Supplementary Methods: All reagents and solvents were commercial reagent grade and were used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on either a Varian Mercury-400 spectrometer or a 600 MHz Varian DirectDrive spectrometer, and chemical shifts were reported on the delta scale in ppm relative to residual chloroform ($\delta = 7.26$ and 77.0 for $^1$H and $^{13}$C, respectively), acetonitrile (MeCN) ($\delta = 1.94$ and 1.32 for $^1$H and $^{13}$C, respectively) and tetrahydrofuran (THF) ($\delta = 3.58$ and 67.2 for $^1$H and $^{13}$C, respectively). High Resolution ESI mass spectrometry was performed using an Ion Spec Fourier Transform mass spectrometer (9.4 T). UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer at room temperature. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. Optical rotations were recorded on an Atago AP-300 automatic polarimeter at the sodium line (589.3 nm) in chloroform. CD spectra were measured using a Jasco J-815 spectropolarimeter. Dynamic light scattering (DLS) measurements were carried out using 200-mW polarized laser source Nd: YAG ($\lambda = 532$ nm). The polarized scattered light data was collected at 90° in a self-beating mode with a Hamamatsu R942/02 photomultiplier. The signals were analyzed using a Malvern 4700 submicrometer particle analyzer system. X-ray crystallographic analyses were carried out on either Rigaku AFC12 diffractometer equipped with Saturn 724+ CCD or Agilent Technologies Super Nova Dual Source diffractometer equipped with a µ-focused Cu K\(\alpha\) radiation source ($\lambda = 1.5418$ Å) with collimating mirror monochromators. CSI-MS measurements were performed using a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS; Apex-Qe 9.4 T, Bruker Daltonics, Inc. Billerica, MA). The heater of the desolvation assembly was turned off in the electrospray ionization source and the temperature was kept around at 310 K. General measurement conditions were as follows: Positive ion mode, capillary voltage, 4.5 kV; dry gas flow rate, 5.0 L/min; nebulizer gas flow rate, 1.0 L/min; and sample flow rate, 120 µL/h. Isotope patterns were calculated by using “Simulate Pattern” packaged in Bruker Daltonics software (Data Analysis, ver. 4.0). Preparative separations were performed by silica gel gravity column chromatography (Sorbent Technologies, Silica Gel 60, particle size 40-63 µm, pH range 6.0-8.0). Compound 1 was synthesized according to a reported method\(^1\) (Supplementary Fig. 1). Although compound 8 was commercially available, it was synthesized from 4-acetylpyridine and (S)-1-chloro-2-methylbutane according to a reported method\(^3\) (Supplementary Fig. 7).
**Supplementary Figure 1.** Synthesis of 1. Ms = methanesulfonyl; TFA = trifluoroacetic acid.

**Supplementary Note 1.** Compound data for 1.

Compound 1: M.p. 220 °C (decomp.); $^1$H NMR (600 MHz, THF-$d_8$): $\delta$ 8.36 (dd, $J_1 = 1.8$ Hz, $J_2 = 4.6$ Hz, 4H), 8.05 (br, 4H), 6.86 (dd, $J_1 = 1.8$ Hz, $J_2 = 4.6$ Hz, 4H), 5.86 (m, 4H), 5.52 (m, 4H), 1.87 (s, 6H), 1.62 (s, 6H), 1.51 (s, 6H) ppm; $^{13}$C NMR (125 MHz, THF-$d_8$): $\delta$ 158.0, 149.9, 139.6, 136.0, 123.1, 106.3, 103.5, 45.4, 35.8, 31.1, 27.0, 26.8 ppm; FTIR (neat): $\nu$ 2973, 1710, 1596, 1493, 1409, 1359, 1328, 1276, 1253, 1220, 1070, 1041, 1007, 825, 773, 710 cm$^{-1}$; HRMS (ESI$^+$) calcd. for C$_{36}$H$_{38}$N$_6$ m/z 555.3231 [M+H]$^+$, found m/z 555.3231.
Supplementary Figure 2. $^1$H and $^{13}$C NMR spectra of I in THF-$d_8$. 
Supplementary Figure 3. NOESY spectrum of 1 in THF-\textit{d}_8. *Indicates solvent impurity.

Supplementary Figure 4. COSY spectrum of 1 in THF-\textit{d}_8.
Supplementary Figure 5. HSQC spectrum of 1 in THF-$d_8$. CH$_3$ and CH carbons are phased up (red), and CH$_2$ carbons are phased down (blue).

Supplementary Figure 6. HRMS (ESI$^+$) spectrum of 1.
Supplementary Figure 7. Synthesis of 3.

Supplementary Note 2. Synthetic procedure of 3 and 9.

Synthesis of 5,10,15,20,22,24-hexahydro-5,5,15,15-tetramethyl-10\(\alpha\),20\(\alpha\)-di-(4-pyridinyl)-10\(\beta\),20\(\beta\)-bis[(2-(S)-(−)-methyl]butyl]-21\(H\),23\(H\)-porphine (3) and its configurational isomer, 5,10,15,20,22,24-hexahydro-5,5,15,15-tetramethyl-10\(\alpha\),20\(\beta\)-di-(4-pyridinyl)-10\(\beta\),20\(\alpha\)-bis[(2-(S)-(−)-methyl]butyl]-21\(H\),23\(H\)-porphine (9): To a solution of 8 (3.88 g, 21.9 mmol) in 45 mL of pyrrole (the solvent) was added methanesulfonic acid (5.7 mL, 87 mmol) dropwise at 0°C. The mixture was allowed to warm to room temperature and then stirred for 8 h under a nitrogen atmosphere. Triethylamine (4.3 mL) was added to the reaction vessel and the resulting mixture was extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with saturated aqueous NaCl, dried over Na\(_2\)SO\(_4\), and concentrated \textit{in vacuo}. The resulting oil was dissolved in acetone (75 mL) and trifluoroacetic acid (1.6 mL, 21 mmol) was added at room temperature. The reaction mixture stirred for 8 hours and quenched with triethylamine (4.0 mL). The resulting mixture was extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with saturated aqueous NaCl, dried over Na\(_2\)SO\(_4\), and concentrated \textit{in vacuo}. Column chromatography on silica gel (0%–30% ethyl acetate in \(n\)-hexane, eluent) gave the desired product 3 (5%, for 2 steps) and its isomer 9 (7%, for 2 steps).

Supplementary Note 3. Compound data for 3 and 9

Compound 3: M.p. 200 °C (decomp.); \([\alpha]^{33}\)_D = −35.7 cm\(^3\)g\(^{-1}\)dm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.47 (dd, \(J_1 = 1.6\) Hz, \(J_2 = 4.4\) Hz, 4H), 7.21 (br, 2H), 7.16 (dd, \(J_1 = 1.6\) Hz, \(J_2 = 4.4\) Hz, 4H), 7.13 (br, 2H), 5.83–5.95 (m, 8H), 2.00–2.24 (m, 4H), 1.54 (s, 6H), 1.44 (s, 6H), 1.42 (m, overlapping, 2H), 0.93–1.13 (m, 4H), 0.73 (t, \(J = 7.4\) Hz, 6H), 0.61 (d, \(J = 6.7\) Hz, 6H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 153.8, 149.3, 139.0, 138.8, 133.9, 133.6, 123.4, 107.1, 106.5, 103.2, 103.1, 48.9, 46.8, 35.1, 31.1, 30.8, 29.4, 28.7, 20.5, 11.3 ppm; FTIR (neat): \(\nu\) 2959, 1719, 1596, 1458, 1415, 1378, 1362, 1206, 1073, 1044, 1003, 767, 709 cm\(^{-1}\); HRMS (ESI\(^+\)) calcd. for C\(_{44}\)H\(_{54}\)N\(_6\)Na \(m/z\) 689.4302 [M+Na]\(^+\), found \(m/z\) 689.4305.

S6
Compound 9: M.p. 220 °C (decomp.); \([\alpha]^{13}_D = -12.0 \, \text{cm}^3\text{g}^{-1}\text{dm}^{-1}\); \(^1\text{H NMR (400 MHz, CDCl}_3\): \(\delta 8.47 \, (dd, J_1 = 1.5 \, \text{Hz}, J_2 = 4.7 \, \text{Hz}, 4\text{H}), 7.24 \, (dd, J_1 = 1.5 \, \text{Hz}, J_2 = 4.7 \, \text{Hz}, 4\text{H}), 7.17 \, (br, 2\text{H}), 7.14 \, (br, 2\text{H}), 5.90–5.95 \, (m, 8\text{H}), 2.05–2.26 \, (m, 4\text{H}), 1.46 \, (s, 6\text{H}), 1.44 \, (s, 6\text{H}), 1.42 \, (m, overlapping, 2\text{H}), 0.90–1.10 \, (m, 4\text{H}), 0.72 \, (t, J = 7.6 \, \text{Hz}, 6\text{H}), 0.61 \, (d, J = 6.6 \, \text{Hz}, 6\text{H})\) ppm; \(^{13}\text{C NMR (100 MHz, CDCl}_3\): \(\delta 153.8, 149.4, 139.0, 133.8, 133.6, 123.2, 106.6, 106.5, 103.2, 103.2, 48.8, 46.7, 35.2, 35.1, 31.0, 30.8, 29.3, 29.2, 20.4, 11.3 \, \text{ppm}; FTIR (neat): \(\nu 2971, 1739, 1601, 1457, 1412, 1380, 1361, 1202, 1074, 1045, 992, 769, 712 \, \text{cm}^{-1}\); HRMS (ESI\(^+\)) calcd. for C\(_{44}\)H\(_{54}\)N\(_6\)Na \(m/z 689.4302 \, [M+Na]^+\), found \(m/z 689.4312\).
Supplementary Figure 8. $^1$H and $^{13}$C NMR spectra of 3 in chloroform-$d$. 
Supplementary Figure 9. NOESY spectrum of 3 in chloroform-\textit{d}.

Supplementary Figure 10. COSY spectrum of 3 in chloroform-\textit{d}.
Supplementary Figure 11. HSQC spectrum of 3 in chloroform-$d$. CH$_3$ and CH carbons are phased up (red), and CH$_2$ carbons are phased down (blue).

Supplementary Figure 12. HRMS (ESI$^+$) spectrum of 3.
Supplementary Figure 13. $^1$H and $^{13}$C NMR spectra of 9 in chloroform-$d$. 
Supplementary Figure 14. NOESY spectrum of 9 in chloroform-\textit{d}.

Supplementary Figure 15. COSY spectrum of 9 in chloroform-\textit{d}.
Supplementary Figure 16. HSQC spectrum of 9 in chloroform-d. CH₃ and CH carbons are phased up (red), and CH₂ carbons are phased down (blue).

Supplementary Figure 17. HRMS (ESI⁺) spectrum of 9.
**Supplementary Figure 18.** Expanded single crystal structure of the helix formed from 1 and AgBF$_4$ highlighting (a) the angle of Pyr(N)-Ag-Pyr(N), the coordination geometry around the Ag(I) center, and (b) the torsion angle between two pyridine moieties.
Supplementary Figure 19. SEM images of [1•Ag]. The scale bars denote 50 µm in (a), 30 µm in (b), 10 µm in (c), 2.0 µm in (d), 1.0 µm in (e), (f), and 0.50 µm in (g).
Supplementary Figure 20. UV-vis spectral absorption changes seen for a 1:1 mixture of 1 and AgBF$_4$ in THF. AgBF$_4$ Total concentrations are (a-h) 0.5, 0.8, 1.0, 2.0, 3.0, 5.0, 6.0, 7.0 x 10$^{-5}$ mol L$^{-1}$. 
### Supplementary Table 1

Cold spray ionization mass spectrometry (CSI-MS) data obtained from a mixture of 1 and AgBF₄ in chloroform/acetonitrile (1:1, v/v).

| m/z obs   | m/z calc | Formula (charge state) | Error /ppm |
|-----------|----------|------------------------|-------------|
| 661.2194  | 661.2203 | Ag₁⁺ (1+)              | −1.5        |
| 1411.4397 | 1411.4458| Ag₂₁₂BF₄⁺ (1+)         | −4.3        |
| 1607.3489 | 1607.3521| Ag₃₁₂(BF₄)₂⁺ (1+)      | −2.0        |
| 2355.5820 | 2355.5805| Ag₄₁₃(BF₄)₃⁺ (1+)      | 0.6         |

### Supplementary Figure 21

CSI-MS spectra of 1 and AgBF₄ complexes: Observed elemental compositions are (a) [1•Ag]⁺, (B) [1•(AgBF₄)•Ag]⁺, (c) [1•(AgBF₄)₂•Ag]⁺ and (d) [1•(AgBF₄)₃•Ag]⁺.
Supplementary Figure 22. CD spectral changes seen for mixtures of 1, 3, and AgBF₄ in THF at 25 °C. The ratios corresponding to the individual spectra are ([1] : [3] : [AgBF₄]) for traces i-viii are, respectively: 10:0:10, 9:1:10, 7:3:10, 4:6:10, 3:7:10, 2:8:10, 1:9:10, 0:10:10. The total concentrations of calix[4]pyrroles ([1] + [3]) and AgBF₄ are 1.3 x 10⁻⁴ mol L⁻¹. The blue line indicates the CD spectrum of 3 in the absence of AgBF₄ recorded at a concentration of 1.3 x 10⁻⁴ mol L⁻¹.
**Supplementary Figure 23.** Changes in the $^1$H NMR spectrum of (a) 1 (8.0 x 10$^{-4}$ mol L$^{-1}$) seen upon the sequential addition of (b) AgBF$_4$ (1.0 equiv.), (c) tetrabutylammonium chloride (TBACl) (1.0 equiv.), (d) the bisTBA salt of 2 (0.5 equiv.), (e) AgBF$_4$ (1.0 equiv.), and (f) TFA (1.0 equiv.). The spectra were recorded in THF-d$_8$. *Indicates solvent impurity.
Supplementary Figure 24. DLS profiles of 1 and its complexes: Changes in the DLS profile seen upon the sequential addition of AgBF₄ and TBACl to the THF solution of 1 at 25°C, highlighting the reversible nature of transformations between monomeric 1 and the helical structure [1•Ag]. The spectra are: (red) 1 (1.0 x 10⁻⁵ molL⁻¹) only; (green) 1 (1.0 x 10⁻⁵ molL⁻¹) + AgBF₄ (1.0 x 10⁻⁵ molL⁻¹); (blue) 1 (1.0 x 10⁻⁵ molL⁻¹) + AgBF₄ (1.0 x 10⁻⁵ molL⁻¹) + TBACl (1.0 x 10⁻⁵ molL⁻¹).
Supplementary Figure 25. $^1$H NMR spectrum of (a) 1 (5.0 x 10$^{-3}$ mol L$^{-1}$), (b) a 2:1 mixture of 1 (5.0 x 10$^{-3}$ mol L$^{-1}$) and the bisTBA salt of 2 (2.5 x 10$^{-3}$ mol L$^{-1}$), and (c) the bisTBA salt of pure 2 (2.5 x 10$^{-3}$ mol L$^{-1}$) as recorded in THF-$d_8$. 
Supplementary Figure 26. NOESY spectrum of a 2:1 mixture of 1 and the bisTBA salt of 2 in THF-$d_8$.

Supplementary Figure 27. COSY spectrum of a 2:1 mixture of 1 and the bisTBA salt of 2 recorded in THF-$d_8$. 
Supplementary Figure 28. HSQC spectrum of a 2:1 mixture of 1 and the bisTBA salt of 2 in THF-<i>d</i><sub>8</sub>. CH<sub>3</sub> and CH carbons are phased up (red), and CH<sub>2</sub> carbons are phased down (blue).
Supplementary Figure 29. (a) Changes in the UV-vis absorption spectrum of the bisTBA salt of 2 (4.0 x 10⁻⁵ mol L⁻¹) seen upon the addition of 1. Concentrations of 1 are (a-k): 0.8, 1.6, 2.4, 3.2, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 12 x 10⁻⁵ mol L⁻¹. The brown and green lines shown in (a) correspond to the UV-vis absorption spectra of the bisTBA salt of 2 (4.0 x 10⁻⁵ mol L⁻¹) and 1 (4.0 x 10⁻⁵ mol L⁻¹), respectively. The spectra were recorded in THF. (b) DLS profiles of (red) 1 (1.0 x 10⁻⁵ mol L⁻¹) and (green) a 2:1 mixture of 1 (1.0 x 10⁻⁵ mol L⁻¹) and the bisTBA salt of 2 (0.50 x 10⁻⁵ mol L⁻¹) in THF at 25 °C. (c) Job plot for a mixture of 1 and the bisTBA salt of 2 ([1] + [2] = 1.0 x 10⁻⁴ mol L⁻¹) in THF. X indicates the mole fraction of 1. ΔAbs’ indicates |Abs₁–Abs₂X–Abs₂(1–X)|. (d) Images exported from HypSpec Graphs showing the fitting over the whole spectrum.
Supplementary Figure 30. (I) Changes in the $^1$H NMR spectra of (a) 1 (2.0 x $10^{-3}$ mol L$^{-1}$) seen upon the sequential addition of (b) the bisTBA salt of 2 (0.5 equiv.) and (c) additional 0.5 equiv. of 2 in MeCN-$d_3$. (II) Changes seen from the same experiments in THF-$d_8$.

Supplementary Figure 31. Changes in the DLS profile seen upon the sequential addition of AgBF$_4$ and the bisTBA salt of 2 to the THF solution of 1 at 25°C. The spectra are: (red) 1 (1.0 x $10^{-5}$ mol L$^{-1}$) only; (green) 1 (1.0 x $10^{-5}$ mol L$^{-1}$) + AgBF$_4$ (1.0 x $10^{-5}$ mol L$^{-1}$); (blue) 1 (1.0 x $10^{-5}$ mol L$^{-1}$) + AgBF$_4$ (1.0 x $10^{-5}$ mol L$^{-1}$) + 2 (0.5 x $10^{-5}$ mol L$^{-1}$).
Supplementary Figure 32. Changes in the $^1$H NMR spectrum of 1 ($2.0 \times 10^{-3}$ mol L$^{-1}$) seen upon the sequential addition of the bisTBA salt of 2. The spectra were recorded in MeCN-$d_3$. 
Supplementary Figure 3.3. Changes in the $^1$H NMR spectrum of 1 (1.0 x $10^{-3}$ mol L$^{-1}$) seen upon the sequential addition of the bisTBA salt of 2. The spectra were recorded in THF-$d_8$. *Indicates solvent impurity.
Supplementary Figure 34. Changes in the $^1$H NMR spectrum of 1 ($2.0 \times 10^{-3}$ mol L$^{-1}$) seen upon the sequential addition of TFA. The spectra were recorded in MeCN-$d_3$. 
Supplementary Figure 35. Changes in the \(^1\)H NMR spectrum of 1 (10 \(\times\) 10\(^{-3}\) mol L\(^{-1}\)) seen upon the sequential addition of TFA. The spectra were recorded in THF-\(d_8\).
Supplementary Figure 36. Changes in the $^1$H NMR spectrum of a 2:1 mixture of 1 (2.0 x 10$^{-3}$ mol L$^{-1}$) and the bisTBA salt of 2 (1.0 x 10$^{-3}$ mol L$^{-1}$) seen upon the sequential addition of TFA. The spectra were recorded in MeCN-$d_3$. 
**Supplementary Figure 37.** Changes in the ^1^H NMR spectrum of a 2:1 mixture of 1 (5.0 x 10^{-3} mol L^{-1}) and bisTBA salt of 2 (2.5 x 10^{-3} mol L^{-1}) seen upon the sequential addition of TFA. The spectra were recorded in THF-d$_8$. *Indicates solvent impurity.
Supplementary Figure 38. (I) Changes in the $^1$H NMR spectra of (a) 1 (2.0 x 10^{-3} mol L^{-1}) in THF-d$_8$ seen upon the sequential addition of (b) the bisTBA salt of 2 (0.5 equiv.), (c) 50% aqueous HBF$_4$ (1.0 equiv.). (II) Changes in the $^1$H NMR spectra of (a) 1 (2.0 x 10^{-3} mol L^{-1}) in THF-d$_8$ seen upon the sequential addition of (b) the bisTBA salt of 2 (0.5 equiv.), and (c) TFA (1.0 equiv.). *Indicates solvent impurity.
Supplementary Figure 39. NOESY spectrum of a 2:1:2 mixture of 1 (2.0 x 10^{-3} mol L^{-1}), the bisTBA salt of 2 (1.0 x 10^{-3} mol L^{-1}) and 50% aqueous HBF_{4} (2.0 x 10^{-3} mol L^{-1}) in THF-d_{8}.

Supplementary Figure 40. HSQC spectrum of a 2:1:2 mixture of 1 (2.0 x 10^{-3} mol L^{-1}), the bisTBA salt of 2 (1.0 x 10^{-3} mol L^{-1}) and 50% aqueous HBF_{4} (2.0 x 10^{-3} mol L^{-1}) in THF-d_{8}. CH_{3} and CH carbons are phased up (red), and CH_{2} carbons are phased down (blue).
Supplementary Figure 41. NOESY spectrum of a 2:1:2 mixture of 1 (2.0 x 10^{-3} \text{ mol L}^{-1}), the bisTBA salt of 2 (1.0 x 10^{-3} \text{ mol L}^{-1}) and TFA (2.0 x 10^{-3} \text{ mol L}^{-1}) in THF-d_8.

Supplementary Figure 42. HSQC spectrum of a 2:1:2 mixture of 1 (2.0 x 10^{-3} \text{ mol L}^{-1}), the bisTBA salt of 2 (1.0 x 10^{-3} \text{ mol L}^{-1}) and TFA (2.0 x 10^{-3} \text{ mol L}^{-1}) in THF-d_8. CH_3 and CH carbons are phased up (red), and CH_2 carbons are phased down (blue).
**Supplementary Figure 43.** Changes in the $^1$H NMR spectra of (a) 1 (2.0 x $10^{-3}$ mol L$^{-1}$) in MeCN-$d_3$ seen upon the sequential addition of (b) the bisTBA salt of 2 (0.5 equiv.), (c) 50% aqueous HBF$_4$ (1.0 equiv.).

**Supplementary Figure 44.** COSY spectrum of a 2:1:2 mixture of 1 (2.0 x $10^{-3}$ mol L$^{-1}$), the bisTBA salt of 2 (1.0 x $10^{-3}$ mol L$^{-1}$), and 50% aqueous HBF$_4$ (2.0 x $10^{-3}$ mol L$^{-1}$) in MeCN-$d_3$. 

S35
**Supplementary Figure 45.** NOESY spectrum of a 2:1:2 mixture of 1 (2.0 x 10^{-3} mol L^{-1}), the bisTBA salt of 2 (1.0 x 10^{-3} mol L^{-1}) and 50% aqueous HBF_{4} (2.0 x 10^{-3} mol L^{-1}) in MeCN-d_{3}.

**Supplementary Figure 46.** HSQC spectrum of a 2:1:2 mixture of 1 (2.0 x 10^{-3} mol L^{-1}), the bisTBA salt of 2 (1.0 x 10^{-3} mol L^{-1}) and TFA (2.0 x 10^{-3} mol L^{-1}) in THF-d_{8}. CH_{3} and CH carbons are phased up (red), and CH_{2} carbons are phased down (blue).
Supplementary Figure 47. Changes in the $^1$H NMR spectrum of (a) 1 (8.0 x 10$^{-4}$ mol L$^{-1}$) seen upon the sequential addition of (b) the bisTBA salt of 2 (0.5 equiv.), (c) AgBF$_4$ (1.0 equiv.), (d) TBACl (1.0 equiv.), and (e) TFA (1.0 equiv.). The spectra were recorded in THF-$d_8$. *Indicates solvent impurity.
Supplementary Figure 48. Changes in the $^1$H NMR spectra of (I-a, III-a) 1 (2.0 x 10$^{-3}$ mol L$^{-1}$) in MeCN-$d_3$ and (II-a, IV-a) 1 (8.0 x 10$^{-4}$ mol L$^{-1}$) in THF-$d_8$ seen upon the sequential addition of (I-b, II-b, III-b, IV-b) AgBF$_4$ (1.0 equiv.), (I-c, II-c) the bisTBA salt of 2 (0.5 equiv.), and (III-d, IV-d) TFA (1.0 equiv.).
**Supplementary Figure 49.** View of 1 showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

**Supplementary Note 4.**

X-ray Experimental for C$_{36}$H$_{38}$N$_6$ – 3/2 CH$_3$CN – H$_2$O: Crystals grew as clusters of colorless prisms by slow evaporation from a 1:1 mixture of chloroform and acetonitrile. The data crystal was cut from a larger crystal and had approximate dimensions; 0.29 x 0.14 x 0.10 mm. The data were collected on a Rigaku SCX-Mini diffractometer with a Mercury 2 CCD using a graphite monochromator with MoKα radiation (λ = 0.71075 Å). A total of 1080 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 26 seconds per frame. The data were collected at 163 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Supplementary Table 2. Data reduction were performed using the Rigaku Americas Corporation’s Crystal Clear version 1.40. The structure was solved by direct methods using SIR97$^6$ and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-97.$^7$ Structure analysis was aided by use of the programs PLATON98$^8$ and WinGX.$^9$ The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms on the water molecule were observed in a ΔF map and refined with isotropic displacement parameters. One of the acetonitrile molecules was disordered about a crystallographic two-fold rotation axis at 1, 1, ¼. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[\sigma(F_o)]^2 + (0.0356 \times P)^2 + (4.1109 \times P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. R$_w$(F$^2$) refined to 0.132, with R(F) equal to 0.0656 and a goodness of fit, S, = 1.15. Definitions used for calculating R(F), R$_w$(F$^2$) and the goodness of fit, S, are given as $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^{1/2}$ where w is the weight given each
reflection, $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ for reflections with $F_o > 4(\sigma(F_o))$, and

$$\Sigma = [\Sigma w(|F_o|^2 - |F_c|^2)^{1/2}(n - p)]^{1/2},$$

where $n$ is the number of reflections and $p$ is the number of refined parameters. The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). All figures were generated using SHELXTL/PC.
Supplementary Table 2. Crystal data and structure refinement for 1.
Supplementary Figure 50. View of [1•Ag]∞ showing the heteroatom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Supplementary Note 5.

X-ray Experimental for \((C_{36}H_{38}N_6)Ag(BF_4) - H_2O - 3CH_3CN\): Crystals grew as yellow plates and prisms by slow evaporation from acetonitrile. The data crystal was cut from a larger crystal and had approximate dimensions; 0.34 x 0.22 x 0.09 mm. The data were collected at -140 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation \((\lambda = 0.71073 \text{ Å})\). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 1836 frames of data were collected using ω and φ-scans with a scan range of 0.5° and a counting time of 30 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Supplementary Table 3. Data reduction were performed using SAINT V8.27B. The structure was solved by direct methods using SUPERFLIP and refined by full-matrix least-squares on \(F^2\) with anisotropic displacement parameters for the non-H atoms using SHELXL-2013. Structure analysis was aided by use of the programs PLATON98 and WinGX. The hydrogen atoms were calculated in idealized positions. The tetrafluoroborate anion was disordered across a crystallographic two-fold rotation axis along \(\frac{1}{2}, y, \frac{1}{4}\). Additionally, a molecule of acetonitrile was also disordered about two orientations of approximately 50% occupancy.

The function, \(\Sigma w(|F_o|^2 - |F_c|^2)^2\), was minimized, where \(w = 1/[(\sigma(F_o))^2 + (0.0607*P)^2 + (9.9 * P)]\) and \(P = (|F_o|^2 + 2|F_c|^2)/3\). \(R_w(F^2)\) refined to 0.151, with \(R(F)\) equal to 0.0565 and a goodness of fit, \(S = 1.10\). Definitions used for calculating \(R(F)\), \(R_w(F^2)\) and the goodness of fit, \(S\), are given as \(R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^4\}^{1/2}\) where \(w\) is the weight given each reflection, \(R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\) for reflections with \(F_o > 4(\sigma(F_o))\), and \(\Sigma = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}\), where \(n\) is...
the number of reflections and \( p \) is the number of refined parameters.

The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).\textsuperscript{10} All figures were generated using SHELXTL/PC.\textsuperscript{11}
Empirical formula \[ \text{C}_{42} \text{H}_{49} \text{Ag B F}_{4} \text{N}_{9} \text{O} \]

Formula weight \[ 890.58 \]

Temperature \[ 133(2) \text{ K} \]

Wavelength \[ 0.71073 \text{ Å} \]

Crystal system \[ \text{monoclinic} \]

Space group \[ \text{P 2/c} \]

Unit cell dimensions \[
\begin{align*}
\text{a} & = 19.692(2) \text{ Å} & \alpha & = 90^\circ. \\
\text{b} & = 10.7710(12) \text{ Å} & \beta & = 107.186(4)^\circ. \\
\text{c} & = 20.408(3) \text{ Å} & \gamma & = 90^\circ.
\end{align*}
\]

Volume \[ 4135.3(9) \text{ Å}^3 \]

\( Z \) \[ 4 \]

Density (calculated) \[ 1.430 \text{ Mg/m}^3 \]

Absorption coefficient \[ 0.551 \text{ mm}^{-1} \]

\( F(000) \) \[ 1840 \]

Crystal size \[ 0.340 \times 0.220 \times 0.090 \text{ mm} \]

Theta range for data collection \[ 2.049 \text{ to } 25.072^\circ. \]

Index ranges \[ -23 \leq h \leq 23, -12 \leq k \leq 12, -24 \leq l \leq 24 \]

Reflections collected \[ 67745 \]

Independent reflections \[ 7341 \text{ [R(int) = 0.0761]} \]

Completeness to theta = 25.242° \[ 98.0 \% \]

Absorption correction \[ \text{Semi-empirical from equivalents} \]

Max. and min. transmission \[ 1.00 \text{ and } 0.840 \]

Refinement method \[ \text{Full-matrix least-squares on F}^2 \]

Data / restraints / parameters \[ 7341 / 154 / 574 \]

Goodness-of-fit on \( F^2 \) \[ 1.079 \]

Final R indices [I>2\sigma(I)] \[ R1 = 0.0565, wR2 = 0.1370 \]

R indices (all data) \[ R1 = 0.0793, wR2 = 0.1510 \]

Extinction coefficient \[ \text{n/a} \]

Largest diff. peak and hole \[ 0.829 \text{ and } -0.810 \text{ e.Å}^{-3} \]

CCDC # \[ 1058559 \]

**Supplementary Table 3.** Crystal data and structure refinement for [1•Ag]∞.
**Supplementary Figure 5.** View of $[\text{Ag}_2\text{I}_2\text{terephthalate}]$ showing the heteroatom labeling scheme. Displacement ellipsoids are scaled to the 40% probability level. The complex resides around a crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Atoms with labels appended by a ′ are related by $1-x, 1-y, 1-z$.

**Supplementary Note 6.**

X-ray Experimental for $[(\text{C}_{36}\text{H}_{38}\text{N}_4)_2(\text{C}_8\text{H}_4\text{O}_4)^2\cdot 2\text{Ag}^{+}] - 4 \text{C}_2\text{H}_4\text{SO} - 2 \text{C}_2\text{H}_3\text{N}$: Crystals grew as clusters of hexagonal shaped colorless prisms by slow evaporation from methanol, acetonitrile and DMSO. The data crystal had approximate dimensions; 0.20 x 0.12 x 0.09 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source ($\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 742 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 22.5 seconds per frame with a detector offset at +/- 41° and a counting time of 55 seconds for frames collected with a detector offset of +/- 108°. The data were collected at 133 K using an Oxford Cryostream low temperature device. Details of crystal, data collection and structure refinement are listed in Supplementary Table 4. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31. The structure was solved by direct methods using SIR97 and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2013. Structure analysis was aided by use of the programs PLATON98 and WinGX. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to nitrogen were located in a $\Delta F$ map and refined with isotropic displacement parameters.
The complex resides around a crystallographic inversion center at 1/2, 1/2, 1/2. Both DMSO molecules were disordered. The disorder was modeled in the same manner for both molecules. For one DMSO molecule, the variable x was assigned to the site occupancy factors for the atoms in one component of the disorder. The variable (1-x) was assigned to the site occupancy factors for the alternate component. A common isotropic displacement parameter was refined while refining the variable x. The geometry of the DMSO molecules was restrained to be equivalent throughout the refinement process. In this way, the major component for one DMSO molecule refined to 55(2)%, while the major component for the second DMSO molecule refined to 73(2)%.

The function, \( \Sigma \text{w}(|F_o|^2 - |F_c|^2)^2 \), was minimized, where \( w = 1/[(\sigma(F_o))^2 + (0.0857*P)^2 + (12.6415*P)] \) and \( P = (|F_o|^2 + 2|F_c|^2)/3 \). \( R_w(F^2) \) refined to 0.198, with R(F) equal to 0.0692 and a goodness of fit, S, = 1.16. Definitions used for calculating \( R(F) \), \( R_w(F^2) \) and the goodness of fit, S, are given as \( R_w(F^2) = \{ \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^4) \}^{1/2} \) where w is the weight given each reflection, \( R(F) = \Sigma |F_o| - |F_c|/\Sigma |F_o| \) for reflections with \( F_o > 4(\sigma(F_o)) \), and \( \Sigma = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2} \), where n is the number of reflections and p is the number of refined parameters. The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).\(^{10}\) All figures were generated using SHELXTL/PC.\(^{11}\)
| Property                        | Value                                      |
|--------------------------------|--------------------------------------------|
| Empirical formula              | C92 H110 Ag2 N14 O8 S4                    |
| Formula weight                 | 1883.91                                    |
| Temperature                    | 133(2) K                                   |
| Wavelength                     | 1.54184 Å                                  |
| Crystal system                 | monoclinic                                 |
| Space group                    | P 21/n                                     |
| Unit cell dimensions           | a = 15.6125(9) Å                           |
|                                | b = 14.9625(10) Å                          |
|                                | c = 20.6736(9) Å                           |
|                                | α = 90°                                    |
|                                | β = 110.917(6)°                            |
| Volume                         | 4511.1(5) Å³                               |
| Z                              | 2                                          |
| Density (calculated)           | 1.387 Mg/m³                                |
| Absorption coefficient         | 4.854 mm⁻¹                                 |
| F(000)                         | 1964                                       |
| Crystal size                   | 0.200 x 0.120 x 0.090 mm                   |
| Theta range for data collection| 3.737 to 69.985°                           |
| Index ranges                   | -18 <= h <= 19, -15 <= k <= 18, -25 <= l <= 17 |
| Reflections collected          | 17684                                      |
| Independent reflections        | 8509 [R(int) = 0.0377]                     |
| Completeness to theta = 67.684°| 99.9 %                                     |
| Absorption correction          | Semi-empirical from equivalents            |
| Max. and min. transmission     | 1.00 and 0.566                             |
| Refinement method              | Full-matrix least-squares on F²            |
| Data / restraints / parameters  | 8509 / 249 / 634                           |
| Goodness-of-fit on F²          | 1.133                                      |
| Final R indices [I>2sigma(I)]  | R1 = 0.0692, wR2 = 0.1809                  |
| R indices (all data)           | R1 = 0.0840, wR2 = 0.1982                  |
| Extinction coefficient         | n/a                                        |
| Largest diff. peak and hole    | 1.490 and -1.028 eÅ⁻³                      |
| CCDC #                         | 1058560                                    |

**Supplementary Table 4.** Crystal data and structure refinement for [Ag₂•1₂•terephthalate].
**Supplementary Figure 52.** View of [Cs$_2$•1$_2$•terephthalate] showing a partial atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

**Supplementary Note 7.**

X-ray Experimental for [(C$_{36}$H$_{38}$N$_6$)Cs]$_2$C$_8$H$_4$O$_4$ - 3CH$_3$N: Crystals grew as colorless prisms by slow evaporation from a 1:1 mixture of chloroform and acetonitrile. The data crystal had approximate dimensions; 0.17 x 0.13 x 0.04 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a µ-focus Cu Kα radiation source (λ = 1.5418 Å) with collimating mirror monochromators. A total of 2284 frames of data were collected using w-scans with a scan range of 2° and a counting time of 30 seconds per frame with a detector offset of +/- 40.5° and 90 seconds per frame with a detector offset of +/- 109.9°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Supplementary Table 5. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31. The structure was solved by direct methods using SIR97 and refined by full-matrix least-squares on F$^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2013. Structure analysis was aided by use of the programs PLATON98 and WinGX. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to nitrogen were located in a ΔF map and refined with isotropic displacement parameters. A molecule of acetonitrile was badly disordered about a crystallographic inversion center at 0, ½, 1. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to the solvent molecule were removed by use of the utility SQUEEZE in PLATON98.
The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0496*P)^2 + (11.5937*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F_2)$ refined to 0.118, with $R(F)$ equal to 0.0462 and a goodness of fit, $S$, = 1.02. Definitions used for calculating $R(F)$, $R_w(F_2)$ and the goodness of fit, $S$, are given below. The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). All figures were generated using SHELXTL/PC.
Empirical formula C$_{86}$H$_{89}$Cs$_{2}$N$_{15}$O$_{4}$
Formula weight 1662.54
Temperature 100(2) K
Wavelength 1.54184 Å
Crystal system triclinic
Space group P -1

Unit cell dimensions
- $a = 11.2373(11)$ Å, $\alpha = 79.728(5)^\circ$.
- $b = 18.3845(8)$ Å, $\beta = 77.533(8)^\circ$.
- $c = 20.4193(15)$ Å, $\gamma = 88.574(6)^\circ$.

Volume 4052.6(5) Å$^3$
Z 2
Density (calculated) 1.362 Mg/m$^3$
Absorption coefficient 7.482 mm$^{-1}$

F(000) 1704
Crystal size 0.170 x 0.130 x 0.040 mm
Theta range for data collection 3.015 to 76.964°.
Index ranges
- $-14 \leq h \leq 14$,
- $-22 \leq k \leq 23$,
- $-25 \leq l \leq 25$

Reflections collected 113961
Independent reflections 16829 [R(int) = 0.0532]
Completeness to theta = 67.684° 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00 and 0.555
Refinement method Full-matrix least-squares on $F^2$
Data / restraints / parameters 16829 / 125 / 998

Goodness-of-fit on $F^2$ 0.982
Final R indices [I>$2\sigma$(I)] $R1 = 0.0462$, $wR2 = 0.1150$
R indices (all data) $R1 = 0.0498$, $wR2 = 0.1177$
Extinction coefficient n/a
Largest diff. peak and hole 1.485 and -0.892 eÅ$^{-3}$

**Supplementary Table 5.** Crystal data and structure refinement for [Cs$_2$I$_2$·terephthalate].
Supplementary Figure 53. Views of [H₂·1,2·terephthalate] (top) and [H₂·1,2·trifluoroacetate] (bottom) showing a partial atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Supplementary Note 8.
X-ray Experimental for complex 2 (C₃₆H₃₉N₆) 0.93(C₈H₄O₄) 0.07(C₂F₃O₂) 4 C₂H₃N: Crystals grew as colorless prisms by evaporation from acetonitrile. The data crystal had approximate dimensions; 0.29 x 0.15 x 0.07 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ =
1.5418 Å) with collimating mirror monochromators. A total of 965 frames of data were collected using \( \omega \)-scans with a scan range of 1° and a counting time of 2 seconds per frame with a detector offset of +/- 40.5° and 5 seconds per frame with a detector offset of +/- 111°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Supplementary Table 6. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31. The structure was solved by direct methods using SuperFlip and refined by full-matrix least-squares on \( F^2 \) with anisotropic displacement parameters for the non-H atoms using SHELXL-2013. Structure analysis was aided by use of the programs PLATON98 and WinGX. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq for the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms on the pyrrole nitrogen atoms were observed in a \( \Delta F \) map and refined with isotropic displacement parameters. The anion encapsulated in the calixpyrrole dimer was composed of both terephthalate and trifluoroacetate ions. The trifluoroacetate ion is present in a small quantity of approximately 7%. The function, \( \Sigma w(|F_o|^2 - |F_c|^2)^2 \), was minimized, where \( w = 1/[(\sigma(F_o))^2 + (0.0446*P)^2 + (1.864*P)] \) and \( P = (|F_o|^2 + 2|F_c|^2)/3 \). \( R_w(F^2) \) refined to 0.102, with \( R(F) \) equal to 0.0401 and a goodness of fit, \( S_i = 1.02 \). Definitions used for calculating \( R(F) \), \( R_w(F^2) \) and the goodness of fit, \( S \), are given as \( R_w(F^2) = \{ \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^4 \}^{1/2} \) where \( w \) is the weight given each reflection, \( R(F) = \Sigma |F_o| - |F_c|/\Sigma |F_o| \) for reflections with \( F_o > 4(\sigma(F_o)) \), and \( S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2} \), where \( n \) is the number of reflections and \( p \) is the number of refined parameters. The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). All figures were generated using SHELXTL/PC.
Empirical formula C87.50 H93.50 F0.50 N16 O4
Formula weight 1442.78
Temperature 100(2) K
Wavelength 1.54184 Å
Crystal system monoclinic
Space group P 21/n
Unit cell dimensions
\[\begin{align*}
a &= 15.1217(4) \text{ Å} & \alpha &= 90^\circ, \\
b &= 15.2911(3) \text{ Å} & \beta &= 99.493(2)^\circ, \\
c &= 16.9007(3) \text{ Å} & \gamma &= 90^\circ.
\end{align*}\]
Volume 3854.39(15) Å³
Z 2
Density (calculated) 1.243 Mg/m³
Absorption coefficient 0.631 mm⁻¹
F(000) 1534
Crystal size 0.290 x 0.150 x 0.068 mm
Theta range for data collection 3.636 to 76.354°.
Index ranges -19<=h<=18, -18<=k<=19, -20<=l<=17
Reflections collected 22578
Independent reflections 7834 [R(int) = 0.0238]
Completeness to theta = 67.684° 99.6 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00 and 0.954
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 7834 / 10 / 542
Goodness-of-fit on F² 1.023
Final R indices [I>2sigma(I)] R1 = 0.0401, wR2 = 0.0973
R indices (all data) R1 = 0.0461, wR2 = 0.1015
Extinction coefficient n/a
Largest diff. peak and hole 0.377 and -0.326 e.Å⁻³
CCDC # 1558007

**Supplementary Table 6.** Crystal data and structure refinement for [H₂•1•terephthalate] + [H₂•1•trifluoroacetate].
Supplementary Figure 54. View of the 9 showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Supplementary Note 9.

X-ray Experimental for C₄4H₅₄N₆ – 2 H₂O: Crystals grew as clear, colorless needles by slow evaporation from acetonitrile. The data crystal was cut from a larger crystal and had approximate dimensions; 0.31 x 0.15 x 0.11 mm. The data were collected at -150 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073 Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 629 frames of data were collected using w and φ-scans with a scan range of 1.1° and a counting time of 85 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Supplementary Table 7. Data reduction were performed using SAINT V8.27B.¹² The structure was solved by direct methods using SHELXT¹¹ and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.⁷ Structure analysis was aided by use of the programs PLATON98⁸ and
WinGX. The hydrogen atoms bound to carbon atoms were calculated in idealized positions. The hydrogen atoms on the water molecule were observed in a ΔF map and constrained in a riding model with Uiso set to 1.5xUeq of the water molecule, O3. The hydrogen atoms on the pyrrole nitrogen atoms were observed in a ΔF map and refined with isotropic displacement parameters.

The calixpyrrole di-hydrate complex resides around a crystallographic inversion center at ½, ½, ½. The pyrrole NH groups H-bond to the water molecule, which, in turn, is H-bound to the pyridine ring. The terminal methyl group of the 2-methylbutyl group is disordered. The disorder was modeled by assigning the variable x to the site occupancy factor for C20 and (1-x) was assigned to the site occupancy factor for the alternate component, C20a, of the disordered atom. A common isotropic displacement parameter was refined for both atoms while refining x. The site occupancy for C20 refined to 52(1)%. The function, \( \Sigma w(\mid F_o \mid^2 - \mid F_c \mid^2)^2 \), was minimized, where \( w = 1/[(s(F_o))^2 + (5.5758*P)] \) and \( P = (\mid F_o \mid^2 + 2\mid F_c \mid^2)/3 \). \( R_w(F^2) \) refined to 0.187, with R(F) equal to 0.0865 and a goodness of fit, \( S = 1.21 \). Definitions used for calculating R(F), \( R_w(F^2) \) and the goodness of fit, \( S \), are given as \( R_w(F^2) = \{ \Sigma w(\mid F_o \mid^2 - \mid F_c \mid^2)^2/\Sigma w(\mid F_o \mid^4)^{1/2} \) where w is the weight given each reflection. \( R_w(F^2) = \{ \Sigma w(\mid F_o \mid^2 - \mid F_c \mid^2)^2/\Sigma w(\mid F_o \mid^4)^{1/2} \) where w is the weight given each reflection, R(F) = \( \Sigma(\mid F_o \mid - \mid F_c \mid)/\Sigma \mid F_o \mid \) for reflections with \( F_o > 4(\sigma(F_o)) \), and \( \Sigma = [\Sigma w(\mid F_o \mid^2 - \mid F_c \mid^2)^2/(n - p)]^{1/2} \), where n is the number of reflections and p is the number of refined parameters. The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). All figures were generated using SHELXTL/PC. Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures may be obtained from the Cambridge Crystallographic Data Centre.
Empirical formula C44 H58 N6 O2
Formula weight 702.96
Temperature 123(2) K
Wavelength 0.71073 Å
Crystal system monoclinic
Space group P 21/n
Unit cell dimensions a = 10.6246(10) Å  α = 90°.
b = 12.3223(13) Å  β = 98.778(6)°.c = 14.8745(14) Å  γ = 90°.
Volume 1924.6(3) Å³
Z 2
Density (calculated) 1.213 Mg/m³
Absorption coefficient 0.075 mm⁻¹
F(000) 760
Crystal size 0.31 x 0.15 x 0.11 mm³
Theta range for data collection 2.157 to 27.640°.
Index ranges -13≤h≤13, -15≤k≤16, -18≤l≤19
Reflections collected 26322
Independent reflections 4419 [R(int) = 0.0895]
Completeness to theta = 25.242° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00 and 0.770
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4419 / 2 / 266
Goodness-of-fit on F² 1.210
Final R indices [I>2sigma(I)] R1 = 0.0865, wR2 = 0.1755
R indices (all data) R1 = 0.1272, wR2 = 0.1871
Extinction coefficient n/a
Largest diff. peak and hole 0.441 and -0.293 e.Å⁻³
CCDC # 1583699

**Supplementary Table 7** Crystal data and structure refinement for 9.
Supplementary References

1. Sokkalingam, P., Kim, D. S., Hwang, H., Sessler, J. L. & Lee, C.-H. A dicationic calix[4]pyrrole derivative and its use for the selective recognition and displacement-based sensing of pyrophosphate. Chem. Sci. 3, 1819–1824 (2012).

2. Kim, D. S., Lynch, V. M., Park, J. S. & Sessler, J. L. Three distinct equilibrium states via self-assembly: simple access to a supramolecular ion-controlled NAND logic gate. J. Am. Chem. Soc. 135, 14889–14894 (2013).

3. Shimada, H. et al. Comparative inhibition of tetrameric carbonyl reductase activity in pig heart cytosol by alkyl 4-pyridyl ketones. J. Enzyme Inhib. Med. Chem. 29, 397–400 (2014).

4. Gans, P., Sabatini, A. & Vacca, A. Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs. Talanta 43, 1739–1753 (1996).

5. Rigaku Americas Corporation. CrystalClear 1.40, The Woodlands, TX. (2008).

6. Altomare, A. et al. SIR97. A program for crystal structure solution. J. Appl. Cryst. 32, 115–119 (1999).

7. Sheldrick, G. M. Program for the refinement of crystal structures. Acta Cryst. A64, 112–122 (2008).

8. Spek, A. L. PLATON. A multipurpose crystallographic tool. Utrecht University, The Netherlands (1998).

9. Farrugia, L. J. WinGX 1.64. An integrated system of windows programs for the solution, refinement and analysis of single crystal X-ray diffraction data. J. Appl. Cryst. 32, 837–838 (1999).

10. A. J. C. Wilson. Tables for X-ray Crystallography Vol. C, Tables 4.2.6.8 and 6.1.1.4, Kluwer Academic Press International (1992).

11. Sheldrick, G. M. SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA (1994).

12. SAINT V8.27B Bruker AXS Inc, Madison, WI (2012).

13. Palatinus, L. & Chapuis, G. Superflip – A computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. J. Appl. Cryst. 40, 786–790 (2007).

14. CrysAlisPro. Agilent Technologies Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlisPro Software System, 1.171.37.31 (2013).

15. van der Sluis, P. & Spek, A. L. SQUEEZE. Acta Cryst. A46, 194–201 (1990).