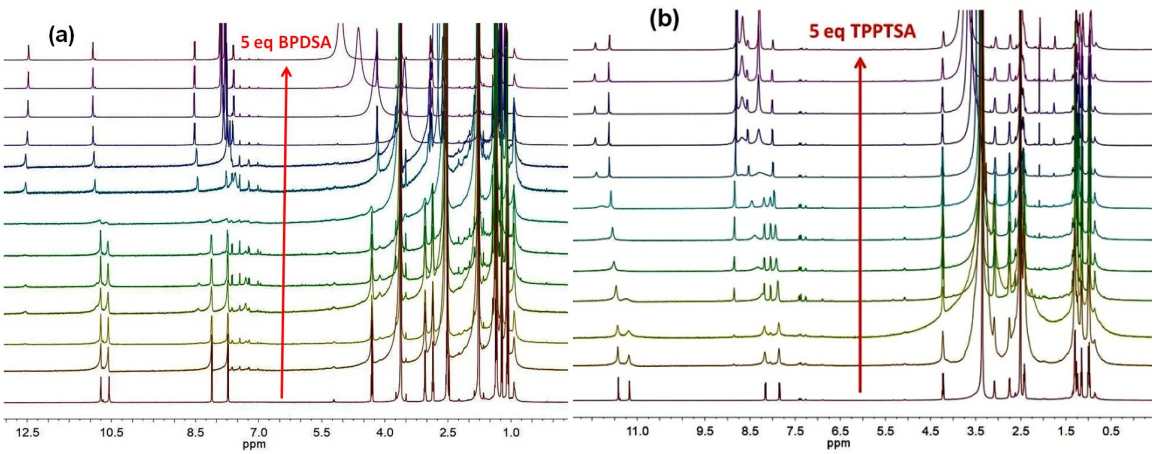


Figure S32. ^{1}H NMR (600 MHz at 298 K) spectroscopic titration results of host **7•7** with 5 equiv of BPDSA (a) and 5 equiv of TPPTSA (b) in THF-d_8 and DMSO-d_6, respectively. **Note**: Due to the poor solubility of TPPTSA in THF-d_8, DMSO-d_6 was used to effectuate the titration.

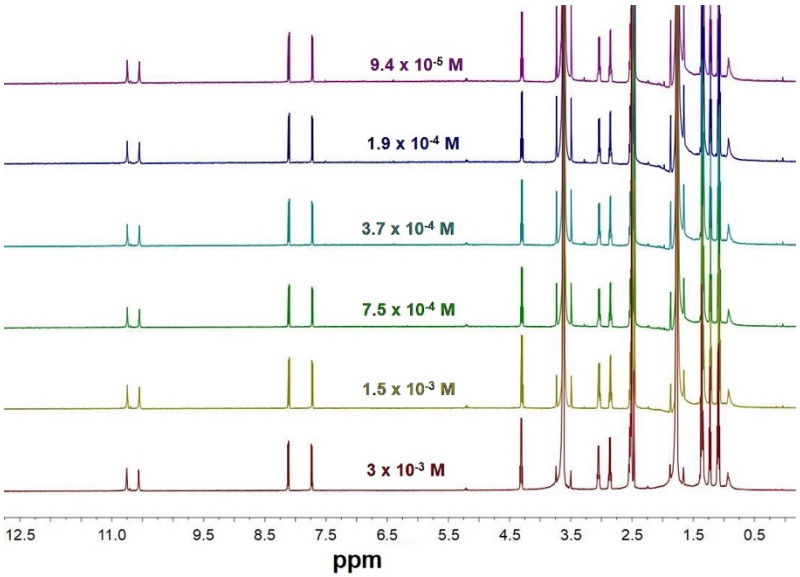


Figure S33. ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectra of the host **7•7** recorded at various concentrations ranging from 3×10^{-3} M to 9.4×10^{-5} M. **Note**: There is no any significant change in the chemical shift of the terminal NH proton signal at 10.75 ppm. All analyses were performed under identical experimental conditions.

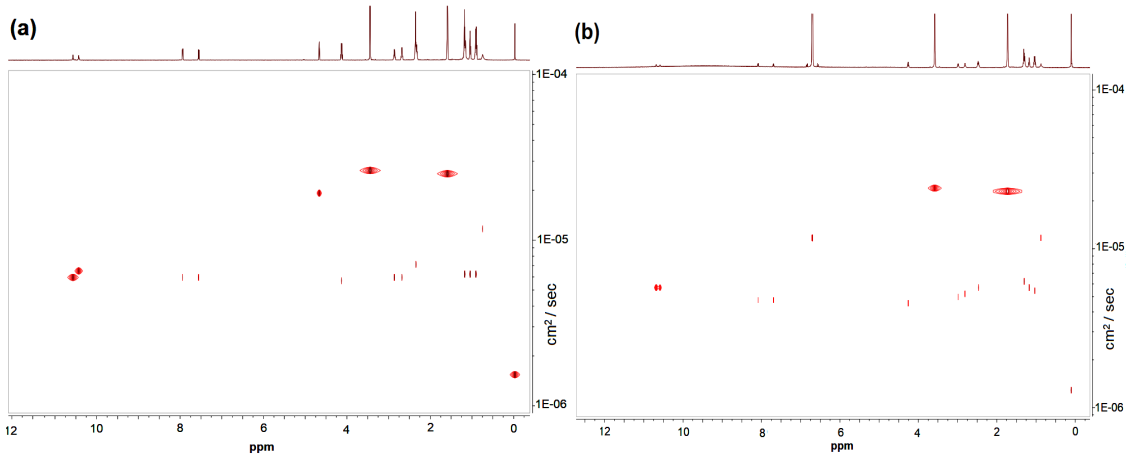


Figure S34. (a) DOSY ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectra of 10 mmol pristine host **7•7** and (b) host in the presence of 50 equiv of fumaric acid, respectively.

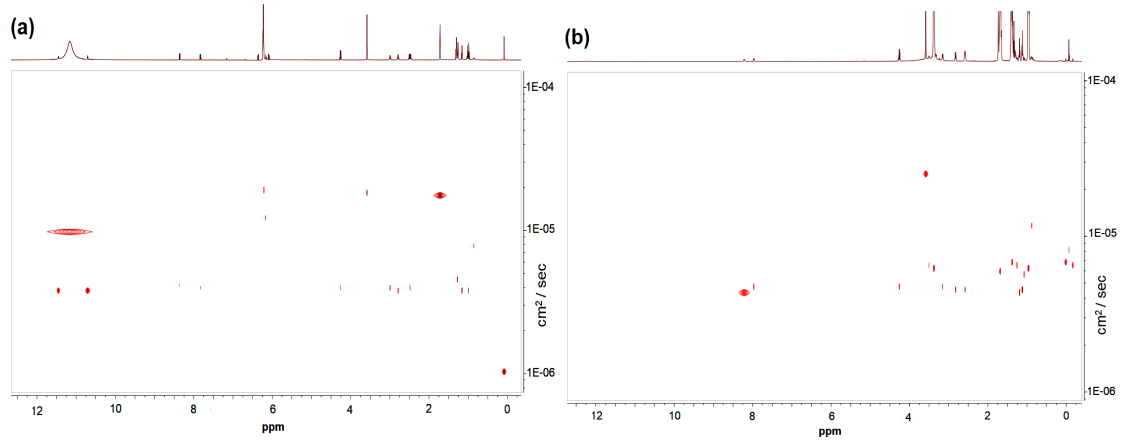


Figure S35. (a) DOSY ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectra of 10 mmol host **7•7** in the presence of 50 equiv of maleic acid and (b) in the presence of 20 equiv of TBAF, respectively.

Table S1. Summary of the diffusion coefficient values (D/cm^{2}sec^{-1}) of host, TBAF and solvent (THF), respectively, determined from the ^{1}H DOSY NMR titration experiments carried out in THF-d_8 at 298 K.

Entry	D_{Guest}	D_{Host}	D_{THF}
Host only	N/A	5.56×10^{-6}	24.8×10^{-6}
TBAF only	6.85×10^{-6}	N/A	24.8×10^{-6}
Host : TBAF (1:20)	6.16×10^{-6}	4.52×10^{-6}	24.8×10^{-6}

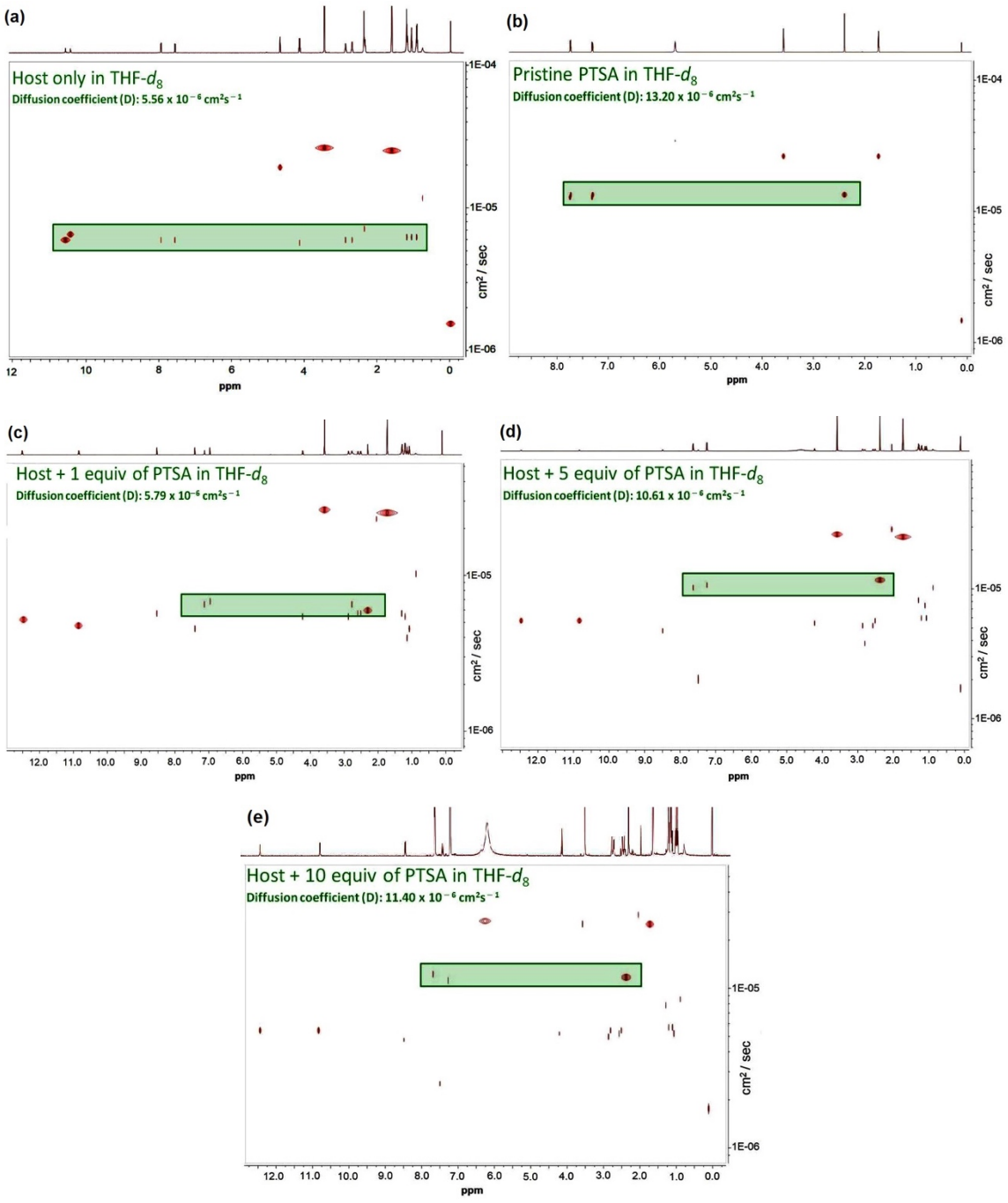


Figure S36. DOSY ^{1}H NMR (600 MHz, THF-d_8 at 298 K) spectroscopic titration results of host **7•7** in the presence of 1 equiv (a), 5 equiv (b), 10 equiv (c), pristine PTSA (d), and pristine host (e), respectively. The corresponding diffusion coefficient values are provided in **Table S2** below.

Table S2. Summary of the diffusion coefficient values (D/cm^2sec^{-1}) of host, guest, and solvent (THF), respectively, as determined from DOSY ^1H NMR spectroscopic analyses (600 MHz, THF-d_8 at 298 K).

Entry	D_{Guest}	D_{Host}	D_{THF}
PTSA only	13.20×10^{-6}	N/A	24.8×10^{-6}
Host : PTSA (1:1)	5.79×10^{-6}	5.56×10^{-6}	24.8×10^{-6}
Host : PTSA (1:5)	10.61×10^{-6}	5.56×10^{-6}	24.8×10^{-6}
Host : PTSA (1:10)	11.40×10^{-6}	5.56×10^{-6}	24.8×10^{-6}
Host only	N/A	5.56×10^{-6}	24.8×10^{-6}

III) Additional Optical Studies

Figure S37. (a) Visible color change of host seen upon adding various guests, under ambient light: (1) only pristine host **7•7**, (2) with acetic acid, (3) with propionic acid, (4) with oxalic acid, (5) with maleic acid, (6) with malonic acid, (7) with fumaric acid, (8) with succinic acid, (9) with adipic acid, (10) with TFA, (11) with PTSA, (12) with TBAF, (13) with TBACl, (14) with BPDSA, and (15) TPPTSA, respectively. (b) The emission behavior of these same glass vials containing the host solution with the various added guests discussed above, under exposure of 365 nm UV light. All host–guest supramolecular complexes were prepared in anhydrous THF at 298 K.

a) Absorption spectroscopic results:

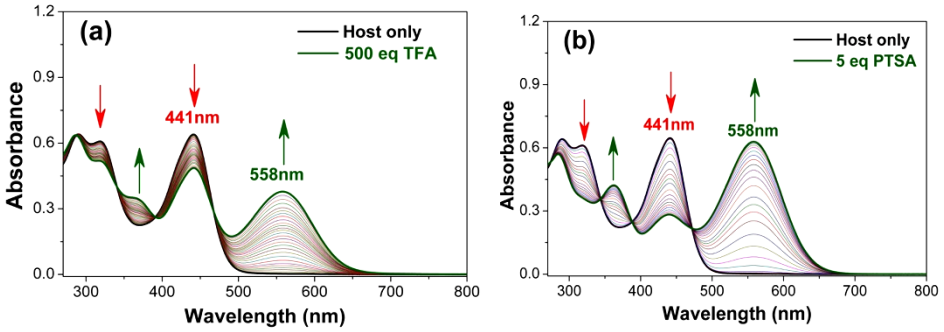


Figure S38. UV–Vis spectroscopic titration (anhydrous THF at 298 K) results of host **7•7** with TFA (a), and PTSA (b), respectively.

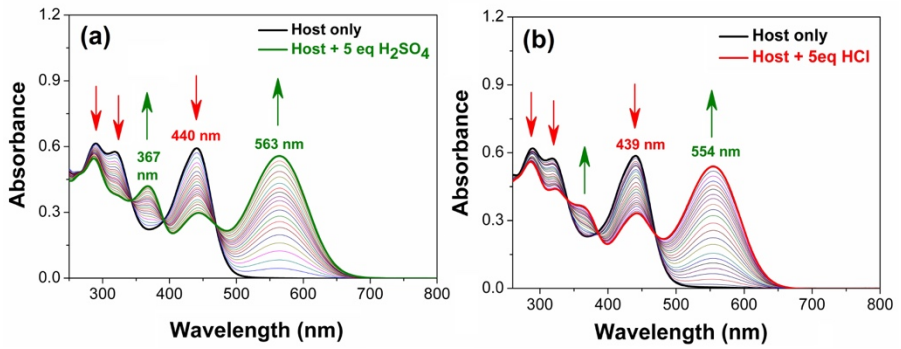


Figure S39. UV–Vis spectroscopic titration (anhydrous THF at 298 K) results of host **7•7** with H_2SO_4 (a), and HCl (b), respectively.

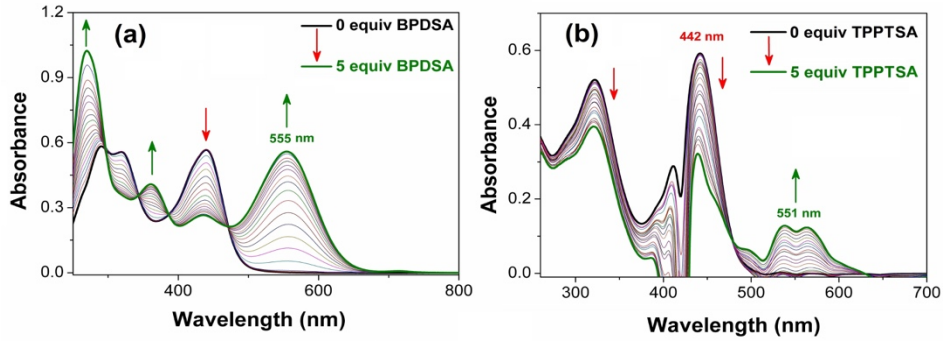


Figure S40. UV–Vis spectroscopic titration (298 K) results of host **7•7** with 5 equiv of BPDSA in anhydrous THF (a), and 5 equiv of TPPTSA in anhydrous DMSO (b), respectively. **Note**: In case of TPPTSA, the porphyrin-based absorptions were subtracted from the original spectra to highlight the change in the 551 nm region which is ascribed to the host–guest complexation process.

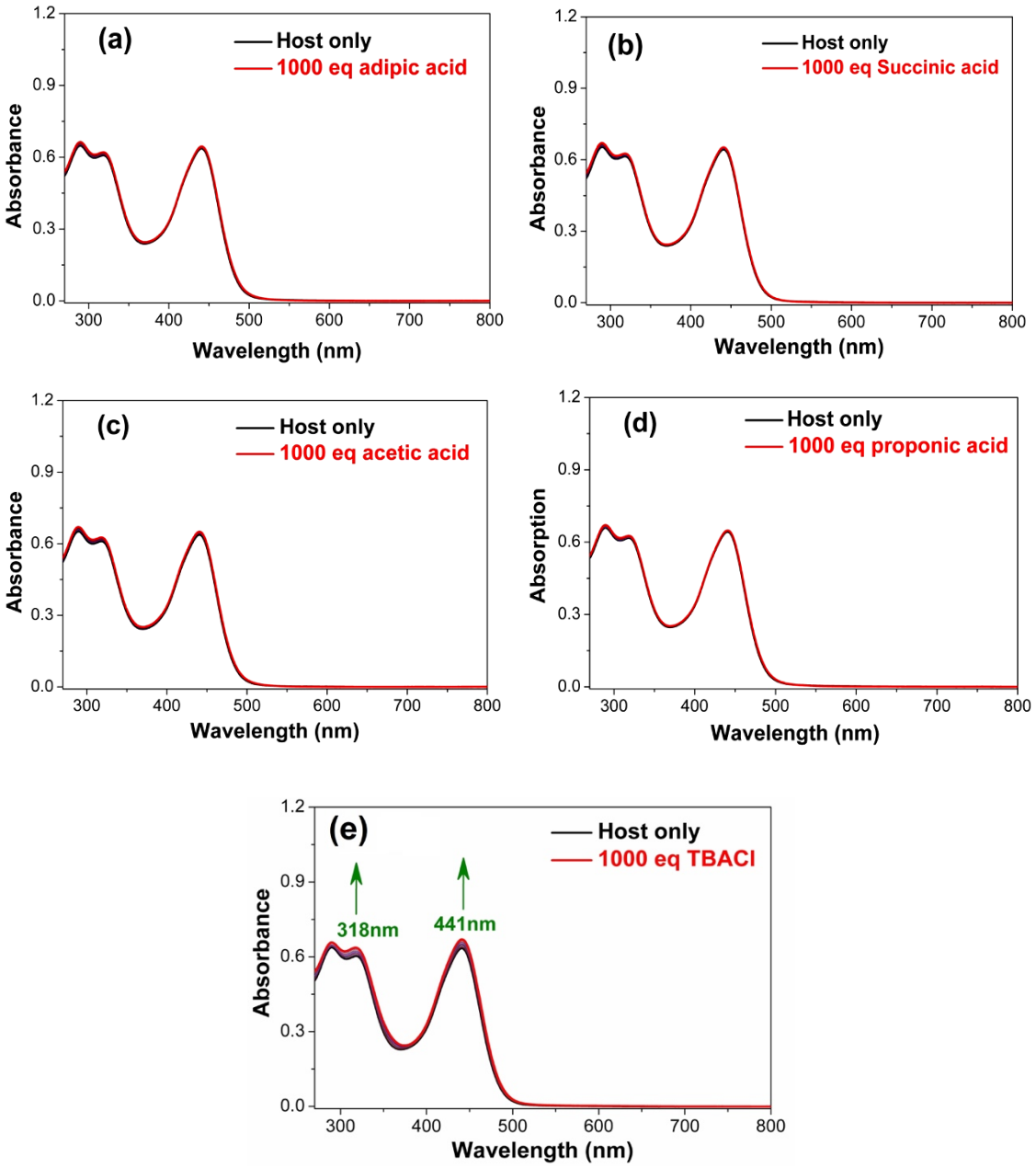


Figure S41. UV–Vis spectroscopic (anhydrous THF at 298 K) titration results of host **7•7** with adipic acid (a), succinic acid (b), acetic acid (c), propionic acid (d), and TBACl (e), respectively.

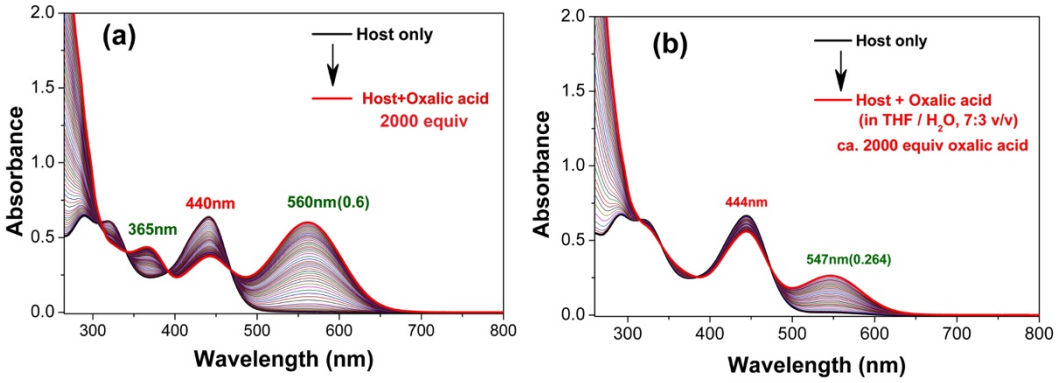


Figure S42. UV–Vis spectroscopic (298 K) titration results of host **7•7** with ca. 2000 equiv of oxalic acid in anhydrous THF (a), and titration of host **7•7** against oxalic acid in THF:H_2O (7:3 v/v) (b), respectively.

b) Emission spectroscopic titration results:

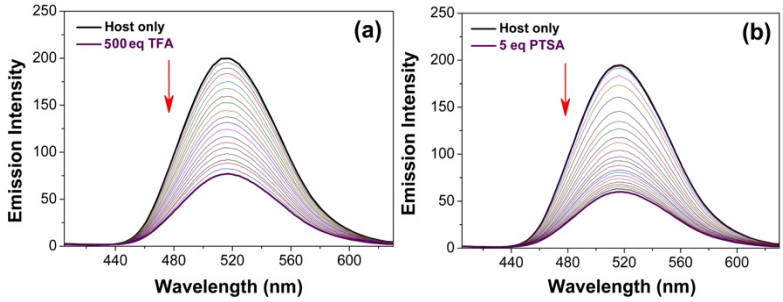


Figure S43. (a,b) Fluorescence spectroscopic (λ_{ex} = 320 nm, anhydrous THF at 298 K) titration results of host **7•7** with TFA and PTSA, respectively.

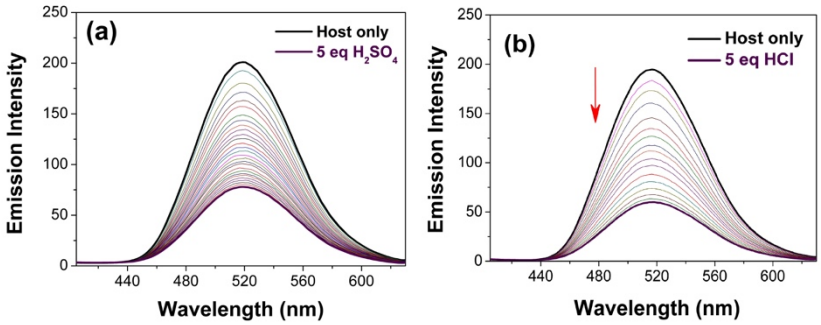


Figure S44. (a,b) Fluorescence spectroscopic (λ_{ex} = 320 nm, anhydrous THF at 298 K) titration results of host **7•7** with up to 5 equiv of H_2SO_4 and HCl, respectively.

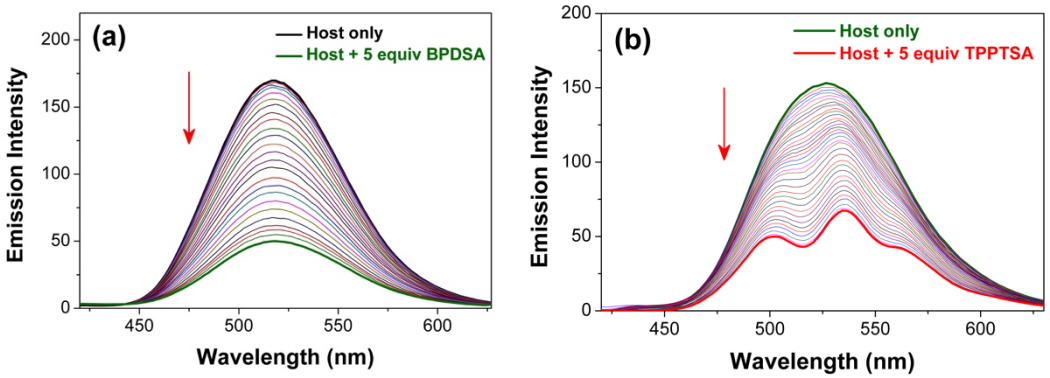


Figure S45. Fluorescence spectroscopic titration (λ_{ex} = 320 nm, at 298 K) results of host **7•7** with up to 5 equiv of BPDSA in anhydrous THF (a), and 5 equiv of TPPTSA in anhydrous DMSO (b), respectively. **Note**: In case of TPPTSA, the porphyrin-based emissions were subtracted from the original spectra to highlight the actual quenching behavior ascribed to the host–guest complexation process.

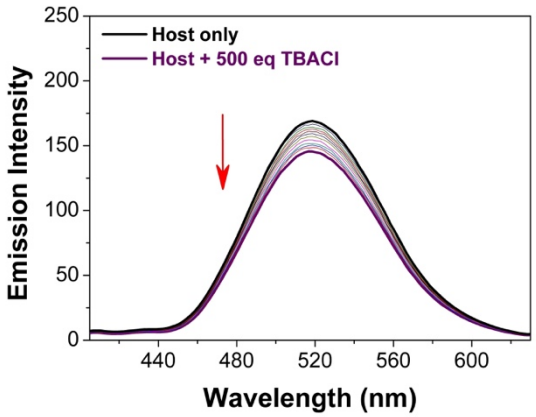


Figure S46. Fluorescence spectroscopic (λ_{ex} = 320 nm, anhydrous THF at 298 K) titration results of host with up to 500 equiv of TBACl.

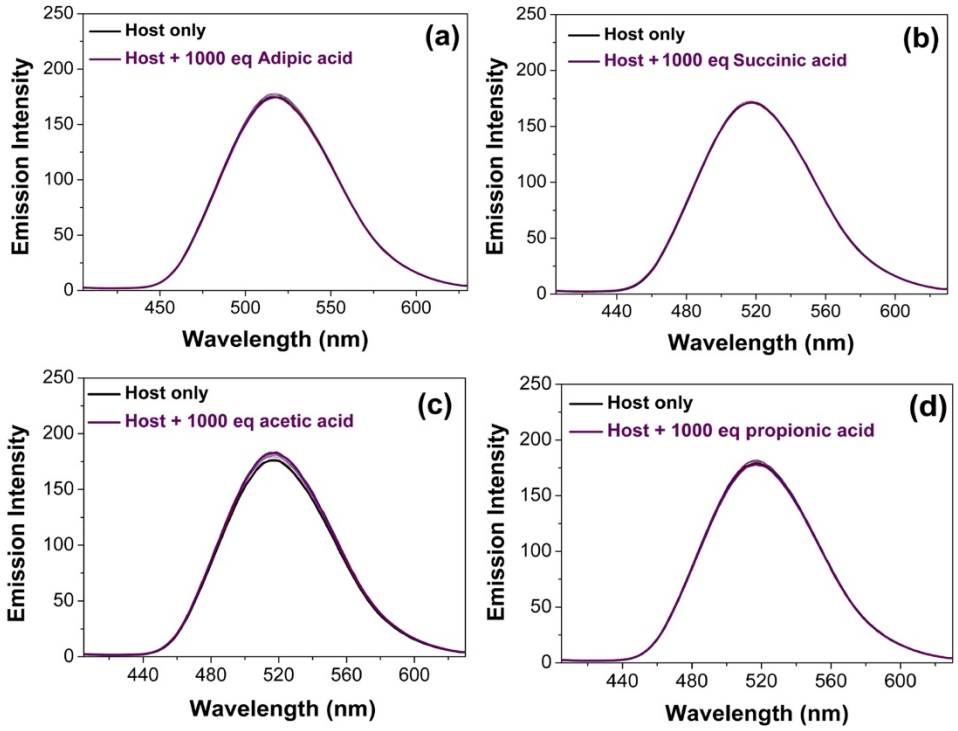


Figure S47. (a–d) Fluorescence spectroscopic (λ_{ex} = 320 nm, anhydrous THF at 298 K) titration results of host **7•7** with adipic acid, succinic acid, acetic acid, and propionic acid, respectively.

c) Isotherms created by fitting the data from selected fluorescence titration studies to standard 1:1 and statistical 1:2 binding equations.

The data from selected fluorescence titration studies (1×10^{-6} M host **7•7** solution in THF, in a quartz cuvette having 1 cm path length, titrated with 10^{-3} M acid guest at constant host concentration) at 516 nm were fitted to standard 1:1 and statistical 1:2 binding profiles using BindFit.[S4] The resulting isotherms are provided below in Figure S48. However, as noted in the main text, the resulting numerical values should not be interpreted in terms of any simple physical model.

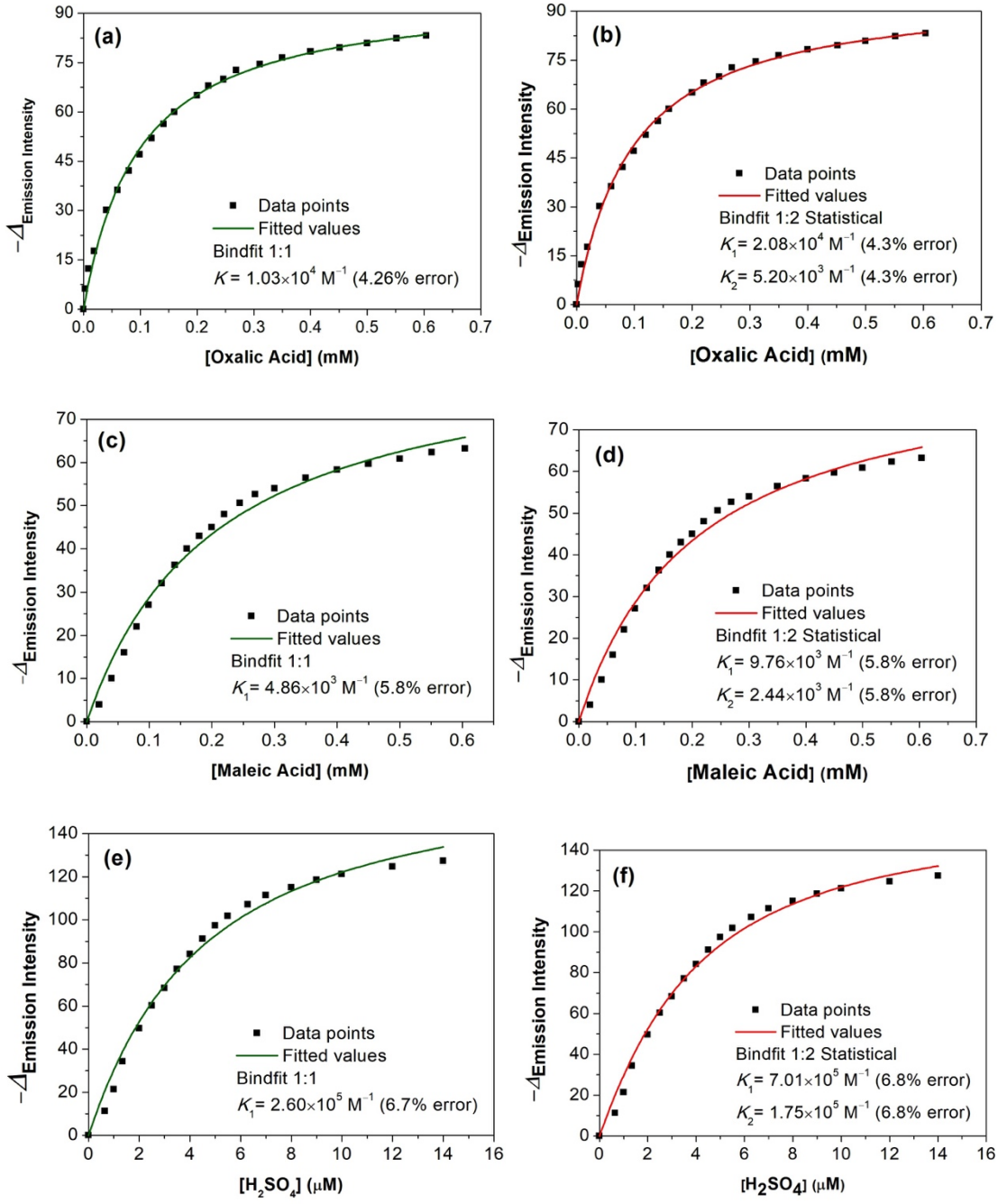


Figure S48. (a–f) Binding isotherms obtained from fluorescence spectroscopic titration results (λ_{ex} = 320 nm, anhydrous THF at 298 K) of host **7•7** with the indicated acids by fitting to standard 1:1 and statistical 1:2 binding equations using BindFit.[S4]

d) Fits of UV–Vis spectroscopic titration data for H_2SO_4

The data from an absorption titration study where H_2SO_4 (1×10^{-5} M host **7•7** solution in THF in a quartz cuvette having 1 cm path length titrated against 10^{-3} M sulfuric acid at constant host concentration) were fitted to standard statistical 1:2 binding profiles using BindFit.[S4] The resulting isotherm is provided below.

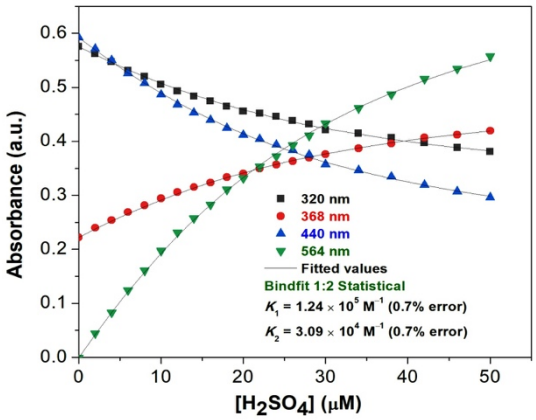


Figure S49. Fittings of UV–Vis spectroscopic titration data of host **7•7** with H_2SO_4 in THF to a statistical 1:2 binding equation using BindFit.[S4]

X-ray crystallographic information

IV) Single crystal X-ray structural analyses of the compounds

X-ray diffraction analysis of single crystals of 3: Yellow block shaped crystals was obtained by vapor diffusion of hexanes into a $CHCl_3$ solution of **3**. The data were collected on a Bruker D8 Venture diffractometer with a PHOTON 100 detector and a μ-focus Cu$K\alpha$ radiation source (λ = 1.5418 Å). The data were collected at 173 K. 9775 frames of data were collected using ϕ- and ω-scans with an oscillation angle of 1°, a scan range of 5.05-68.23°, a exposing time of 1.0 s per frame and a detector distance of 40 mm. Crystallographic data are listed in the **Table S3**. Data were collected using Bruker APEX III software. Unit cell refinement and data reduction were performed using Bruker SAINT V8.37A

software.[S5] The structure was solved by direct methods using SHELXT[S6] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. The hydrogen atoms were calculated in ideal positions with a riding mode.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: **1937460**. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

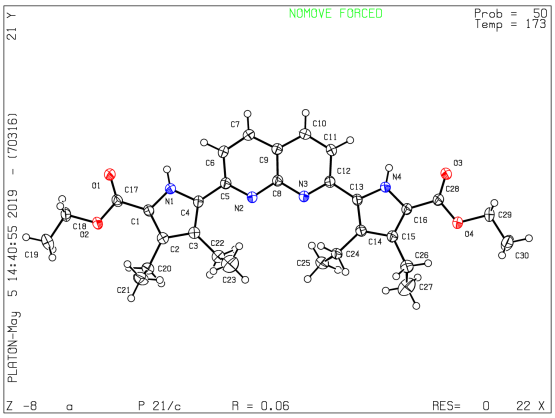


Figure S50. Asymmetric unit of the precursor **3** obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled to the 30% probability level.

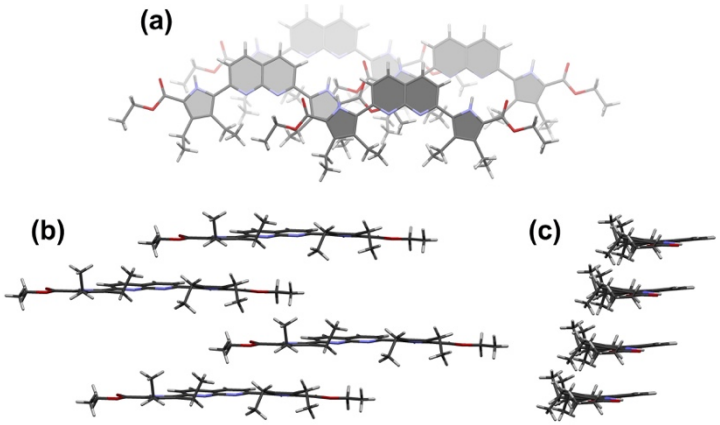


Figure S51. Different views of *J*-type aggregated pattern of precursor **3** obtained from a single crystal X-ray diffraction analysis.

Table S3. Crystallographic data and structure refinement parameters for **3**.

Identification code	**3**
Empirical formula	$C_{30}H_{36}N_4O_4$
Formula weight	516.63
Temperature	173 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 2_1/c
Unit cell dimensions	a = 11.0628(2) Å α = 90°
	b = 26.8155(4) Å β = 98.755(1)°
	c = 9.3804(1) Å γ = 90°
Volume	2750.31(7) Å^3
Z	4
Calculated density	1.248 g/m^3
Absorption coefficient	0.673 mm^{-1}
F(000)	1104
Crystal size	0.200 × 0.180 × 0.150 mm^3
Theta range for data collection	4.043 to 66.578°
Limiting indices	$-13 \le h \le 13, -31 \le k \le 31, -11 \le l \le 11$
Reflections collected/unique	45743 / 4831 [R_{int} = 0.0258]
Completeness to θ = 24.295°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.906 and 0.877
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4831 / 0 / 349
Goodness-of-fit on F^2	1.028
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0619, wR_2 = 0.1635
R indices (all data)	R_1 = 0.0650, wR_2 = 0.1664
Extinction coefficient	n/a
Largest diff. peak and hole	1.301 and -0.485 e·Å^{-3}
CCDC No 1937460	

X-ray diffraction analysis of single crystals of [7•7(CHCl$_3$)$_4$]: Yellow rod shaped crystals were obtained by vapor diffusion of petroleum ether into a chloroform solution of **7**. The data were collected on an X-ray diffractometer Bruker/ARINAX MD2 equipped with a MarCCD-300 detector (λ = 0.68875 Å), at beam line station BL17B of Shanghai Synchrotron Radiation Facility (SSRF). Suitable single crystals were mounted

on a Nylon loop with the protection of Paratone-N oil for diffraction at 100 K. 360 frames of data were collected using ω-scans with an oscillation angle of 1°, a scan range of 0.00-361.00°, a exposing time of 1.0 s per frame and a detector distance of 90 mm. Crystallographic data are listed in the **Table S4**. Data were collected using BlueIce software package.[S7] Unit cell refinement and data reduction were performed using HKL3000 software package.[S8] The structure was solved by direct methods using SHELXT[S6] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. The hydrogen atoms were calculated in ideal positions with a riding mode.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: **1937464**. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

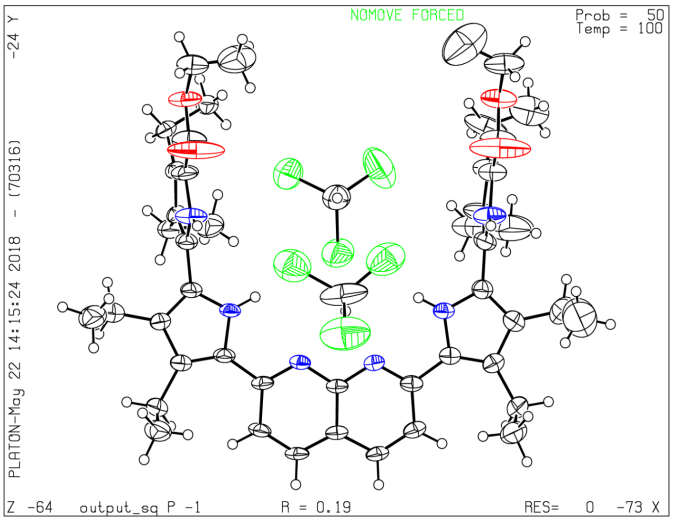


Figure S52. Asymmetric unit of [**7**•**7**$(CHCl_3)_4$], obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled to the 30% probability level.

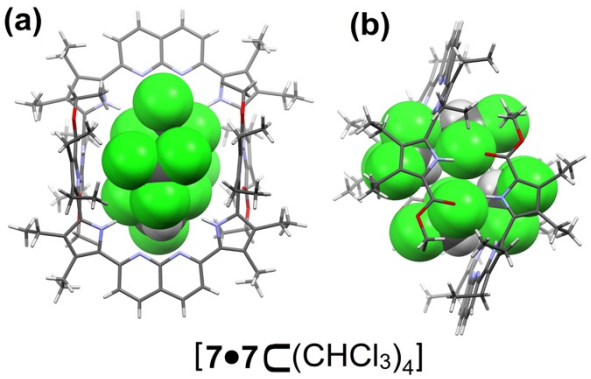


Figure S53. Single crystal X-ray structure of [**7•7**$(CHCl_3)_4$] showing four encapsulated solvent ($CHCl_3$) molecules inside the capsule.

Table S4. Crystallographic data and structure refinement parameters for [**7•7**$(CHCl_3)_4$].

Identification code	**7•7**$(CHCl_3)_4$
Empirical formula	$C_{48}H_{57}Cl_6N_{12}O_4$
Formula weight	994.69
Temperature	100(2) K
Wavelength	0.68875 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.130(2) Å α = 78.46(3)°
	b = 14.831(3) Å β = 88.91(3)°
	c = 16.344(3) Å γ = 69.37(3)°
Volume	2691.9(10) Å^3
Z	2
Calculated density	1.227 g/m^3
Absorption coefficient	0.336 mm^{-1}
F(000)	1042
Crystal size	0.300 × 0.120 × 0.030 mm^3
Theta range for data collection	1.701 to 24.295°
Limiting indices	$0 \le h \le 7$, $-17 \le k \le 21$, $-23 \le l \le 23$
Reflections collected/unique	8980 / 8980 [R_{int} = 0.00]
Completeness to θ = 24.295°	93.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.990 and 0.906
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8980 / 15 / 587
Goodness-of-fit on F^2	1.016

Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.1903$, $wR_2 = 0.3995$
R indices (all data)	$R_1 = 0.2016$, $wR_2 = 0.4041$
Extinction coefficient	0.084(10)
Largest diff. peak and hole	1.667 and -1.235 e.Å^{-3}
CCDC No 1937464	

X-ray diffraction analysis of single crystals of [(**7**•**7**H_2)$^{2+}$⊂(Hmaleate$^-$)$_2$]. Single crystals grew as yellow rods by vapor diffusion of hexanes into a THF solution containing **7** and maleic acid. The data were collected on a Bruker D8 QUEST diffractometer using a μ-focus Cu$K\alpha$ radiation source (λ = 1.5418 Å) with collimating mirror monochromators. The data were collected at 150 K. 720 frames of data were collected using ϕ- and ω-scans with an oscillation angle of 1°, a scan range of 2.74–67.06°, a exposing time of 1.0 s per frame and a detector distance of 45 mm. Crystallographic data are listed in the **Table S5**. Data were collected using Bruker APEX III software. Unit cell refinement and data reduction were performed using SAINT V8.378A software.[S5] The structure was solved by direct methods using SHELXT[S6] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. The hydrogen atoms were calculated in ideal positions with a riding mode. SQUEEZE routine was applied by using PLATON[S9] for some electron densities which could not reasonably modeled.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: **1951164**. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

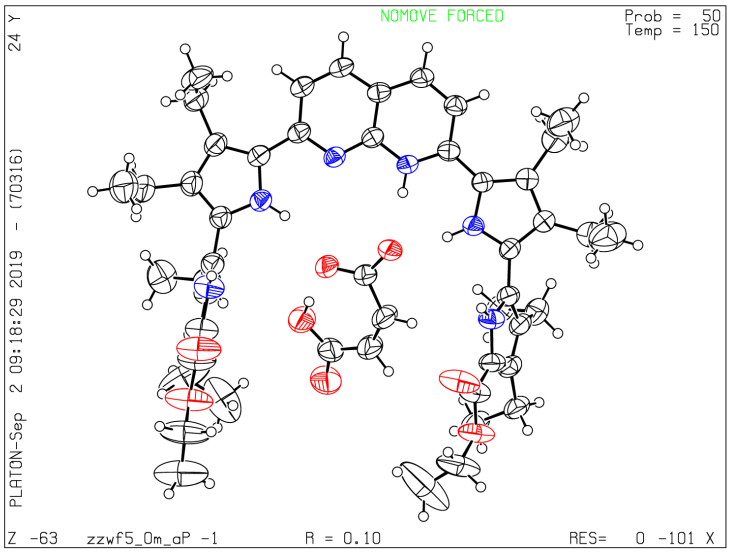


Figure S54. Asymmetric unit of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset(\text{Hmaleate}^-)_2]$, obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled to the 30% probability level.

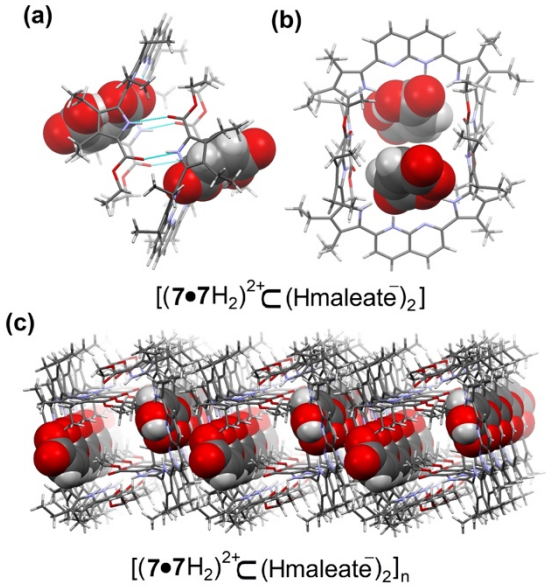


Figure S55. (a,b) The single crystal X-ray structure of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset(\text{Hmaleate}^-)_2]$ showing two encapsulated maleate anions inside the capsule. (c) 3D view of Hmaleate guests inside the infinite channel of capsules.

Table S5. Crystallographic data and structure refinement parameters for $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset(Hmaleate^{-})_2]$ supramolecular ensemble.

Identification code	**7**•**7**(maleic acid)$_2$
Empirical formula	$C_{50}H_{62}N_6O_8$
Formula weight	875.05
Temperature	150(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.8492(11) Å α = 102.285(4)°
	b = 14.4967(12) Å β = 91.716(4)°
	c = 16.6539(14) Å γ = 112.279(4)°
Volume	2783.8(4) Å^3
Z	2
Calculated density	1.044 g/m^3
Absorption coefficient	0.575 mm^{-1}
F(000)	936
Crystal size	0.118 × 0.113 × 0.098 mm^3
Theta range for data collection	2.736 to 67.062°
Limiting indices	$-15 \le h \le 15$, $-17 \le k \le 16$, $-19 \le l \le 19$
Reflections collected/unique	84912 / 9833 [R_{int} = 0.1073]
Completeness to θ = 67.684°	98.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.946 and 0.935
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9833 / 2 / 589
Goodness-of-fit on F^2	1.078
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0963, wR_2 = 0.2107
R indices (all data)	R_1 = 0.1597, wR_2 = 0.2422
Extinction coefficient	0.00151(14)
Largest diff. peak and hole	0.790 and -0.469 e·Å^{-3}
CCDC No 1951164	

X-ray diffraction analysis of single crystals of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset\{(Hoxalate^{-})_2(THF)_2\}]$: Red needle like crystals were grown by vapor diffusion of hexanes into a THF solution containing **7** and oxalic acid. The data were collected on the same

diffractometer as $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset(Hmaleate^{-})_2]$ with the same radiation source. The strategy for collection was also the same except that a scan range of 2.70–67.07° and a exposing time of 3.0 s per frame. Crystallographic data are listed in the **Table S6**. Data were collected using Bruker APEX III software. Unit cell refinement and data reduction were performed using SAINT V8.38A software.[S5] The structure was solved by direct methods using SHELXT[S6] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. The hydrogen atoms were calculated in ideal positions with a riding mode. SQUEEZE routine was applied by using PLATON[S9] for some electron densities which could not reasonably modeled.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: **1951162**. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

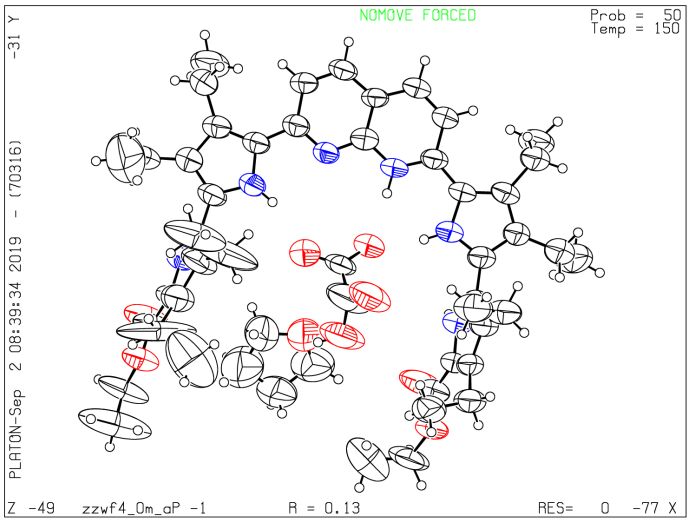


Figure S56. Asymmetric unit of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset\{(Hoxalate^{-})_2(THF)_2\}]$ obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled to the 30% probability level.

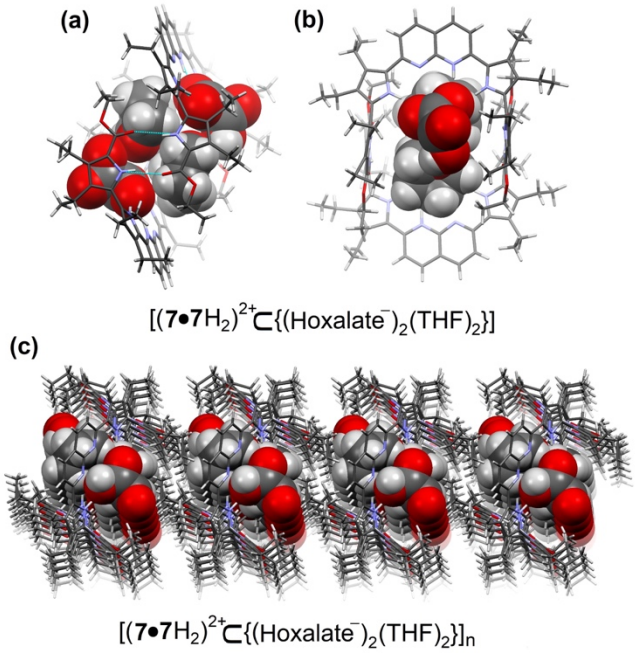


Figure S57. (a,b) Single crystal X-ray structure of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset\{(Hoxalate^{-})_2(THF)_2\}]$, showing two encapsulated oxalate anions along with two solvent (THF) molecules inside the capsule. (c) 3D view of guests inside the infinite channel made up of capsules **7•7**.

Table S6. Crystallographic data and structure refinement parameters for $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset\{(Hoxalate^{-})_2(THF)_2\}]$ supramolecular ensemble.

Identification code	**7•7**(oxalic acid)$_2$(THF)$_2$	
Empirical formula	$C_{52}H_{68}N_6O_9$	
Formula weight	921.12	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.0076(6) Å	α = 73.739(2)°
	b = 14.8684(7) Å	β = 86.373(3)°
	c = 17.0843(8) Å	γ = 68.275(2)°
Volume	2717.3(2) Å^3	
Z	2	
Calculated density	1.126 g/m^3	
Absorption coefficient	0.625 mm^{-1}	
F(000)	988	
Crystal size	0.224 × 0.092 × 0.091 mm^3	
Theta range for data collection	2.697 to 67.075°	

Limiting indices	$-14 \le h \le 14$, $-17 \le k \le 17$, $-20 \le l \le 20$
Reflections collected/unique	103564 / 9699 [R_{int} = 0.2760]
Completeness to θ = 67.054°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.945 and 0.873
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9699 / 25 / 617
Goodness-of-fit on F^2	1.003
Final R indices [$I>2\sigma(I)$]	R_1 = 0.1250, wR_2 = 0.2221
R indices (all data)	R_1 = 0.2511, wR_2 = 0.2804
Extinction coefficient	0.00092(7)
Largest diff. peak and hole	0.762 and -0.395 e·Å^{-3}
CCDC No 1951162	

X-ray diffraction analysis of single crystals of [(**7**•**7**H_2)$^{2+}$⊂{(Hmalonate$^-$)$_2$(THF)$_2$}]. Single crystals grew as yellow rods by vapor diffusion of hexanes into a THF solution containing **7** and malonic acid. The data were collected on a Rigaku XtaLAB AFC12 diffractometer with a μ-focus Cu$K\alpha$ radiation source (λ = 1.5418 Å) and a Kappa goniometer. The data were collected at 173 K. 3357 frames of data were collected using ϕ- and ω-scans with an oscillation angle of 1º, a scan range of 3.60–67.06º, a exposing time of 1.0 s per frame and a detector distance of 60 mm. Crystallographic data are listed in the **Table S7**. Data were collected using CrysAlisPro 1.171.39.32a software.[S10] Unit cell refinement and data reduction were performed using the same software. The structure was solved by direct methods using SHELXT[S6] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. The hydrogen atoms were calculated in ideal positions with a riding mode.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: **1951163**. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

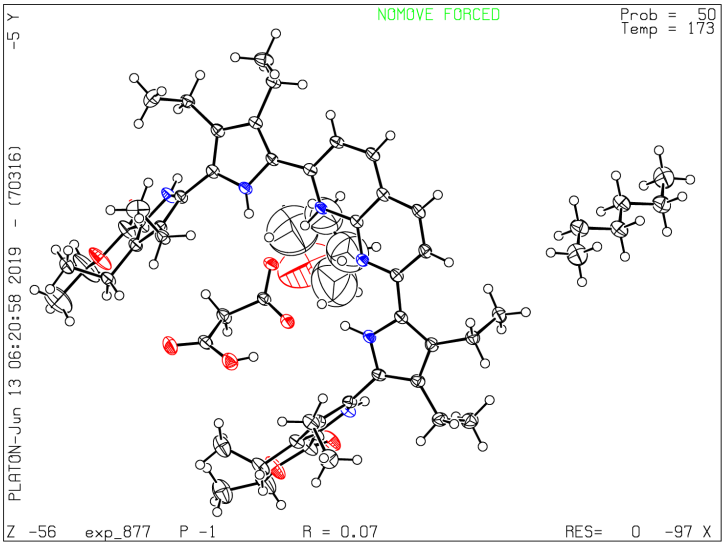


Figure S58. Asymmetric unit of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset\{(Hmalonate^{-})_2(THF)_2\}]$ obtained from the single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled to the 30% probability level.

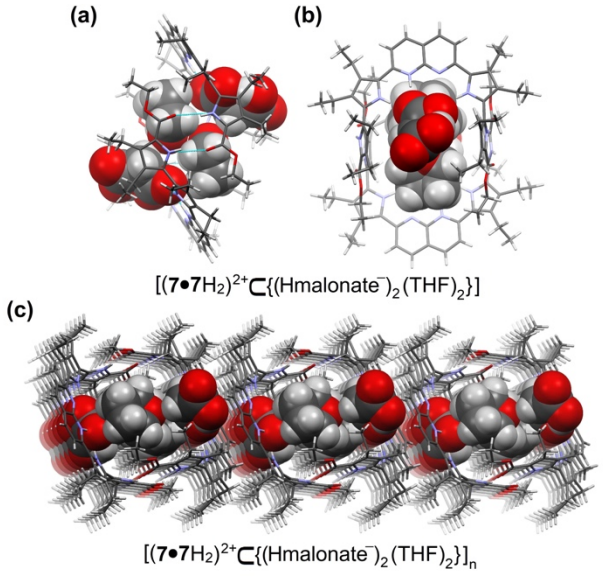


Figure S59. (a,b) Single crystal X-ray structure of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset\{(Hmalonate^{-})_2(THF)_2\}]$, showing two encapsulated oxalate anions along with two solvent (THF) molecules inside capsule **7•7**. (c) 3D view of the guests inside the infinite channel formed from capsules **7•7**.

Table S7. Crystallographic data and structure refinement parameters for $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset\{(Hmalonate^-)_2(THF)_2\}]$.

Identification code	**7•7**(malonic acid)$_2$(THF)$_2$
Empirical formula	$C_{56}H_{77}N_6O_9$
Formula weight	978.23
Temperature	173(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.7856(2) Å α = 68.685(2)^o
	b = 15.0499(4) Å β = 71.465(3)^o
	c = 17.5779(4) Å γ = 71.534(2)^o
Volume	2681.50(12) Å^3
Z	2
Calculated density	1.212 g/m^3
Absorption coefficient	0.661 mm^{-1}
F(000)	1054
Crystal size	0.200 × 0.080 × 0.080 mm^3
Theta range for data collection	3.595 to 67.064°
Limiting indices	$-14 \le h \le 14$, $-17 \le k \le 17$, $-20 \le l \le 20$
Reflections collected/unique	63220 / 9511 [R_{int} = 0.0665]
Completeness to θ = 67.064°	99.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.72442
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9511 / 40 / 654
Goodness-of-fit on F^2	1.037
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0725, wR_2 = 0.1925
R indices (all data)	R_1 = 0.0844, wR_2 = 0.2013
Extinction coefficient	n/a
Largest diff. peak and hole	1.362 and -0.733 e·Å^{-3}
CCDC No 1951163	

X-ray diffraction analysis of single crystals of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset(HSO_4^-)_2]$: A single crystal suitable for X-ray analysis was grown from a THF solution of capsule **7•7** in the presence of 100 equiv of H_2SO_4, slowly diffused with hexanes. Deep red rod-shaped crystals appeared after approximately seven days. The data were collected on a Bruker

D8 Venture diffractometer with a METALJET Ga$K\alpha$ radiation source (λ = 1.3414 Å). The data were collected at 213 K. The data were collected using ϕ- and ω-scans with a scan range of 2.71–52.99° and an exposing time of 3 s per frame. Crystallographic data are listed in the **Table S8**. Data were collected using Bruker APEX III software. Unit cell refinement and data reduction were performed using SAINT V8.378A software.[S5] The structure was solved by direct methods using SHELXT[S6] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. The hydrogen atoms were calculated in ideal positions with a riding mode. SQUEEZE routine was applied by using PLATON[S9] for some electron densities which could not reasonably modeled.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: **1951161**. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

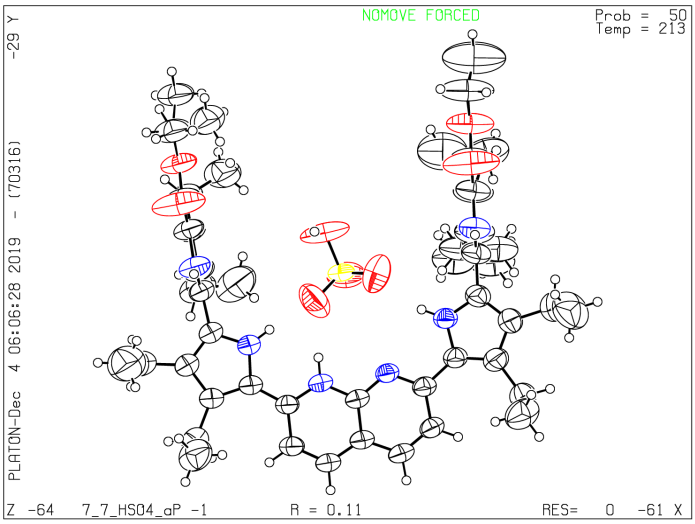


Figure S60. Asymmetric unit of $[(\mathbf{7}\bullet 7H_2)^{2+}\subset(HSO_4^-)_2]$ obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled to the 30% probability level.

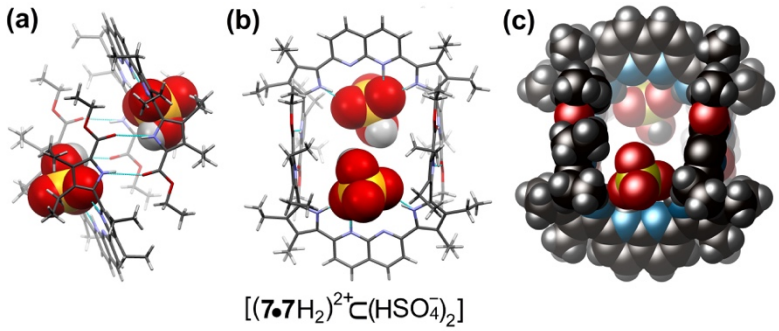


Figure S61. (a,b) Two different views of the single crystal X-ray structure of $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset(HSO_4^-)_2]$, showing two encapsulated sulfate anions inside the capsule. (c) The space-filling model of encapsulated guests inside the capsule.

Table S8. Crystallographic data and structure refinement parameters for $[(\mathbf{7}\bullet\mathbf{7}H_2)^{2+}\subset(HSO_4^-)_2]$.

Identification code	$\mathbf{7}\bullet\mathbf{7}(H_2SO_4)_2$
Empirical formula	$C_{46}H_{58}N_6O_8S$
Formula weight	855.04
Temperature	213(2) K
Wavelength	1.34139 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.9458(5) Å α = 76.623(2)°
	b = 15.1939(5) Å β = 88.347(2)°
	c = 16.5538(6) Å γ = 73.614(2)°
Volume	2802.19(18) Å^3
Z	2
Calculated density	1.013 g/m^3
Absorption coefficient	0.583 mm^{-1}
F(000)	912
Crystal size	0.160 × 0.110 × 0.090 mm^3
Theta range for data collection	2.712 to 52.990°
Limiting indices	$-14 \le h \le 14$, $-18 \le k \le 15$, $-19 \le l \le 19$
Reflections collected	37633
Independent reflections	9864 [R_{int} = 0.0560]
Completeness to θ = 52.990°	99.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.872442
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9864 / 495 / 529

Goodness-of-fit on F^2	1.077
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.1152$, $wR_2 = 0.2274$
R indices (all data)	$R_1 = 0.1592$, $wR_2 = 0.2482$
Extinction coefficient	n/a
Largest diff. peak and hole	0.839 and -0.693 e·Å^{-3}
CCDC No 1951161	

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