Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Binding Properties and Supramolecular Polymerization of a Water-Soluble Resorcin[4]arene

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2 Experimental Section

2.1 General Information

2.1.1 Materials and Instrumentation

Reagents were purchased from commercial suppliers Sigma-Aldrich Corp. or TCI America and were used without further purification. All sodium salts were of purity ≥98% and were used as received. All solvents were purchased from Fisher Scientific, or VWR and were used as received. ^{1}H NMR spectra were collected on a Bruker 300 MHz, Bruker 500 MHz or Varian 400 MHz spectrometer at 25 ˚C. All ^{13}C NMR spectra were collected on a Bruker 300 MHz (75 MHz ^{13}C) at 25 ˚C. All spectra utilized deuterated solvents as described for the individual experiments (Cambridge Isotopes, 99.9%+) and changes in chemical shift (Δδ) were referenced to the residual solvent signal. Spectral processing was performed using MestReNova software (Mestrelab Research, S.L.) with results for complexation models fitted using either the online software BINDFIT[1] or Microsoft Excel. MALDI-MS and ESI-MS spectra were collected using a Bruker Autoflex III MALDI-TOF mass spectrometer and a Bruker microTOF mass spectrometer, respectively. Dynamic light scattering (DLS) measurements were performed on a Nicomp ZLS Z3000 particle size analyzer (Particle Sizing Systems—Port Richey, FL) with a 50 mW laser diode (660 nm wavelength) and an avalanche photodiode (APD) detector. Measurements of scattered light were made at 90˚, with data collected at 23 ˚C and processed using a non-negative least squares Nicomp analysis

2.1.2 NMR solution sample preparation

For resorcinarene **1** solutions for titrations of host with guest were prepared at either 0.5 mM or 1.0 mM with an initial volume of 0.6 mL. The concentration of the solution was confirmed by titration in triplicate with separate solutions of sodium ethanesulfonate (SES, 30 mM). Integration of the methyl peak of SES and the H_l, and H_m methylene of the host gave the

concentration of the host and hence the number of waters of crystallization. For organic guests, concentrated guest solutions were prepared and titrated as per the procedure for the hosts. Solutions of organic cation guest were prepared between 30–100 mM. Solutions of hosts and guests prepared in D_2O or other (unbuffered) deuterated solvents were uncorrected. and the concentration confirmed by titration with SES. For titrations involving incrementally increasing the host concentration, a 0.25 mM host solution was titrated with a concentrated stock of host solution prepared at 25 mM. The stock solution was prepared by mass and the molecular weight of **1** was determined by titration with SES.

2.1.3 DLS solution preparation procedures

All solutions were prepared using 18.2 MΩ·cm H_2O, in 40 mM phosphate buffer pH 7.35 ± 0.05, 40 mM phosphate buffer pH 3.05 ± 0.05, or 100 mM NaCl. All host solutions were prepared at a concentration of 25.0 mM and solutions of **1** were diluted serially by ½ with their respective buffers until reaching a final concentration of 0.781 mM. Samples were centrifuged for 10 minutes at 10,000 rpm prior to each titration but not centrifuged thereafter. Solutions of host were diluted, then shaken and vortexed to ensure mixing before acquiring DLS measurements. All analyses were performed in duplicate at a channel width of 1 μs; the data presented herein is representative of one data set. Results shown (diameter) are representative of the volume-weighted distribution. Surface plots of the raw, volume-weighted hydrodynamic diameter distribution data were plotted using OriginPro software.

2.1.4 ESI-MS sample procedure

All samples were prepared as 10–100 μM concentration solutions in distilled H_2O (dH_2O), 18.2 MΩ·cm H_2O, or HPLC grade Methanol (MeOH). ESI-MS spectra acquisitions were acquired

using a Bruker microTOF mass spectrometer in positive mode and averaged from 1.0–10.0 minutes. Ions were continuously generated by infusing the solution samples into the source with a syringe pump at flow rates of 6 μL/min. The parameters were adjusted and are typically as follows for negative mode: capillary voltage (–4.1 kV); capillary exit voltage (70 V); skimmer voltage (40 V); drying gas temperature (200 °C). The experiments were carried out with a nebulizer gas pressure of 0.3 Bar and a drying gas flow of 4.0 L/min.

2.1.5 MALDI-TOF sample procedure

All samples were prepared using the dried-droplet method with a mix ratio of matrix-analyte-salt of 2:1:1 as 2.0–2.5 μL droplet. The matrix utilized was α-cyano-4-hydroxycinnamic acid (α-cyano, 10 mg · mL^{-1} in acetone). The salts used were silver trifluoroacetate or sodium trifluoroacetate (1 mg · mL^{-1} in THF). Analytes were prepared as ~2.0 mM solutions in MeOH.

2.1.6 Errors

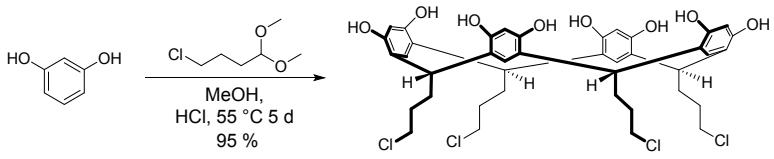
Results are expressed as the average when possible with the coefficient of variation (CV) expressed as a percentage of the mean when applicable, where s is the sample standard deviation and μ is the sample mean:

$$CV\% = \frac{s}{\mu} \times 100 \qquad \text{Eq. S1}$$

2.2 Experimental procedures

All reactions were performed under a nitrogen atmosphere (balloon) and reaction temperatures were monitored by monitoring the temperature of the oil bath. The synthesis of known compound **2** is an improvement upon a literature protocol reported previously.[2]

2.2.1 Synthesis of tetrachloro resorcinarene **2**.



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Resorcinol (20.0 g, 182 mmol) was added to 120 mL of methanol and 30 mL of 36% HCl at 0 °C (ice bath). To the stirred solution was added 28 mL (191 mmol) of 4-chlorobutanal dimethyl acetal dropwise over 20 minutes (syringe pump). The solution was then stirred for 30 min. at 0°C, before being slowly warmed to rt and then heated to 60 °C. After a few hours the solution turned red, and within 6-12 h a precipitate formed. The reaction was left for 4 d from when a significant amount of precipitate was apparent.

The solution was cooled to room temperature and filtered and rinsed once with EtOH/Water (1:1, ~50 mL). The solids were then taken up in water (300 mL) and sonicated and then filtered and washing repeated until the filtrate pH >6. The resulting cream-colored solid was dried under reduced pressure at rt overnight and then at 110 °C overnight to give 31.1 g of pure **2** as a slightly yellow powder (95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 (s, 8H), 6.91 (s, 4H), 6.14 (s, 4H), 4.31 (t, J = 7.8 Hz, 4H), 3.56 (t, J = 6.7 Hz, 8H), 1.94 (m, 8H), 1.54 (m, 8H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 152.71, 125.73, 122.38, 102.78, 45.90, 32.97, 32.63, 31.43. *MALDI-TOF MS* m/z: $[M+Ag]^+$ Calcd for $C_{40}H_{44}Cl_4O_8$ 899.08; Found 899.05. Anal. Calcd for $C_{40}H_{44}Cl_4O_8 \cdot 2H_2O$: C, 57.84; H, 5.83. Found: C, 57.99; H, 5.81.

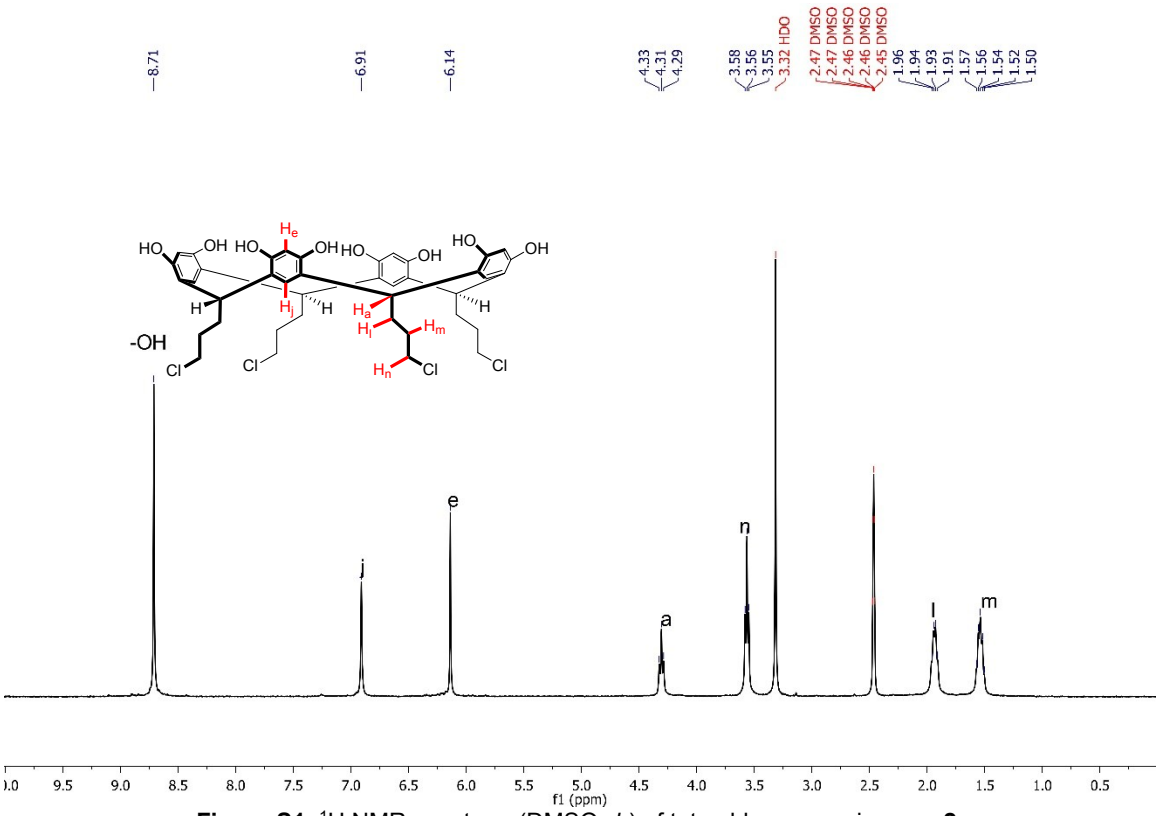


Figure S1. ^{1}H NMR spectrum (DMSO-d_6) of tetrachloro resorcinarene **2**.

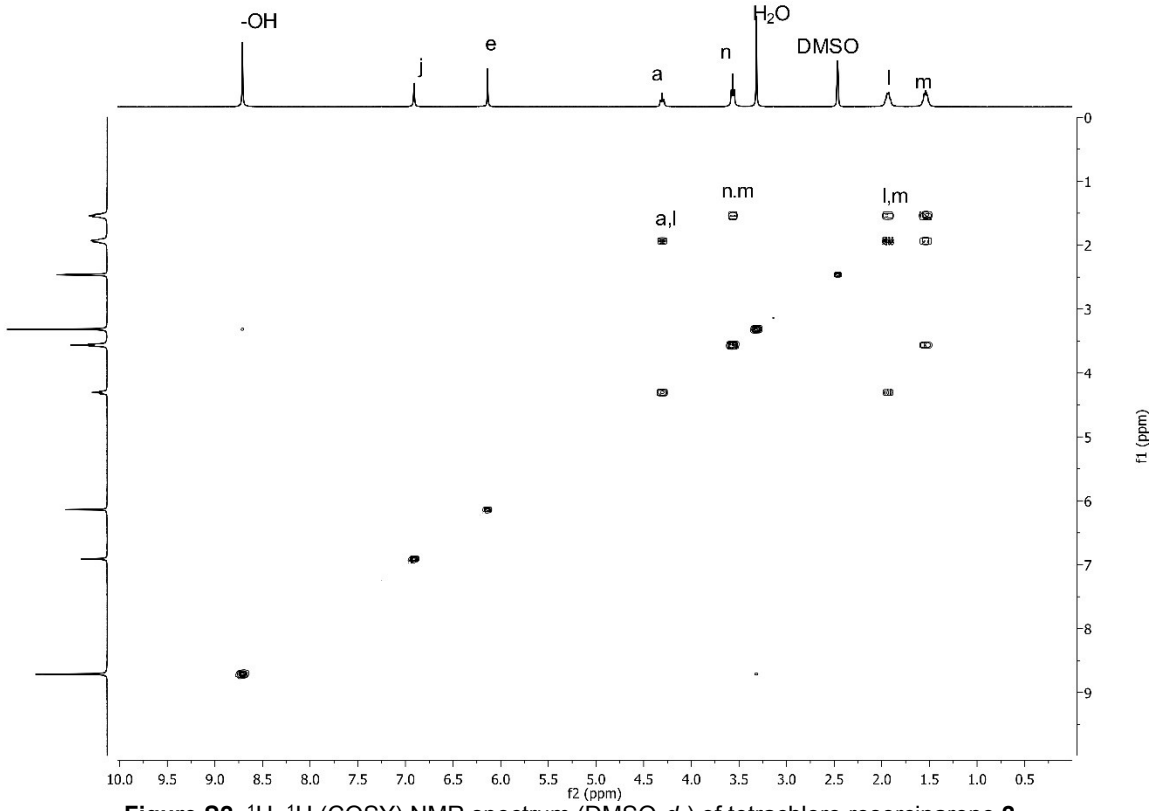


Figure S2. ^{1}H–^{1}H (COSY) NMR spectrum (DMSO-d_6) of tetrachloro resorcinarene **2.**

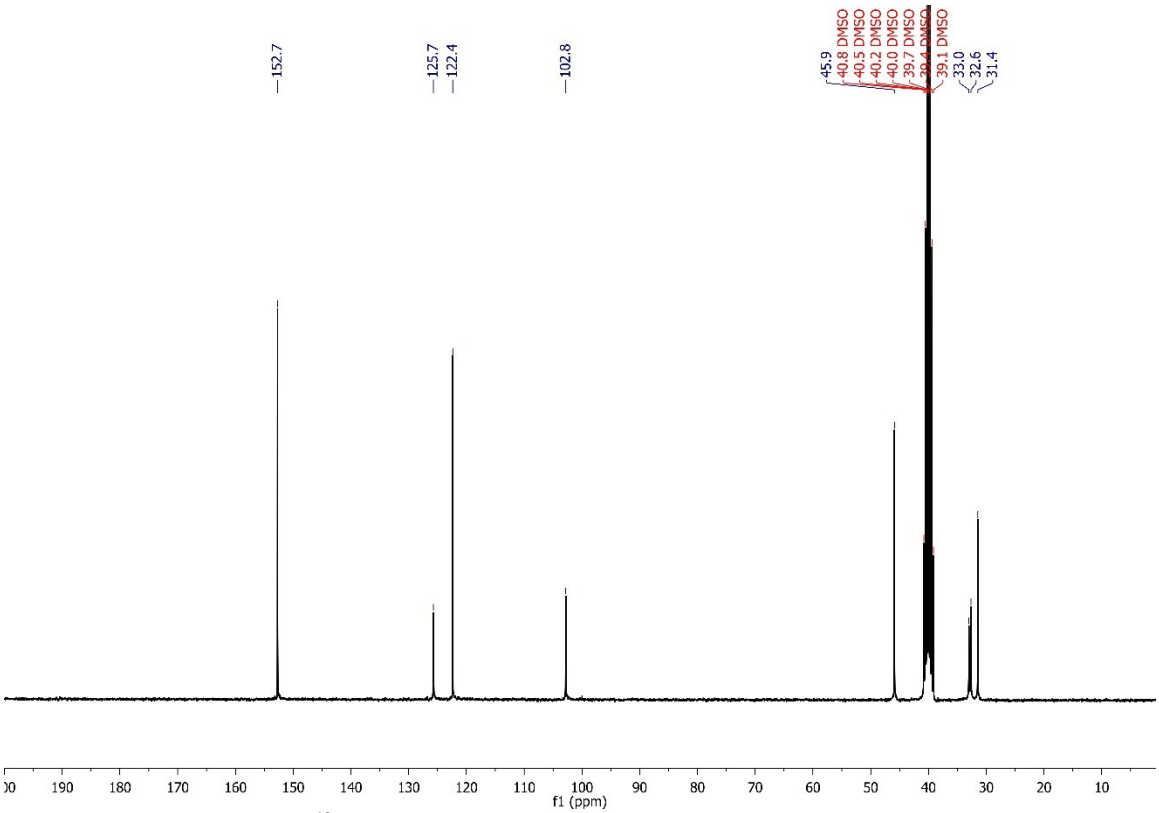


Figure S3. ^{13}C NMR spectrum (DMSO-d_6) of tetrachloro resorcinarene **2.**

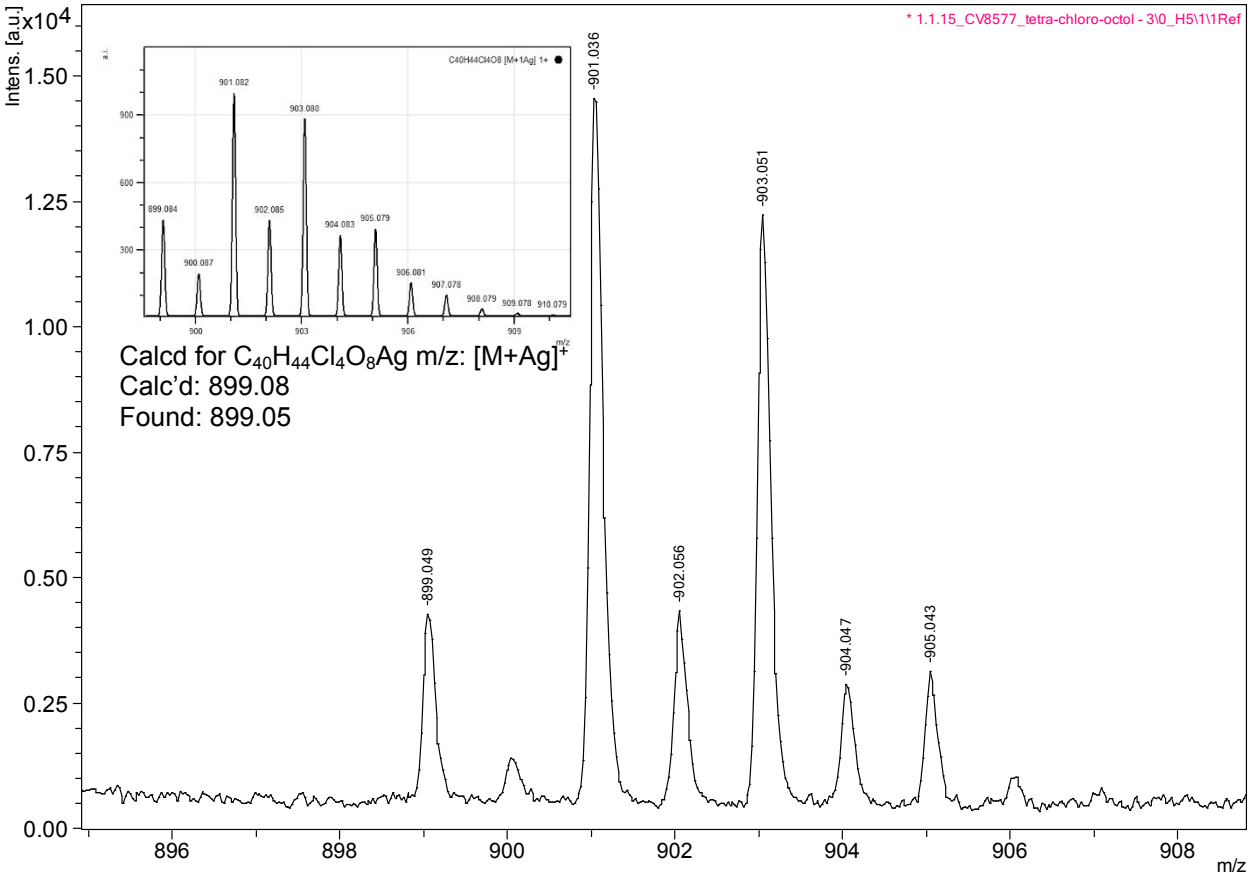


Figure S4. MALDI-TOF of tetrachloro cavitand **2** (X = Cl), $[M+Ag]^+$, with theoretical calculation inset

2.2.2 Synthesis of tetrakis(pyridinium) octol **1**

Resorcinarene **2** (1.0 g, 1.26 mmol) was added to a 100 mL RBF. To this was added 50 mL of pyridine and the solution heated to 80 °C for 3 d. After, the reaction was cooled to rt and poured over Et_2O (200 mL). The white precipitate was collected by filtration and washed with additional Et_2O (3 × 50 mL). The solids were taken up in EtOH (20 mL) and the suspension brought to reflux, cooled, filtered and washed with cold EtOH (2 × 25 mL) to afford 1.33 g of **1** as an off-white solid (92%). ^{1}H NMR (500 MHz, D_2O) δ 8.72 (d, *J* = 6.3 Hz, 8H), 8.45 (t, *J* = 8.0 Hz, 4H), 7.95 (t, *J* = 7.2 Hz, 8H), 6.65 (s, 4H), 6.23 (s, 4H), 4.57 (t, *J* = 7.4 Hz, 8H), 4.27 (t, *J* = 7.8 Hz, 4H), 2.15 – 1.74 (m, 16H). ^{13}C NMR (75 MHz, D_2O) δ 151.99, 145.42, 143.94, 128.08, 125.90, 123.00, 102.65, 61.26, 33.00, 30.44, 28.61. HRMS (ESI) m/z: $[M-4Cl-H]^{3+}$ Calcd for $C_{60}H_{63}N_4O_8$ 322.4876; Found 322.4892. $[M-3Cl]^{3+}$ Calcd for $C_{60}H_{64}N_4O_8Cl$ 334.4799; Found 334.4810.

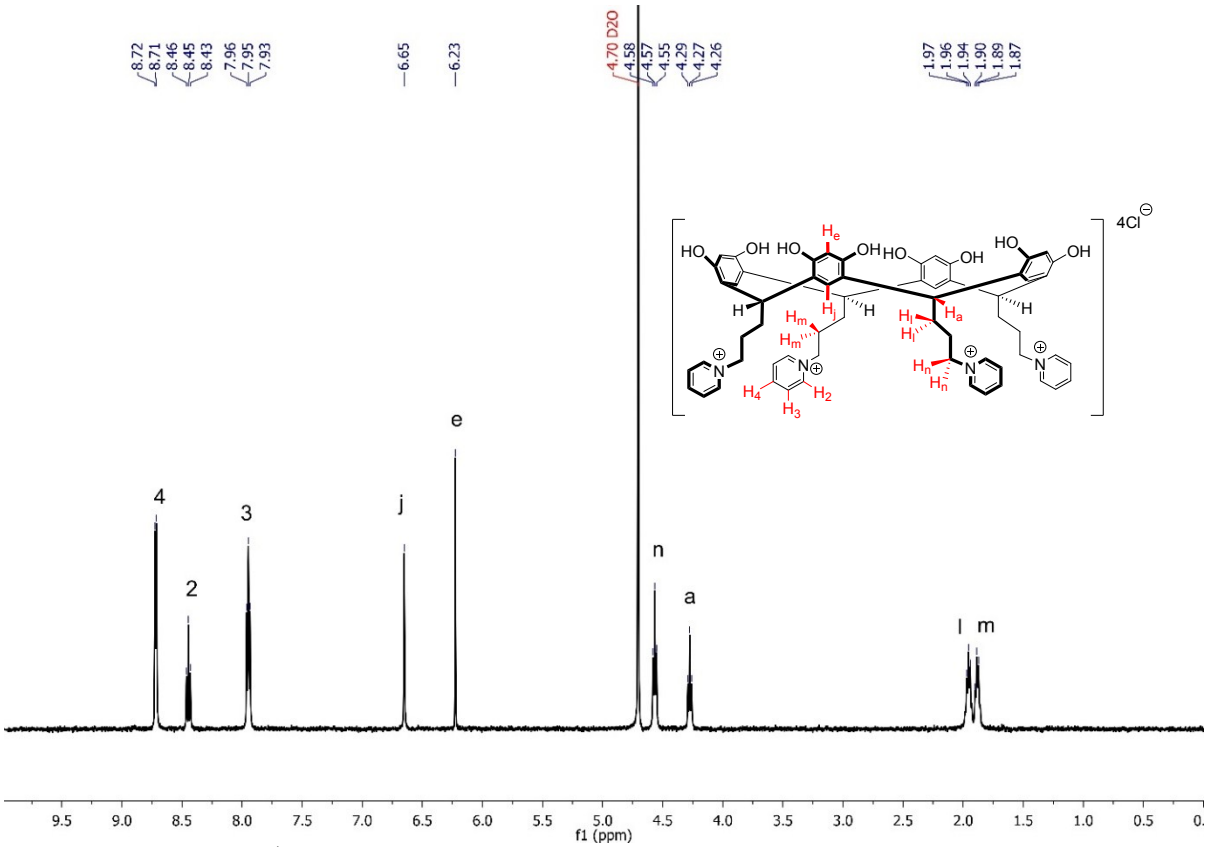


Figure S5. ^{1}H NMR spectrum (500 MHz, D_2O) of tetrakis(pyridinium) resorcinarene **1**.

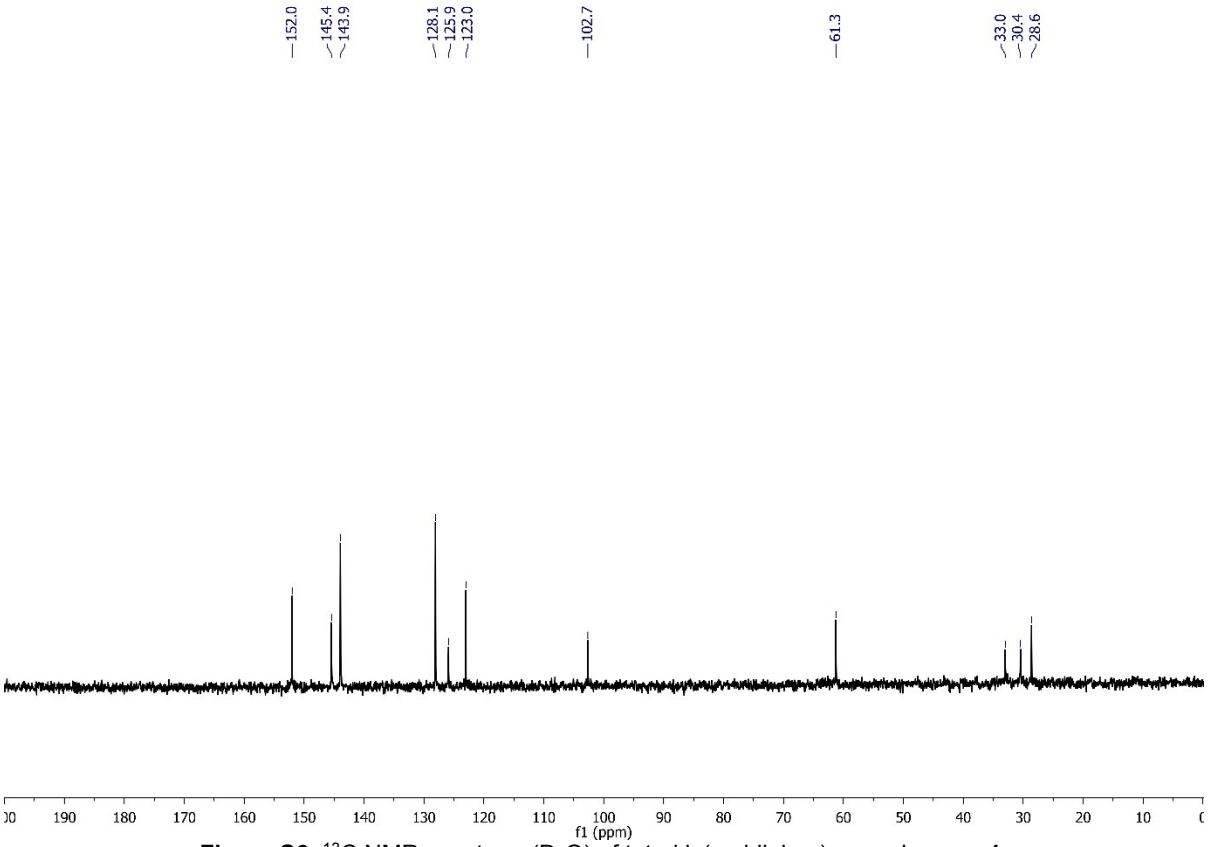


Figure S6. ^{13}C NMR spectrum (D_2O) of tetrakis(pyridinium) resorcinarene **1**.

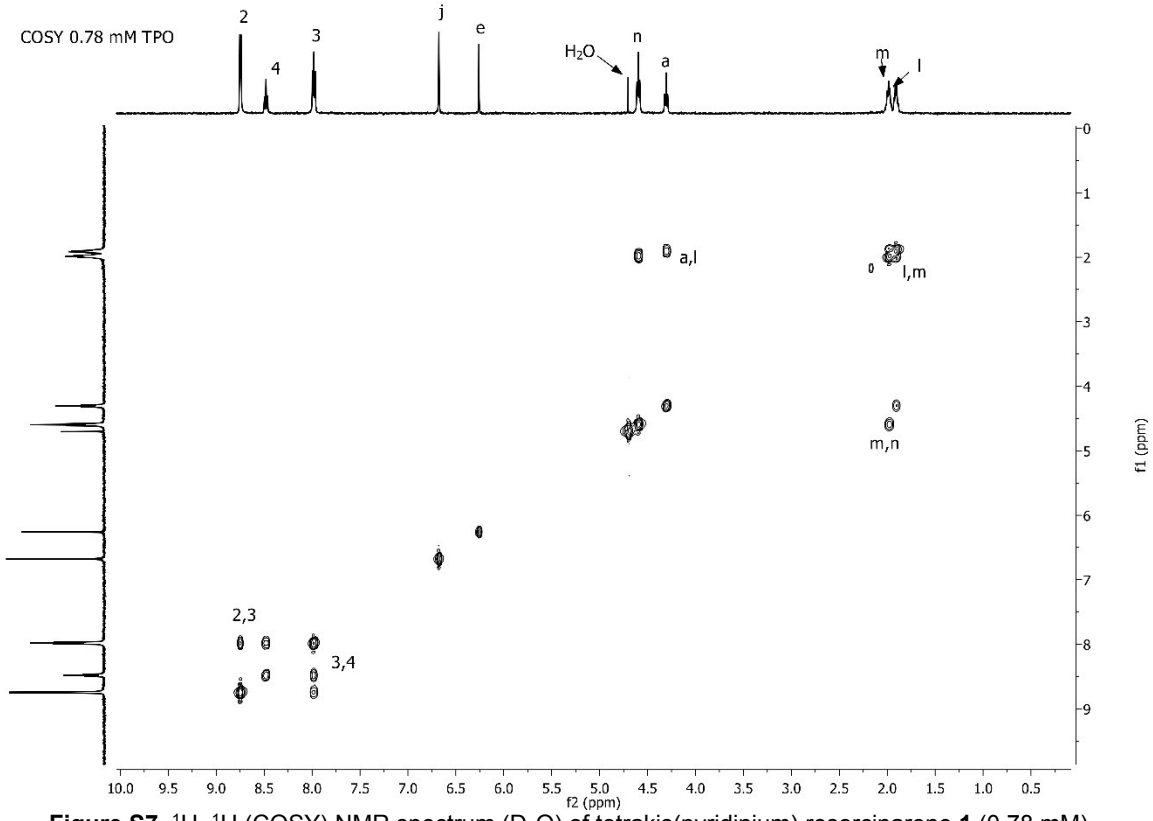


Figure S7. $^{1}H–^{1}H$ (COSY) NMR spectrum (D_2O) of tetrakis(pyridinium) resorcinarene **1** (0.78 mM).

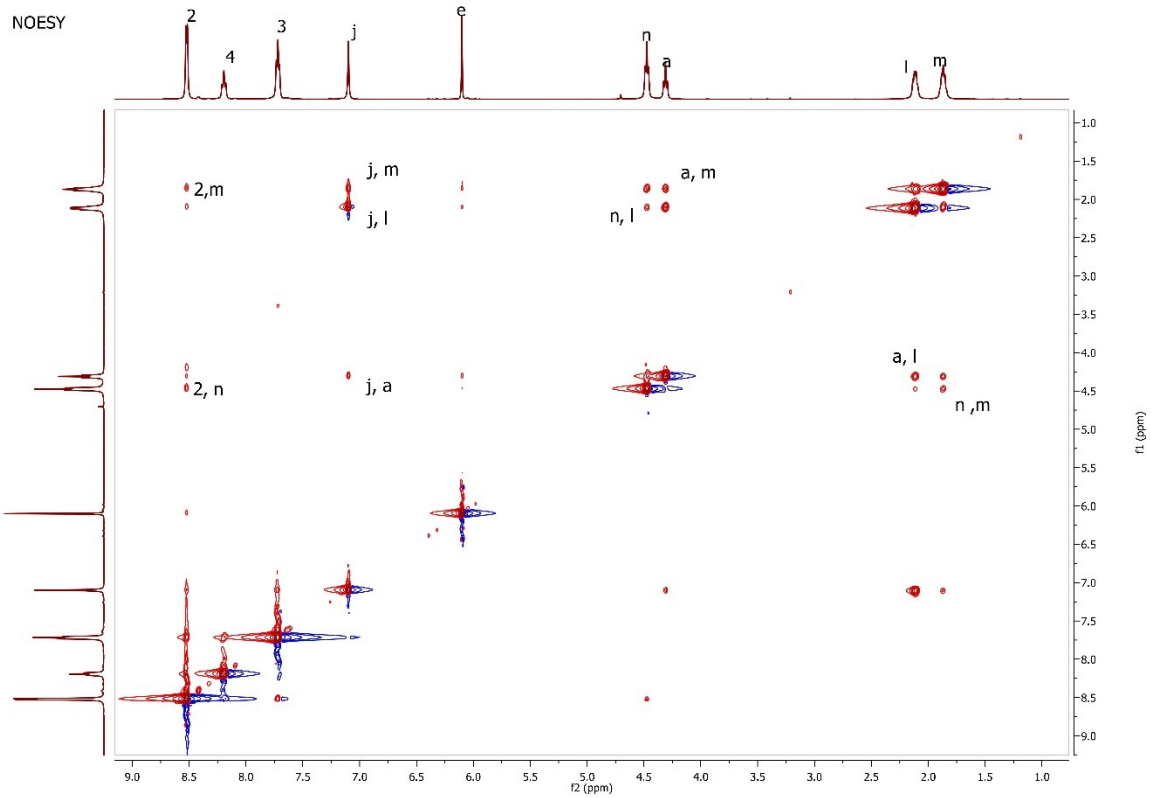


Figure S8. $^{1}H–^{1}H$ (NOESY) NMR spectrum (D_2O) of tetrakis(pyridinium) resorcinarene **1** (25 mM).

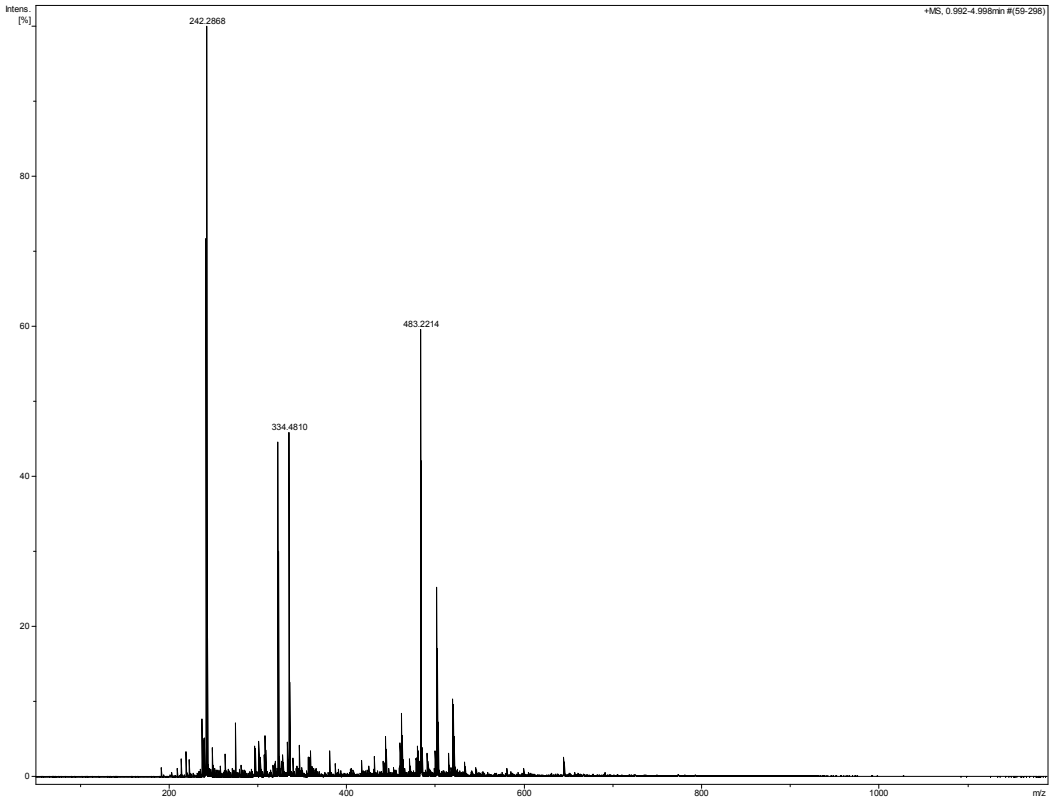


Figure S9. ESI-MS of tetrakis(pyridinium) resorcinarene **1** (100 μM).

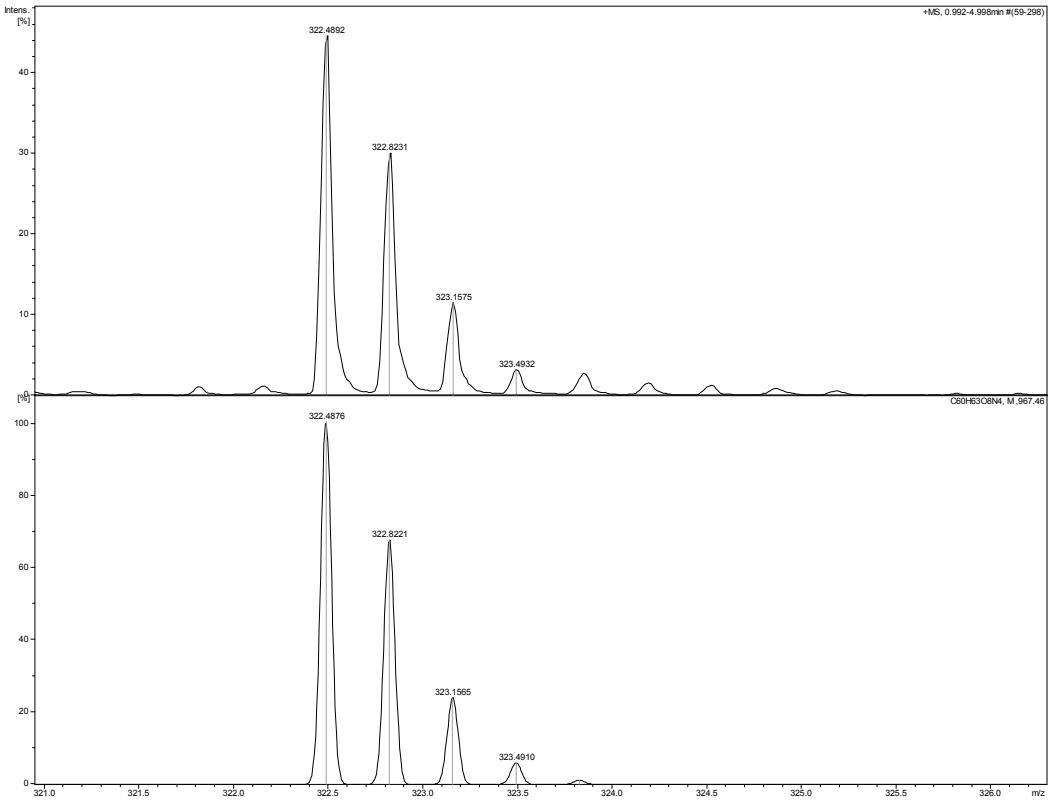


Figure S10. HRMS (ESI) Expanded view of tetrakis(pyridinium) resorcinarene **1** M–4Cl⁻–H⁺ with theoretical calculation below.

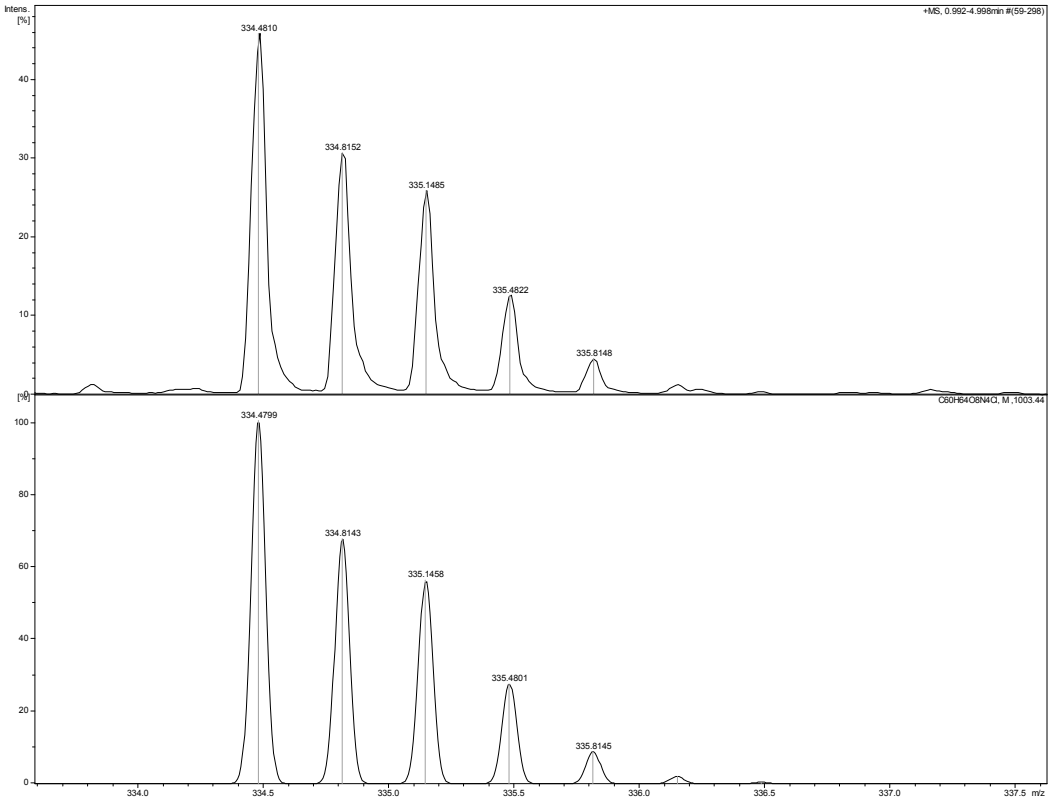
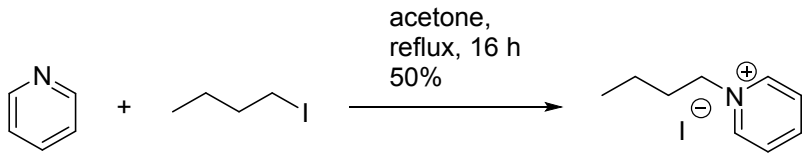


Figure S11. HRMS (ESI) Expanded view of tetrakis(pyridinium) resorcinarene **1** M–3Cl⁻ with theoretical calculation below.

2.2.3 General synthesis of pyridinium guests.

To a solution of alkyl halide (5-8 mmol) in acetone (10 mL) was added pyridine in excess and the solution heated to reflux for 2–16 h. The iodide salts were obtained by precipitation and/or trituration (50–94%). The chloride salts were obtained by subsequent ion exchange of the organic iodide salt using a Dowex™ anion exchange resin. (>95%).

A) synthesis of butyl pyridinium iodide.



Iodobutane (5 mmol, 570 µL) was added to 10 mL of acetone and 2.4 mL of pyridine and heated to reflux for 16 h. The yellow solution was cooled to rt and the solvent removed under reduced pressure. The residue was dried at rt for 2 h, then suspended in Et_2O, sonicated, collected by filtration, and washed with Et_2O (2 × 50 mL) to afford 658 mg of an off-white solid (50%). ^{1}H NMR (500 MHz, D_2O) δ 8.76 (d, *J* = 6.3 Hz, 2H), 8.45 (t, *J* = 8.1 Hz, 1H), 7.98 (t, *J* = 7.1 Hz, 2H), 4.53 (t, *J* = 7.5 Hz, 2H), 1.91 (p, *J* = 7.5 Hz, 2H), 1.28 (dt, *J* = 15.3, 7.5 Hz, 2H), 0.85 (t, *J* = 7.6 Hz, 3H). (See Figure S12).

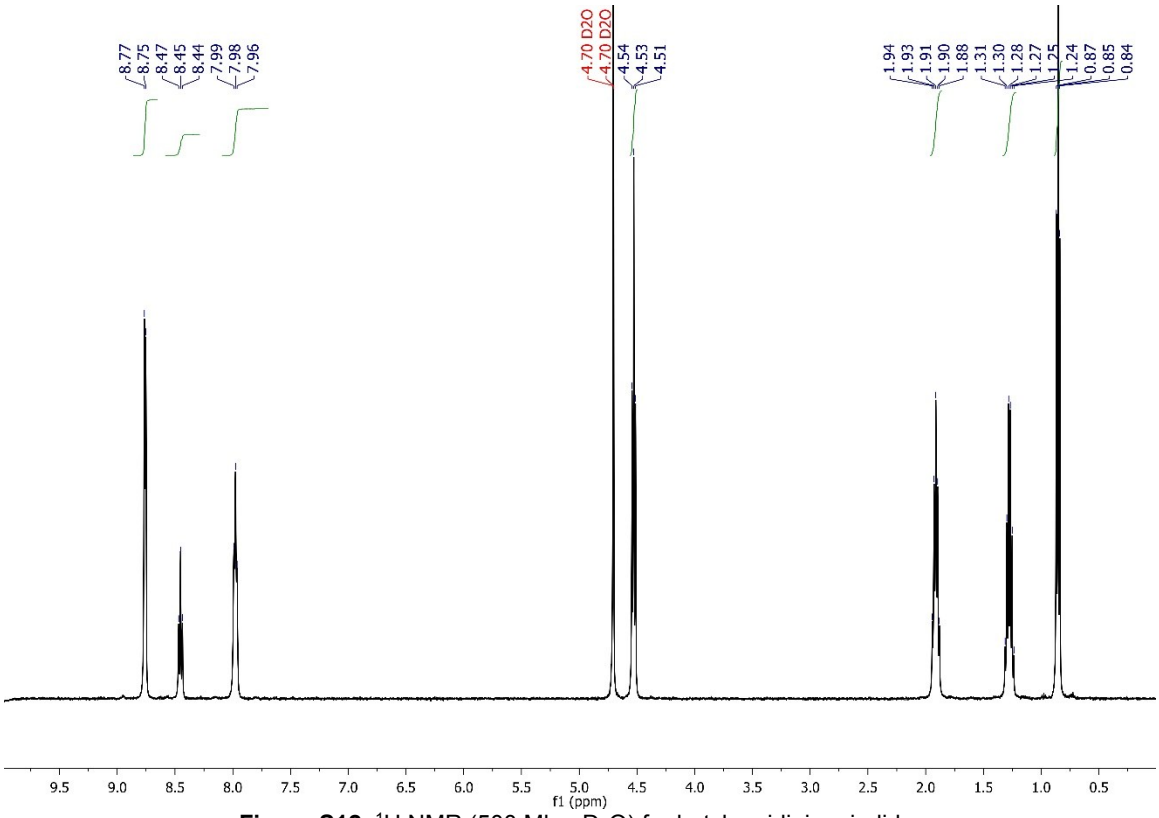
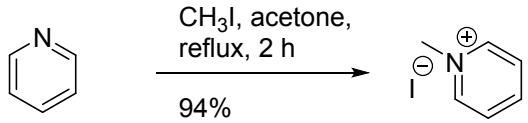


Figure S12. ^{1}H NMR (500 Mhz, D_2O) for butyl pyridinium iodide.

B) synthesis of methyl pyridinium iodide.



Iodomethane (8 mmol, 500 µL) was added to 10 mL of acetone and 4 mL of pyridine (50 mmol) and heated to reflux for 16 h. The colorless solution was cooled to rt and poured over Et_2O (50 mL), sonicated, collected by filtration, and washed with Et_2O (2 × 50 mL) to afford 1.67 g of an off-white solid (94%). ^{1}H NMR (400 MHz, D_2O) δ 8.60 (d, *J* = 6.0 Hz, 2H), 8.35 (t, *J* = 7.7 Hz, 1H), 7.86 (t, *J* = 6.9 Hz, 2H), 4.21 (s, 3H). See Figure S13.

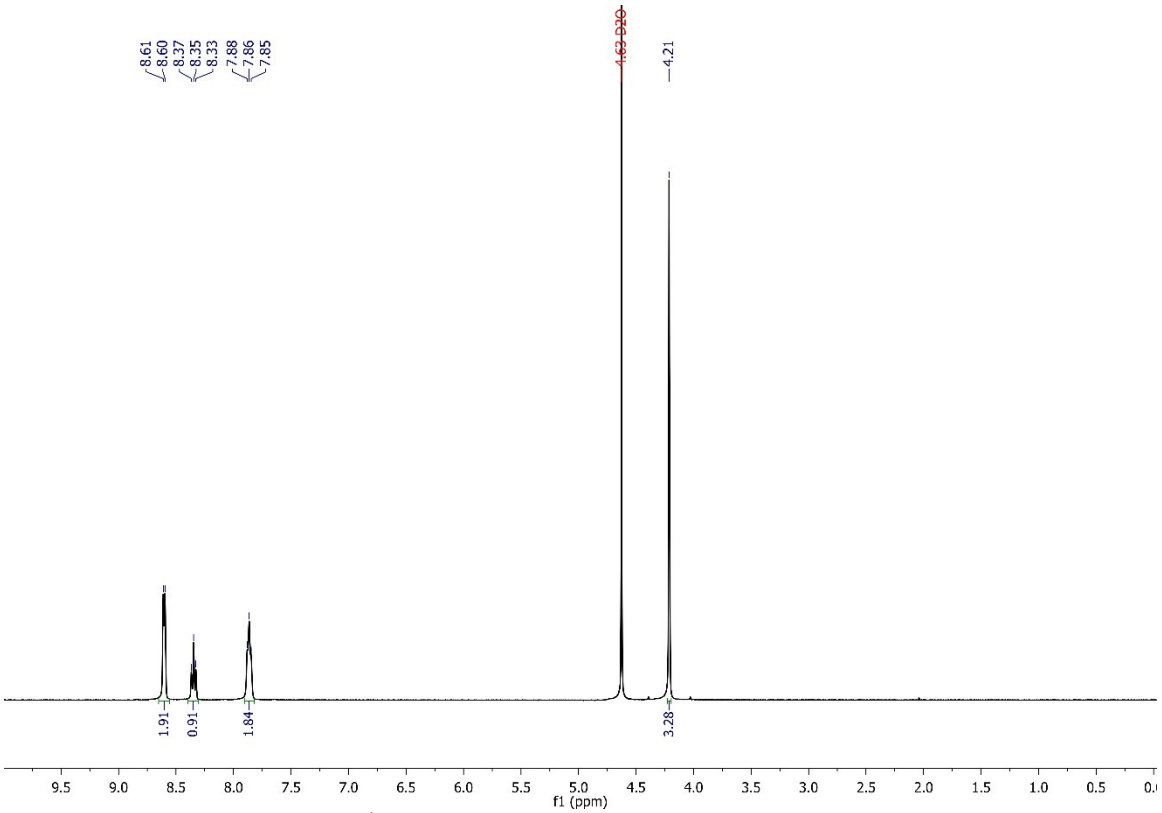


Figure S13. ^{1}H NMR (500 Mhz, D_2O) for methyl pyridinium iodide.

2.3 Analytical Data

The properties of host **1** were examined by a combination of UV-Vis and ^{1}H NMR spectroscopy, and dynamic light scattering; concentration, and pH dependent data were collected. Host **1** was found to be soluble in unbuffered solutions up to ~50 mM. Serial dilution of the host revealed well-resolved concentration dependent chemical induced shifts (Δδ ppm) in the ^{1}H NMR spectrum of **1** (Figure S14); upon successive dilutions of **1** nearly all resonances experience Δδ values of 0.05 – 1.0 ppm. DOSY experiments were conducted from 0.78 to 50 mM host. DOSY measurements indicate while the host is mostly monomeric (D = 2.32 × 10^{-10} $m^2 \cdot s^{-1}$) at low concentration (~1.56 mM, Figure S15), a higher order aggregate (D = 1.14 ×10^{-10} $m^2 \cdot s^{-1}$) results at higher concentrations (~25 mM, Figure S16).

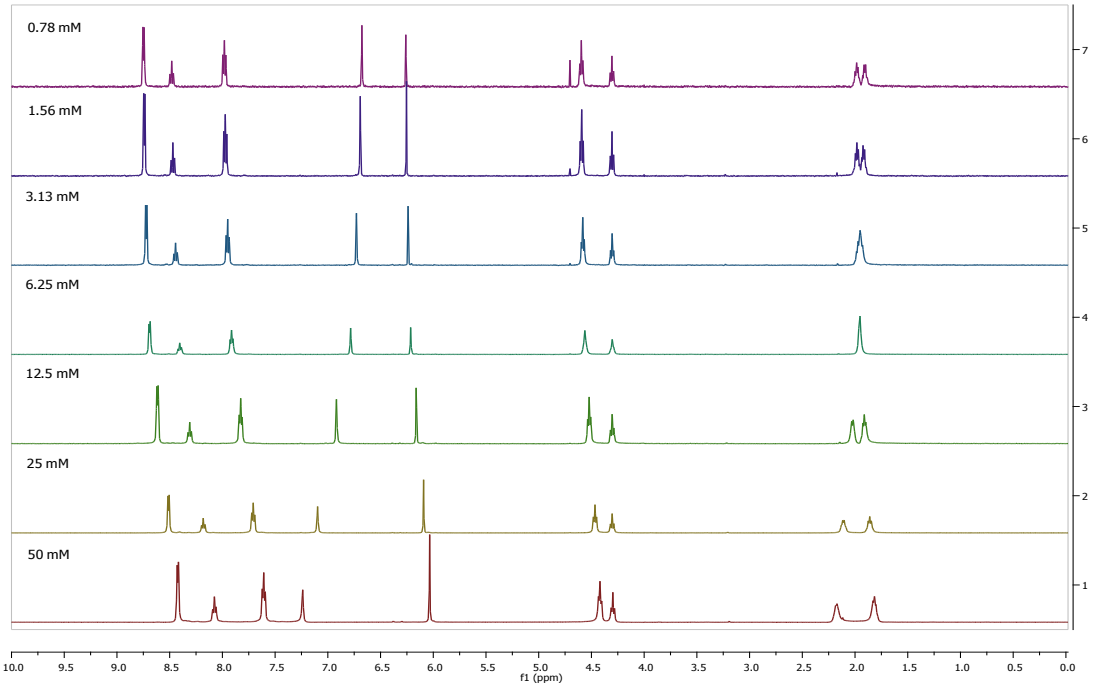


Figure S14. ^{1}H NMR (500 MHz, D_2O) showing concentration dependence of **1** from 50 to 0.78 mM by serial ½ dilution. The PGSE pulse sequence was used to minimize the water signal and visualize the shift in H_n.

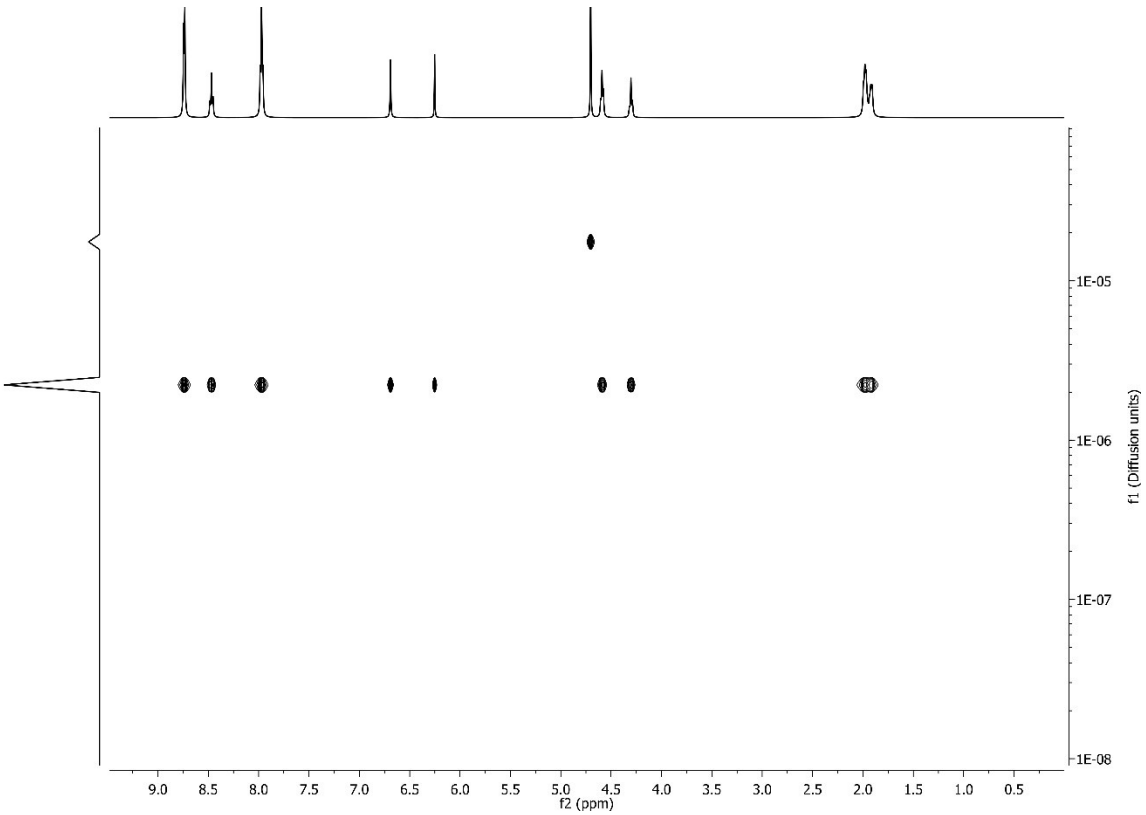


Figure S15. 2D DOSY NMR spectrum of tetrakis(pyridinium) resorcinarene **1** (1.56 mM, D_2O).

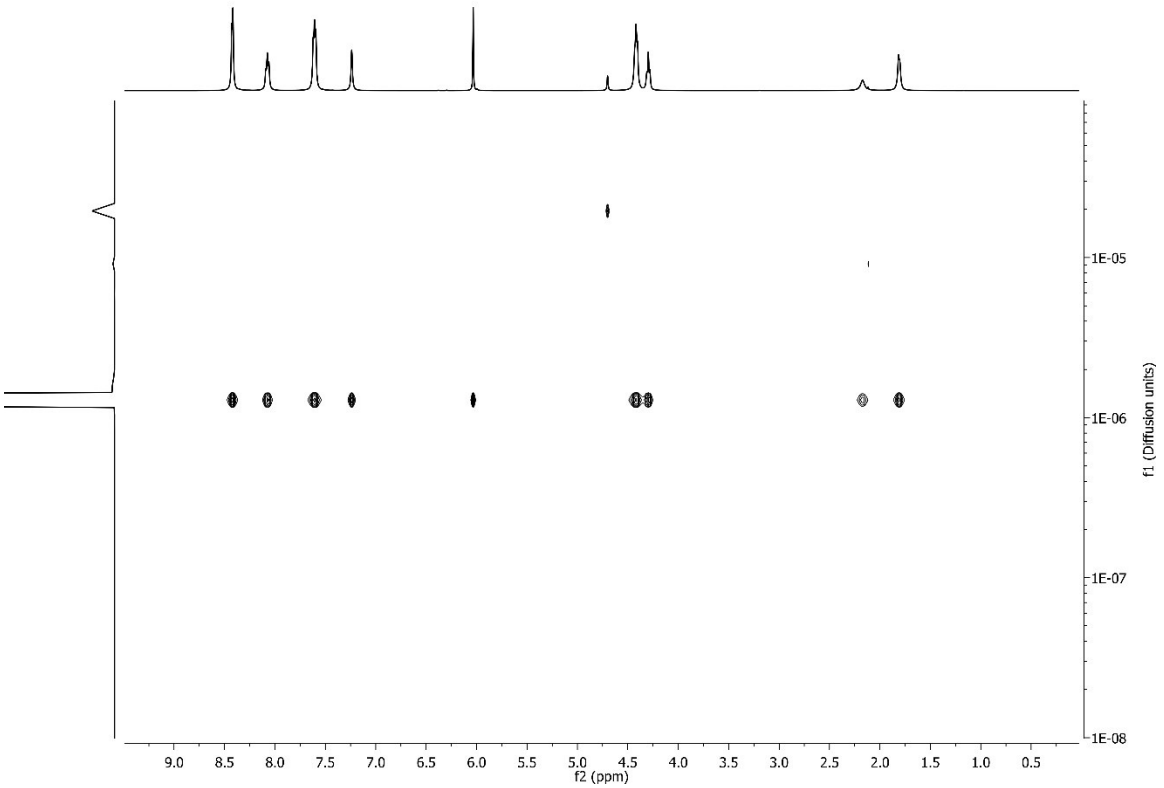


Figure S16. 2D DOSY NMR spectrum of tetrakis(pyridinium) resorcinarene **1** (25 mM, D_2O).

Halide complexation with a related cavitand bearing a crown of trimethylammonium cations[3] resulted in a downfield ($\Delta\delta \approx 0.2–0.3$ ppm) shift for H_j and H_l (Figure S5); similar shifts are observed for **1**, although the shifts for **1** are larger. However, upfield shifts ($\Delta\delta \approx 0.3$) in H_2, H_3, and H_4 of the pyridinium moiety suggests that these changes in the ^{1}H NMR spectrum do not correspond to halide complexation; upon titration of Cl^- up to 200 mM, $\Delta\delta$ values were < 0.05 (*vide infra*).

Titration of an unbuffered solution of **1** with NaOH resulted in line-broadening, aggregation, precipitation, and no discernable signals (pH ≈ 12.5). This process is reversible by addition of DCl (Figure S17). Small changes in the ^{1}H NMR spectrum were noted and attributed to changes in concentration and bound ratio of Cl^- to host **1**.

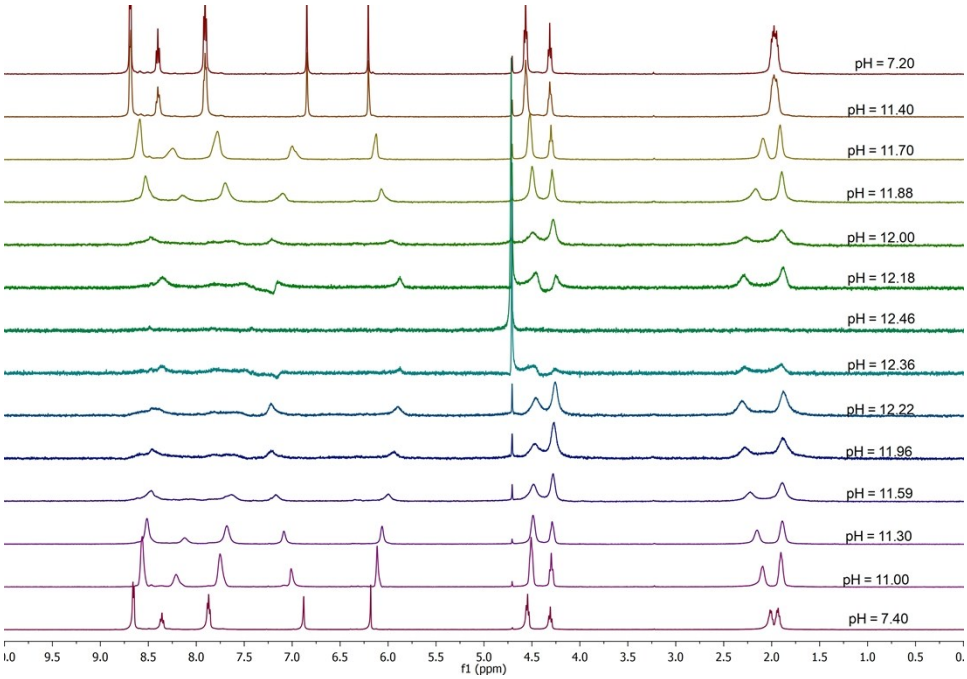


Figure S17. ^{1}H NMR titration of **1** with 100 mM NaOD (up to pH 12.46) and subsequent titration with 100 mM DCl to pH 7.2.

Upon addition of an excess of various organic salts, large shits were observed in the host resonances H_j, and H_l, and minor changes observed for the other resonances (Figure S18).

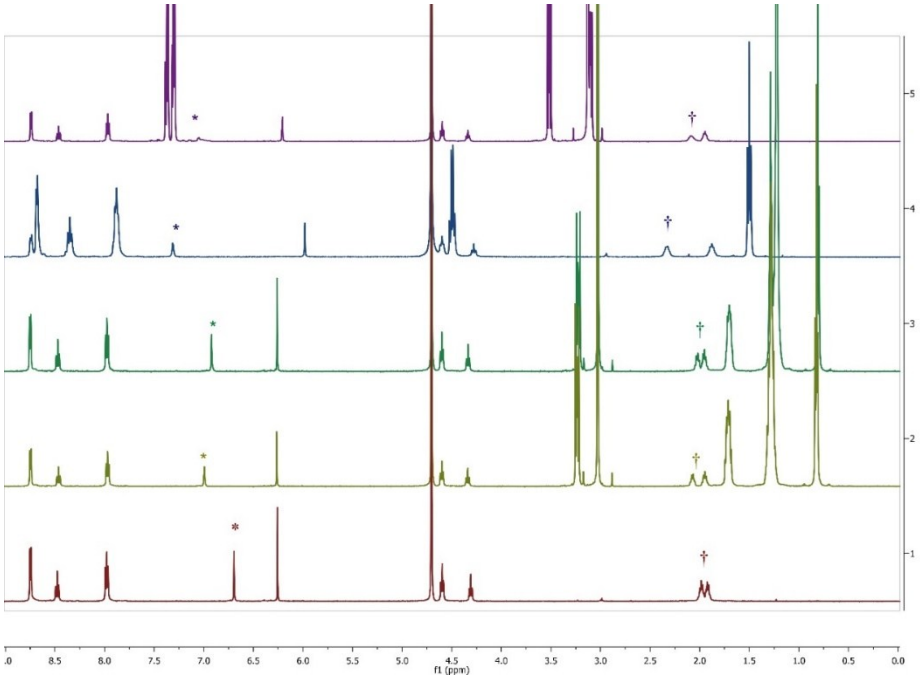


Figure S18. ^{1}H NMR (500 Mhz, D_2O) of 1) host **1** (1.0 mM) in the presence of: 2) hexyl trimethylammonium chloride, 3) decyl trimethylammonium chloride, 4) ethyl pyridinium iodide and 5) phenethyl trimethylammonium chloride.

In all cases, significant changes were observed in H_j and H_l upon addition of organic salts due to counterion complexation. Only minor changes in the aromatic proton (H_e) at the upper face of the host was observed upon addition of the various trimethylammonium cations. The observed Δδ for H_e upon complexation with the pyridinium guest was significant, however, so ^{1}H NMR spectroscopic titration data was collected for methyl and butyl pyridinium to host **1** as the chloride and iodide salts.

2.3.1 ^{1}H NMR Titration Data

^{1}H NMR spectroscopic titration experiments were used to monitor changes as a function of guest concentration. Anion affinities for Cl^- and I^- were determined as the sodium salt as they were selected as the counterion for the organic salts. Titrations performed with sodium chloride and iodide monitored the changes in H_j and H_l for binding constant determination fit to a 1:1 model using BINDFIT or iteratively using SOLVER in Excel by the following equation (Eq. S2):

$$\Delta\delta = \frac{K_a[G]}{1 + K_a[G]} \qquad \text{Eq. S2}$$

Where, Δδ is the chemical shift of the host-guest complex, $[G_0]$ and $[H_0]$ are the total guest and host concentration respectively, and [G] is the free guest concentration which can be solved for using equation S3.

$$[G] = \frac{1}{2}\left(G_0 - H_0 - \frac{1}{K_a}\right) - \sqrt{\left(G_0 - H_0 - \frac{1}{K_a}\right)^2 + 4\frac{G_0}{K_a}} \qquad \text{Eq. S3}$$

Titrations involving incrementally increasing the anion concentration predominately showed changes in the H_l and H_j resonances indicative of anion complexation. Affinities for Cl^- (Figure S19 to Figure S20) and I^- (Figure S21 and Figure S22) were measured in unbuffered D_2O (K_a = 14 ± 3, and 200 M^{-1} ± 20, respectively). Comparison of the results obtained from fitting H_j to a fit of H_l gives approximately the same affinity for I^- (K_a = 193 ± 33 M^{-1}), although

the shifts in H_l are smaller, the signal is coincident with H_m, and thus provides a larger inherent error in the measurements. Global fitting of both H_l and H_j, likewise provides similar results (K_a = 192 ± 14 M^{-1}). Since the data for H_j and H_l do not differ significantly irrespective of the model chosen, it suggests minimal cooperativity from Na^+ complexation at the rim. Thus, in these instances it was determined that a simple 1:1 model fitting H_j was sufficient for halide complexation to the crown independent of sodium complexation to the rim.

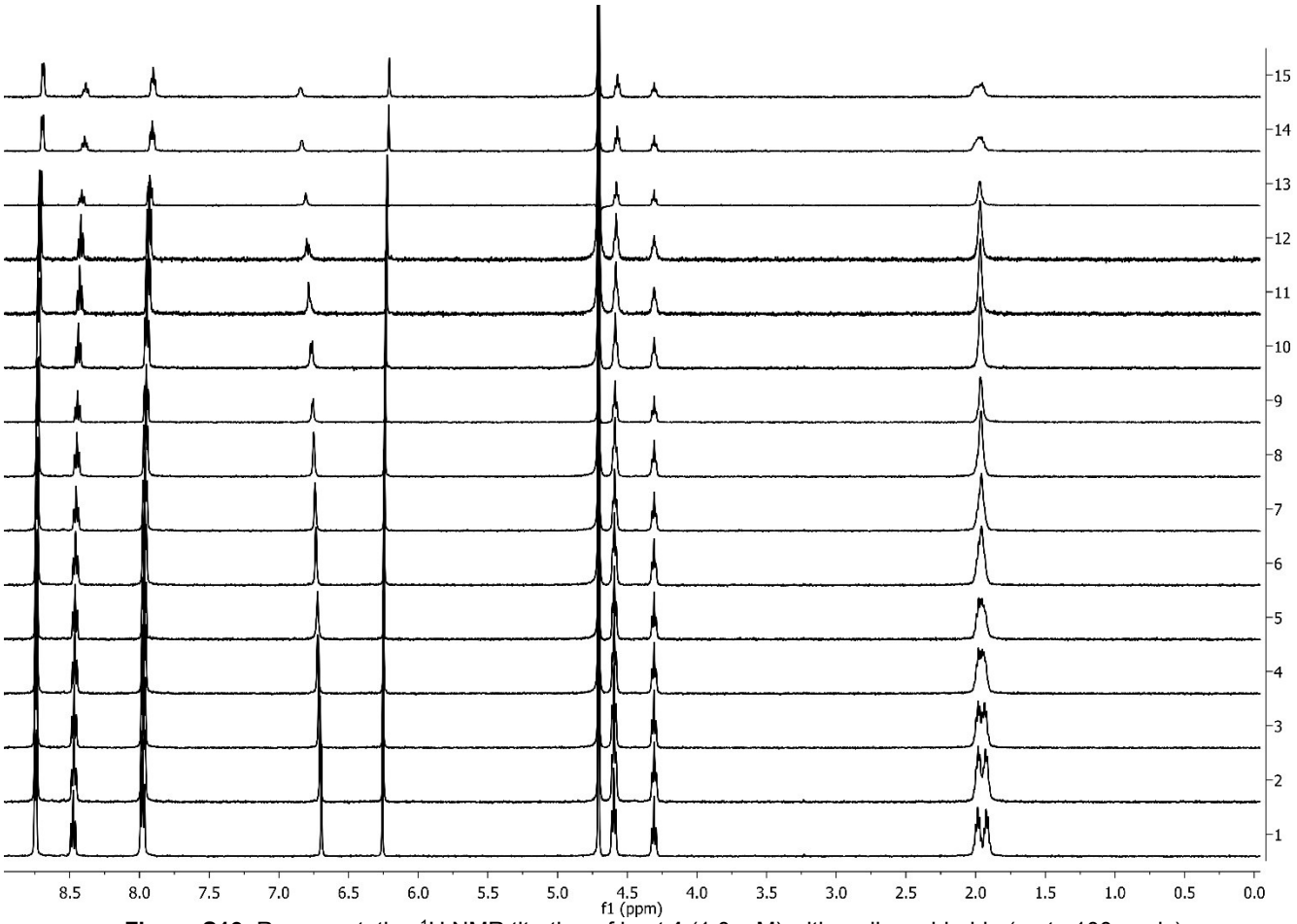


Figure S19. Representative ^1H NMR titration of host **1** (1.0 mM) with sodium chloride (up to 100 equiv).

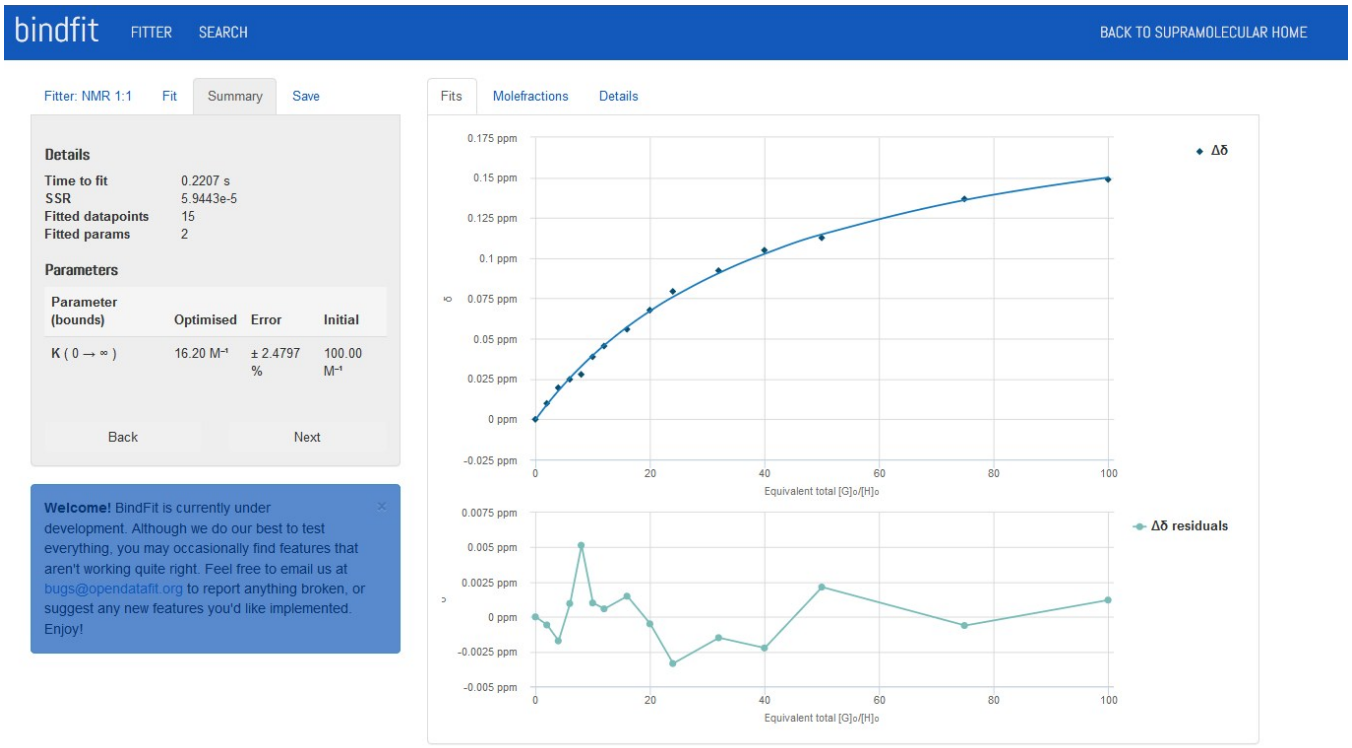


Figure S20. Fit of the data for H_j (Δδ ppm) from Figure S19 to a 1:1 model.

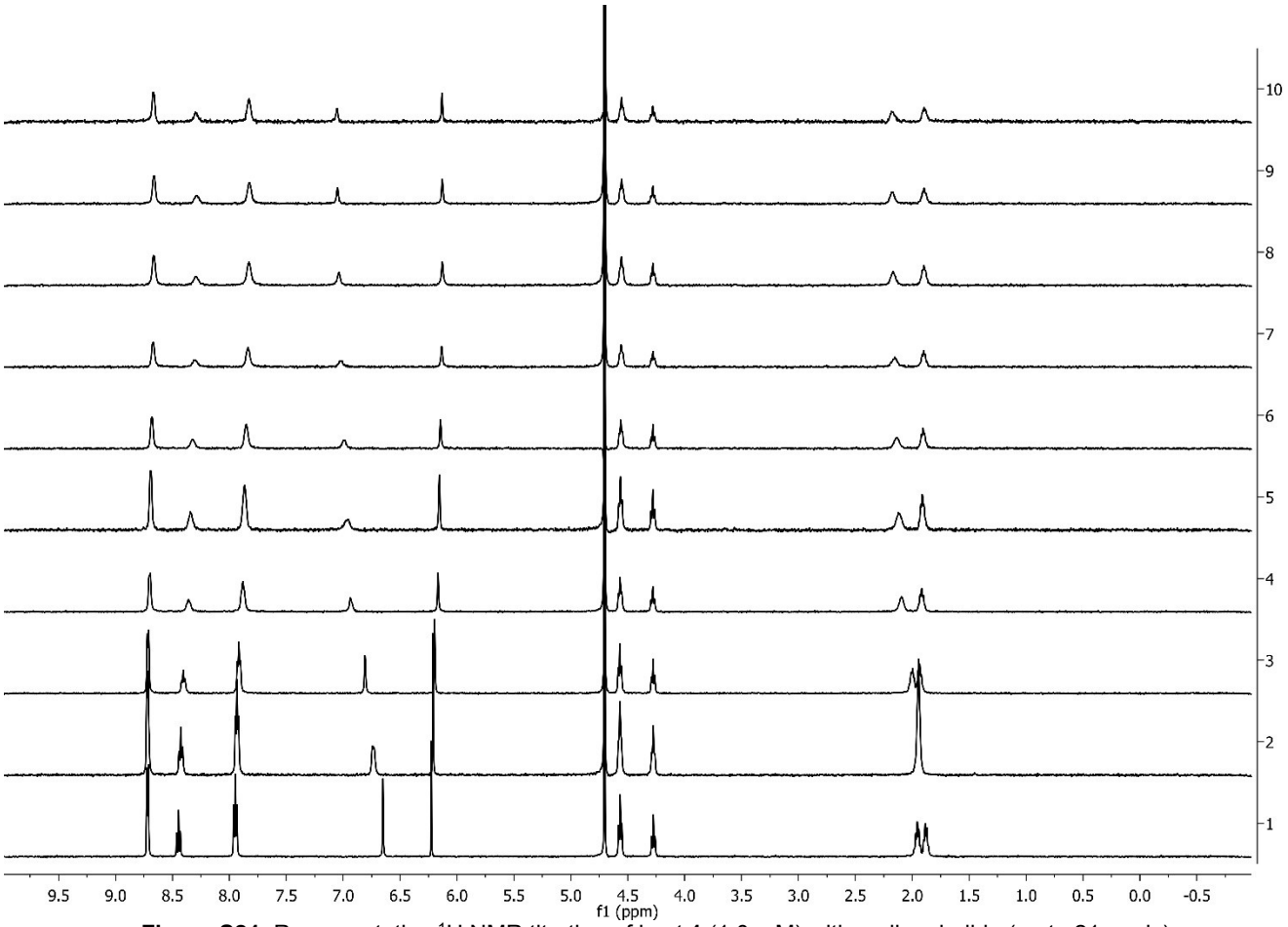
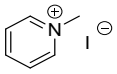
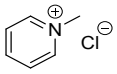
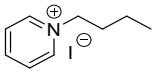
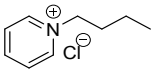


Figure S21. Representative ^{1}H NMR titration of host **1** (1.0 mM) with sodium iodide (up to 21 equiv).

Figure S22. Fit of the data for H_j (Δδ ppm) from Figure S21 to a 1:1 model.

The host signal H_e at the rim of the cavity was used to determine the affinity of the organic cations. Titrations were performed with the Cl^- and I^- salts of methyl and butyl pyridinium cations and fit to a 1:1 model. The results are summarized in Table S1 and representative examples for each titration are shown with their corresponding isotherm obtained from BINDFIT (Figure S23 – Figure S30).

Table S1 Selected guests, affinities, and free energies of complexation for host **1**.

Guest	NaCl	NaI				
K_a^{cation} (M^{-1})	—	—	300 ± 3%	53 ± 4%	560 ± 6%	89 ± 17%
K_a^{anion} (M^{-1})	14 ± 21%	200 ± 10%	440 ± 5%	50 ± 8%	520 ± 11%	57 ± 7%
ΔG^{cation} (kJ mol^{-1})	—	—	−14.1 ± 0.1	−9.8 ± 0.1	−15.7± 0.1	−11.1 ± 0.4
ΔG^{anion} (kJ mol^{-1})	−6.5 ± 0.5	−13.1 ± 0.2	−15.1 ± 0.1	−9.7 ± 0.2	−15.5 ± 0.3	−10.0 ± 0.3

Titrations of host and guest were performed on 1.0 mM solutions of **1** in unbuffered D_2O and monitored either H_j/H_l or H_e of the host resonances.

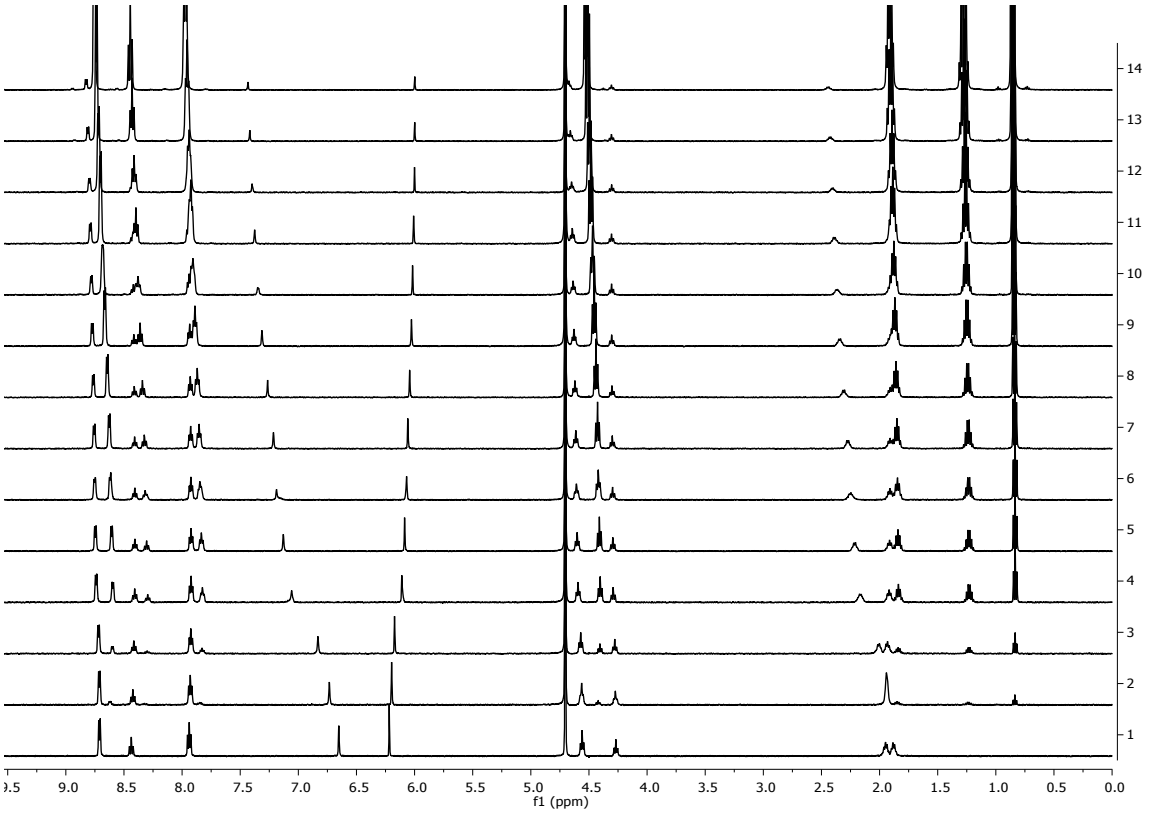


Figure S23. Representative ^{1}H NMR titration of host **1** (1.0 mM) with butyl pyridinium iodide (up to 100 equiv).

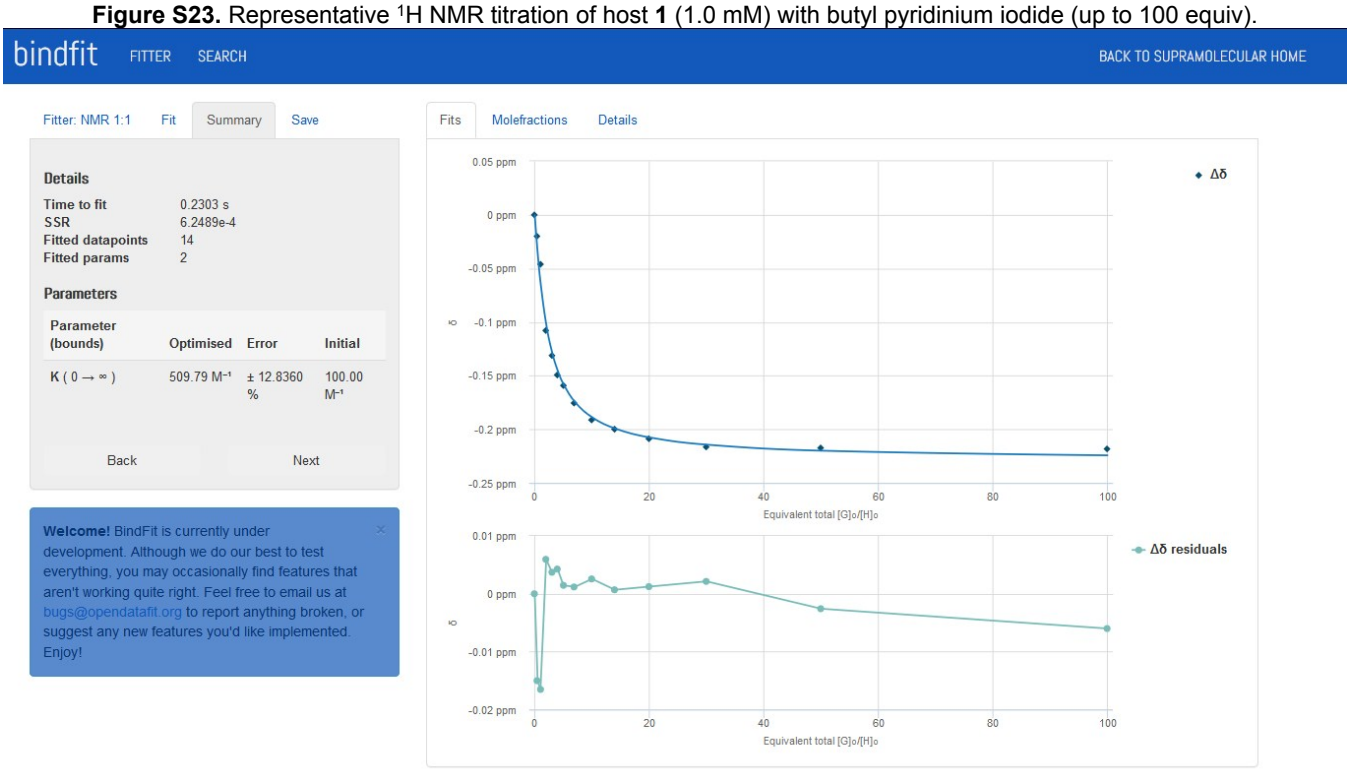


Figure S24. Fit of the data for H_e (Δδ ppm) from Figure S23 to a 1:1 model.

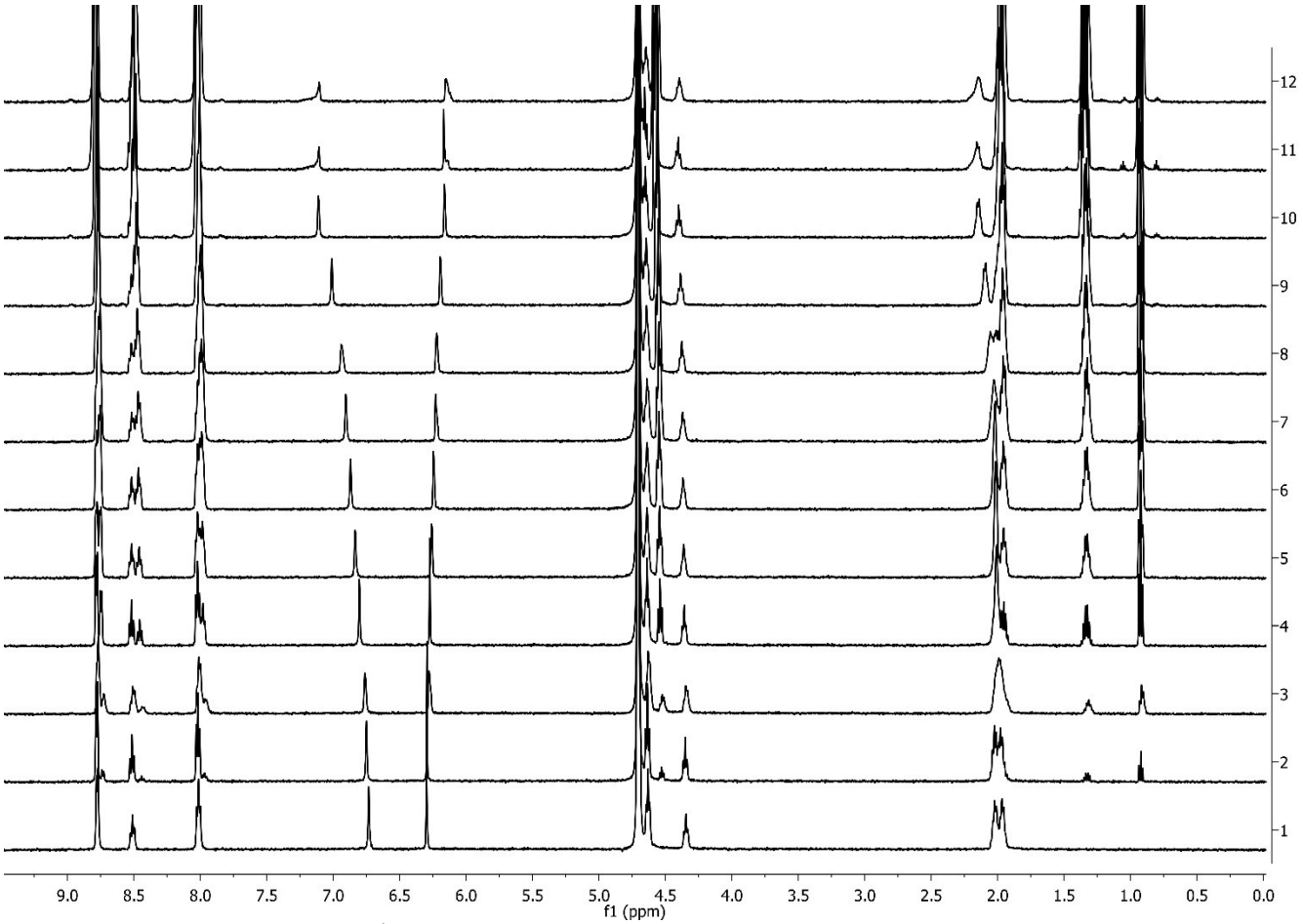


Figure S25. Representative ^{1}H NMR titration of host **1** (1.0 mM) with butyl pyridinium chloride (up to 100 equiv).

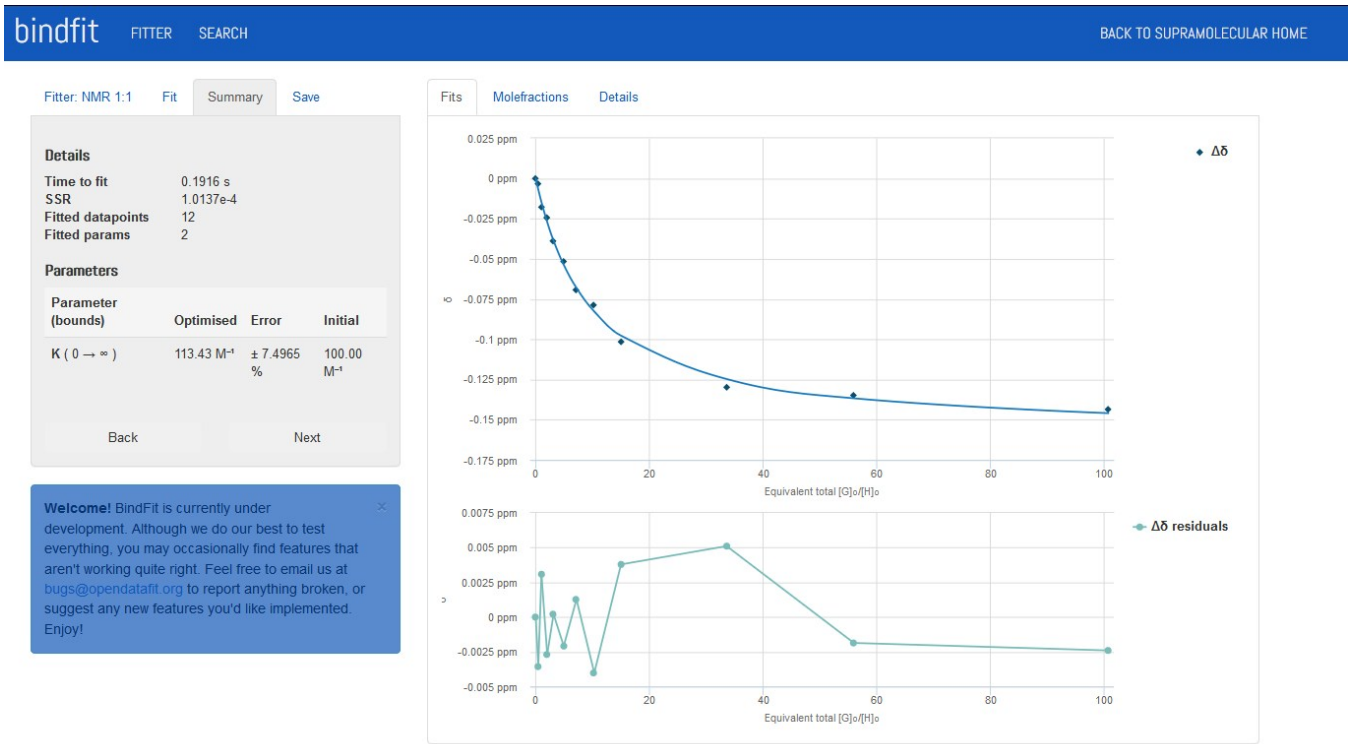


Figure S26. Fit of the data for H_e (Δδ ppm) from Figure S25 to a 1:1 model.

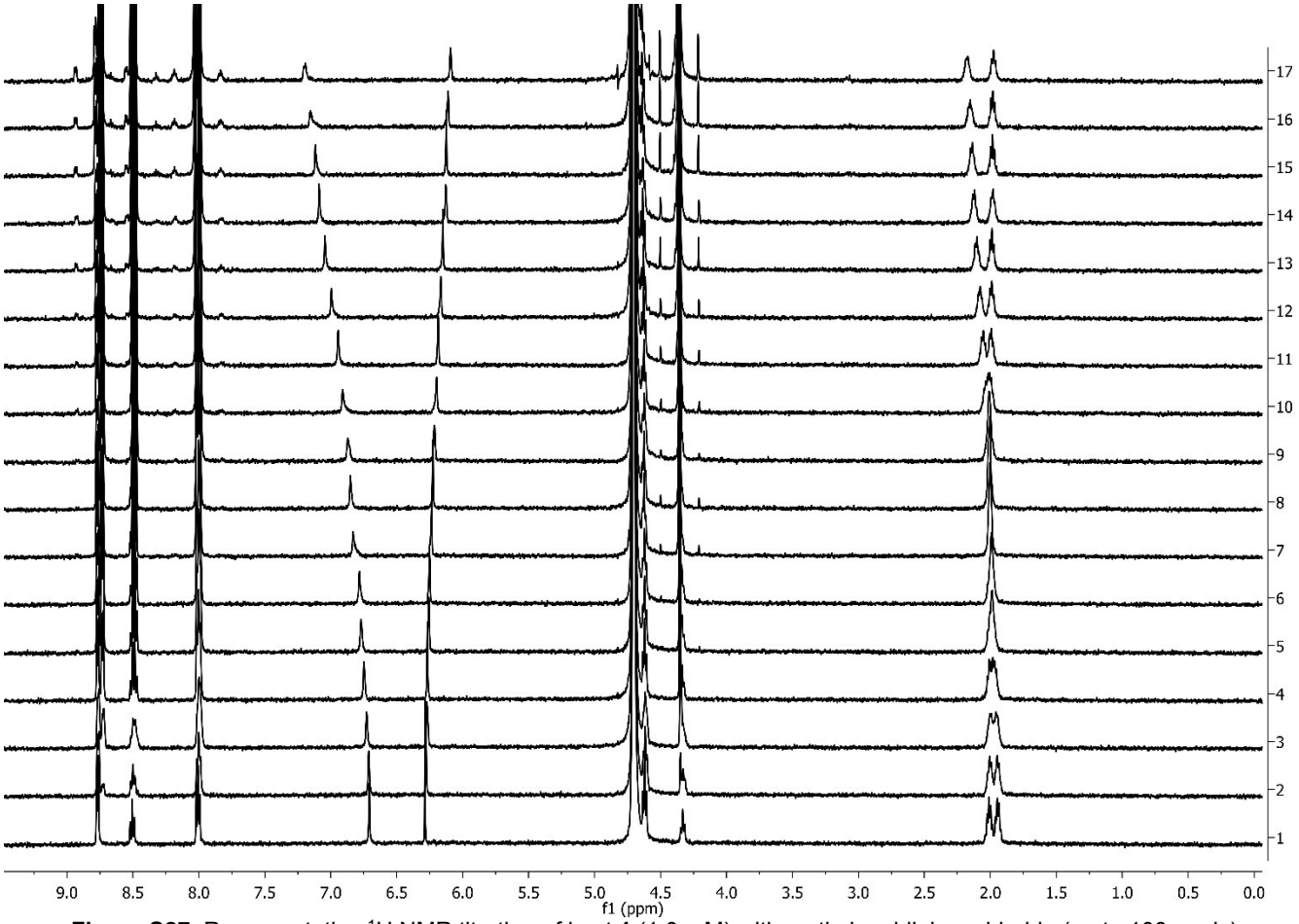


Figure S27. Representative ^{1}H NMR titration of host **1** (1.0 mM) with methyl pyridinium chloride (up to 100 equiv).

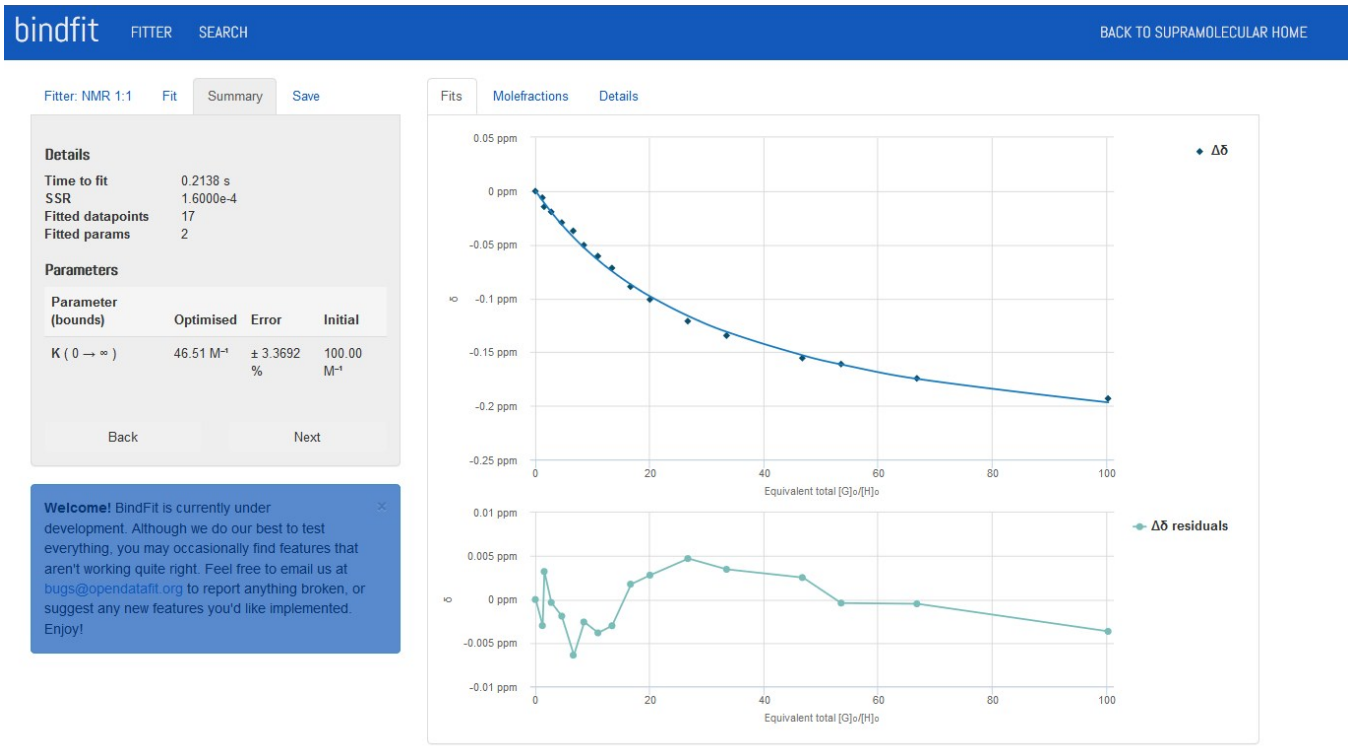


Figure S28. Fit of the data for H_e (Δδ ppm) from Figure S27 to a 1:1 model.

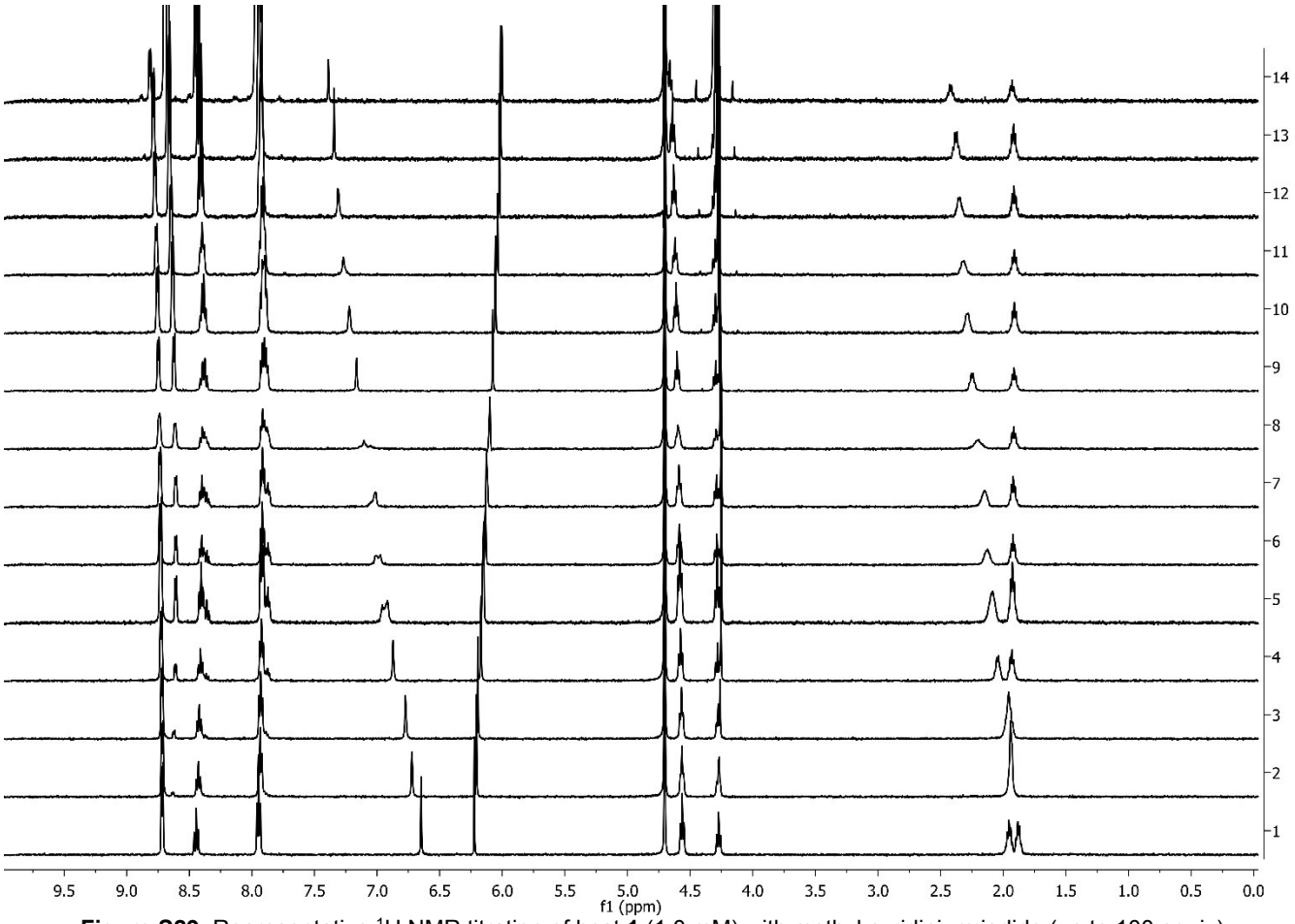


Figure S29. Representative ^{1}H NMR titration of host **1** (1.0 mM) with methyl pyridinium iodide (up to 100 equiv).

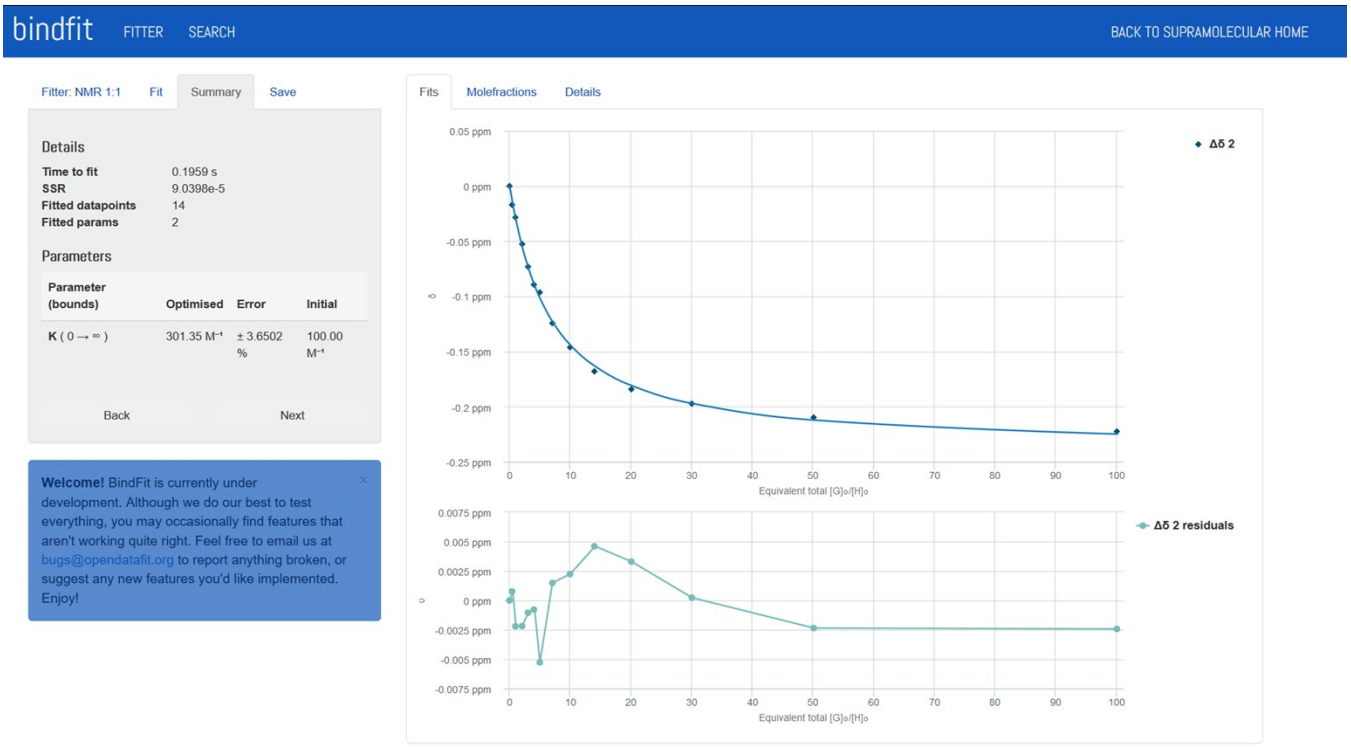


Figure S30. Fit of the data for H_e (Δδ ppm) from Figure S29 to a 1:1 model.

2.3.2 Supramolecular polymerization

An experiment was conducted whereby the concentration of host **1** was incrementally increased in the absence of guest and the chemical induced changes of H_e monitored in the NMR spectrum. As there is no other guest, these changes correspond to changes resulting from aggregate formation. Homogenous (one-component) linear type continuous aggregation, can be described by the following relation:

$$H + H \overset{K_2}{\rightleftharpoons} H_2 + H \overset{K_3}{\rightleftharpoons} H_3 + H \overset{K_4}{\rightleftharpoons} \ldots \overset{K_n}{\rightleftharpoons} H_n$$

This refers to a system where there is a known monomer initial concentration described by one of three aggregation models:

Dimerization model: $K_D = K_2, K_3 \ldots K_n = 0$

EK (equal *K,* linear aggregate) model: $K_E = K_2 = K_3 \ldots = K_n$

CoEK (Cooperative, equal *K*) aggregation model, where ρ is the cooperativity factor

ρ < 1: positive cooperativity

ρ = 1: non-cooperative

ρ > 1: negative cooperativity

The details of these derivations have been given previously[4-5] and are discussed briefly in context of host **1** here. For the dimerization model K_D is the equilibrium constant for the formation of a dimer. The EK–aggregation model describes the isodesmic model for K_E, where $K_E = K_D = K_3 = K_n$:

A + A $\overset{K_2}{\rightleftharpoons}$ AA, and AA + A $\overset{K_3}{\rightleftharpoons}$ AAA

[A] = C_1 is the concentration of monomer, and [AA] = C_2 the concentration of dimer. It follows that $C_2 = K_2[A][A] = K_2C_1^2$, since C_1 = [A]. Continuing the derivation gives: [AAA] = C_3, which from the equilibrium relation gives: $C_3 = K_3[AA][A]$. Insertion of the definition of C_2 and C_1 gives a relation for $C_3 = K_3C_2C_1 = K_3K_2C_1^2C_1 = K_3K_2C_1^3$, which can be extrapolated indefinitely, and thus, $C_n = K^{n-1}C_1^n$. This can be used to derive *N* the number average of polymer aggregates in terms of the total concentration (C_T) and C_N (Equation S4):

Equation S4
$$N = \frac{C_T}{C_N} = \frac{C_T}{C_1 + C_2 + \ldots C_n} = \frac{2KC_T}{-1 + \sqrt{4KC_T + 1}}$$

Equation S4 assumes no cooperativity, but can be used to model the number average of the aggregates in solution at a given concentration with increasing host concentration. A plot of Δδ vs $[H]_0$ and fit to a linear aggregation model gives a value for $K_E \approx 800\ M^{-1} \pm 5\%$. The least squares fit of the obtained sizes from DOSY versus calculated values for *N* provide a comparable value ($K_E = 830\ M^{-1}$). This corresponds to $N \approx 5$ at 25 mM host. A presumed aggregate is shown in Figure S31.

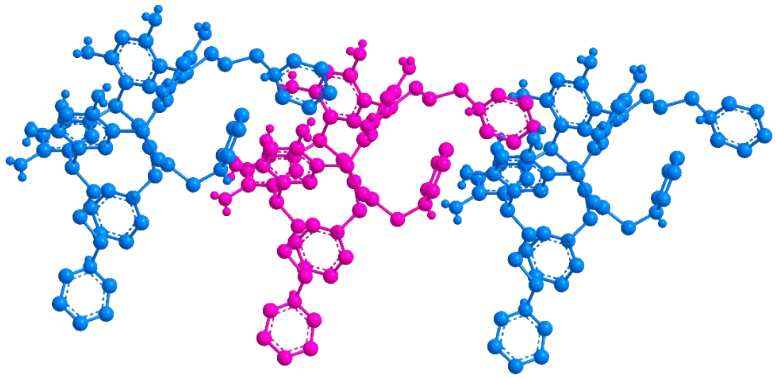
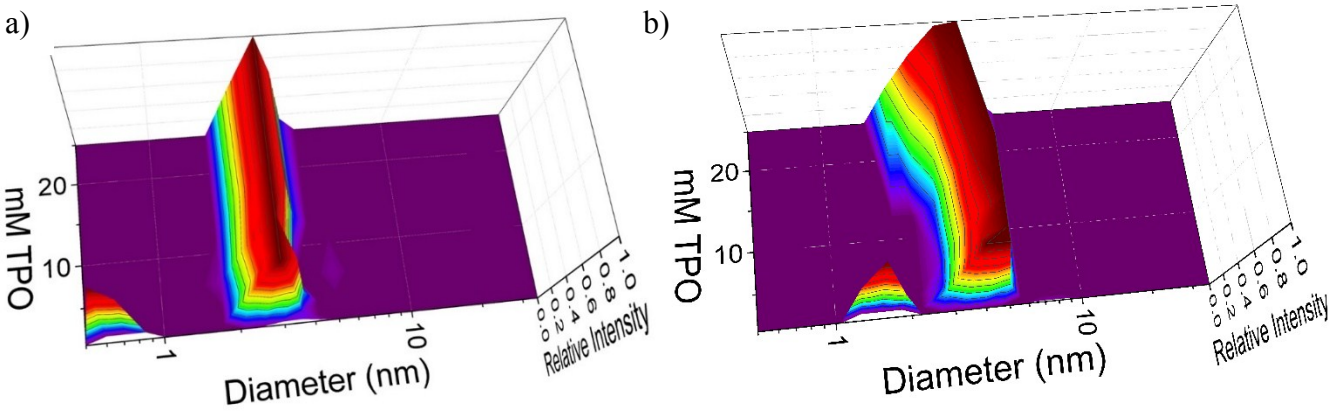


Figure S31. proposed linear aggregate MMC minimized structure, image shows plausible “head-to-tail” aggregation and intercalation of a pyridinium unit in the boat conformation of **1**.

2.3.3 Light Scattering Data

Due to limitations imposed by the DLS instrument, unbuffered data could not be reliably collected. Light scattering data for the free host was collected under four different conditions: (1) in the presence of 100 mM NaCl, (2) in 40 mM phosphate buffer, pH 7.3, (3) in 40 mM phosphate buffer, pH 3.0, and (4) 97 mM phosphate buffer, pH 3.0.



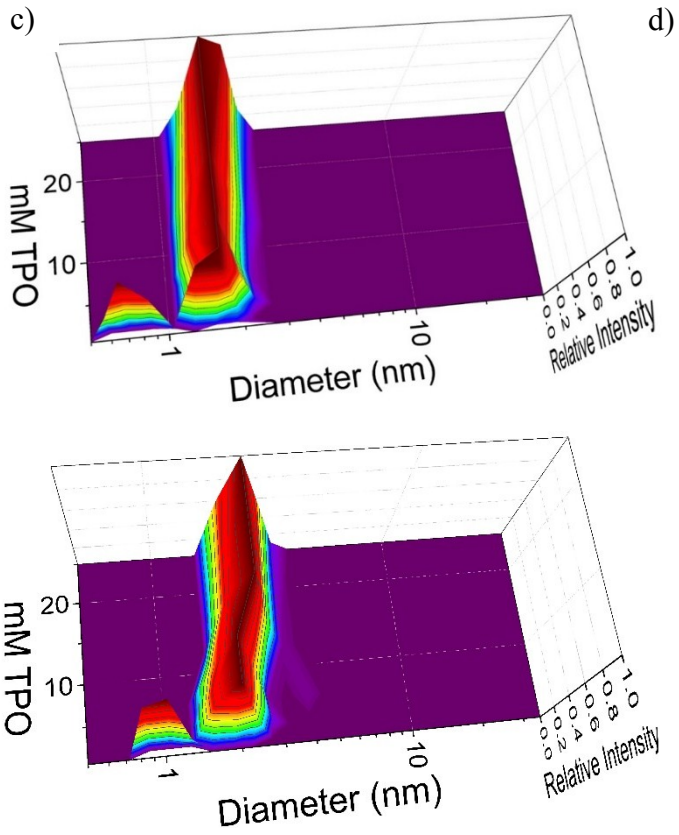


Figure S32. Light scattering data (DLS) for solutions of host **1** by serial ½ dilution of a 25 mM stock in a) 100 mM NaCl b) 40 mM phosphate buffer, pH 7.30, c) 40 mM phosphate buffer 3.00, d) 97 mM phosphate buffer pH 3.00.

Above a concentration of 1 mM the observed size of the host suggests the presence of at higher order aggregate (N ≥ 2) under all conditions. Dilution below 1 mM renders **1** mostly monomeric. The host appears on average slightly larger under basic conditions than in the presence of sodium chloride. Under the two acidic conditions tested, the hydrodynamic radius is slightly smaller with the lower ionic strength solution giving smaller sizes.

2.4 Crystallographic Data

Crystallography data was submitted to the Cambridge Crystallographic Data Center (CCDC, identifier: 1894952).

2.4.1 Analysis of solid-state data

Host **1** was recrystallized from refluxing EtOH-H_2O (4:1) to give crystals suitable for structural determination (Figure S33); which lend support to the linear aggregate model. Host **1** adopts a boat-shaped conformation with favorable phenol-pyridinium interactions consistent with the proposed model.

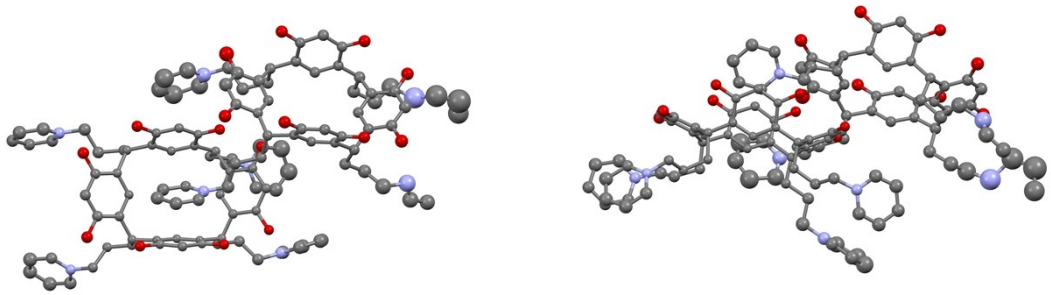


Figure S33. X-ray structural determination of **1**. Solvent and counterions removed for clarity Top view of **1** and rotation 90° about the x-axis.

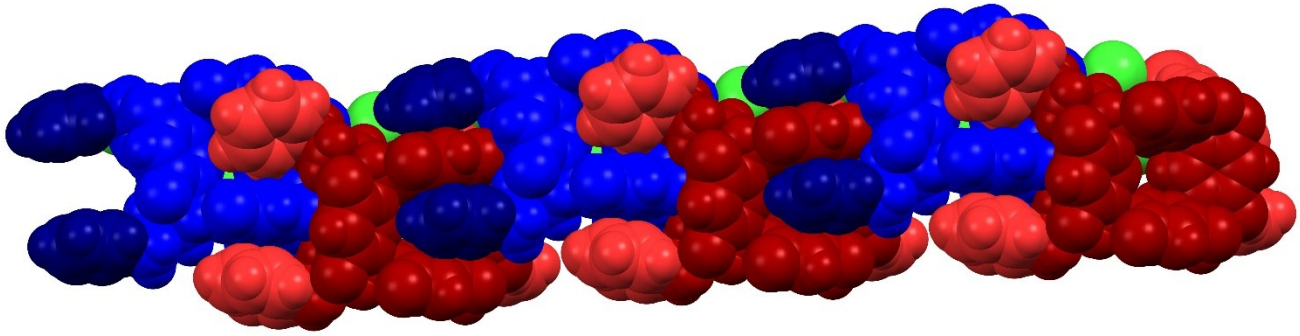


Figure S34. Partial packed slice from the cell of 1. Alternating host **1** molecules are shown in blue and red. Dark blue and light red indicate the pypridinium cations at the feet positions for clarity. Light green are chloride atoms.

2.4.2 Structural Analysis of TPO, **1**

A colorless block-like specimen of $C_{120}H_{156}Cl_4N_8O_{32}$, approximate dimensions 0.182 mm x 0.206 mm x 0.226 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE PHOTON 100 CMOS system equipped with a INCOATEC IμS micro--focus source (Cu-Kα, λ = 1.54184 Å) and a mirror monochromator.

Table S2. Data collection details for **TPO, 1**.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	50.030	77.15	-105.60	90.00	54.74	0.50	371	60.00	1.54184	50	1.0	n/a
Omega	50.030	107.15	-74.85	-144.00	54.74	0.50	368	60.00	1.54184	50	1.0	n/a
Omega	50.030	107.15	-74.85	-36.00	54.74	0.50	368	60.00	1.54184	50	1.0	n/a
Omega	50.030	19.91	-161.84	-120.00	54.74	0.50	367	30.00	1.54184	50	1.0	n/a
Omega	50.030	107.15	-74.85	36.00	54.74	0.50	368	60.00	1.54184	50	1.0	n/a
Omega	50.030	107.15	-74.85	108.00	54.74	0.50	368	60.00	1.54184	50	1.0	n/a
Omega	50.030	92.15	-90.60	0.00	54.74	0.50	371	60.00	1.54184	50	1.0	n/a

A total of 2581 frames were collected. The total exposure time was 39.96 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 57489 reflections to a maximum θ angle of 72.30° (0.81 Å resolution), of which 25199 were independent (average redundancy 2.281, completeness = 94.3%, R_{int} = 4.83%, R_{sig} = 5.54%) and 18616 (73.88%) were greater than $2\sigma(F^2)$. The final cell constants of a = 15.267(9) Å, b = 19.087(10) Å, c = 24.390(15) Å, α = 87.94(3)°, β = 83.839(18)°, γ = 73.08(2)°, volume = 6760.(7) Å^3, are based upon the refinement of the XYZ-centroids of 9643 reflections above 20 σ(I) with 6.082° < 2θ < 143.8°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.870. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7520 and 0.8644.

The final anisotropic full-matrix least-squares refinement on F^2 with 1523 variables converged at R1 = 16.46%, for the observed data and wR2 = 43.66% for all data. The goodness-of-fit was 2.916. The largest peak in the final difference electron density synthesis was 2.780 e^-/Å^3 and the largest hole was -1.035 e^-/Å^3 with an RMS deviation of 0.152 e^-/Å^3. On the basis of the final model, the calculated density was 1.161 g/cm^3 and F(000), 2512 e^-.

Table S3. Sample and crystal data for TPO, **1**.

Identification code	TPO, 1	
Chemical formula	$C_{120}H_{156}Cl_4N_8O_{32}$	
Formula weight	2364.32 g/mol	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal size	0.182 x 0.206 x 0.226 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 15.267(9) Å	α = 87.94(3)°
	b = 19.087(10) Å	β = 83.839(18)°
	c = 24.390(15) Å	γ = 73.08(2)°
Volume	6760.(7) Å^3	
Z	2	
Density (calculated)	1.161 g/cm^3	
Absorption coefficient	1.389 mm^{-1}	
F(000)	2512	

Table S4. Data collection and structure refinement for TPO, 1.

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS	
Radiation source	INCOATEC IμS micro--focus source (Cu-Kα, λ = 1.54184 Å)	
Theta range for data collection	3.02 to 72.30°	
Index ranges	-18<=h<=18, -23<=k<=23, -30<=l<=30	
Reflections collected	57489	
Independent reflections	25199 [R(int) = 0.0483]	
Coverage of independent reflections	94.3%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8644 and 0.7520	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	*SHELXL-2018/1* (Sheldrick, 2015*a*)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	25199 / 350 / 1523	
Goodness-of-fit on F^2	2.916	
Δ/σ_{max}	0.006	
Final R indices	18616 data; I>2σ(I)	R1 = 0.1646, wR2 = 0.4164
	all data	R1 = 0.1896, wR2 = 0.4366
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1000P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.780 and -1.035 eÅ^{-3}	
R.M.S. deviation from mean	0.152 eÅ^{-3}	

Table S5. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for TPO, **1**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
O1	0.4159(3)	0.7097(2)	0.97611(16)	0.0385(9)
O2	0.2326(3)	0.5426(2)	0.99533(17)	0.0429(9)
O3	0.2051(3)	0.3849(3)	0.95300(17)	0.0530(12)
O4	0.1143(3)	0.4437(3)	0.77054(17)	0.0516(12)
O5	0.1260(3)	0.6211(3)	0.73006(18)	0.0463(10)
O6	0.3207(3)	0.7750(2)	0.71853(16)	0.0405(9)
O7	0.4997(3)	0.7979(2)	0.72341(16)	0.0433(10)
O8	0.5869(3)	0.7546(2)	0.90824(15)	0.0396(9)
N1	0.4135(4)	0.1915(3)	0.95534(18)	0.0396(11)
N2	0.2359(4)	0.2889(3)	0.6671(2)	0.0509(14)
N3	0.8239(4)	0.5465(4)	0.6577(2)	0.0639(17)
N4	0.8395(4)	0.6322(3)	0.8880(2)	0.0500(13)
C1	0.4720(4)	0.5930(3)	0.93340(19)	0.0297(11)

C2	0.4031(4)	0.6428(3)	0.9663(2)	0.0311(11)
C3	0.3240(4)	0.6261(3)	0.9880(2)	0.0348(11)
C4	0.3108(4)	0.5602(3)	0.9752(2)	0.0334(11)
C5	0.3767(4)	0.5089(3)	0.94198(19)	0.0305(11)
C6	0.4567(4)	0.5271(3)	0.92245(19)	0.0306(11)
C7	0.3626(4)	0.4349(3)	0.9311(2)	0.0334(11)
C8	0.2931(4)	0.4408(3)	0.8895(2)	0.0346(12)
C9	0.2170(4)	0.4145(4)	0.9016(2)	0.0409(13)
C10	0.1570(4)	0.4167(4)	0.8629(2)	0.0442(14)
C11	0.1721(4)	0.4430(3)	0.8102(2)	0.0377(12)
C12	0.2479(4)	0.4687(3)	0.7953(2)	0.0314(11)
C13	0.3067(4)	0.4672(3)	0.8360(2)	0.0327(11)
C14	0.2700(4)	0.4914(3)	0.7360(2)	0.0341(11)
C15	0.2865(4)	0.5662(3)	0.7316(2)	0.0325(11)
C16	0.2126(4)	0.6301(3)	0.7285(2)	0.0341(12)
C17	0.2259(4)	0.6979(3)	0.7242(2)	0.0340(11)
C18	0.3138(4)	0.7056(3)	0.7209(2)	0.0319(11)
C19	0.3906(4)	0.6438(3)	0.72128(19)	0.0313(11)
C20	0.3749(4)	0.5750(3)	0.7274(2)	0.0326(11)
C21	0.4868(4)	0.6532(3)	0.7151(2)	0.0348(12)
C22	0.5057(4)	0.6852(3)	0.76772(19)	0.0311(11)
C23	0.5180(4)	0.7540(3)	0.7692(2)	0.0353(12)
C24	0.5439(4)	0.7793(3)	0.8161(2)	0.0335(11)
C25	0.5570(4)	0.7336(3)	0.8626(2)	0.0306(11)
C26	0.5410(4)	0.6656(3)	0.8635(2)	0.0329(11)
C27	0.5150(4)	0.6426(3)	0.8158(2)	0.0322(11)
C28	0.5589(4)	0.6132(3)	0.9117(2)	0.0314(11)
C29	0.4531(4)	0.3764(3)	0.9147(2)	0.0356(12)
C30	0.4446(4)	0.2994(3)	0.9090(2)	0.0365(12)
C31	0.4108(5)	0.2682(3)	0.9633(2)	0.0399(13)
C32	0.4923(5)	0.1384(4)	0.9611(3)	0.0540(16)
C33	0.4980(7)	0.0675(4)	0.9507(3)	0.067(2)
C34	0.4209(9)	0.0505(4)	0.9359(3)	0.080(3)
C35	0.3418(7)	0.1045(5)	0.9311(3)	0.073(3)
C36	0.3384(5)	0.1764(4)	0.9410(3)	0.0535(17)
C37	0.3492(4)	0.4316(3)	0.7079(2)	0.0411(13)
C38	0.3279(5)	0.3593(4)	0.7054(3)	0.0498(15)
C39	0.2633(6)	0.3589(4)	0.6624(3)	0.0582(19)
C40	0.1459(6)	0.2931(4)	0.6791(3)	0.0629(19)
C41	0.1204(7)	0.2292(5)	0.6841(4)	0.071(2)
C42	0.1863(6)	0.1629(4)	0.6766(3)	0.0569(18)
C43	0.2779(6)	0.1611(4)	0.6650(3)	0.0543(17)
C44	0.3010(6)	0.2237(4)	0.6603(2)	0.0518(16)
C45	0.5638(4)	0.5839(3)	0.6983(2)	0.0387(12)
C46	0.6576(4)	0.5993(4)	0.6861(3)	0.0485(15)
C47	0.7328(5)	0.5323(5)	0.6690(4)	0.070(2)
C48	0.8447(6)	0.5770(8)	0.6090(4)	0.106(4)
C49	0.9264(8)	0.5895(12)	0.5973(5)	0.166(9)
C50	0.9898(6)	0.5722(8)	0.6359(5)	0.111(5)
C51	0.9662(6)	0.5452(6)	0.6845(4)	0.077(3)
C52	0.8841(5)	0.5331(4)	0.6961(3)	0.0593(18)
C53	0.6409(4)	0.5466(3)	0.8960(2)	0.0362(12)
C54	0.7281(4)	0.5651(3)	0.8724(2)	0.0394(13)
C55	0.7681(4)	0.5995(4)	0.9149(2)	0.0470(15)
C56	0.8241(6)	0.7044(5)	0.8896(3)	0.0633(19)
C57	0.8867(5)	0.7366(5)	0.8636(4)	0.066(2)
C58	0.9646(5)	0.6926(5)	0.8355(3)	0.064(2)
C59	0.9805(6)	0.6184(5)	0.8356(4)	0.072(2)
C60	0.9154(5)	0.5912(5)	0.8616(3)	0.0599(18)
O9	0.8090(4)	0.1052(4)	0.4240(2)	0.0813(18)
O10	0.9129(3)	0.0570(3)	0.23370(19)	0.0590(13)
O11	0.8843(3)	0.8775(3)	0.1951(2)	0.0547(11)
O12	0.6575(4)	0.7559(3)	0.18852(18)	0.0539(11)

O13	0.4752(4)	0.7461(3)	0.21957(18)	0.0653(15)
O14	0.3875(4)	0.7687(3)	0.41420(18)	0.0623(14)
O15	0.5658(4)	0.7948(3)	0.46005(19)	0.0557(12)
O16	0.7701(3)	0.9434(3)	0.46113(19)	0.0566(12)
N5	0.7526(4)	0.2443(3)	0.1110(2)	0.0489(13)
C61	0.7185(5)	0.0606(4)	0.3679(2)	0.0500(16)
C62	0.7958(5)	0.0831(5)	0.3739(3)	0.062(2)
C63	0.8617(5)	0.0812(6)	0.3289(3)	0.070(2)
C64	0.8498(4)	0.0580(4)	0.2783(3)	0.0483(15)
C65	0.7732(4)	0.0357(3)	0.2704(2)	0.0390(12)
C66	0.7107(4)	0.0371(3)	0.3166(2)	0.0395(12)
C67	0.7591(4)	0.0153(3)	0.2129(2)	0.0377(12)
C68	0.7281(4)	0.9465(3)	0.2107(2)	0.0372(12)
C69	0.7942(4)	0.8798(4)	0.1993(2)	0.0430(13)
C70	0.7672(5)	0.8169(4)	0.1932(2)	0.0455(14)
C71	0.6770(4)	0.8194(3)	0.1972(2)	0.0420(13)
C72	0.6078(4)	0.8860(3)	0.2090(2)	0.0395(13)
C73	0.6357(4)	0.9482(3)	0.2153(2)	0.0367(12)
C74	0.5074(4)	0.8857(4)	0.2134(2)	0.0444(15)
C75	0.4818(4)	0.8502(4)	0.2666(2)	0.0452(15)
C76	0.4621(5)	0.7837(4)	0.2686(2)	0.0505(16)
C77	0.4323(5)	0.7546(5)	0.3173(3)	0.0571(18)
C78	0.4218(5)	0.7942(4)	0.3656(2)	0.0518(17)
C79	0.4430(4)	0.8595(4)	0.3661(2)	0.0446(15)
C80	0.4727(4)	0.8862(4)	0.3162(2)	0.0445(14)
C81	0.4286(4)	0.9050(4)	0.4186(2)	0.0457(15)
C82	0.5183(4)	0.9177(4)	0.4297(2)	0.0418(14)
C83	0.5851(4)	0.8603(4)	0.4519(2)	0.0473(15)
C84	0.6678(4)	0.8690(4)	0.4633(2)	0.0487(15)
C85	0.6866(4)	0.9346(4)	0.4513(2)	0.0448(15)
C86	0.6243(4)	0.9923(4)	0.4281(2)	0.0434(14)
C87	0.5394(4)	0.9831(4)	0.4186(2)	0.0439(14)
C88	0.6468(4)	0.0642(4)	0.4169(2)	0.0449(15)
C89	0.6980(5)	0.0808(4)	0.1829(2)	0.0448(14)
C90	0.7496(5)	0.1346(4)	0.1644(3)	0.0494(15)
C91	0.6955(5)	0.1979(4)	0.1290(3)	0.0607(19)
C92	0.7433(5)	0.3086(4)	0.1370(2)	0.0442(14)
C93	0.8029(5)	0.3474(4)	0.1211(3)	0.0555(17)
C94	0.8731(5)	0.3248(5)	0.0805(3)	0.061(2)
C95	0.8812(5)	0.2586(4)	0.0541(3)	0.0597(18)
C96	0.8218(5)	0.2201(4)	0.0701(3)	0.0518(15)
C97	0.4398(5)	0.9627(4)	0.2067(2)	0.0513(16)
C98	0.3390(6)	0.9611(5)	0.2110(3)	0.0606(18)
C99	0.3203(8)	0.9245(8)	0.1639(5)	0.055(3)
N6	0.2363(5)	0.8858(5)	0.1904(3)	0.0557(19)
C100	0.1573(6)	0.9287(5)	0.1689(4)	0.061(3)
C101	0.0720(5)	0.9202(7)	0.1882(5)	0.084(3)
C102	0.0657(6)	0.8687(7)	0.2291(5)	0.099(4)
C103	0.1448(8)	0.8258(6)	0.2506(5)	0.116(5)
C104	0.2301(6)	0.8343(5)	0.2312(4)	0.094(4)
C98A	0.3390(6)	0.9611(5)	0.2110(3)	0.0606(18)
C99B	0.3241(10)	0.8927(9)	0.1749(8)	0.055(3)
N6B	0.2216(6)	0.9473(7)	0.1550(5)	0.0557(19)
C10B	0.1704(8)	0.9081(7)	0.1866(6)	0.061(3)
C11B	0.0767(8)	0.9234(10)	0.1823(7)	0.084(3)
C12B	0.0341(7)	0.9779(10)	0.1464(8)	0.099(4)
C13B	0.0853(10)	0.0170(9)	0.1148(7)	0.116(5)
C14B	0.1790(9)	0.0017(8)	0.1191(6)	0.094(4)
C105	0.3486(5)	0.9760(5)	0.4138(3)	0.061(2)
C106	0.2564(6)	0.9639(6)	0.4078(4)	0.084(3)
C107	0.2179(11)	0.9296(8)	0.4475(6)	0.115(4)
N7	0.1413(8)	0.9003(7)	0.4362(5)	0.110(4)
C108	0.1583(7)	0.8254(7)	0.4293(6)	0.115(5)

C109	0.0873(9)	0.7973(6)	0.4190(6)	0.134(7)
C110	0.9993(8)	0.8441(8)	0.4155(6)	0.097(4)
C111	0.9822(7)	0.9190(7)	0.4224(6)	0.143(7)
C112	0.0533(9)	0.9471(6)	0.4327(6)	0.130(6)
C17A	0.2179(11)	0.9296(8)	0.4475(6)	0.115(4)
N7A	0.1367(16)	0.9461(15)	0.4166(11)	0.110(4)
C18A	0.1550(15)	0.8743(14)	0.3991(11)	0.115(5)
C19A	0.0829(18)	0.8466(14)	0.3905(12)	0.134(7)
C20A	0.9925(17)	0.8906(16)	0.3994(12)	0.097(4)
C21A	0.9742(15)	0.9624(15)	0.4170(11)	0.143(7)
C22A	0.0463(18)	0.9901(14)	0.4256(12)	0.130(6)
C113	0.5605(5)	0.1292(4)	0.4106(2)	0.0539(17)
C114	0.5782(7)	0.2036(5)	0.4037(3)	0.066(2)
C115	0.6197(11)	0.2231(8)	0.4538(5)	0.049(3)
N8	0.6403(6)	0.2911(4)	0.4421(3)	0.0481(18)
C116	0.5710(5)	0.3565(5)	0.4386(4)	0.070(3)
C117	0.5933(6)	0.4208(4)	0.4241(5)	0.081(3)
C118	0.6850(7)	0.4196(4)	0.4132(5)	0.079(3)
C119	0.7543(5)	0.3541(5)	0.4167(5)	0.084(4)
C120	0.7320(5)	0.2898(4)	0.4312(4)	0.069(3)
C15B	0.5896(15)	0.2404(11)	0.4572(7)	0.035(4)
N8B	0.6010(10)	0.3127(6)	0.4454(5)	0.0481(18)
C16B	0.5229(8)	0.3725(8)	0.4524(6)	0.070(3)
C17B	0.5293(10)	0.4427(7)	0.4407(7)	0.081(3)
C18B	0.6138(12)	0.4532(7)	0.4220(8)	0.079(3)
C19B	0.6920(10)	0.3934(9)	0.4150(8)	0.084(4)
C20B	0.6856(9)	0.3232(7)	0.4267(6)	0.069(3)
Cl1	0.65377(14)	0.88917(9)	0.90248(7)	0.0592(5)
Cl2	0.06418(15)	0.59301(14)	0.19161(10)	0.0777(6)
Cl3	0.07631(19)	0.11856(17)	0.23675(15)	0.0819(9)
Cl3A	0.9994(6)	0.1184(6)	0.4351(4)	0.0819(9)
Cl4	0.2889(3)	0.8216(3)	0.05151(17)	0.0936(12)
Cl4A	0.9590(4)	0.1848(4)	0.4252(2)	0.0936(12)
O18	0.7361(4)	0.8434(3)	0.7791(2)	0.0629(13)
O19	0.4171(4)	0.6052(3)	0.2260(2)	0.0717(16)
O20	0.0863(3)	0.2838(4)	0.9720(2)	0.0732(17)
O21	0.6076(4)	0.8849(3)	0.6996(2)	0.0721(16)
O22	0.9948(4)	0.7418(4)	0.6933(3)	0.093(2)
O23	0.7266(5)	0.7928(5)	0.6132(3)	0.104(2)
O24	0.3565(7)	0.6131(4)	0.4187(3)	0.119(3)
O25	0.2754(7)	0.9386(4)	0.9805(4)	0.114(3)
O26	0.8139(5)	0.7218(5)	0.7053(4)	0.106(2)
O27	0.0926(7)	0.6541(6)	0.3064(4)	0.132(3)
O28	0.1045(6)	0.6356(5)	0.0723(4)	0.125(3)
O29	0.1118(10)	0.7857(9)	0.0798(6)	0.098(4)
O30	0.0285(11)	0.7576(8)	0.1909(6)	0.095(4)
O31	0.2548(11)	0.6753(9)	0.3157(7)	0.104(4)
O32	0.1709(13)	0.1168(12)	0.0362(8)	0.131(6)
O33	0.0258(14)	0.6018(11)	0.4106(8)	0.128(6)
O34	0.2946(15)	0.6695(13)	0.1444(9)	0.142(7)
O35	0.8527(7)	0.8286(7)	0.5322(4)	0.141(3)
O36	0.6638(3)	0.6914(2)	0.54010(19)	0.0539(13)

Table S6. Bond lengths (Å) for TPO, **1**.

O1-C2	1.378(6)	O1-H1	0.84
O2-C4	1.369(6)	O2-H2A	0.84
O3-C9	1.373(7)	O3-H3A	0.84
O4-C11	1.375(6)	O4-H4	0.84
O5-C16	1.378(6)	O5-H5A	0.84
O6-C18	1.357(6)	O6-H6A	0.84
O7-C23	1.374(6)	O7-H7A	0.84
O8-C25	1.363(6)	O8-H8	0.84

N1-C36	1.345(8)	N1-C32	1.345(9)
N1-C31	1.471(7)	N2-C44	1.351(10)
N2-C40	1.353(10)	N2-C39	1.510(8)
N3-C52	1.349(9)	N3-C48	1.351(11)
N3-C47	1.488(9)	N4-C60	1.312(10)
N4-C56	1.332(10)	N4-C55	1.489(8)
C1-C6	1.384(7)	C1-C2	1.395(8)
C1-C28	1.523(7)	C2-C3	1.385(7)
C3-C4	1.382(8)	C3-H3B	0.95
C4-C5	1.391(8)	C5-C6	1.396(7)
C5-C7	1.527(7)	C6-H6B	0.95
C7-C8	1.525(6)	C7-C29	1.528(9)
C7-H7B	1.0	C8-C9	1.394(7)
C8-C13	1.398(7)	C9-C10	1.374(8)
C10-C11	1.383(8)	C10-H10E	0.95
C11-C12	1.395(7)	C12-C13	1.401(7)
C12-C14	1.525(7)	C13-H13B	0.95
C14-C15	1.519(7)	C14-C37	1.520(9)
C14-H14B	1.0	C15-C20	1.401(7)
C15-C16	1.406(8)	C16-C17	1.366(8)
C17-C18	1.386(7)	C17-H17	0.95
C18-C19	1.401(8)	C19-C20	1.401(7)
C19-C21	1.522(7)	C20-H20	0.95
C21-C45	1.527(9)	C21-C22	1.529(7)
C21-H21	1.0	C22-C23	1.382(8)
C22-C27	1.398(7)	C23-C24	1.395(7)
C24-C25	1.401(7)	C24-H24	0.95
C25-C26	1.387(7)	C26-C27	1.393(7)
C26-C28	1.511(7)	C27-H27	0.95
C28-C53	1.529(8)	C28-H28	1.0
C29-C30	1.526(7)	C29-H29A	0.99
C29-H29B	0.99	C30-C31	1.535(7)
C30-H30A	0.99	C30-H30B	0.99
C31-H31A	0.99	C31-H31B	0.99
C32-C33	1.360(11)	C32-H32	0.95
C33-C34	1.394(14)	C33-H33	0.95
C34-C35	1.354(15)	C34-H34	0.95
C35-C36	1.386(11)	C35-H35	0.95
C36-H36	0.95	C37-C38	1.512(8)
C37-H37A	0.99	C37-H37B	0.99
C38-C39	1.516(9)	C38-H38A	0.99
C38-H38B	0.99	C39-H39A	0.99
C39-H39B	0.99	C40-C41	1.383(11)
C40-H40	0.95	C41-C42	1.371(12)
C41-H41	0.95	C42-C43	1.387(11)
C42-H42	0.95	C43-C44	1.338(9)
C43-H43	0.95	C44-H44	0.95
C45-C46	1.541(8)	C45-H45A	0.99
C45-H45B	0.99	C46-C47	1.486(11)
C46-H46A	0.99	C46-H46B	0.99
C47-H47A	0.99	C47-H47B	0.99
C48-C49	1.337(16)	C48-H48	0.95
C49-C50	1.385(16)	C49-H49	0.95
C50-C51	1.332(14)	C50-H50	0.95
C51-C52	1.337(12)	C51-H51	0.95
C52-H52	0.95	C53-C54	1.525(7)
C53-H53A	0.99	C53-H53B	0.99
C54-C55	1.515(8)	C54-H54A	0.99
C54-H54B	0.99	C55-H55A	0.99
C55-H55B	0.99	C56-C57	1.369(11)
C56-H56	0.95	C57-C58	1.370(12)
C57-H57	0.95	C58-C59	1.366(13)
C58-H58	0.95	C59-C60	1.342(11)

C59-H59	0.95	C60-H60	0.95
O9-C62	1.359(8)	O9-H9A	0.84
O10-C64	1.371(8)	O10-H10A	0.84
O11-C69	1.357(8)	O11-H11	0.84
O12-C71	1.357(7)	O13-C76	1.382(8)
O13-H13	0.84	O14-C78	1.376(7)
O14-H14A	0.84	O15-C83	1.368(8)
O15-H15A	0.84	O16-C85	1.379(7)
O16-H16A	0.84	N5-C96	1.360(9)
N5-C92	1.365(9)	N5-C91	1.440(9)
C61-C66	1.374(9)	C61-C62	1.392(9)
C61-C88	1.519(8)	C62-C63	1.400(10)
C63-C64	1.374(10)	C63-H63	0.95
C64-C65	1.389(8)	C65-C66	1.392(8)
C65-C67	1.522(8)	C66-H66	0.95
C67-C68	1.525(8)	C67-C89	1.539(8)
C67-H67	1.0	C68-C69	1.390(9)
C68-C73	1.394(8)	C69-C70	1.395(9)
C70-C71	1.357(9)	C70-H70	0.95
C71-C72	1.412(9)	C72-C73	1.391(8)
C72-C74	1.527(8)	C73-H73	0.95
C74-C75	1.510(7)	C74-C97	1.545(10)
C74-H74	1.0	C75-C76	1.385(9)
C75-C80	1.388(9)	C76-C77	1.383(9)
C77-C78	1.392(10)	C77-H77	0.95
C78-C79	1.375(10)	C79-C80	1.386(8)
C79-C81	1.532(9)	C80-H80	0.95
C81-C82	1.513(8)	C81-C105	1.548(11)
C81-H81	1.0	C82-C87	1.388(9)
C82-C83	1.399(10)	C83-C84	1.378(9)
C84-C85	1.379(10)	C84-H84	0.95
C85-C86	1.379(10)	C86-C87	1.401(8)
C86-C88	1.518(9)	C87-H87	0.95
C88-C113	1.542(10)	C88-H88	1.0
C89-C90	1.497(8)	C89-H89A	0.99
C89-H89B	0.99	C90-C91	1.545(9)
C90-H90A	0.99	C90-H90B	0.99
C91-H91A	0.99	C91-H91B	0.99
C92-C93	1.349(10)	C92-H92	0.95
C93-C94	1.360(12)	C93-H93	0.95
C94-C95	1.406(12)	C94-H94	0.95
C95-C96	1.343(10)	C95-H95	0.95
C96-H96	0.95	C97-C98A	1.540(10)
C97-C98	1.540(10)	C97-H97A	0.99
C97-H97B	0.99	C98-C99	1.460(15)
C98-H98A	0.99	C98-H98B	0.99
C99-N6	1.716(11)	C99-H99A	0.99
C99-H99B	0.99	N6-C100	1.39
N6-C104	1.39	C100-C101	1.39
C100-H100	0.95	C101-C102	1.39
C101-H101	0.95	C102-C103	1.39
C102-H102	0.95	C103-C104	1.39
C103-H103	0.95	C104-H104	0.95
C98A-C99B	1.68(2)	C98A-H98C	0.99
C98A-H98D	0.99	C99B-N6B	1.717(11)
C99B-H99C	0.99	C99B-H99D	0.99
N6B-C10B	1.39	N6B-C14B	1.39
C10B-C11B	1.39	C10B-H10B	0.95
C11B-C12B	1.39	C11B-H11B	0.95
C12B-C13B	1.39	C12B-H12B	0.95
C13B-C14B	1.39	C13B-H13B	0.95
C14B-H14B	0.95	C105-C106	1.513(11)
C105-H10B	0.99	C105-H10C	0.99

C106-C17A	1.329(17)	C106-C107	1.329(17)
C106-N7A	1.94(2)	C106-H10D	0.99
C106-H10F	0.99	C107-N7	1.490(17)
C107-H10G	0.99	C107-H10H	0.99
N7-C108	1.39	N7-C112	1.39
C108-C109	1.39	C108-H108	0.95
C109-C110	1.39	C109-H109	0.95
C110-C111	1.39	C110-H110	0.95
C111-C112	1.39	C111-H111	0.95
C112-H112	0.95	C17A-N7A	1.47(3)
C17A-H17A	0.99	C17A-H17D	0.99
N7A-C18A	1.39	N7A-C22A	1.39
C18A-C19A	1.39	C18A-H18A	0.95
C19A-C20A	1.39	C19A-H19A	0.95
C20A-C21A	1.39	C20A-H20A	0.95
C21A-C22A	1.39	C21A-H21A	0.95
C22A-H22A	0.95	C113-C114	1.520(11)
C113-H11A	0.99	C113-H11C	0.99
C114-C115	1.540(14)	C114-C15B	1.555(19)
C114-H11D	0.99	C114-H11E	0.99
C115-N8	1.434(14)	C115-H11F	0.99
C115-H11G	0.99	N8-C116	1.39
N8-C120	1.39	C116-C117	1.39
C116-H116	0.95	C117-C118	1.39
C117-H117	0.95	C118-C119	1.39
C118-H118	0.95	C119-C120	1.39
C119-H119	0.95	C120-H120	0.95
C15B-N8B	1.45(2)	C15B-H11H	0.99
C15B-H11I	0.99	N8B-C16B	1.39
N8B-C20B	1.39	C16B-C17B	1.39
C16B-H16B	0.95	C17B-C18B	1.39
C17B-H17B	0.95	C18B-C19B	1.39
C18B-H18B	0.95	C19B-C20B	1.39
C19B-H19B	0.95	C20B-H20B	0.95
Cl3A-Cl4A	1.264(12)	O19-H19C	0.87
O19-H19D	0.87	O20-H20C	0.8701
O20-H20D	0.87	O21-H21B	0.8709
O21-H21C	0.8705	O22-H22C	0.8701
O23-H23A	0.8702	O23-H23B	0.87
O24-H24A	0.8684	O24-H24B	0.8726
O25-H25A	0.8702	O25-H25B	0.8702
O26-H26A	0.8704	O26-H26B	0.8703
O27-H27A	0.87	O27-H27B	0.87
O28-H28A	0.8701	O28-H28B	0.8701
O29-H29C	0.8701	O29-H29D	0.87
O30-H30C	0.8716	O30-H30D	0.8701
O31-H31C	0.8701	O31-H31D	0.8701
O32-H32A	0.8701	O32-H32B	0.8702
O33-H33A	0.8705	O33-H33B	0.87
O34-H34A	0.8701	O34-H34B	0.87
O35-H35A	0.8702	O35-H35B	0.8705
O36-H36A	0.8702	O36-H36B	0.8705

Table S7. Bond angles (°) for TPO, **1**.

C2-O1-H1	109.5	C4-O2-H2A	109.5
C9-O3-H3A	109.5	C11-O4-H4	109.5
C16-O5-H5A	109.5	C18-O6-H6A	109.5
C23-O7-H7A	109.5	C25-O8-H8	109.5
C36-N1-C32	121.6(6)	C36-N1-C31	119.4(6)
C32-N1-C31	119.0(5)	C44-N2-C40	121.3(6)
C44-N2-C39	119.9(6)	C40-N2-C39	118.8(6)
C52-N3-C48	119.2(7)	C52-N3-C47	121.4(7)

C48-N3-C47	119.3(6)	C60-N4-C56	119.8(6)
C60-N4-C55	121.1(6)	C56-N4-C55	119.1(7)
C6-C1-C2	117.1(5)	C6-C1-C28	123.7(5)
C2-C1-C28	119.2(5)	O1-C2-C3	120.9(5)
O1-C2-C1	117.9(5)	C3-C2-C1	121.2(5)
C4-C3-C2	119.7(5)	C4-C3-H3B	120.1
C2-C3-H3B	120.1	O2-C4-C3	121.1(5)
O2-C4-C5	117.5(5)	C3-C4-C5	121.4(5)
C4-C5-C6	116.9(5)	C4-C5-C7	120.1(4)
C6-C5-C7	122.8(5)	C1-C6-C5	123.6(5)
C1-C6-H6B	118.2	C5-C6-H6B	118.2
C8-C7-C5	112.0(4)	C8-C7-C29	111.7(5)
C5-C7-C29	112.4(4)	C8-C7-H7B	106.8
C5-C7-H7B	106.8	C29-C7-H7B	106.8
C9-C8-C13	116.9(4)	C9-C8-C7	121.3(5)
C13-C8-C7	121.6(4)	O3-C9-C10	121.1(5)
O3-C9-C8	117.8(5)	C10-C9-C8	121.0(5)
C9-C10-C11	120.9(5)	C9-C10-H10E	119.5
C11-C10-H10E	119.5	O4-C11-C10	121.8(5)
O4-C11-C12	117.5(5)	C10-C11-C12	120.7(5)
C11-C12-C13	117.0(5)	C11-C12-C14	121.1(4)
C13-C12-C14	121.6(4)	C8-C13-C12	123.4(5)
C8-C13-H13B	118.3	C12-C13-H13B	118.3
C15-C14-C37	112.8(5)	C15-C14-C12	113.2(4)
C37-C14-C12	109.7(4)	C15-C14-H14B	106.9
C37-C14-H14B	106.9	C12-C14-H14B	106.9
C20-C15-C16	116.9(5)	C20-C15-C14	122.4(5)
C16-C15-C14	120.7(4)	C17-C16-O5	121.6(5)
C17-C16-C15	121.6(5)	O5-C16-C15	116.8(5)
C16-C17-C18	120.6(5)	C16-C17-H17	119.7
C18-C17-H17	119.7	O6-C18-C17	116.8(5)
O6-C18-C19	122.7(5)	C17-C18-C19	120.4(5)
C18-C19-C20	117.8(5)	C18-C19-C21	119.6(5)
C20-C19-C21	122.6(5)	C19-C20-C15	122.5(5)
C19-C20-H20	118.7	C15-C20-H20	118.7
C19-C21-C45	114.5(5)	C19-C21-C22	110.6(4)
C45-C21-C22	110.6(4)	C19-C21-H21	106.9
C45-C21-H21	106.9	C22-C21-H21	106.9
C23-C22-C27	118.1(4)	C23-C22-C21	122.4(4)
C27-C22-C21	119.4(5)	O7-C23-C22	117.3(4)
O7-C23-C24	121.2(5)	C22-C23-C24	121.5(4)
C23-C24-C25	118.7(5)	C23-C24-H24	120.7
C25-C24-H24	120.7	O8-C25-C26	118.0(4)
O8-C25-C24	120.6(4)	C26-C25-C24	121.4(4)
C25-C26-C27	117.9(4)	C25-C26-C28	122.9(4)
C27-C26-C28	119.0(5)	C26-C27-C22	122.3(5)
C26-C27-H27	118.9	C22-C27-H27	118.9
C26-C28-C1	110.7(4)	C26-C28-C53	110.4(4)
C1-C28-C53	113.1(4)	C26-C28-H28	107.4
C1-C28-H28	107.4	C53-C28-H28	107.4
C30-C29-C7	114.9(4)	C30-C29-H29A	108.6
C7-C29-H29A	108.6	C30-C29-H29B	108.6
C7-C29-H29B	108.6	H29A-C29-H29B	107.5
C29-C30-C31	113.2(4)	C29-C30-H30A	108.9
C31-C30-H30A	108.9	C29-C30-H30B	108.9
C31-C30-H30B	108.9	H30A-C30-H30B	107.7
N1-C31-C30	109.5(5)	N1-C31-H31A	109.8
C30-C31-H31A	109.8	N1-C31-H31B	109.8
C30-C31-H31B	109.8	H31A-C31-H31B	108.2
N1-C32-C33	120.0(7)	N1-C32-H32	120.0
C33-C32-H32	120.0	C32-C33-C34	119.4(8)
C32-C33-H33	120.3	C34-C33-H33	120.3
C35-C34-C33	119.9(7)	C35-C34-H34	120.1

C33-C34-H34	120.1	C34-C35-C36	119.4(8)
C34-C35-H35	120.3	C36-C35-H35	120.3
N1-C36-C35	119.7(8)	N1-C36-H36	120.2
C35-C36-H36	120.2	C38-C37-C14	113.0(5)
C38-C37-H37A	109.0	C14-C37-H37A	109.0
C38-C37-H37B	109.0	C14-C37-H37B	109.0
H37A-C37-H37B	107.8	C37-C38-C39	112.7(5)
C37-C38-H38A	109.1	C39-C38-H38A	109.1
C37-C38-H38B	109.1	C39-C38-H38B	109.1
H38A-C38-H38B	107.8	N2-C39-C38	109.7(5)
N2-C39-H39A	109.7	C38-C39-H39A	109.7
N2-C39-H39B	109.7	C38-C39-H39B	109.7
H39A-C39-H39B	108.2	N2-C40-C41	119.1(8)
N2-C40-H40	120.5	C41-C40-H40	120.5
C42-C41-C40	119.7(8)	C42-C41-H41	120.1
C40-C41-H41	120.1	C41-C42-C43	119.4(7)
C41-C42-H42	120.3	C43-C42-H42	120.3
C44-C43-C42	119.9(7)	C44-C43-H43	120.0
C42-C43-H43	120.0	C43-C44-N2	120.6(7)
C43-C44-H44	119.7	N2-C44-H44	119.7
C21-C45-C46	111.8(5)	C21-C45-H45A	109.3
C46-C45-H45A	109.3	C21-C45-H45B	109.3
C46-C45-H45B	109.3	H45A-C45-H45B	107.9
C47-C46-C45	112.2(6)	C47-C46-H46A	109.2
C45-C46-H46A	109.2	C47-C46-H46B	109.2
C45-C46-H46B	109.2	H46A-C46-H46B	107.9
C46-C47-N3	112.6(7)	C46-C47-H47A	109.1
N3-C47-H47A	109.1	C46-C47-H47B	109.1
N3-C47-H47B	109.1	H47A-C47-H47B	107.8
C49-C48-N3	120.7(8)	C49-C48-H48	119.6
N3-C48-H48	119.6	C48-C49-C50	119.6(11)
C48-C49-H49	120.2	C50-C49-H49	120.2
C51-C50-C49	118.5(9)	C51-C50-H50	120.7
C49-C50-H50	120.7	C50-C51-C52	121.6(8)
C50-C51-H51	119.2	C52-C51-H51	119.2
C51-C52-N3	120.1(7)	C51-C52-H52	119.9
N3-C52-H52	119.9	C54-C53-C28	114.4(5)
C54-C53-H53A	108.7	C28-C53-H53A	108.7
C54-C53-H53B	108.7	C28-C53-H53B	108.7
H53A-C53-H53B	107.6	C55-C54-C53	112.2(5)
C55-C54-H54A	109.2	C53-C54-H54A	109.2
C55-C54-H54B	109.2	C53-C54-H54B	109.2
H54A-C54-H54B	107.9	N4-C55-C54	110.7(5)
N4-C55-H55A	109.5	C54-C55-H55A	109.5
N4-C55-H55B	109.5	C54-C55-H55B	109.5
H55A-C55-H55B	108.1	N4-C56-C57	120.7(8)
N4-C56-H56	119.7	C57-C56-H56	119.7
C56-C57-C58	118.3(8)	C56-C57-H57	120.9
C58-C57-H57	120.9	C59-C58-C57	120.3(7)
C59-C58-H58	119.8	C57-C58-H58	119.8
C60-C59-C58	117.7(9)	C60-C59-H59	121.2
C58-C59-H59	121.2	N4-C60-C59	123.2(8)
N4-C60-H60	118.4	C59-C60-H60	118.4
C62-O9-H9A	109.5	C64-O10-H10A	109.5
C69-O11-H11	109.5	C76-O13-H13	109.5
C78-O14-H14A	109.5	C83-O15-H15A	109.5
C85-O16-H16A	109.5	C96-N5-C92	119.7(6)
C96-N5-C91	118.6(7)	C92-N5-C91	121.5(6)
C66-C61-C62	116.9(6)	C66-C61-C88	123.4(5)
C62-C61-C88	119.7(6)	O9-C62-C61	120.0(6)
O9-C62-C63	119.6(6)	C61-C62-C63	120.4(6)
C64-C63-C62	120.1(6)	C64-C63-H63	119.9
C62-C63-H63	119.9	O10-C64-C63	120.8(6)

O10-C64-C65	117.8(6)	C63-C64-C65	121.4(6)
C64-C65-C66	116.3(5)	C64-C65-C67	119.8(5)
C66-C65-C67	123.8(5)	C61-C66-C65	124.8(5)
C61-C66-H66	117.6	C65-C66-H66	117.6
C65-C67-C68	114.5(4)	C65-C67-C89	111.8(5)
C68-C67-C89	112.6(5)	C65-C67-H67	105.7
C68-C67-H67	105.7	C89-C67-H67	105.7
C69-C68-C73	118.1(6)	C69-C68-C67	118.9(5)
C73-C68-C67	122.8(5)	O11-C69-C68	118.5(6)
O11-C69-C70	121.5(6)	C68-C69-C70	120.0(6)
C71-C70-C69	121.4(6)	C71-C70-H70	119.3
C69-C70-H70	119.3	C70-C71-O12	117.0(6)
C70-C71-C72	120.4(6)	O12-C71-C72	122.6(6)
C73-C72-C71	117.6(5)	C73-C72-C74	124.0(6)
C71-C72-C74	118.4(5)	C72-C73-C68	122.5(6)
C72-C73-H73	118.7	C68-C73-H73	118.7
C75-C74-C72	110.9(4)	C75-C74-C97	110.8(6)
C72-C74-C97	113.1(5)	C75-C74-H74	107.2
C72-C74-H74	107.2	C97-C74-H74	107.2
C76-C75-C80	117.1(5)	C76-C75-C74	123.1(5)
C80-C75-C74	119.8(6)	O13-C76-C77	120.6(6)
O13-C76-C75	117.2(5)	C77-C76-C75	122.2(6)
C76-C77-C78	118.2(7)	C76-C77-H77	120.9
C78-C77-H77	120.9	C79-C78-O14	118.5(6)
C79-C78-C77	122.0(6)	O14-C78-C77	119.5(6)
C78-C79-C80	117.6(6)	C78-C79-C81	122.5(5)
C80-C79-C81	119.8(6)	C79-C80-C75	123.0(6)
C79-C80-H80	118.5	C75-C80-H80	118.5
C82-C81-C79	109.9(5)	C82-C81-C105	114.3(6)
C79-C81-C105	109.6(5)	C82-C81-H81	107.6
C79-C81-H81	107.6	C105-C81-H81	107.6
C87-C82-C83	117.4(5)	C87-C82-C81	123.9(6)
C83-C82-C81	118.7(6)	O15-C83-C84	121.7(6)
O15-C83-C82	117.2(5)	C84-C83-C82	121.1(6)
C83-C84-C85	119.8(6)	C83-C84-H84	120.1
C85-C84-H84	120.1	O16-C85-C84	120.4(6)
O16-C85-C86	118.2(6)	C84-C85-C86	121.4(5)
C85-C86-C87	117.8(6)	C85-C86-C88	119.7(5)
C87-C86-C88	122.4(6)	C82-C87-C86	122.3(6)
C82-C87-H87	118.8	C86-C87-H87	118.8
C86-C88-C61	113.0(6)	C86-C88-C113	112.7(5)
C61-C88-C113	110.7(5)	C86-C88-H88	106.7
C61-C88-H88	106.7	C113-C88-H88	106.7
C90-C89-C67	110.9(5)	C90-C89-H89A	109.5
C67-C89-H89A	109.5	C90-C89-H89B	109.5
C67-C89-H89B	109.5	H89A-C89-H89B	108.0
C89-C90-C91	113.6(5)	C89-C90-H90A	108.8
C91-C90-H90A	108.8	C89-C90-H90B	108.8
C91-C90-H90B	108.8	H90A-C90-H90B	107.7
N5-C91-C90	109.2(5)	N5-C91-H91A	109.8
C90-C91-H91A	109.8	N5-C91-H91B	109.8
C90-C91-H91B	109.8	H91A-C91-H91B	108.3
C93-C92-N5	119.1(7)	C93-C92-H92	120.4
N5-C92-H92	120.4	C92-C93-C94	122.8(7)
C92-C93-H93	118.6	C94-C93-H93	118.6
C93-C94-C95	117.2(7)	C93-C94-H94	121.4
C95-C94-H94	121.4	C96-C95-C94	119.8(8)
C96-C95-H95	120.1	C94-C95-H95	120.1
C95-C96-N5	121.4(7)	C95-C96-H96	119.3
N5-C96-H96	119.3	C98A-C97-C74	112.2(6)
C98-C97-C74	112.2(6)	C98-C97-H97A	109.2
C74-C97-H97A	109.2	C98-C97-H97B	109.2
C74-C97-H97B	109.2	H97A-C97-H97B	107.9

C99-C98-C97	112.0(7)	C99-C98-H98A	109.2
C97-C98-H98A	109.2	C99-C98-H98B	109.2
C97-C98-H98B	109.2	H98A-C98-H98B	107.9
C98-C99-N6	104.2(8)	C98-C99-H99A	110.9
N6-C99-H99A	110.9	C98-C99-H99B	110.9
N6-C99-H99B	110.9	H99A-C99-H99B	108.9
C100-N6-C104	120.0	C100-N6-C99	104.1(7)
C104-N6-C99	135.0(7)	C101-C100-N6	120.0
C101-C100-H100	120.0	N6-C100-H100	120.0
C100-C101-C102	120.0	C100-C101-H101	120.0
C102-C101-H101	120.0	C101-C102-C103	120.0
C101-C102-H102	120.0	C103-C102-H102	120.0
C104-C103-C102	120.0	C104-C103-H103	120.0
C102-C103-H103	120.0	C103-C104-N6	120.0
C103-C104-H104	120.0	N6-C104-H104	120.0
C97-C98A-C99B	113.3(8)	C97-C98A-H98C	108.9
C99B-C98A-H98C	108.9	C97-C98A-H98D	108.9
C99B-C98A-H98D	108.9	H98C-C98A-H98D	107.7
C98A-C99B-N6B	91.9(9)	C98A-C99B-H99C	113.3
N6B-C99B-H99C	113.3	C98A-C99B-H99D	113.3
N6B-C99B-H99D	113.3	H99C-C99B-H99D	110.6
C10B-N6B-C14B	120.0	C10B-N6B-C99B	93.0(9)
C14B-N6B-C99B	146.3(10)	C11B-C10B-N6B	120.0
C11B-C10B-H10B	120.0	N6B-C10B-H10B	120.0
C10B-C11B-C12B	120.0	C10B-C11B-H11B	120.0
C12B-C11B-H11B	120.0	C11B-C12B-C13B	120.0
C11B-C12B-H12B	120.0	C13B-C12B-H12B	120.0
C14B-C13B-C12B	120.0	C14B-C13B-H13B	120.0
C12B-C13B-H13B	120.0	C13B-C14B-N6B	120.0
C13B-C14B-H14B	120.0	N6B-C14B-H14B	120.0
C106-C105-C81	114.7(8)	C106-C105-H10B	108.6
C81-C105-H10B	108.6	C106-C105-H10C	108.6
C81-C105-H10C	108.6	H10B-C105-H10C	107.6
C17A-C106-C105	119.9(10)	C107-C106-C105	119.9(10)
C17A-C106-N7A	49.1(11)	C105-C106-N7A	168.1(11)
C107-C106-H10D	107.4	C105-C106-H10D	107.4
C107-C106-H10F	107.4	C105-C106-H10F	107.4
H10D-C106-H10F	106.9	C106-C107-N7	119.9(12)
C106-C107-H10G	107.3	N7-C107-H10G	107.3
C106-C107-H10H	107.3	N7-C107-H10H	107.3
H10G-C107-H10H	106.9	C108-N7-C112	120.0
C108-N7-C107	119.5(10)	C112-N7-C107	120.5(10)
C109-C108-N7	120.0	C109-C108-H108	120.0
N7-C108-H108	120.0	C110-C109-C108	120.0
C110-C109-H109	120.0	C108-C109-H109	120.0
C109-C110-C111	120.0	C109-C110-H110	120.0
C111-C110-H110	120.0	C112-C111-C110	120.0
C112-C111-H111	120.0	C110-C111-H111	120.0
C111-C112-N7	120.0	C111-C112-H112	120.0
N7-C112-H112	120.0	C106-C17A-N7A	87.8(14)
C106-C17A-H17A	114.0	N7A-C17A-H17A	114.0
C106-C17A-H17D	114.0	N7A-C17A-H17D	114.0
H17A-C17A-H17D	111.2	C18A-N7A-C22A	120.0
C18A-N7A-C17A	93.7(15)	C22A-N7A-C17A	134.9(16)
C18A-N7A-C106	103.9(13)	C22A-N7A-C106	134.8(13)
C17A-N7A-C106	43.1(9)	C19A-C18A-N7A	120.0
C19A-C18A-H18A	120.0	N7A-C18A-H18A	120.0
C18A-C19A-C20A	120.0	C18A-C19A-H19A	120.0
C20A-C19A-H19A	120.0	C19A-C20A-C21A	120.0
C19A-C20A-H20A	120.0	C21A-C20A-H20A	120.0
C22A-C21A-C20A	120.0	C22A-C21A-H21A	120.0
C20A-C21A-H21A	120.0	C21A-C22A-N7A	120.0
C21A-C22A-H22A	120.0	N7A-C22A-H22A	120.0

C114-C113-C88	114.9(6)	C114-C113-H11A	108.5
C88-C113-H11A	108.5	C114-C113-H11C	108.5
C88-C113-H11C	108.5	H11A-C113-H11C	107.5
C113-C114-C115	111.7(7)	C113-C114-C15B	116.3(8)
C113-C114-H11D	109.3	C115-C114-H11D	109.3
C113-C114-H11E	109.3	C115-C114-H11E	109.3
H11D-C114-H11E	107.9	N8-C115-C114	108.0(9)
N8-C115-H11F	110.1	C114-C115-H11F	110.1
N8-C115-H11G	110.1	C114-C115-H11G	110.1
H11F-C115-H11G	108.4	C116-N8-C120	120.0
C116-N8-C115	121.5(8)	C120-N8-C115	118.4(8)
C117-C116-N8	120.0	C117-C116-H116	120.0
N8-C116-H116	120.0	C116-C117-C118	120.0
C116-C117-H117	120.0	C118-C117-H117	120.0
C119-C118-C117	120.0	C119-C118-H118	120.0
C117-C118-H118	120.0	C120-C119-C118	120.0
C120-C119-H119	120.0	C118-C119-H119	120.0
C119-C120-N8	120.0	C119-C120-H120	120.0
N8-C120-H120	120.0	N8B-C15B-C114	110.9(12)
N8B-C15B-H11H	109.5	C114-C15B-H11H	109.5
N8B-C15B-H11I	109.5	C114-C15B-H11I	109.5
H11H-C15B-H11I	108.0	C16B-N8B-C20B	120.0
C16B-N8B-C15B	117.5(12)	C20B-N8B-C15B	122.5(12)
N8B-C16B-C17B	120.0	N8B-C16B-H16B	120.0
C17B-C16B-H16B	120.0	C18B-C17B-C16B	120.0
C18B-C17B-H17B	120.0	C16B-C17B-H17B	120.0
C19B-C18B-C17B	120.0	C19B-C18B-H18B	120.0
C17B-C18B-H18B	120.0	C18B-C19B-C20B	120.0
C18B-C19B-H19B	120.0	C20B-C19B-H19B	120.0
C19B-C20B-N8B	120.0	C19B-C20B-H20B	120.0
N8B-C20B-H20B	120.0	H19C-O19-H19D	104.5
H20C-O20-H20D	103.9	H21B-O21-H21C	104.0
H23A-O23-H23B	104.5	H24A-O24-H24B	104.5
H25A-O25-H25B	104.0	H26A-O26-H26B	104.0
H27A-O27-H27B	104.0	H28A-O28-H28B	104.0
H29C-O29-H29D	104.5	H30C-O30-H30D	103.9
H31C-O31-H31D	104.0	H32A-O32-H32B	104.0
H33A-O33-H33B	104.0	H34A-O34-H34B	104.0
H35A-O35-H35B	104.0	H36A-O36-H36B	104.0

Table S8. Torsion angles (°) for TPO, **1**.

C6-C1-C2-O1	-177.9(4)	C28-C1-C2-O1	2.1(6)
C6-C1-C2-C3	1.6(6)	C28-C1-C2-C3	-178.4(4)
O1-C2-C3-C4	176.6(4)	C1-C2-C3-C4	-2.9(7)
C2-C3-C4-O2	-178.9(4)	C2-C3-C4-C5	2.0(7)
O2-C4-C5-C6	-179.0(4)	C3-C4-C5-C6	0.1(7)
O2-C4-C5-C7	-2.6(6)	C3-C4-C5-C7	176.6(4)
C2-C1-C6-C5	0.6(7)	C28-C1-C6-C5	-179.4(4)
C4-C5-C6-C1	-1.5(7)	C7-C5-C6-C1	-177.8(4)
C4-C5-C7-C8	76.2(6)	C6-C5-C7-C8	-107.6(5)
C4-C5-C7-C29	-157.1(4)	C6-C5-C7-C29	19.1(6)
C5-C7-C8-C9	-126.1(6)	C29-C7-C8-C9	106.9(6)
C5-C7-C8-C13	59.3(7)	C29-C7-C8-C13	-67.7(7)
C13-C8-C9-O3	176.7(6)	C7-C8-C9-O3	1.8(9)
C13-C8-C9-C10	-2.0(10)	C7-C8-C9-C10	-176.8(6)
O3-C9-C10-C11	-176.4(6)	C8-C9-C10-C11	2.1(11)
C9-C10-C11-O4	178.1(6)	C9-C10-C11-C12	-0.9(10)
O4-C11-C12-C13	-179.5(6)	C10-C11-C12-C13	-0.5(9)
O4-C11-C12-C14	-4.5(9)	C10-C11-C12-C14	174.5(6)
C9-C8-C13-C12	0.6(9)	C7-C8-C13-C12	175.4(6)
C11-C12-C13-C8	0.6(9)	C14-C12-C13-C8	-174.4(5)
C11-C12-C14-C15	130.2(6)	C13-C12-C14-C15	-55.0(7)

C11-C12-C14-C37	-102.8(6)	C13-C12-C14-C37	72.0(7)
C37-C14-C15-C20	-28.8(6)	C12-C14-C15-C20	96.5(6)
C37-C14-C15-C16	147.7(5)	C12-C14-C15-C16	-87.0(6)
C20-C15-C16-C17	-3.0(7)	C14-C15-C16-C17	-179.7(5)
C20-C15-C16-O5	177.1(4)	C14-C15-C16-O5	0.4(7)
O5-C16-C17-C18	-177.8(5)	C15-C16-C17-C18	2.3(8)
C16-C17-C18-O6	-178.0(4)	C16-C17-C18-C19	0.6(7)
O6-C18-C19-C20	176.0(4)	C17-C18-C19-C20	-2.4(7)
O6-C18-C19-C21	-4.1(7)	C17-C18-C19-C21	177.5(4)
C18-C19-C20-C15	1.6(7)	C21-C19-C20-C15	-178.3(4)
C16-C15-C20-C19	1.1(7)	C14-C15-C20-C19	177.7(4)
C18-C19-C21-C45	-161.8(4)	C20-C19-C21-C45	18.1(6)
C18-C19-C21-C22	72.4(6)	C20-C19-C21-C22	-107.6(6)
C19-C21-C22-C23	-114.0(6)	C45-C21-C22-C23	118.0(6)
C19-C21-C22-C27	68.8(7)	C45-C21-C22-C27	-59.2(6)
C27-C22-C23-O7	-173.7(5)	C21-C22-C23-O7	9.1(8)
C27-C22-C23-C24	3.5(8)	C21-C22-C23-C24	-173.7(5)
O7-C23-C24-C25	176.7(5)	C22-C23-C24-C25	-0.4(9)
C23-C24-C25-O8	176.6(5)	C23-C24-C25-C26	-2.7(8)
O8-C25-C26-C27	-176.8(5)	C24-C25-C26-C27	2.5(8)
O8-C25-C26-C28	-2.4(8)	C24-C25-C26-C28	176.9(5)
C25-C26-C27-C22	0.7(8)	C28-C26-C27-C22	-173.8(5)
C23-C22-C27-C26	-3.7(8)	C21-C22-C27-C26	173.6(5)
C25-C26-C28-C1	123.5(6)	C27-C26-C28-C1	-62.2(7)
C25-C26-C28-C53	-110.4(6)	C27-C26-C28-C53	63.8(6)
C6-C1-C28-C26	102.6(6)	C2-C1-C28-C26	-77.4(6)
C6-C1-C28-C53	-21.9(6)	C2-C1-C28-C53	158.1(4)
C8-C7-C29-C30	-59.1(5)	C5-C7-C29-C30	174.1(4)
C7-C29-C30-C31	-63.6(6)	C36-N1-C31-C30	-91.8(7)
C32-N1-C31-C30	86.3(6)	C29-C30-C31-N1	-174.3(5)
C36-N1-C32-C33	1.9(10)	C31-N1-C32-C33	-176.1(6)
N1-C32-C33-C34	-2.1(11)	C32-C33-C34-C35	1.1(12)
C33-C34-C35-C36	0.0(12)	C32-N1-C36-C35	-0.8(9)
C31-N1-C36-C35	177.3(6)	C34-C35-C36-N1	-0.2(11)
C15-C14-C37-C38	-172.2(4)	C12-C14-C37-C38	60.6(6)
C14-C37-C38-C39	75.0(7)	C44-N2-C39-C38	-60.2(8)
C40-N2-C39-C38	118.7(7)	C37-C38-C39-N2	-173.0(6)
C44-N2-C40-C41	-0.4(10)	C39-N2-C40-C41	-179.3(6)
N2-C40-C41-C42	-0.2(11)	C40-C41-C42-C43	1.0(11)
C41-C42-C43-C44	-1.1(10)	C42-C43-C44-N2	0.5(9)
C40-N2-C44-C43	0.3(9)	C39-N2-C44-C43	179.1(6)
C19-C21-C45-C46	173.2(4)	C22-C21-C45-C46	-61.0(5)
C21-C45-C46-C47	-179.4(5)	C45-C46-C47-N3	-179.4(6)
C52-N3-C47-C46	97.2(10)	C48-N3-C47-C46	-79.2(11)
C52-N3-C48-C49	4.(2)	C47-N3-C48-C49	-179.1(15)
N3-C48-C49-C50	-1.(3)	C48-C49-C50-C51	-2.(3)
C49-C50-C51-C52	2.(2)	C50-C51-C52-N3	1.7(16)
C48-N3-C52-C51	-4.6(14)	C47-N3-C52-C51	178.9(9)
C26-C28-C53-C54	53.4(5)	C1-C28-C53-C54	178.1(4)
C28-C53-C54-C55	67.2(6)	C60-N4-C55-C54	-63.4(8)
C56-N4-C55-C54	114.5(7)	C53-C54-C55-N4	-167.1(5)
C60-N4-C56-C57	0.3(11)	C55-N4-C56-C57	-177.6(7)
N4-C56-C57-C58	0.8(12)	C56-C57-C58-C59	-2.6(12)
C57-C58-C59-C60	3.3(12)	C56-N4-C60-C59	0.3(12)
C55-N4-C60-C59	178.2(7)	C58-C59-C60-N4	-2.1(13)
C66-C61-C62-O9	-178.3(8)	C88-C61-C62-O9	3.0(12)
C66-C61-C62-C63	-0.2(12)	C88-C61-C62-C63	-179.0(8)
O9-C62-C63-C64	179.0(8)	C61-C62-C63-C64	0.9(14)
C62-C63-C64-O10	178.9(8)	C62-C63-C64-C65	-0.3(13)
O10-C64-C65-C66	179.8(6)	C63-C64-C65-C66	-1.1(10)
O10-C64-C65-C67	-3.3(9)	C63-C64-C65-C67	175.8(7)
C62-C61-C66-C65	-1.3(11)	C88-C61-C66-C65	177.4(6)
C64-C65-C66-C61	1.9(10)	C67-C65-C66-C61	-174.9(6)

C64-C65-C67-C68	136.7(6)	C66-C65-C67-C68	-46.6(8)
C64-C65-C67-C89	-93.6(7)	C66-C65-C67-C89	83.0(7)
C65-C67-C68-C69	-94.6(6)	C89-C67-C68-C69	136.2(5)
C65-C67-C68-C73	90.7(6)	C89-C67-C68-C73	-38.5(7)
C73-C68-C69-O11	-179.5(5)	C67-C68-C69-O11	5.5(8)
C73-C68-C69-C70	-0.5(8)	C67-C68-C69-C70	-175.5(5)
O11-C69-C70-C71	-179.7(5)	C68-C69-C70-C71	1.4(9)
C69-C70-C71-O12	177.5(5)	C69-C70-C71-C72	-1.7(8)
C70-C71-C72-C73	1.1(8)	O12-C71-C72-C73	-177.9(5)
C70-C71-C72-C74	-179.6(5)	O12-C71-C72-C74	1.3(7)
C71-C72-C73-C68	-0.3(7)	C74-C72-C73-C68	-179.5(5)
C69-C68-C73-C72	0.0(7)	C67-C68-C73-C72	174.8(5)
C73-C72-C74-C75	-106.6(6)	C71-C72-C74-C75	74.1(7)
C73-C72-C74-C97	18.6(7)	C71-C72-C74-C97	-160.6(5)
C72-C74-C75-C76	-111.6(7)	C97-C74-C75-C76	121.9(7)
C72-C74-C75-C80	71.6(8)	C97-C74-C75-C80	-54.9(7)
C80-C75-C76-O13	-177.1(6)	C74-C75-C76-O13	6.0(10)
C80-C75-C76-C77	1.7(10)	C74-C75-C76-C77	-175.2(7)
O13-C76-C77-C78	178.9(7)	C75-C76-C77-C78	0.2(11)
C76-C77-C78-C79	-2.1(11)	C76-C77-C78-O14	176.5(7)
O14-C78-C79-C80	-176.5(6)	C77-C78-C79-C80	2.1(10)
O14-C78-C79-C81	-0.8(10)	C77-C78-C79-C81	177.8(6)
C78-C79-C80-C75	-0.1(10)	C81-C79-C80-C75	-175.9(6)
C76-C75-C80-C79	-1.7(10)	C74-C75-C80-C79	175.3(6)
C78-C79-C81-C82	123.5(7)	C80-C79-C81-C82	-60.9(8)
C78-C79-C81-C105	-110.1(7)	C80-C79-C81-C105	65.5(7)
C79-C81-C82-C87	102.7(7)	C105-C81-C82-C87	-21.0(8)
C79-C81-C82-C83	-76.4(7)	C105-C81-C82-C83	159.9(5)
C87-C82-C83-O15	-176.7(5)	C81-C82-C83-O15	2.5(8)
C87-C82-C83-C84	1.4(9)	C81-C82-C83-C84	-179.4(6)
O15-C83-C84-C85	176.1(6)	C82-C83-C84-C85	-1.9(9)
C83-C84-C85-O16	-178.2(6)	C83-C84-C85-C86	0.1(9)
O16-C85-C86-C87	-179.6(5)	C84-C85-C86-C87	2.1(9)
O16-C85-C86-C88	-3.2(8)	C84-C85-C86-C88	178.5(6)
C83-C82-C87-C86	0.9(8)	C81-C82-C87-C86	-178.2(5)
C85-C86-C87-C82	-2.7(9)	C88-C86-C87-C82	-178.9(5)
C85-C86-C88-C61	73.8(7)	C87-C86-C88-C61	-110.0(7)
C85-C86-C88-C113	-159.9(5)	C87-C86-C88-C113	16.4(7)
C66-C61-C88-C86	53.5(9)	C62-C61-C88-C86	-127.9(7)
C66-C61-C88-C113	-73.9(9)	C62-C61-C88-C113	104.7(8)
C65-C67-C89-C90	74.0(6)	C68-C67-C89-C90	-155.4(5)
C67-C89-C90-C91	174.3(6)	C96-N5-C91-C90	74.9(8)
C92-N5-C91-C90	-100.0(7)	C89-C90-C91-N5	-177.1(6)
C96-N5-C92-C93	0.4(8)	C91-N5-C92-C93	175.2(6)
N5-C92-C93-C94	-0.7(9)	C92-C93-C94-C95	1.0(10)
C93-C94-C95-C96	-1.0(10)	C94-C95-C96-N5	0.8(10)
C92-N5-C96-C95	-0.5(9)	C91-N5-C96-C95	-175.4(6)
C75-C74-C97-C98A	-55.0(7)	C72-C74-C97-C98A	179.7(5)
C75-C74-C97-C98	-55.0(7)	C72-C74-C97-C98	179.7(5)
C74-C97-C98-C99	-68.7(9)	C97-C98-C99-N6	149.1(7)
C98-C99-N6-C100	107.5(9)	C98-C99-N6-C104	-60.5(14)
C104-N6-C100-C101	0	C99-N6-C100-C101	-170.2(8)
N6-C100-C101-C102	0	C100-C101-C102-C103	0
C101-C102-C103-C104	0	C102-C103-C104-N6	0
C100-N6-C104-C103	0	C99-N6-C104-C103	166.6(11)
C74-C97-C98A-C99B	-44.7(9)	C97-C98A-C99B-N6B	-141.7(8)
C98A-C99B-N6B-C10B	-111.6(10)	C98A-C99B-N6B-C14B	79.6(19)
C14B-N6B-C10B-C11B	0	C99B-N6B-C10B-C11B	-172.8(11)
N6B-C10B-C11B-C12B	0	C10B-C11B-C12B-C13B	0
C11B-C12B-C13B-C14B	0	C12B-C13B-C14B-N6B	0
C10B-N6B-C14B-C13B	0	C99B-N6B-C14B-C13B	167.1(19)
C82-C81-C105-C106	-174.8(6)	C79-C81-C105-C106	61.4(8)
C81-C105-C106-C17A	61.3(13)	C81-C105-C106-C107	61.3(13)

C81-C105-C106-N7A	82.(6)	C105-C106-C107-N7	-163.9(11)
C106-C107-N7-C108	104.7(14)	C106-C107-N7-C112	-75.6(17)
C112-N7-C108-C109	0	C107-N7-C108-C109	179.7(12)
N7-C108-C109-C110	0	C108-C109-C110-C111	0
C109-C110-C111-C112	0	C110-C111-C112-N7	0
C108-N7-C112-C111	0	C107-N7-C112-C111	-179.7(12)
C105-C106-C17A-N7A	174.5(14)	C106-C17A-N7A-C18A	106.4(12)
C106-C17A-N7A-C22A	-113.0(19)	C22A-N7A-C18A-C19A	0
C17A-N7A-C18A-C19A	148.8(18)	C106-N7A-C18A-C19A	-168.8(15)
N7A-C18A-C19A-C20A	0	C18A-C19A-C20A-C21A	0
C19A-C20A-C21A-C22A	0	C20A-C21A-C22A-N7A	0
C18A-N7A-C22A-C21A	0	C17A-N7A-C22A-C21A	-133.(2)
C106-N7A-C22A-C21A	165.(2)	C86-C88-C113-C114	175.6(5)
C61-C88-C113-C114	-56.8(7)	C88-C113-C114-C115	-60.8(10)
C88-C113-C114-C15B	-79.8(12)	C113-C114-C115-N8	175.9(9)
C114-C115-N8-C116	68.7(12)	C114-C115-N8-C120	-107.8(10)
C120-N8-C116-C117	0	C115-N8-C116-C117	-176.4(9)
N8-C116-C117-C118	0	C116-C117-C118-C119	0
C117-C118-C119-C120	0	C118-C119-C120-N8	0
C116-N8-C120-C119	0	C115-N8-C120-C119	176.5(8)
C113-C114-C15B-N8B	-176.8(12)	C114-C15B-N8B-C16B	95.4(15)
C114-C15B-N8B-C20B	-83.2(16)	C20B-N8B-C16B-C17B	0
C15B-N8B-C16B-C17B	-178.7(13)	N8B-C16B-C17B-C18B	0
C16B-C17B-C18B-C19B	0	C17B-C18B-C19B-C20B	0
C18B-C19B-C20B-N8B	0	C16B-N8B-C20B-C19B	0
C15B-N8B-C20B-C19B	178.6(14)		

Table S9. Anisotropic atomic displacement parameters (Å^2) for TPO, **1**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.046(2)	0.0320(19)	0.041(2)	-0.0013(16)	-0.0064(17)	-0.0158(18)
O2	0.035(2)	0.051(2)	0.046(2)	0.0133(19)	0.0018(16)	-0.021(2)
O3	0.048(3)	0.084(3)	0.042(2)	0.024(2)	-0.0093(18)	-0.044(3)
O4	0.044(3)	0.080(3)	0.046(2)	0.020(2)	-0.0195(19)	-0.040(2)
O5	0.028(2)	0.058(3)	0.057(3)	0.002(2)	-0.0069(17)	-0.020(2)
O6	0.047(2)	0.040(2)	0.038(2)	0.0092(17)	-0.0046(17)	-0.0197(19)
O7	0.054(3)	0.055(2)	0.0345(19)	0.0222(18)	-0.0177(17)	-0.035(2)
O8	0.049(2)	0.046(2)	0.0351(19)	0.0070(17)	-0.0105(16)	-0.031(2)
N1	0.057(3)	0.040(3)	0.027(2)	0.0056(19)	-0.002(2)	-0.025(2)
N2	0.075(4)	0.045(3)	0.041(3)	0.004(2)	-0.010(3)	-0.029(3)
N3	0.042(3)	0.102(5)	0.048(3)	-0.001(3)	-0.006(2)	-0.021(3)
N4	0.040(3)	0.064(4)	0.052(3)	0.004(3)	-0.009(2)	-0.023(3)
C1	0.036(3)	0.033(3)	0.025(2)	0.011(2)	-0.0088(19)	-0.018(2)
C2	0.036(3)	0.035(3)	0.027(2)	0.008(2)	-0.010(2)	-0.016(2)
C3	0.035(3)	0.041(3)	0.027(2)	0.009(2)	-0.004(2)	-0.008(2)
C4	0.031(3)	0.042(3)	0.030(2)	0.012(2)	-0.004(2)	-0.016(2)
C5	0.032(3)	0.040(3)	0.023(2)	0.012(2)	-0.0039(19)	-0.018(2)
C6	0.033(3)	0.042(3)	0.021(2)	0.006(2)	-0.0029(18)	-0.018(2)
C7	0.038(3)	0.042(3)	0.028(2)	0.011(2)	-0.007(2)	-0.024(2)
C8	0.035(3)	0.043(3)	0.032(3)	0.005(2)	-0.007(2)	-0.020(2)
C9	0.041(3)	0.056(4)	0.033(3)	0.011(3)	-0.003(2)	-0.027(3)
C10	0.039(3)	0.059(4)	0.043(3)	0.011(3)	-0.005(2)	-0.030(3)
C11	0.034(3)	0.046(3)	0.039(3)	0.009(2)	-0.009(2)	-0.021(3)
C12	0.030(3)	0.035(3)	0.033(3)	0.009(2)	-0.008(2)	-0.016(2)
C13	0.033(3)	0.042(3)	0.030(2)	0.006(2)	-0.005(2)	-0.021(2)
C14	0.037(3)	0.039(3)	0.031(2)	0.004(2)	-0.009(2)	-0.018(2)
C15	0.037(3)	0.043(3)	0.025(2)	0.011(2)	-0.008(2)	-0.023(2)
C16	0.023(3)	0.052(3)	0.031(2)	0.004(2)	-0.0050(19)	-0.015(2)
C17	0.033(3)	0.040(3)	0.029(2)	0.007(2)	-0.005(2)	-0.011(2)
C18	0.037(3)	0.039(3)	0.024(2)	0.007(2)	-0.0043(19)	-0.018(2)
C19	0.035(3)	0.044(3)	0.020(2)	0.006(2)	-0.0050(19)	-0.020(2)
C20	0.031(3)	0.042(3)	0.028(2)	0.007(2)	-0.0081(19)	-0.015(2)

C21	0.036(3)	0.053(3)	0.023(2)	0.006(2)	-0.0040(19)	-0.025(3)
C22	0.030(3)	0.046(3)	0.022(2)	0.005(2)	-0.0027(18)	-0.019(2)
C23	0.036(3)	0.048(3)	0.029(2)	0.013(2)	-0.006(2)	-0.023(3)
C24	0.032(3)	0.041(3)	0.032(3)	0.009(2)	-0.004(2)	-0.020(2)
C25	0.031(3)	0.037(3)	0.029(2)	0.004(2)	-0.0054(19)	-0.018(2)
C26	0.035(3)	0.044(3)	0.025(2)	0.009(2)	-0.005(2)	-0.022(2)
C27	0.030(3)	0.041(3)	0.031(2)	0.005(2)	-0.005(2)	-0.019(2)
C28	0.036(3)	0.039(3)	0.026(2)	0.007(2)	-0.009(2)	-0.021(2)
C29	0.044(3)	0.041(3)	0.029(2)	0.009(2)	-0.009(2)	-0.023(3)
C30	0.048(3)	0.042(3)	0.026(2)	0.004(2)	-0.003(2)	-0.024(3)
C31	0.062(4)	0.035(3)	0.029(3)	-0.001(2)	-0.006(2)	-0.024(3)
C32	0.058(4)	0.048(4)	0.052(4)	0.010(3)	0.008(3)	-0.015(3)
C33	0.082(6)	0.043(4)	0.068(5)	0.010(3)	0.017(4)	-0.013(4)
C34	0.162(10)	0.044(4)	0.039(4)	0.003(3)	0.013(5)	-0.044(6)
C35	0.122(8)	0.075(6)	0.050(4)	0.016(4)	-0.024(4)	-0.071(6)
C36	0.075(5)	0.055(4)	0.045(3)	0.009(3)	-0.023(3)	-0.035(4)
C37	0.045(3)	0.043(3)	0.037(3)	0.002(2)	-0.001(2)	-0.017(3)
C38	0.067(4)	0.043(3)	0.044(3)	0.005(3)	-0.004(3)	-0.023(3)
C39	0.089(6)	0.046(4)	0.051(4)	0.011(3)	-0.017(4)	-0.035(4)
C40	0.076(5)	0.053(4)	0.066(4)	-0.003(3)	-0.011(4)	-0.027(4)
C41	0.073(6)	0.080(6)	0.074(5)	0.009(4)	-0.016(4)	-0.041(5)
C42	0.081(5)	0.047(4)	0.049(4)	0.003(3)	-0.015(3)	-0.026(4)
C43	0.082(5)	0.047(4)	0.040(3)	-0.003(3)	-0.003(3)	-0.029(4)
C44	0.074(5)	0.052(4)	0.033(3)	-0.002(3)	0.002(3)	-0.027(4)
C45	0.033(3)	0.054(3)	0.030(3)	-0.001(2)	-0.002(2)	-0.016(3)
C46	0.038(3)	0.064(4)	0.045(3)	0.007(3)	-0.001(2)	-0.019(3)
C47	0.043(4)	0.092(6)	0.078(5)	-0.020(4)	0.004(4)	-0.025(4)
C48	0.052(5)	0.217(14)	0.051(4)	0.021(6)	-0.011(4)	-0.042(7)
C49	0.058(7)	0.34(3)	0.089(8)	0.079(12)	-0.006(6)	-0.048(11)
C50	0.036(5)	0.182(13)	0.108(8)	0.044(8)	-0.008(5)	-0.025(6)
C51	0.041(4)	0.102(7)	0.085(6)	0.004(5)	-0.023(4)	-0.010(4)
C52	0.052(4)	0.070(5)	0.054(4)	0.005(3)	-0.015(3)	-0.012(4)
C53	0.035(3)	0.043(3)	0.034(3)	0.007(2)	-0.007(2)	-0.017(3)
C54	0.031(3)	0.048(3)	0.043(3)	0.003(3)	-0.005(2)	-0.017(3)
C55	0.037(3)	0.073(4)	0.038(3)	0.001(3)	-0.001(2)	-0.030(3)
C56	0.049(4)	0.071(5)	0.070(5)	0.007(4)	-0.008(3)	-0.018(4)
C57	0.048(4)	0.065(5)	0.089(6)	0.010(4)	-0.009(4)	-0.025(4)
C58	0.049(4)	0.092(6)	0.060(4)	0.006(4)	-0.005(3)	-0.035(4)
C59	0.067(5)	0.083(6)	0.075(5)	-0.014(4)	0.008(4)	-0.041(5)
C60	0.050(4)	0.063(4)	0.071(5)	-0.013(4)	0.007(3)	-0.025(4)
O9	0.072(4)	0.144(5)	0.050(3)	-0.016(3)	-0.004(2)	-0.064(4)
O10	0.037(2)	0.095(4)	0.051(3)	0.011(3)	0.0033(19)	-0.031(3)
O11	0.038(3)	0.046(2)	0.075(3)	0.004(2)	0.011(2)	-0.010(2)
O12	0.077(3)	0.051(3)	0.040(2)	-0.0023(19)	-0.005(2)	-0.030(2)
O13	0.092(4)	0.086(4)	0.035(2)	-0.006(2)	0.001(2)	-0.054(3)
O14	0.064(3)	0.102(4)	0.035(2)	0.013(2)	0.002(2)	-0.050(3)
O15	0.062(3)	0.071(3)	0.046(2)	0.011(2)	-0.013(2)	-0.035(3)
O16	0.036(2)	0.091(4)	0.052(3)	-0.001(2)	-0.0109(19)	-0.030(3)
N5	0.051(3)	0.055(3)	0.042(3)	0.017(2)	-0.011(2)	-0.017(3)
C61	0.045(4)	0.079(5)	0.032(3)	0.006(3)	-0.001(2)	-0.030(3)
C62	0.061(5)	0.106(6)	0.036(3)	0.005(4)	-0.009(3)	-0.048(5)
C63	0.049(4)	0.128(7)	0.052(4)	0.012(4)	-0.009(3)	-0.056(5)
C64	0.038(3)	0.070(4)	0.042(3)	0.014(3)	-0.001(2)	-0.026(3)
C65	0.039(3)	0.046(3)	0.034(3)	0.008(2)	-0.001(2)	-0.018(3)
C66	0.037(3)	0.048(3)	0.039(3)	0.003(2)	-0.004(2)	-0.019(3)
C67	0.033(3)	0.047(3)	0.033(3)	0.004(2)	0.004(2)	-0.015(3)
C68	0.041(3)	0.045(3)	0.025(2)	0.008(2)	0.004(2)	-0.015(3)
C69	0.040(3)	0.047(3)	0.039(3)	0.003(3)	0.004(2)	-0.012(3)
C70	0.052(4)	0.044(3)	0.039(3)	0.004(3)	0.001(3)	-0.014(3)
C71	0.052(4)	0.048(3)	0.029(3)	0.002(2)	-0.005(2)	-0.020(3)
C72	0.046(3)	0.053(3)	0.023(2)	0.003(2)	-0.004(2)	-0.021(3)
C73	0.036(3)	0.050(3)	0.025(2)	0.009(2)	-0.004(2)	-0.015(3)
C74	0.050(4)	0.070(4)	0.021(2)	0.008(3)	-0.004(2)	-0.031(3)

C75	0.047(4)	0.073(4)	0.025(3)	0.004(3)	-0.004(2)	-0.032(3)
C76	0.061(4)	0.074(4)	0.030(3)	-0.003(3)	-0.001(3)	-0.042(4)
C77	0.063(5)	0.082(5)	0.038(3)	0.004(3)	0.000(3)	-0.043(4)
C78	0.053(4)	0.086(5)	0.029(3)	0.010(3)	-0.005(3)	-0.041(4)
C79	0.040(3)	0.073(4)	0.029(3)	0.007(3)	-0.006(2)	-0.031(3)
C80	0.043(3)	0.071(4)	0.028(3)	-0.003(3)	-0.005(2)	-0.030(3)
C81	0.038(3)	0.079(4)	0.026(2)	0.002(3)	0.001(2)	-0.028(3)
C82	0.033(3)	0.074(4)	0.024(2)	-0.002(3)	-0.001(2)	-0.025(3)
C83	0.047(4)	0.078(5)	0.024(2)	0.003(3)	-0.003(2)	-0.028(3)
C84	0.041(4)	0.072(4)	0.034(3)	0.002(3)	-0.007(2)	-0.018(3)
C85	0.035(3)	0.077(4)	0.029(3)	-0.004(3)	-0.001(2)	-0.026(3)
C86	0.042(3)	0.074(4)	0.021(2)	0.000(3)	-0.001(2)	-0.027(3)
C87	0.040(3)	0.073(4)	0.022(2)	0.002(3)	-0.002(2)	-0.023(3)
C88	0.044(3)	0.073(4)	0.026(2)	-0.001(3)	0.002(2)	-0.031(3)
C89	0.047(4)	0.048(3)	0.038(3)	0.007(3)	0.000(2)	-0.014(3)
C90	0.046(4)	0.059(4)	0.046(3)	0.012(3)	-0.002(3)	-0.022(3)
C91	0.055(4)	0.064(4)	0.070(5)	0.014(4)	-0.019(4)	-0.025(4)
C92	0.055(4)	0.050(3)	0.031(3)	0.008(3)	-0.009(2)	-0.020(3)
C93	0.062(5)	0.059(4)	0.047(4)	0.010(3)	-0.018(3)	-0.018(4)
C94	0.061(5)	0.076(5)	0.055(4)	0.020(4)	-0.013(3)	-0.035(4)
C95	0.059(5)	0.065(5)	0.057(4)	0.011(4)	-0.007(3)	-0.023(4)
C96	0.053(4)	0.059(4)	0.040(3)	0.001(3)	0.004(3)	-0.013(3)
C97	0.052(4)	0.074(5)	0.033(3)	0.010(3)	-0.004(3)	-0.027(4)
C98	0.059(2)	0.065(2)	0.059(2)	-0.0030(18)	-0.0064(18)	-0.0190(18)
C99	0.052(3)	0.057(3)	0.056(3)	-0.001(2)	-0.0041(19)	-0.018(2)
N6	0.054(3)	0.058(3)	0.057(3)	-0.0014(18)	-0.0089(19)	-0.0184(19)
C100	0.059(3)	0.061(3)	0.063(3)	0.002(2)	-0.007(2)	-0.018(2)
C101	0.082(3)	0.086(3)	0.087(3)	-0.003(2)	-0.010(2)	-0.027(2)
C102	0.098(5)	0.101(5)	0.100(5)	-0.001(2)	-0.010(2)	-0.031(2)
C103	0.115(6)	0.116(6)	0.117(6)	0.000(2)	-0.012(2)	-0.034(3)
C104	0.093(5)	0.095(5)	0.096(5)	0.000(2)	-0.010(2)	-0.028(2)
C98A	0.059(2)	0.065(2)	0.059(2)	-0.0030(18)	-0.0064(18)	-0.0190(18)
C99B	0.052(3)	0.057(3)	0.056(3)	-0.001(2)	-0.0041(19)	-0.018(2)
N6B	0.054(3)	0.058(3)	0.057(3)	-0.0014(18)	-0.0089(19)	-0.0184(19)
C10B	0.059(3)	0.061(3)	0.063(3)	0.002(2)	-0.007(2)	-0.018(2)
C11B	0.082(3)	0.086(3)	0.087(3)	-0.003(2)	-0.010(2)	-0.027(2)
C12B	0.098(5)	0.101(5)	0.100(5)	-0.001(2)	-0.010(2)	-0.031(2)
C13B	0.115(6)	0.116(6)	0.117(6)	0.000(2)	-0.012(2)	-0.034(3)
C14B	0.093(5)	0.095(5)	0.096(5)	0.000(2)	-0.010(2)	-0.028(2)
C105	0.040(4)	0.101(6)	0.043(3)	-0.014(4)	-0.001(3)	-0.019(4)
C106	0.045(5)	0.109(8)	0.097(7)	-0.025(6)	-0.003(4)	-0.020(5)
C107	0.113(4)	0.118(4)	0.115(4)	-0.003(2)	-0.014(2)	-0.034(2)
N7	0.108(5)	0.113(5)	0.111(5)	-0.002(2)	-0.013(2)	-0.033(2)
C108	0.113(6)	0.116(6)	0.116(6)	-0.001(2)	-0.012(2)	-0.035(3)
C109	0.134(7)	0.134(7)	0.134(7)	-0.002(2)	-0.013(2)	-0.040(3)
C110	0.095(5)	0.100(5)	0.097(5)	-0.001(2)	-0.012(2)	-0.030(2)
C111	0.141(8)	0.144(8)	0.144(8)	0.000(2)	-0.014(2)	-0.042(3)
C112	0.129(7)	0.130(7)	0.131(7)	0.000(2)	-0.013(2)	-0.038(3)
C17A	0.113(4)	0.118(4)	0.115(4)	-0.003(2)	-0.014(2)	-0.034(2)
N7A	0.108(5)	0.113(5)	0.111(5)	-0.002(2)	-0.013(2)	-0.033(2)
C18A	0.113(6)	0.116(6)	0.116(6)	-0.001(2)	-0.012(2)	-0.035(3)
C19A	0.134(7)	0.134(7)	0.134(7)	-0.002(2)	-0.013(2)	-0.040(3)
C20A	0.095(5)	0.100(5)	0.097(5)	-0.001(2)	-0.012(2)	-0.030(2)
C21A	0.141(8)	0.144(8)	0.144(8)	0.000(2)	-0.014(2)	-0.042(3)
C22A	0.129(7)	0.130(7)	0.131(7)	0.000(2)	-0.013(2)	-0.038(3)
C113	0.060(4)	0.079(5)	0.028(3)	0.002(3)	-0.002(3)	-0.029(4)
C114	0.097(6)	0.080(5)	0.028(3)	0.009(3)	-0.011(3)	-0.037(5)
C115	0.051(4)	0.051(4)	0.043(4)	0.004(3)	-0.004(3)	-0.013(3)
N8	0.049(3)	0.051(3)	0.044(2)	0.0021(18)	-0.0049(19)	-0.014(2)
C116	0.070(4)	0.070(3)	0.070(3)	-0.002(2)	-0.008(2)	-0.020(2)
C117	0.083(4)	0.080(4)	0.078(4)	0.002(2)	-0.011(2)	-0.022(2)
C118	0.082(4)	0.079(4)	0.076(4)	0.001(2)	-0.009(2)	-0.024(2)
C119	0.086(4)	0.085(4)	0.084(4)	0.001(2)	-0.006(2)	-0.028(2)

C120	0.069(4)	0.070(4)	0.069(3)	0.000(2)	-0.007(2)	-0.022(2)
C15B	0.034(5)	0.036(5)	0.031(5)	0.003(3)	-0.002(3)	-0.007(3)
N8B	0.049(3)	0.051(3)	0.044(2)	0.0021(18)	-0.0049(19)	-0.014(2)
C16B	0.070(4)	0.070(3)	0.070(3)	-0.002(2)	-0.008(2)	-0.020(2)
C17B	0.083(4)	0.080(4)	0.078(4)	0.002(2)	-0.011(2)	-0.022(2)
C18B	0.082(4)	0.079(4)	0.076(4)	0.001(2)	-0.009(2)	-0.024(2)
C19B	0.086(4)	0.085(4)	0.084(4)	0.001(2)	-0.006(2)	-0.028(2)
C20B	0.069(4)	0.070(4)	0.069(3)	0.000(2)	-0.007(2)	-0.022(2)
Cl1	0.0759(12)	0.0490(9)	0.0613(10)	-0.0021(7)	-0.0025(8)	-0.0328(9)
Cl2	0.0693(13)	0.0942(15)	0.0839(13)	0.0193(12)	-0.0150(10)	-0.0457(12)
Cl3	0.0614(15)	0.0839(18)	0.115(2)	-0.0219(16)	0.0263(14)	-0.0534(14)
Cl3A	0.0614(15)	0.0839(18)	0.115(2)	-0.0219(16)	0.0263(14)	-0.0534(14)
Cl4	0.0612(18)	0.166(4)	0.0745(18)	-0.042(2)	0.0065(13)	-0.066(2)
Cl4A	0.0612(18)	0.166(4)	0.0745(18)	-0.042(2)	0.0065(13)	-0.066(2)
O18	0.056(3)	0.079(4)	0.062(3)	-0.001(3)	-0.010(2)	-0.032(3)
O19	0.065(3)	0.095(4)	0.076(3)	0.024(3)	-0.013(3)	-0.056(3)
O20	0.043(3)	0.103(4)	0.085(4)	0.032(3)	0.001(2)	-0.045(3)
O21	0.084(4)	0.078(4)	0.075(3)	0.022(3)	-0.026(3)	-0.052(3)
O22	0.056(4)	0.115(5)	0.101(5)	-0.004(4)	-0.034(3)	-0.004(4)
O23	0.094(5)	0.145(7)	0.086(5)	0.005(5)	-0.012(4)	-0.053(5)
O24	0.242(8)	0.063(3)	0.061(3)	0.029(3)	-0.048(4)	-0.049(4)
O25	0.158(6)	0.091(5)	0.111(5)	-0.011(4)	0.012(5)	-0.070(5)
O26	0.094(5)	0.117(5)	0.114(5)	-0.005(4)	-0.028(4)	-0.034(4)
O27	0.118(6)	0.142(6)	0.143(6)	-0.019(5)	-0.028(5)	-0.042(5)
O28	0.107(6)	0.104(5)	0.158(7)	-0.015(5)	0.017(5)	-0.028(5)
O29	0.086(7)	0.113(8)	0.095(7)	-0.023(6)	0.010(6)	-0.033(6)
O30	0.105(8)	0.076(7)	0.094(7)	-0.002(6)	-0.005(6)	-0.016(6)
O31	0.090(7)	0.124(9)	0.107(8)	0.004(7)	-0.005(6)	-0.049(7)
O32	0.109(9)	0.163(10)	0.143(10)	-0.030(8)	-0.022(7)	-0.070(8)
O33	0.129(9)	0.127(9)	0.113(9)	-0.021(7)	-0.034(7)	-0.005(7)
O34	0.126(10)	0.166(11)	0.138(10)	-0.021(8)	-0.013(8)	-0.045(8)
O35	0.122(6)	0.185(8)	0.129(6)	0.028(6)	-0.044(5)	-0.058(6)
O36	0.064(3)	0.044(2)	0.064(3)	0.028(2)	-0.057(2)	-0.018(2)

Table S10. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for TPO, **1**.

	x/a	y/b	z/c	U(eq)
H1	0.3667	0.7377	0.9911	0.058
H2A	0.2023	0.5735	1.0191	0.064
H3A	0.1540	0.3761	0.9571	0.08
H4	0.0738	0.4239	0.7831	0.077
H5A	0.0920	0.6560	0.7133	0.069
H6A	0.3765	0.7737	0.7151	0.061
H7A	0.5298	0.8285	0.7220	0.065
H8	0.6267	0.7764	0.8986	0.059
H3B	0.2790	0.6597	1.0117	0.042
H6B	0.5032	0.4924	0.9004	0.037
H7B	0.3358	0.4185	0.9668	0.04
H10E	0.1045	0.4000	0.8725	0.053
H13B	0.3584	0.4850	0.8267	0.039
H14B	0.2148	0.4948	0.7163	0.041
H17	0.1744	0.7402	0.7236	0.041
H20	0.4263	0.5327	0.7287	0.039
H21	0.4880	0.6901	0.6851	0.042
H24	0.5525	0.8266	0.8165	0.04
H27	0.5031	0.5964	0.8159	0.039
H28	0.5758	0.6393	0.9419	0.038
H29A	0.4807	0.3909	0.8791	0.043
H29B	0.4960	0.3752	0.9426	0.043
H30A	0.5054	0.2664	0.8950	0.044
H30B	0.4013	0.3004	0.8813	0.044
H31A	0.4505	0.2709	0.9923	0.048
H31B	0.3471	0.2974	0.9755	0.048

H32	0.5438	0.1503	0.9724	0.065
H33	0.5541	0.0300	0.9535	0.081
H34	0.4239	0.0011	0.9292	0.097
H35	0.2890	0.0933	0.9210	0.087
H36	0.2833	0.2148	0.9376	0.064
H37A	0.3643	0.4476	0.6699	0.049
H37B	0.4041	0.4245	0.7281	0.049
H38A	0.2996	0.3486	0.7420	0.06
H38B	0.3861	0.3199	0.6970	0.06
H39A	0.2078	0.4015	0.6679	0.07
H39B	0.2943	0.3628	0.6251	0.07
H40	0.1008	0.3393	0.6840	0.075
H41	0.0576	0.2311	0.6926	0.086
H42	0.1693	0.1187	0.6794	0.068
H43	0.3242	0.1154	0.6604	0.065
H44	0.3637	0.2222	0.6520	0.062
H45A	0.5491	0.5631	0.6650	0.046
H45B	0.5676	0.5472	0.7283	0.046
H46A	0.6534	0.6366	0.6564	0.058
H46B	0.6724	0.6197	0.7195	0.058
H47A	0.7181	0.5123	0.6354	0.084
H47B	0.7364	0.4949	0.6985	0.084
H48	0.8007	0.5897	0.5828	0.127
H49	0.9409	0.6102	0.5627	0.2
H50	1.0489	0.5794	0.6278	0.134
H51	1.0085	0.5343	0.7116	0.092
H52	0.8683	0.5151	0.7314	0.071
H53A	0.6545	0.5155	0.9292	0.043
H53B	0.6234	0.5175	0.8685	0.043
H54A	0.7746	0.5198	0.8583	0.047
H54B	0.7139	0.5994	0.8410	0.047
H55A	0.7183	0.6380	0.9351	0.056
H55B	0.7958	0.5617	0.9419	0.056
H56	0.7692	0.7340	0.9089	0.076
H57	0.8763	0.7881	0.8650	0.079
H58	1.0078	0.7138	0.8158	0.077
H59	1.0358	0.5871	0.8178	0.086
H60	0.9248	0.5398	0.8608	0.072
H9A	0.7770	1.1487	0.4294	0.122
H10A	0.9139	1.1000	0.2258	0.089
H11	0.9158	0.8402	0.1774	0.082
H13	0.4872	0.7010	0.2262	0.098
H14A	0.4165	0.7245	0.4186	0.093
H15A	0.6076	0.7656	0.4763	0.084
H16A	0.8043	0.9034	0.4718	0.085
H63	0.9148	1.0960	0.3334	0.084
H66	0.6588	1.0207	0.3122	0.047
H67	0.8212	1.0036	0.1914	0.045
H70	0.8128	0.7714	0.1862	0.055
H73	0.5901	0.9935	0.2231	0.044
H74	0.5011	0.8550	0.1825	0.053
H77	0.4193	0.7088	0.3178	0.069
H80	0.4874	0.9313	0.3159	0.053
H81	0.4098	0.8757	0.4501	0.055
H84	0.7116	0.8300	0.4793	0.058
H87	0.4947	1.0231	0.4041	0.053
H88	0.6743	1.0745	0.4500	0.054
H89A	0.6769	1.0631	0.1505	0.054
H89B	0.6431	1.1053	0.2080	0.054
H90A	0.8079	1.1084	0.1427	0.059
H90B	0.7655	1.1554	0.1973	0.059
H91A	0.6772	1.1780	0.0966	0.073
H91B	0.6390	1.2268	0.1510	0.073

H92	0.6955	1.3259	0.1658	0.053
H93	0.7955	1.3924	0.1391	0.067
H94	0.9148	1.3526	0.0703	0.073
H95	0.9286	1.2411	0.0251	0.072
H96	0.8282	1.1751	0.0523	0.062
H97A	0.4466	0.9952	0.2357	0.062
H97B	0.4555	0.9833	0.1704	0.062
H98A	0.3253	0.9353	0.2453	0.073
H98B	0.2978	1.0119	0.2131	0.073
H99A	0.3762	0.8865	0.1489	0.066
H99B	0.2983	0.9601	0.1343	0.066
H100	0.1616	0.9639	0.1409	0.073
H101	0.0180	0.9495	0.1735	0.101
H102	0.0074	0.8629	0.2423	0.119
H103	0.1405	0.7906	0.2786	0.139
H104	0.2841	0.8050	0.2460	0.113
H98C	0.3005	1.0083	0.1974	0.073
H98D	0.3174	0.9559	0.2503	0.073
H99C	0.3174	0.8506	0.1982	0.066
H99D	0.3720	0.8760	0.1437	0.066
H10B	0.1995	0.8710	0.2112	0.073
H11B	0.0417	0.8967	0.2039	0.101
H12B	-0.0300	0.9883	0.1435	0.119
H13B	0.0562	1.0542	0.0903	0.139
H14B	0.2140	1.0284	0.0975	0.113
H10B	0.3424	1.0060	0.4471	0.074
H10C	0.3647	1.0044	0.3816	0.074
H10D	0.2122	1.0125	0.4025	0.101
H10F	0.2631	0.9362	0.3733	0.101
H10G	0.1948	0.9640	0.4788	0.138
H10H	0.2674	0.8881	0.4603	0.138
H108	0.2185	0.7933	0.4316	0.138
H109	0.0989	0.7461	0.4143	0.16
H110	-0.0493	0.8249	0.4085	0.116
H111	-0.0779	0.9511	0.4201	0.172
H112	0.0416	0.9983	0.4374	0.156
H17A	0.2063	0.9539	0.4839	0.138
H17D	0.2499	0.8767	0.4506	0.138
H18A	0.2168	0.8442	0.3929	0.138
H19A	0.0954	0.7975	0.3784	0.16
H20A	-0.0567	0.8716	0.3935	0.116
H21A	-0.0876	0.9925	0.4231	0.172
H22A	0.0337	1.0392	0.4376	0.156
H11A	0.5313	1.1203	0.3782	0.065
H11C	0.5160	1.1308	0.4436	0.065
H11D	0.5196	1.2416	0.3987	0.079
H11E	0.6209	1.2032	0.3701	0.079
H11F	0.5753	1.2279	0.4872	0.058
H11G	0.6765	1.1840	0.4606	0.058
H116	0.5083	1.3574	0.4461	0.084
H117	0.5459	1.4656	0.4217	0.097
H118	0.7002	1.4635	0.4033	0.094
H119	0.8170	1.3533	0.4093	0.101
H120	0.7794	1.2451	0.4336	0.083
H11H	0.5347	1.2449	0.4840	0.042
H11I	0.6440	1.2094	0.4741	0.042
H16B	0.4651	1.3653	0.4652	0.084
H17B	0.4759	1.4836	0.4455	0.097
H18B	0.6182	1.5012	0.4140	0.094
H19B	0.7498	1.4006	0.4022	0.101
H20B	0.7390	1.2823	0.4219	0.083
H19C	0.3714	0.5965	0.2119	0.107
H19D	0.3993	0.6522	0.2318	0.107

H20C	0.1030	0.2364	0.9755	0.11
H20D	0.0637	0.2915	0.9403	0.11
H21B	0.5775	0.8760	0.7301	0.108
H21C	0.6490	0.8433	0.6918	0.108
H22C	-0.0340	0.7221	0.7192	0.139
H23A	0.7496	0.7552	0.6339	0.157
H23B	0.7728	0.8096	0.6023	0.157
H24A	0.3235	0.6028	0.4474	0.179
H24B	0.4045	0.5748	0.4144	0.179
H25A	1.2239	0.9714	-0.0251	0.171
H25B	1.2594	0.9106	0.0062	0.171
H26A	0.8136	0.7060	0.7392	0.159
H26B	0.8031	0.6872	0.6871	0.159
H27A	0.0505	0.6537	0.3334	0.197
H27B	0.0662	0.6908	0.2859	0.197
H28A	0.0739	0.6092	1.0590	0.188
H28B	0.0866	0.6775	1.0554	0.188
H29C	0.1503	0.7717	1.0505	0.147
H29D	0.1347	0.7550	1.1054	0.147
H30C	0.0133	0.8043	0.1979	0.142
H30D	0.0069	0.7556	0.1596	0.142
H31C	0.2861	0.6605	0.3439	0.156
H31D	0.2929	0.6892	0.2917	0.156
H32A	0.1809	1.0800	0.0591	0.196
H32B	0.1231	1.1490	0.0522	0.196
H33A	-0.0006	0.6377	0.4334	0.192
H33B	0.0839	0.5992	0.4087	0.192
H34A	0.2541	0.7123	0.1438	0.213
H34B	0.3143	0.6604	0.1098	0.213
H35A	0.8919	0.8470	0.5455	0.211
H35B	0.8867	0.7875	0.5174	0.211
H36A	0.7024	0.6656	0.5144	0.081
H36B	0.6463	0.6589	0.5609	0.081

Table S11. Hydrogen bond distances (Å) and angles (°) for TPO, **1**.

	Donor-H	**Acceptor-H**	**Donor-Acceptor**	**Angle**
O2-H2A···O28	0.84	2.00	2.816(11)	165.1
O3-H3A···O20	0.84	2.29	3.002(6)	143.3
O5-H5A···O22	0.84	1.95	2.771(8)	165.0
O6-H6A···O7	0.84	2.09	2.905(6)	162.3
O7-H7A···O21	0.84	1.85	2.670(6)	163.9
C30-H30B···O12	0.99	2.43	3.337(7)	152.8
C31-H31A···O1	0.99	2.39	3.302(7)	153.3
C31-H31A···O8	0.99	2.50	3.149(7)	123.2
C31-H31B···O3	0.99	2.42	3.309(8)	148.6
C38-H38A···O12	0.99	2.55	3.317(8)	134.1
C51-H51···O4	0.95	2.52	3.385(9)	150.9
C55-H55B···O2	0.99	2.58	3.425(8)	143.7
C59-H59···O5	0.95	2.59	3.223(10)	124.7
O11-H11···O30	0.84	2.01	2.671(15)	134.4
O13-H13···O19	0.84	2.37	3.061(7)	139.7
O14-H14A···O24	0.84	2.55	3.136(9)	128.0
O15-H15A···O36	0.84	2.14	2.929(6)	155.9
O16-H16A···O35	0.84	2.05	2.825(11)	152.2
C90-H90B···O6	0.99	2.51	3.303(9)	136.5
C101^{a-H101}a···O10	0.95	2.59	3.144(13)	117.2
C103^{a-H103}a···O31	0.95	2.58	3.321(19)	134.8
C107^{a-H10G}a···O16	0.99	2.54	3.407(16)	145.8
C108^{a-H108}a···O14	0.95	2.48	3.331(11)	149.7
C111^{a-H111}a···O16	0.95	2.47	3.178(12)	131.3
C114-H11E^a···O6	0.99	2.32	3.275(9)	162.1
C115^{a-H11F}a···O14	0.99	2.54	3.217(13)	125.6

C115$^{a\text{-}H11F}$a···O15	0.99	2.53	3.433(15)	151.7
C115$^{a\text{-}H11G}$a···O9	0.99	2.26	3.135(18)	147.2
C120$^{a\text{-}H120}$a···O9	0.95	2.59	3.380(11)	140.8
O19-H19C···O34	0.87	2.31	2.87(2)	122.7
O19-H19D···O13	0.87	2.40	3.061(7)	133.5
O21-H21B···O7	0.87	2.18	2.670(6)	115.2
O21-H21C···O23	0.87	2.23	2.900(11)	133.3
O22-H22C···O26	0.87	2.39	2.881(11)	116.5
O23-H23A···O26	0.87	2.08	2.833(11)	144.4
O23-H23B···O35	0.87	2.08	2.817(13)	142.5
O27-H27A···O33	0.87	2.14	2.89(2)	143.2
O28-H28B···O29	0.87	2.32	2.913(19)	125.9
O30-H30C···O11	0.87	2.06	2.671(15)	126.0
O31-H31C···O24	0.87	2.25	3.110(17)	173.0

3.0 References

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