Electronic Supplementary Information

Construction and interconversion of anion-coordination-based ('aniono') grids and double helicates modulated by counter-cations

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S1. General considerations

The *o*-nitrophenylisocyanate and *p*-nitrophenylisocyanate were purchased from Alfa Aesar and used as received. All solvents and other reagents were of reagent grade quality. NMR spectra were obtained at 296 K by using Bruker AVANCE III-400 MHz spectrometers unless noted otherwise. ^{1}H and ^{13}C NMR chemical shifts were reported relative to residual solvent peaks (^{1}H NMR: 2.50 ppm for DMSO-d_6, 1.94 ppm for CD_3CN respectively;^{13}C NMR: 39.5 for DMSO-d_6). ESI-MS measurements were carried out using a Bruker microTOF-Q II ESI-Q-TOF LC/MS/MS spectrometer, or a Waters Synapt HDMS G2 instrument with a LockSpray ESI source, or a Waters Synapt G2 mass spectrometer with traveling wave ion mobility. Computer fitting of the data was performed using the VP-ITC software. Single crystal diffraction analyses were done on a Bruker SMART APEX II diffractometer.

S2. Computer-aided design of A_2L_2 helicate

The S_4 symmetric geometry for the complex formed between two tris-urea ligands and phosphate, Figure S1a,[1] serves as the starting point for the design of an $A_2\mathbf{L}_2$ assembly. The 3D design of ligands for high-symmetry assemblies involves identifying hydrocarbon links that will connect two ligand fragments on one anion, A, to two ligand fragments on a second anion, A, such that both ligands, **L**, have identical shapes.[2] With analogous M_2L_2 assemblies, the most common structures are D_2 symmetric helicates where both M lie on a common C_2 axis, perpendicular C_2 axes through the center of each L, and M centers have the same configuration (ΔΔ or ΛΛ). Given the way that the two tris-urea fragments wrap around each phosphate center, however, the A_2L_2 assemblies that are possible when the ends of these fragments are connected to yield L lack these C_2 axes and D_2 symmetry is not possible. When the two phosphate centers adopt opposite configurations (ΔΛ), it is possible to achieve a C_i symmetric assembly in which both ligands have identical shapes. Hydrocarbon links yielding **L** conformations that compliment this C_i symmetric $A_2\mathbf{L}_2$ mesocate assembly were identified using computer-aided molecular design software HostDesigner.[3] A synthetically tractable ligand candidate, **L**, is obtained when the tris-urea fragments are connected with *p*-xylene to yield the assembly shown in Figure S1b.

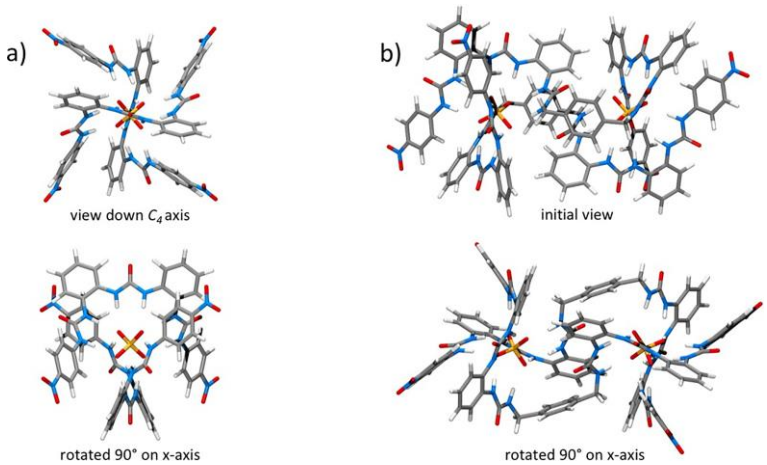
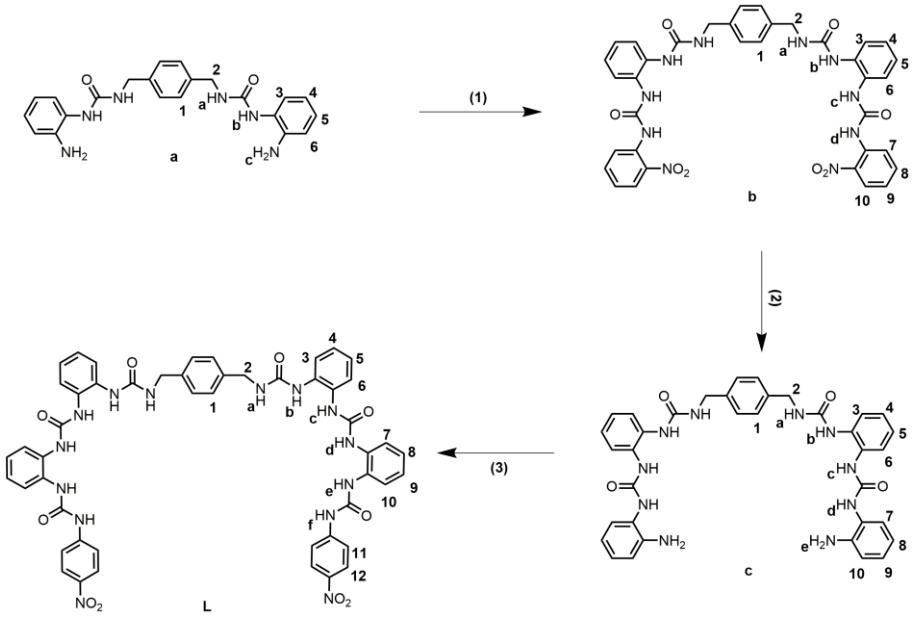


Fig. S1. a) Geometry of the 2:1 bis(tris-urea)-PO_4^{3-} complex.[1] b) Designed geometry for the C_i symmetric mesocate $A_2\mathbf{L}_2$ assembly obtained when p-xylene links are used to connect the tris-urea fragment ends between PO_4^{3-} complexes.

S3. Synthesis of ligand L



Scheme S1. Synthesis of **L**, (1) 2-nitrophenyl isocyanate, THF, DMF, reflux; (2) Pd/C 10% cat., NH_2NH_2 ·H_2O, MeOH, reflux; (3) 4-nitrophenyl isocyanate, THF, DMF, reflux.

1,1'-(1,4-Phenylenebis(methylene))bis(3-(2-aminophenyl)urea) (a)

Compound **a** was prepared according to reported literature procedures.[4] ^{1}H NMR (400 MHz, [D_6]DMSO, ppm): δ 7.60 (s, 1H, Hb), 7.27 (s, 3H, H1, Ha), 6.79 (t, *J* = 8.0 Hz, 1H, H4), 6.70 (d, *J* = 8.0 Hz, 1H, H3), 6.60 (d, *J* = 8.0 Hz,1H, H6), 6.53 (t, *J* = 8.0 Hz, 1H, H5), 4.70 (s, 1H, Hc,), 4.27 (d, *J* = 8.0 Hz, 2H, H2).

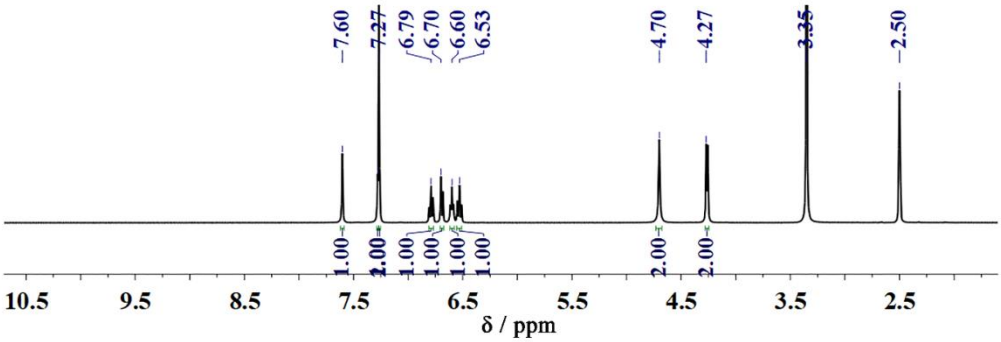


Fig. S2. ^{1}H NMR spectrum of compound **a** (400 MHz, DMSO-d_6, 296 K).

Compound b

1,1'-(1,4-Phenylenebis(methylene))bis(3-(2-aminophenyl)urea) (**a**, 0.2 g, 0.74 mmol) dissolved in 3 mL DMF was added to a refluxing THF solution (20 mL) of o-nitrophenylisocyanate (0.48 g, 2.93 mmol). The mixture was refluxed for 4 hours and the precipitate was filtered off and washed several times with THF and diethyl ether and then dried over vacuum to give pure compound **b** as a light yellow solid (0.53 g, 95 %). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.71 (s, 1H, Hd), 9.13 (s, 1H, Hc), 8.32(d, *J* = 8.0 Hz, 1H, H10), 8.08 (d, *J* = 8.0 Hz, 1H, H7), 7.91 (s, 1H, Hb), 7.84 (d, *J* = 8.0 Hz, 1H, H6), 7.68 (t, *J* = 8.0 Hz , 1H, H9), 7.35 (d, *J* = 8.0 Hz, 1H, H3), 7.26 (s,

2H, H1), 7.17 (t, *J* = 8.0 Hz , 1H, H8), 7.14 (m, 2H, H4/5), 6.98 (t, *J* = 8.0 Hz , 1H, Ha), 4.28 (d, *J* = 8.0 Hz , 2H, H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.4 (CO), 152.9 (CO), 138.7 (CH), 137.5 (CH), 135.1 (CH), 135.0 (CH), 134.4 (C), 127.7 (C), 127.3 (CH), 125.9 (C), 125.5 (C), 125.3 (CH), 122.4 (CH), 122.3 (CH), 122.1 (CH), 121.6 (C), 42.7 (CH_2). IR (KBr, ν/cm^{-1}): 3352, 3298, 3130, 1647, 1587, 1540, 1510, 1342, 1290. ESI-MS: *m*/*z* 755.2279, $[M+Na]^+$.

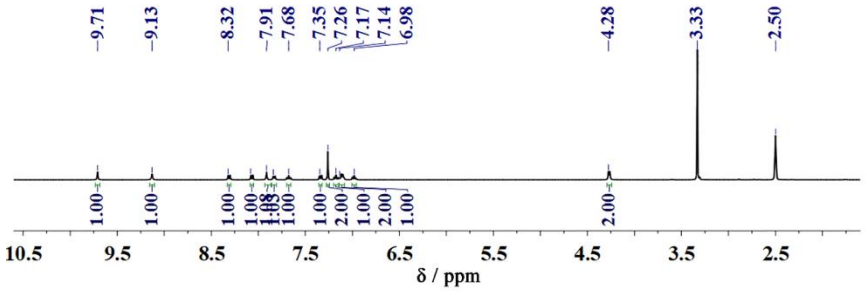


Fig. S3. ^{1}H NMR spectrum of compound **b** (400 MHz, DMSO-d_6, 296 K).

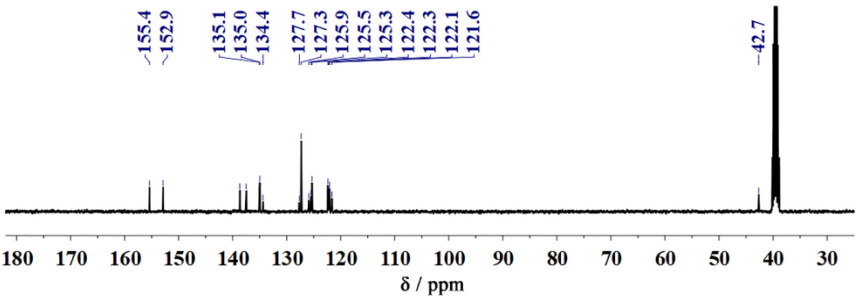


Fig. S4. ^{13}C NMR spectrum of compound **b** (400 MHz, DMSO-d_6, 296 K).

Compound c

Hydrazine monohydrate (9.0 mL) was added dropwise to a suspension of compound **b** (1.40 g, 1.9 mmol) and Pd/C 10% (0.14 g, cat.) in methanol (150 mL). After refluxing for 12 hours, the solid was filtered off, dissolved in DMF (60 mL), and filtered through Celite to remove Pd/C. The DMF solution was poured in water (500 mL) and the precipitate thus obtained was filtered off, washed several times with ethanol and diethyl ether and then dried over vacuum to give compound **c** as a brown solid (0.90g, 70 %). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 8.09 (s, 2H, Hd/a), 7.93 (s, 1H, Hb), 7.54 (m, 2H, H7/6), 7.33 (d, *J* = 8.0 Hz, 1H, H3), 7.29 (s, 2H, H1), 7.03 (m, 3H, H4/5/8), 6.84 (t, *J* = 8.0 Hz, 1H, H9), 6.74 (d, *J* = 8.0 Hz,1H, H10), 6.56 (t, *J* = 8.0 Hz, 1H, Ha). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.9 (CO), 153.9 (CO), 131.1 (CH), 138.8 (CH), 132.0 (CH), 131.0 (CH), 127.3 (CH), 124.6 (C), 124.5 (CH), 124.2 (CH), 124.0 (C), 123.7 (C), 123.4 (C), 123.3 (C), 116.7 (CH), 115.8 (CH), 42.8 (CH_2). IR (KBr, ν/cm^{-1}): 3306, 3267, 3066, 1638, 1594, 1543, 1458, 1244. ESI-MS: *m*/*z* 695.2806, $[M+Na]^+$.

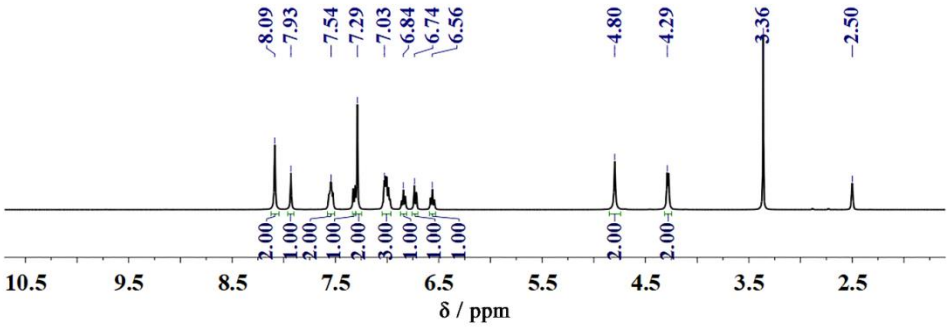


Fig. S5. [1]H NMR spectrum of compound **c** (400 MHz, DMSO-d_6, 296 K).

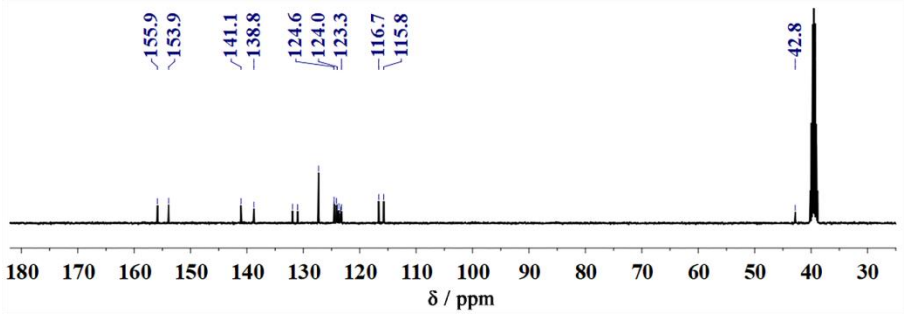


Fig. S6. [13]C NMR spectrum of compound **c** (400 MHz, DMSO-d_6, 296 K).

Ligand L

Compound **c** (0.67 g, 1.00 mmol) dissolved by 8 ml DMF was added to a refluxing THF solution (20 mL) of p-nitrophenylisocyanate (0.65 g, 4.00 mmol). The mixture was refluxed for 4 hours and the precipitate was filtered off and washed several times with THF and diethyl ether and then dried over vacuum to give pure d as a light yellow solid (0.82 g, 82 %). [1]H NMR (400 MHz, DMSO-d_6, ppm): δ 9.91 (s, 1H, Hf), 8.49 (s, 1H, Hd), 8.38 (s, 1H, Hc), 8.28 (s, 1H, He), 8.19 (d, *J* = 8.0 Hz, 2H,H12), 7.95 (s, 1H, Hb), 7.70 (d, *J* = 8.0 Hz, 2H, H11), 7.58 (m, 3H, H10/9/8), 7.51 (d, *J* = 12.0 Hz, 1H, H7), 7.22 (s, 2H, H1), 7.10 (m, 4H, H6/3), 7.01 (m, 3H, H5/4/a), 4.24 (d, *J* = 8.0 Hz, 4H, H2). [13]C NMR (100 MHz, DMSO-d_6): δ 155.8 (CO), 154.1 (CO), 152.6 (CO), 146.6 (CH), 141.0 (C), 140.9 (C), 138.6 (CH), 132.5(CH), 131.6 (CH), 130.8 (C), 130.7 (C), 130.3 (C), 127.2 (CH), 125.2 (CH), 124.6 (CH), 124.5 (C), 124.3 (C), 124.2 (CH), 124.1 (CH), 123.2 (CH), 117.4 (CH), 42.7 (CH_2). IR (KBr, ν/cm^{-1}): 3347, 3269, 3161, 1630, 1599, 1557, 1507, 1327, 1300. ESI-MS: *m*/*z* 1023.3262, $[M+Na]^+$.

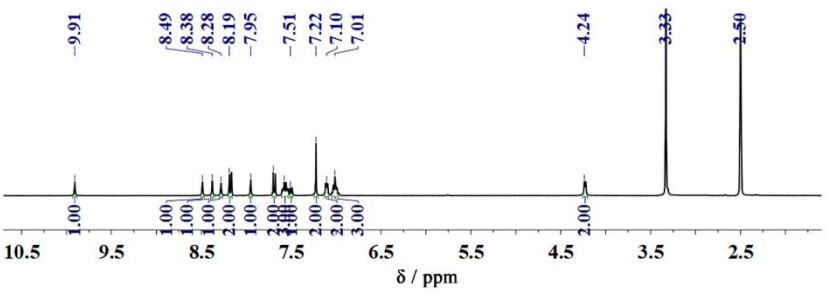


Fig. S7. [1]H NMR spectrum of ligand **L** (400 MHz, DMSO-d_6, 296 K).

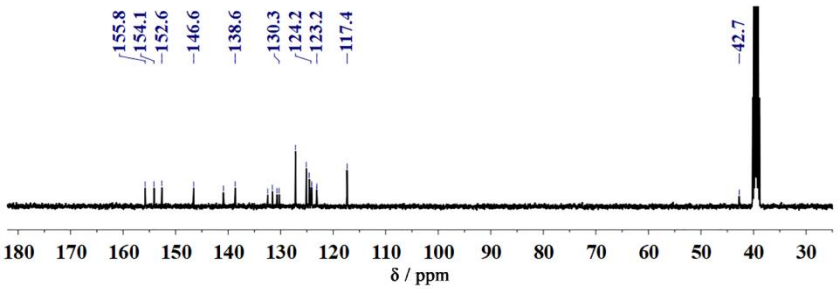


Fig. S8. ^{13}C NMR spectrum of ligand **L** (400 MHz, DMSO-d_6, 296 K).

S4. Synthesis, H[1] NMR spectra and crystal structures of complexes 1a−1d and 2

$(TMA)_5[TMA\subset(PO_4)_2\mathbf{L}_2]$ (1a)

$(TMA)_3PO_4$ (16 μL, 0.625 mol/L; generated in situ from (TMA)OH and H_3PO_4) was added to a suspension of **L** (10 mg, 10 μmol) in acetone (1 mL). After stirring overnight at room temperature, a clear yellow solution was obtained. Slow vapor diffusion of diethyl ether into this solution provided yellow crystals of $(TMA)_5[TMA\subset(PO_4)_2\mathbf{L}_2]$ within two weeks (yield > 90 %). ^{1}H NMR (400 MHz, CD_3CN, ppm): δ 12.80 (s, 1H, NHf), 12.40 (s, 1H, NHe), 11.79-11.31 (3H, NHd/NHc/ NHb), 9.90 (t, 1H, NHa), 8.40 (s, 1H, H10), 8.10 (m, 1H, H6), 7.95 (m, 2H, H3/H7), 7.64 (d, J = 8 Hz, 2H, H12), 7.28 (d, J = 8.0 Hz, 2H, H11), 7.14 (t, J = 8 Hz, 1H, H9), 7.03-6.95 (m, 3H, H4/H5/H8), 6.50 (s, 2H, H1), 4.35 (s, 1H, H2), 3.23 (d, J = 4 Hz,1H, H2).

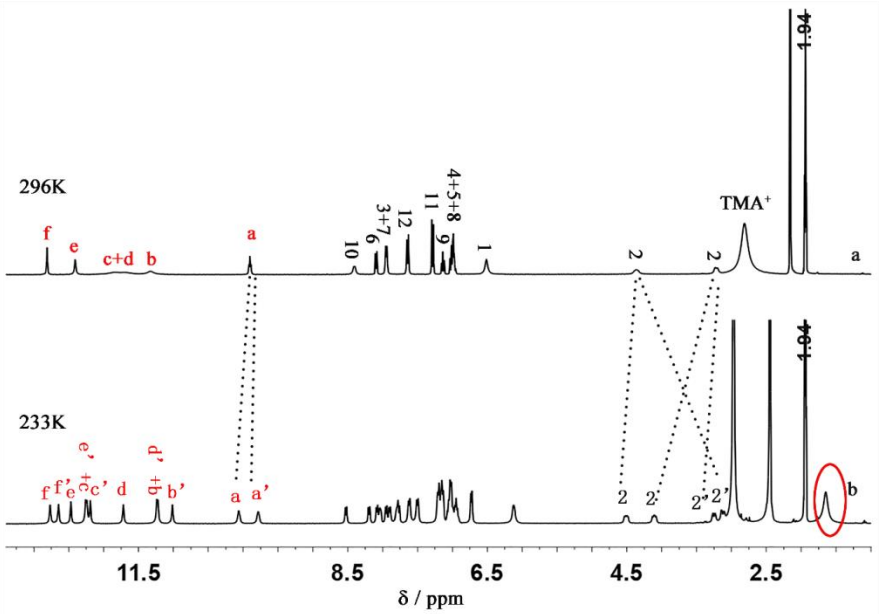


Fig. S9. ^{1}H NMR spectra of $(TMA)_5[TMA\subset(PO_4)_2\mathbf{L}_2]$ (**1a**) (400 MHz, CD_3CN) at different temperatures (296 K and 233 K).

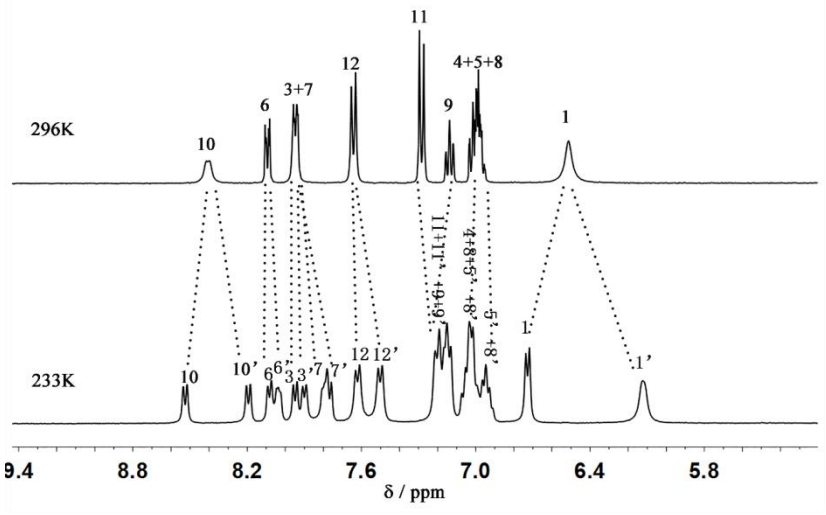


Fig. S10. Partial ^{1}H NMR spectrum of $(TMA)_5[TMA\subset(PO_4)_2\mathbf{L}_2]$ (400 MHz, CD_3CN).

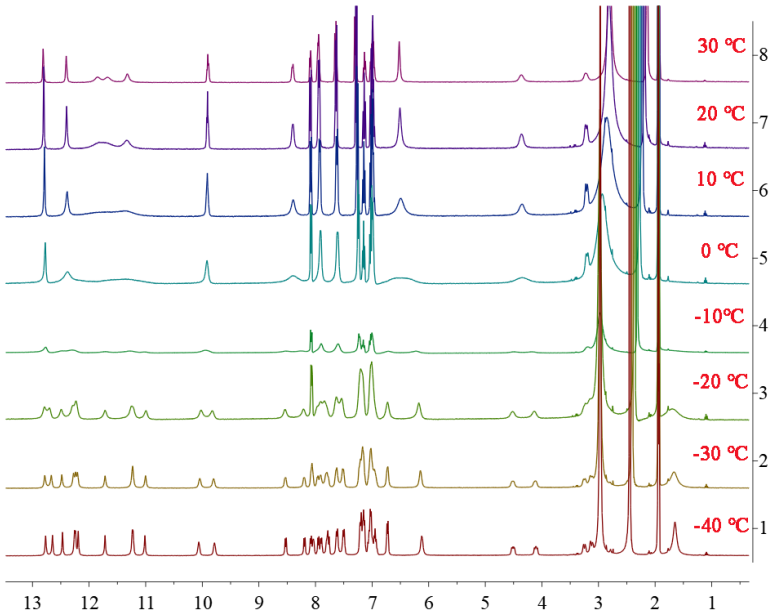


Fig. S11. Variable-temperature ^{1}H NMR spectra of $(TMA)_5[TMA\subset(PO_4)_2\mathbf{L}_2]$ (**1a**) (400 MHz, CD_3CN).

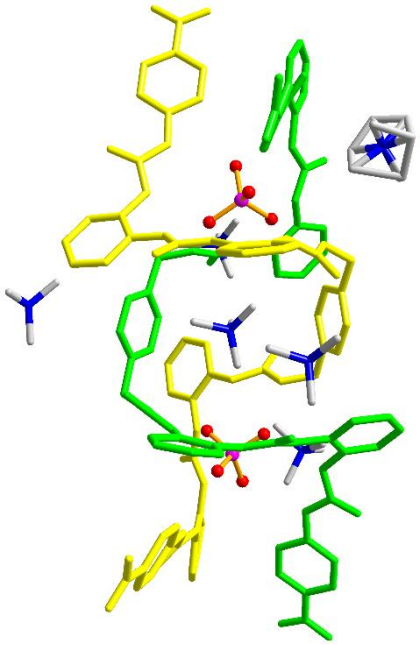


Fig. S12. Crystal structure of the double helicate $[(TMA)\subset(PO_4)_2\mathbf{L}_2]^{5-}$ (**1a**) (Only an *M* enantiomer is shown) and solvents are omitted for clarity.

$(TPA)_6[(PO_4)_2\mathbf{L}_2]$ (1b)

$(TPA)_3PO_4$ (16 μL, 0.625 mol/L; generated in situ from (TPA)OH and H_3PO_4) was added to a suspension of **L** (10 mg, 10 μmol) in acetone (1 mL). After stirring overnight at room temperature, a clear yellow solution was obtained. Diethyl ether was added to this solution to give a yellow precipitate, which was collected by centrifugation and washed with diethyl ether for several times, and dried to obtain the yellow complex of complex **1b**, $(TPA)_6[(PO_4)_2\mathbf{L}_2]$ (yield > 90 %). ^{1}H NMR (400 MHz, CD_3CN, ppm): δ 13.05 (s, 2H, Hf), 12.72 (s, 2H, He), 11.93 (s, 2H, Hd), 11.69 (s, 2H, Hc),11.61 (s, 2H, Hb), 9.97 (s, 2H, Ha), 8.46 (d, *J* = 8 Hz, 2H, H10), 8.12 (d, *J* = 8 Hz, 2H, H6), 7.90 (d, *J* = 8 Hz, 2H, H7), 7.72 (d, *J* = 12 Hz, 4H, H12), 7.43 (s, 2H, H3), 7.33 (d, *J* = 8 Hz, 4H, H11), 7.11 (s, 4H, H1) ,7.07 (t, *J* = 8 Hz, 2H, H9), 6.97 (t, *J* = 8 Hz, 2H, H8), 7.92 (t, *J* = 8 Hz, 2H, H5), 6.77 (t, *J* = 8 Hz, 2H, H4), 3.80 (s, H2).

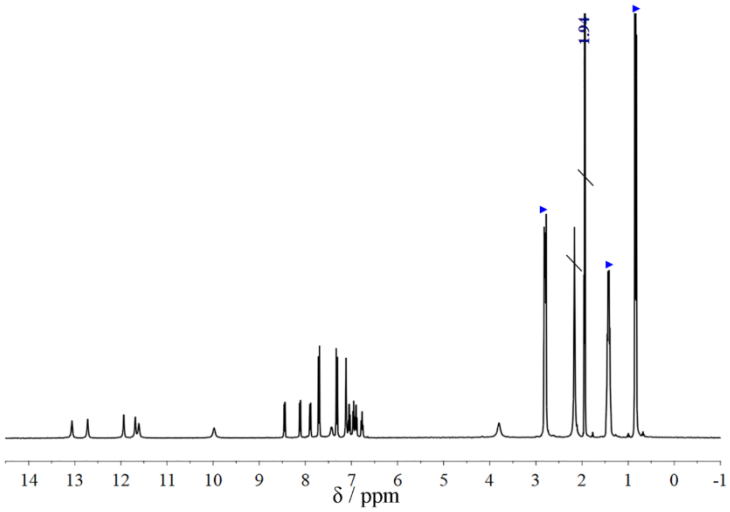


Fig. S13. ^{1}H NMR spectrum of $(TPA)_6[(PO_4)_2\mathbf{L}_2]$ (**1b**) (400 MHz, CD_3CN, 296 K). The signals of TPA^+ are marked with ▶.

$(TBA)_6[(PO_4)_2L_2]$ (1c)

$(TBA)_3PO_4$ (16 µL, 0.625 mol/L; generated in situ from (TBA)OH and H_3PO_4) was added to a suspension of **L** (10 mg, 10 µmol) in acetone (1 mL). After stirring overnight at room temperature, a clear yellow solution was obtained. Similar work up as in the case of **1b** led to the yellow complex $(TBA)_6[(PO_4)_2\mathbf{L}_2]$ (yield > 90 %). ^{1}H NMR (400 MHz, CD_3CN, ppm): δ 13.08 (s, 2H, Hf), 12.79 (s, 2H, He), 11.91 (s, 2H, Hd), 11.71 (s, 2H, Hc), 11.58 (s, 2H, Hb), 9.95 (s, 2H, Ha), 8.43 (d, *J* = 8 Hz, 2H, H10), 8.13 (d, *J* = 8 Hz, 2H, H6), 7.90 (d, *J* = 8 Hz, 2H, H7), 7.71 (d, *J* = 8 Hz, 4H, H12), 7.54 (d, *J* = 8 Hz, 2H, H3), 7.32 (d, *J* = 8 Hz, 4H, H11), 7.07 (s, 4H, H1) ,7.03 (t, *J* = 8 Hz, 2H, H9), 6.94 (t, *J* = 8 Hz, 2H, H8), 7.88 (t, *J* = 8 Hz, 2H, H5), 6.57 (t, *J* = 8 Hz, 2H, H4), 3.77 (s, H2).

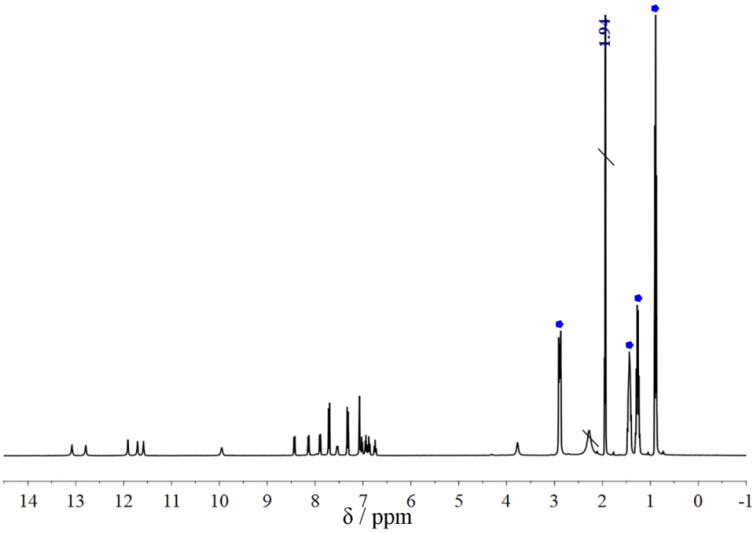


Fig. S14. ^{1}H NMR spectrum of $(TBA)_6[(PO_4)_2\mathbf{L}_2]$ (**1c**) (400 MHz, CD_3CN, 296 K). The signals of TBA^+ are marked with ●.

$(TBA)_5[TMA\subset(PO_4)_2L_2]$ (1d)

$(TBA)_3PO_4$ (13 μL, 0.625 mol/L; generated in situ from (TBA)OH and H_3PO_4) and $(TMA)_3PO_4$ (3 μL, 0.625 mol/L; generated in situ from (TMA)OH and H_3PO_4) was added to a suspension of **L** (10 mg, 10 μmol) in acetone (1 mL). After stirring overnight at room temperature, a clear yellow solution was obtained. Slow vapor diffusion of diethyl ether into this solution provided yellow crystals of $(TBA)_5[TMA\subset(PO_4)_2\mathbf{L}_2]$ within two weeks (yield > 90 %). ^{1}H NMR (400 MHz, CD_3CN, ppm): δ 12.86 (s, 1H, NHf), 12.43 (s, 1H, NHe), 11.94-11.29 (3H, NHd/NHc/NHb), 9.90 (t, 1H, NHa), 8.41 (s, 1H, H10), 8.11 (d, J = 8 Hz, 1H, H6), 7.97 (m, 2H, H3/H7), 7.67 (d, J = 8 Hz, 2H, H12), 7.29 (d, J = 8.0 Hz, 2H, H11), 7.13 (t, J = 8 Hz, 1H, H9), 7.02-6.94 (m, 3H, H4/H5/H8), 6.51 (s, 2H, H1), 4.37 (s, 1H, H2), 3.23 (d, J = 12 Hz, 1H, H2).

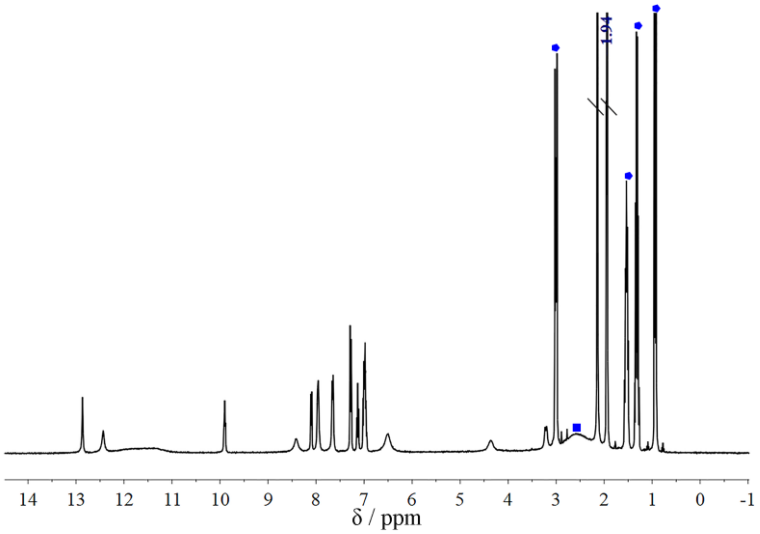


Fig. S15. ^{1}H NMR spectrum of $(TBA)_5[TMA\subset(PO_4)_2\mathbf{L}_2]$ (400 MHz, CD_3CN, 296 K). The signals of the TMA^+ ions are marked with ■, and those of TBA^+ with ⬟.

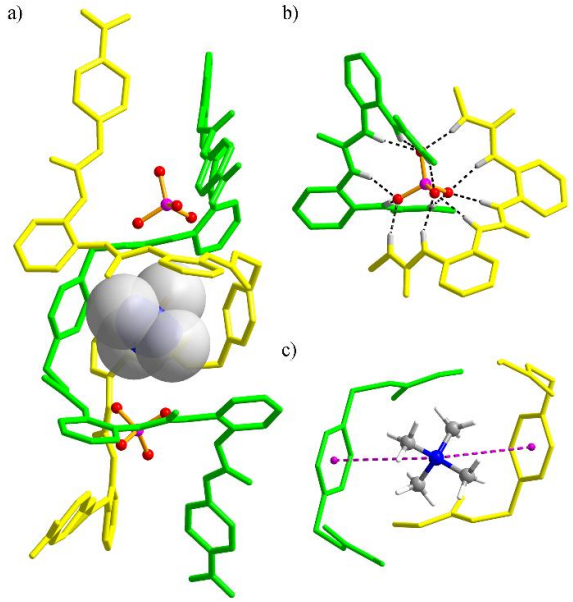


Fig. S16. a) Crystal structure of complex **1d** $(TBA)_5[(TMA)\subset(PO_4)_2\mathbf{L}_2]$; b) hydrogen bonds around the PO_4^{3-} ion (N ··O distances range from 2.708 to 2.894 Å, average 2.790 Å; N−H ··O angles range from 151 to 176°, average 161.6°); c) the TMA^+ was trapped in the half-cavity through cation-π interactions (N···centroid distances is the same 4.423 Å). All TBA^+ ions were omitted for clarity.

$(TEA)_{10}[(TEA)_2\subset(PO_4)_4\mathbf{L}_4]$ (2)

$(TEA)_3PO_4$ (16 µL, 0.625 mol/L; generated in situ from (TEA)OH and H_3PO_4) was added to a suspension of **L** (10 mg, 10 µmol) in acetone (1 mL). After stirring overnight at room temperature, a clear yellow solution was obtained. Slow vapor diffusion of diethyl ether into this solution provided yellow crystals of $(TEA)_{10}[(TEA)_2\subset(PO_4)_4\mathbf{L}_4]$ within two weeks (yield > 90 %). ^{1}H NMR (400 MHz, CD_3CN, ppm): δ 13.01 (s, 1H, NHf), 12.63 (s, 1H, NHe), 11.86 (2H, NHd/NHc/ NHb), 11.55 (s, 1H, NHe), 9.92 (t, 1H, NHa), 8.44 (s, *J* = 8 Hz, 1H, H10), 8.08 (t, *J* = 8 Hz, 1H, H6), 7.94 (m, 2H, H3/H7), 7.69 (d, *J* = 8 Hz, 2H, H12), 7.30 (d, *J* = 12.0 Hz, 2H, H11), 7.11 (t, *J* = 8 Hz, 1H, H9), 7.01 (t, *J* = 8 Hz, 1H, H8), 6.89 (m, 2H, H4/H5), 6.73 (s, 2H, H1), 4.31 (s, 1H, H2), 3.29 (s, 1H, H2).

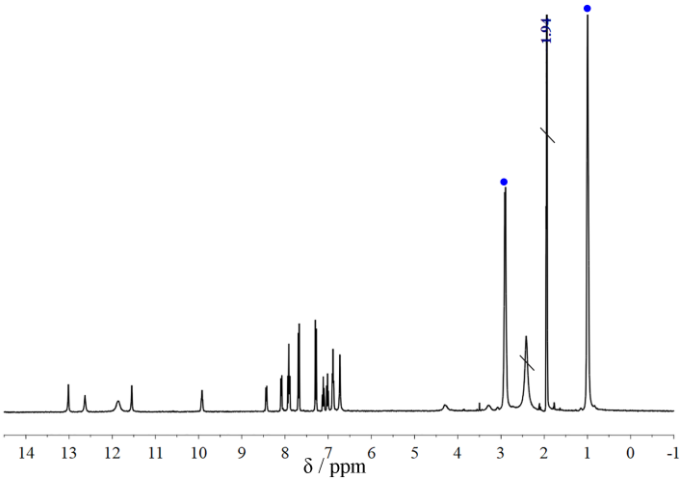


Fig. S17. ^{1}H NMR spectrum of $(TEA)_{10}[(TEA)_2\subset(PO_4)_4\mathbf{L}_4]$ (**2**) (400 MHz, CD_3CN, 296 K). The signals of the TEA^+ are marked with ● ,

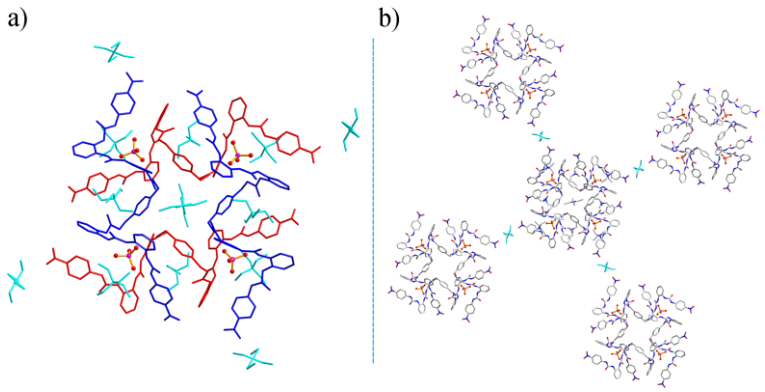


Fig. S18. a) Complete crystal structure of complex **2** $(TEA)_{10}[(TEA)_2\subset(PO_4)_4\mathbf{L}_4]$ with all counter cations shown. The third type of TEA^+ ions are encapsulated in a 'half cavity'; b) Type-II TEA^+ (cyan) cations that link to nearby grids by hydrogen bonding.

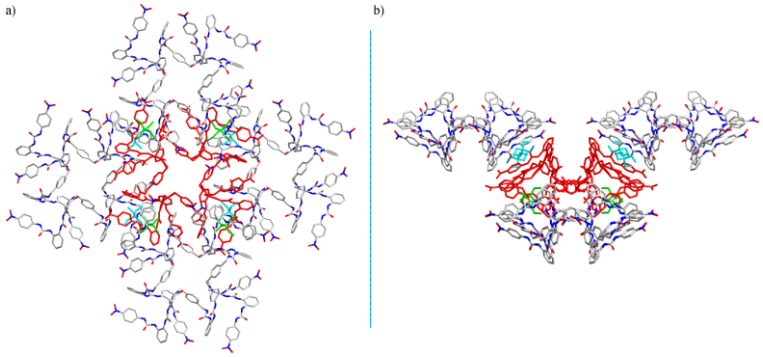


Fig. S19. a) Stacking diagram of the complex **2** showing the type-IV TEA^{+} cations (cyan and bright green) linked to nearby grids by electrostatic interactions; b) side view of the stacking grids.

S5. High-resolution ESI-MS spectra

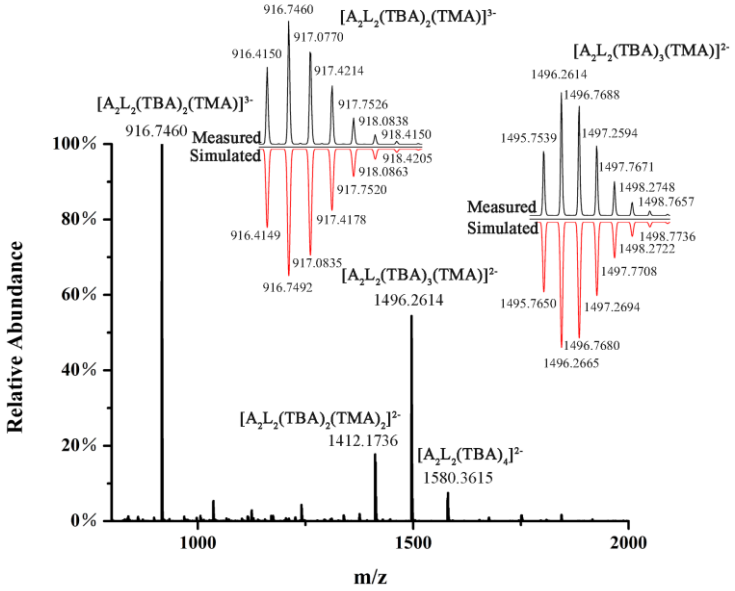


Fig. S20. High-resolution ESI-MS of $(TBA)_5[TMA\subset(PO_4)_2\mathbf{L}_2]$ (**1d**).

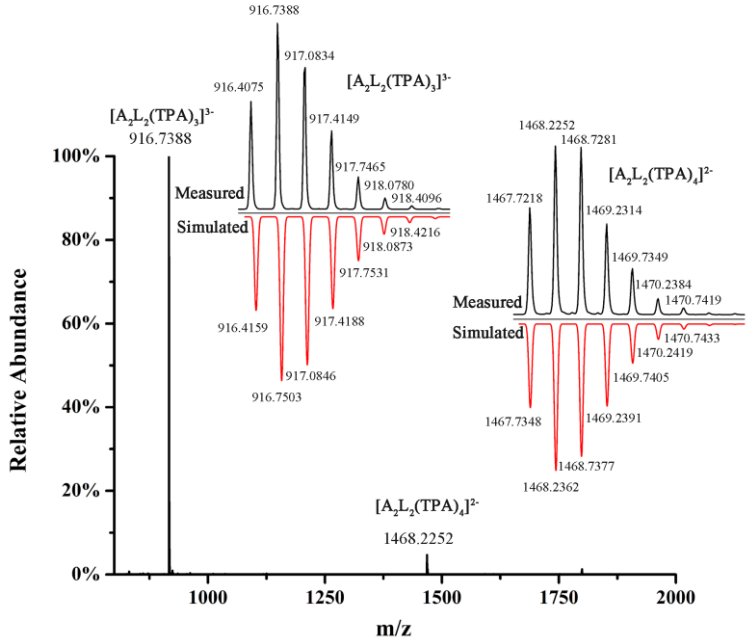


Fig. S21. High-resolution ESI-MS of $(TPA)_6[(PO_4)_2\mathbf{L}_2]$ (**1b**).

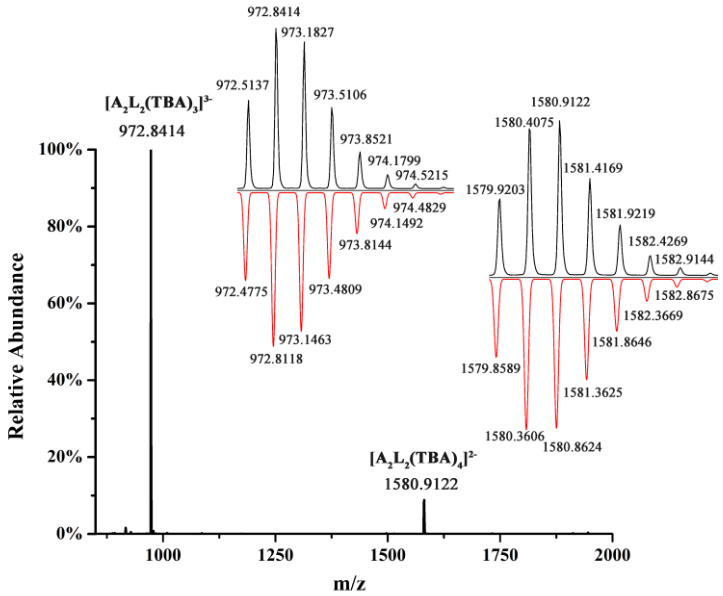


Fig. S22. High-resolution ESI-MS of $(TBA)_6[(PO_4)_2\mathbf{L}_2]$ (**1c**).

S6. ^{1}H NMR Titration experiments

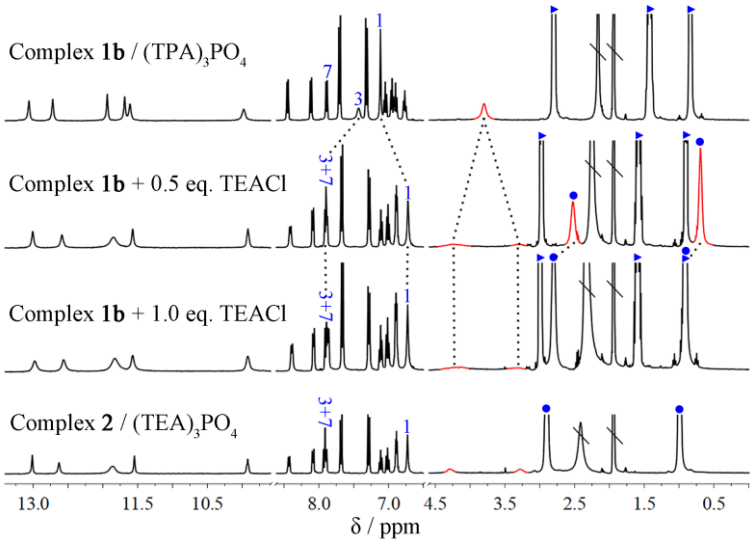


Fig. S23. ^{1}H NMR spectra (400 MHz, CD_3CN, 296 K) of complex **1b** alone and in the presence of TEACl (equivalents are labeled by numbers), and the spectrum of complex **2**.

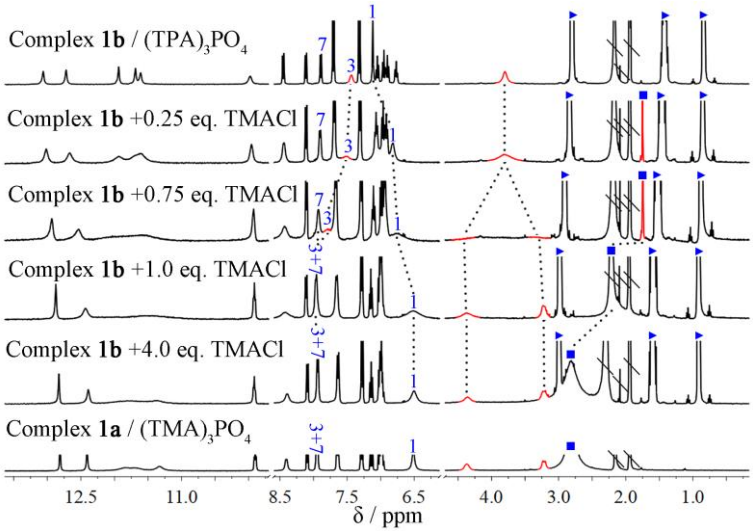


Fig. S24. ^{1}H NMR spectra (400 MHz, CD_3CN, 296 K) of complex **1b** alone and in the presence of TMACl (equivalents are labeled by numbers), and the spectrum of complex **1a**.

S7. 2D NMR and diffusion spectra spectroscopy

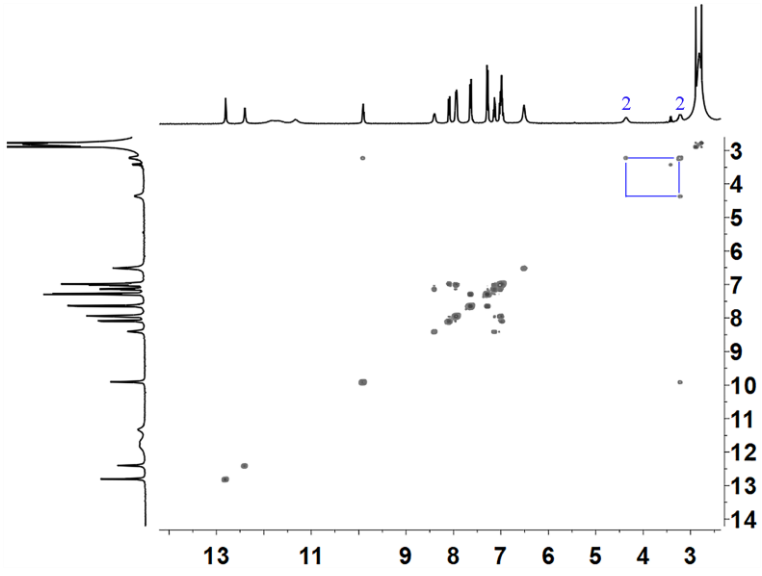


Fig. S25. Partial COSY spectrum of $(TMA)_5[(PO_4)_2\mathbf{L}_2\supset TMA]$ (**1a**) (400 MHz, CD_3CN, 269 K).

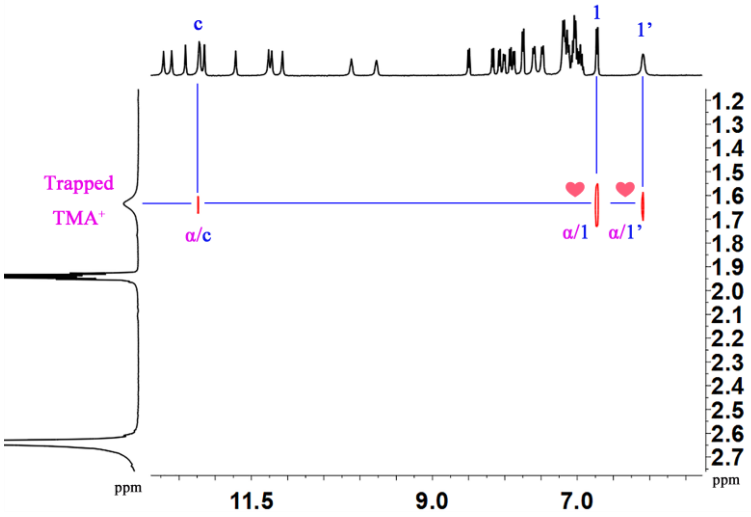


Fig. S26. Partial ^1H-^1H NOESY spectrum of $(TMA)_5[(PO_4)_2\mathbf{L}_2\supset TMA]$ (**1a**) (400 MHz, CD_3CN, 233 K).

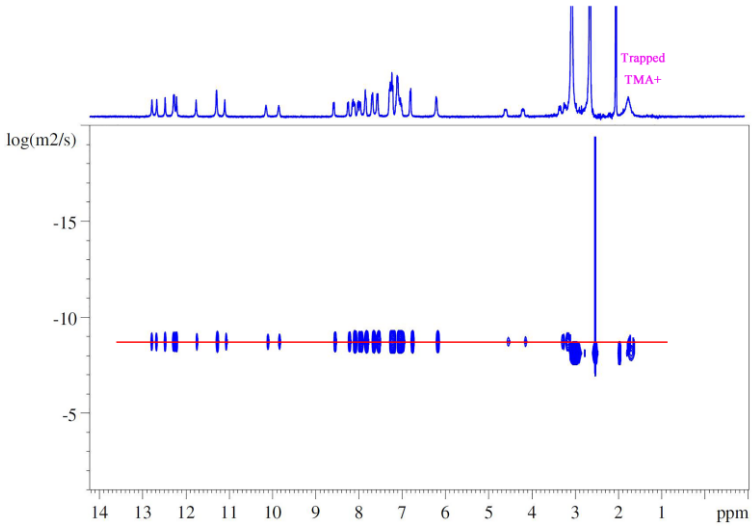


Fig. S27. Partial ^1H-^1H DOSY spectrum of $(TMA)_5[(PO_4)_2\mathbf{L}_2\supset TMA]$ (**1a**) (400 MHz, CD_3CN, 233 K).

S8. X-ray crystallography

Diffraction data were collected on a Bruker APEX-II CCD at 150 K (**1a**⊃TMA^+) Mo-Kα radiation (λ = 0.71073 Å), Rigaku XtaLAB Pro diffractometer at 100 K (**2**⊃TEA^+) with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and Bruker SMART APEX II diffractometer at 100 K (**1d**⊃ TMA^+) with graphite-monochromated Cu-K radiation (λ = 1.54178 Å). An empirical absorption correction using SADABS was applied for all data. All of the structures were solved by intrinsic phasing 1 using the APEX III program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the SHELXL program. Hydrogen atoms bonded to carbon and nitrogen were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The high *R*1 and *wR*2 values for the complexes may be due to the presence of a considerable amount of weak diffractions. The remaining solvents could not be successfully resolved despite numerous attempts at modeling and consequently the SQUEEZE function of PLATON was required to account for these highly disordered solvents. Limit order was used for part of the benzene ring and nitro during crystal structure refinement. CCDC 1892629-1892631.

Table S1. Crystal data and refinement details of the complexes **1a**, **1d** and **2**.

	1a ⊃ TMA^+	**1d** ⊃ TMA^+	**2** ⊃ TEA^+
Empirical formula	$C_{124.5}H_{160.75}N_{34.25}O_{26}P_2$	$C_{95}H_{147}N_{17}O_{15}P$	$C_{84}H_{126}N_{17}O_{17}P$
Formula weight	2615.05	1798.26	1676.98
Crystal System	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/c$	$C2$	$I4_1/a$
a (Å)	21.5380(8)	22.5953(16)	35.9168(11)
b (Å)	15.2994(7)	26.3348(18)	35.9168(11)
c (Å)	51.669(2)	19.0456(12)	32.8056(14)
α (deg)	90	90	90
β (deg)	94.6020(10)	103.180(4)	90
γ (deg)	90	90	90
V (Å^3)	16970.9(12)	11034.4(13)	42320(3)
Z	4	4	16
$D_{calc,}$ g/cm^3	1.023	1.082	1.053
No. of unique data	30060	14700	18551
T (K)	99.99	100(2)	100(2)
Total no. of data	287127	25064	68954
Crystal size (mm)	0.76×0.48×0.26	1.8×1.2×0.8	0.8×0.6×0.4
θ range	1.548-25.068	2.38-66.95	1.947-24.998
Completeness to θ	99.7 %	97.0 %	99.6 %
Goodness-of-fit on F^2	1.061	1.174	1.034
*R*1	0.0916	0.1031	0.0894
*wR*2	0.2709	0.3010	0.2473

Table S2. Hydrogen bonds around the PO_4^{3-} ion in **1a**

PO_4	D–H ··A	d(D–H)	d(H ··A)	d(D–A)	∠(DHA)
P1	N(2)–H(2A) ··O(21)	0.88	1.96	2.826(10)	166
	N(3)–H(3A) ··O(24)	0.88	1.88	2.750(9)	169
	N(4)–H(4) ··O(24)	0.88	1.92	2.772(10)	161
	N(5)–H(5A) ··O(23)	0.88	1.92	2.794(11)	175
	N(6)–H(6A) ··O(23)	0.88	2.04	2.854(10)	153
	N(7)–H(7) ··O(22)	0.88	1.99	2.793(10)	150
	N(16)–H(16A) ··O(24)	0.88	1.97	2.815(9)	161
	N(17)–H(17A) ··O(22)	0.88	1.88	2.732(9)	164
	N(18)–H(18A) ··O(22)	0.88	1.85	2.710(19)	165
	N(19)–H(19A) ··O(21)	0.88	1.95	2.814(9)	167
	N(20)–H(20) ··O(21)	0.88	1.97	2.782(9)	154
	N(21)–H(21) ··O(23)	0.88	2.13	2.967(9)	159
P2	N(8)–H(8) ··O(25)	0.88	2.03	2.833(9)	152
	N(9)–H(9A) ··O(27)	0.88	1.89	2.745(9)	163
	N(10)–H(10A) ··O(27)	0.88	1.95	2.814(10)	165
	N(11)–H(11A) ··O(26)	0.88	1.86	2.698(10)	158
	N(12)–H(12A) ··O(26)	0.88	1.85	2.713(10)	166
	N(13)–H(13) ··O(28)	0.88	1.98	2.808(10)	156
	N(22)–H(22) ··O(26)	0.88	1.96	2.798(10)	160
	N(23)–H(23) ··O(25)	0.88	2.06	2.865(9)	152
	N(24)–H(24A) ··O(25)	0.88	1.91	2.785(9)	176
	N(25)–H(25A) ··O(28)	0.88	1.99	2.826(10)	159
	N(26)–H(26) ··O(28)	0.88	1.92	2.780(9)	165
	N(27)–H(27A) ··O(27)	0.88	1.93	2.785(10)	163

Table S3. Hydrogen bonds around the PO_4^{3-} ion in **1d**

D–H ··A	d(D–H)	d(H ··A)	d(D–A)	∠(DHA)
N(13)–H(13) ··O(11)	0.88	1.94	2.786(10)	162
N(12)–H(12A) ··O(14)	0.88	1.92	2.787(10)	167
N(11)–H(11A) ··O(14)	0.88	1.93	2.787(11)	163
N(10)–H(10A) ··O(12)	0.88	1.91	2.785(10)	177
N(9)–H(9A) ··O(12)	0.88	2.04	2.865(10)	157
N(8)–H(8) ··O(13)	0.88	1.96	2.771(12)	153
N(7)–H(7) ··O(12)	0.88	2.08	2.903(9)	155
N(6)–H(6A) ··O(11)	0.88	1.93	2.751(11)	155
N(5)–H(5A) ··O(11)	0.88	1.95	2.821(10)	169
N(4)–H(4) ··O(13)	0.88	1.85	2.702(11)	161
N(3)–H(3A) ··O(13)	0.88	1.86	2.719(8)	166
N(2)–H(2A) ··O(14)	0.88	1.97	2.831(8)	165

Table S4. Hydrogen bonds around the PO_4^{3-} ion in **2**

D–H ··A	d(D–H)	d(H ··A)	d(D–A)	∠(DHA)
N(13)–H(13) ··O(12)	0.88	1.96	2.752(13)	149
N(12)–H(12A) ··O(14)	0.88	1.88	2.721(14)	160
N(11)–H(11A) ··O(14)	0.88	1.96	2.827(13)	167
N(10)–H(10A) ··O(11)	0.88	1.81	2.674(14)	166
N(9)–H(9A) ··O(11)	0.88	1.93	2.790(13)	164
N(8)–H(8) ··O(13)	0.88	2.09	2.971(13)	176
N(7)–H(7) ··O(11)	0.88	1.97	2.821(13)	164
N(6)–H(6A) ··O(12)	0.88	2.07	2.905(13)	157
N(5)–H(5A) ··O(12)	0.88	1.84	2.714(13)	171
N(4)–H(4) ··O(13)	0.88	1.98	2.817(13)	159
N(3)–H(3A) ··O(13)	0.88	1.88	2.749(13)	171
N(2)–H(2A) ··O(14)	0.88	1.96	2.805(13)	160

S9. Density Functional Theory (DFT) computations

The geometry optimizations for the racemic double helicate without any guests and mesomeric double helicate were performed by the Gaussian16 package.[5] The Density Functional Theory (DFT) method with B97D functional[6] has been utilized. The correlation-consistent polarized (cc-pVDZ) basis sets[7] were employed for hydrogen and carbon elements, while aug-cc-pVDZ for the rest.[8] Polarizable Continuum Model (PCM)[9] was used to account the solvation effect in acetonitrile.

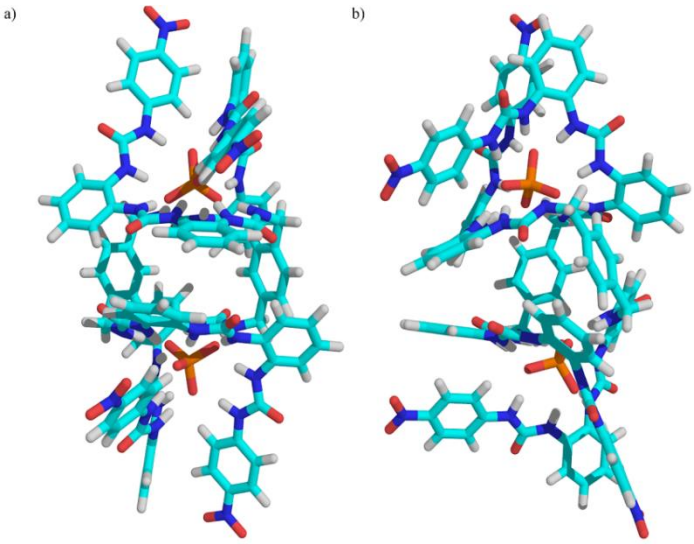


Fig. S28. DFT optimized structure of racemic double helicate without any guests. a) front view; b) side view.

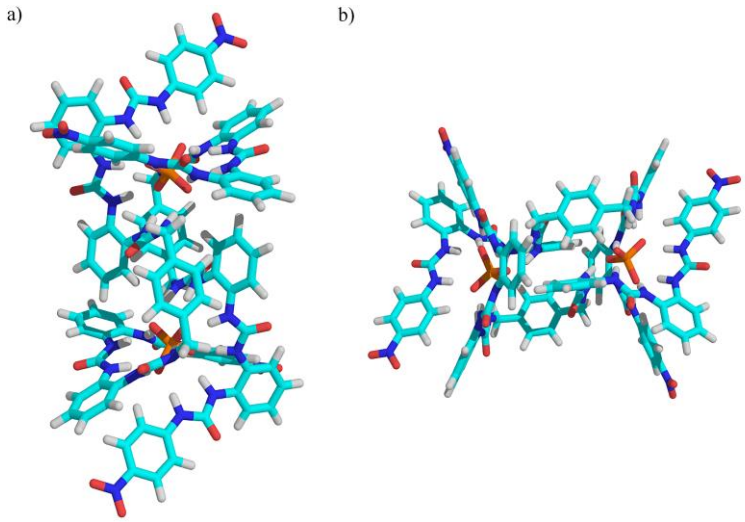


Fig. S29. DFT optimized structure of mesomeric double helicate. a) front view; b) pours view.

Cartesian coordinates (Å) for the optimized geometries of racemic double helicate.

C	-10.928293	-2.060959	2.440978
C	-10.551757	-1.409824	3.636869
H	-11.294810	-1.262707	4.425341
C	-9.246432	-0.955654	3.812416
H	-8.960218	-0.450832	4.734336
C	-8.276217	-1.143936	2.782786
C	-8.679881	-1.815338	1.586838
H	-7.941030	-1.974941	0.799757
C	-9.981496	-2.263376	1.409797
H	-10.269830	-2.759954	0.479705
C	-6.299140	-0.098383	3.917416
C	-4.025972	0.662742	4.557641
C	-4.064579	0.346916	5.932437
H	-4.844469	-0.331811	6.286811
C	-3.127431	0.884653	6.827014
H	-3.180339	0.624637	7.891056
C	-2.114422	1.731116	6.343942
H	-1.359899	2.141421	7.026063
C	-2.041679	2.032092	4.976616
H	-1.236018	2.656669	4.587337
C	-2.991771	1.521011	4.062770
C	-2.462303	2.963167	2.086861
C	-2.265805	3.912077	-0.248723
C	-1.918655	5.229104	0.129230
H	-1.911154	5.471140	1.191234
C	-1.568858	6.200141	-0.820958
H	-1.290521	7.205227	-0.483612
C	-1.579953	5.875661	-2.184536
H	-1.319980	6.624012	-2.943313
C	-1.941630	4.581542	-2.587182
H	-1.968311	4.320476	-3.645226
C	-2.278476	3.578540	-1.650219
C	-2.494360	1.682362	-3.300105
C	-2.752520	-0.469971	-4.474417
H	-2.729075	0.107477	-5.413333
H	-3.567999	-1.213717	-4.535620
C	-1.423148	-1.179371	-4.258177
C	-1.335133	-2.239871	-3.330331
H	-2.234632	-2.557848	-2.795076
C	-0.112616	-2.874349	-3.077362
H	-0.068115	-3.695633	-2.352625
C	1.058416	-2.466612	-3.753645
C	0.975154	-1.404517	-4.672996
H	1.878681	-1.061089	-5.191428
C	-0.253657	-0.765725	-4.920477
H	-0.298567	0.071420	-5.626292
C	2.381979	-3.173365	-3.491006
H	3.176637	-2.694592	-4.093405
H	2.316102	-4.234517	-3.791097
C	2.516815	-4.150972	-1.210308
C	2.762489	-4.694265	1.205905
C	1.760936	-5.672453	1.373835
H	0.953984	-5.713304	0.638722
C	1.796012	-6.566867	2.454587
H	1.007064	-7.321236	2.561051
C	2.827135	-6.470551	3.405710
H	2.854073	-7.148786	4.267500
C	3.819818	-5.487100	3.268526
H	4.616153	-5.390200	4.009875
C	3.817208	-4.602869	2.166958
C	6.156833	-3.732791	2.264929
C	8.246422	-2.389499	1.887278
C	9.208023	-3.407326	2.092659
H	8.865994	-4.442667	2.135760
C	10.568452	-3.098080	2.242495
H	11.289496	-3.907583	2.408907
C	11.003916	-1.764683	2.150540
H	12.067611	-1.515790	2.243649
C	10.068999	-0.747906	1.908623
H	10.392296	0.291038	1.806437
C	8.692951	-1.033723	1.793307
C	7.780521	1.239057	2.151328
C	6.546056	3.408718	1.996808
C	5.495178	4.070516	1.293337
H	4.914292	3.503368	0.564039
C	5.199452	5.408050	1.520118
H	4.372672	5.886558	0.988839
C	5.966114	6.133537	2.460677
C	7.010801	5.501778	3.170754
H	7.591149	6.075626	3.898295
C	7.302730	4.158114	2.946218
H	8.107848	3.672343	3.495954
N	-12.290217	-2.526877	2.272583
N	-6.956890	-0.728543	2.841927
H	-6.434397	-0.846235	1.935893
N	-4.960482	0.092134	3.654548
H	-4.567357	-0.216829	2.732087
N	-2.926490	1.793385	2.680357

H	-3.188002	0.998210	2.059493
N	-2.632083	2.927869	0.701837
H	-3.249507	2.167077	0.364568
N	-2.659340	2.281895	-2.052601
H	-3.292897	1.760461	-1.416798
N	-3.095799	0.439016	-3.372627
H	-3.332965	-0.052171	-2.493686
N	2.774789	-3.129094	-2.086155
H	3.025911	-2.188642	-1.728263
N	2.711545	-3.786089	0.123264
H	3.017581	-2.820163	0.317889
N	4.802587	-3.603329	1.999777
H	4.480509	-2.691719	1.601463
N	6.873681	-2.665024	1.725912
H	6.367671	-2.050346	1.059335
N	7.755322	0.001520	1.538803
H	7.007651	-0.210789	0.840868
N	6.744692	2.070643	1.694714
H	5.983348	1.642020	1.104676
N	5.684918	7.537204	2.694657
O	-13.122697	-2.305510	3.179978
O	-12.592856	-3.137465	1.224646
O	-6.869651	0.241557	4.967486
O	-1.974768	3.915505	2.720220
O	-1.900704	2.198423	-4.268969
O	2.175691	-5.301131	-1.563354
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C	9.981177	-2.264326	-1.408552
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C	-10.068851	-0.748624	-1.908094	H	-4.480485	-2.692697	-1.600333
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H	-7.589826	6.073681	-3.901119	O	1.975049	3.914481	-2.721746
C	-7.301956	4.156693	-2.947808	O	1.900329	2.200929	4.268228
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N	6.956477	-0.730430	-2.841465	O	-8.617924	1.579760	-3.002314
H	6.434098	-0.847460	-1.935278	O	-6.303138	8.132957	-3.605895
N	4.960095	0.090137	-3.654253	O	-4.833721	8.107234	-1.982971
H	4.567101	-0.218213	-2.731562	O	4.529092	1.131700	0.35671
N	2.926509	1.792274	-2.680691				

Cartesian coordinates (Å) for the optimized geometries of mesocate.

C	-5.355340	-3.260380	2.273554	O	-0.300338	-3.140830	-0.692845
C	-8.279009	-0.950766	-2.855739	O	-2.952860	-2.599026	-5.395200
C	-5.172134	3.990698	-2.065342	O	-9.173077	-1.060325	-3.710667
C	-1.024808	-2.162079	-0.419096	O	-5.756714	-4.073564	3.122280
C	-6.041152	1.984556	2.980913	O	-6.469716	2.523214	4.017152
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N	-5.290496	-3.537948	0.895994	C	-4.189635	-1.689538	6.222009
N	-5.364179	0.769033	2.958177	C	-10.493018	1.084840	-2.301086
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O	-3.653749	0.524917	-1.693279	C	8.277453	0.956451	2.854080
O	-5.038590	-1.596091	-1.050071	O	9.171605	1.067520	3.708727
O	-5.133312	5.201120	-2.372399	O	6.471430	-2.524512	-4.015609
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C	-8.286759	5.627377	1.785808	O	5.134439	-5.200589	2.374290
C	-8.116756	6.097669	0.474931	O	0.300124	3.140087	0.692220
C	-7.304366	5.382804	-0.417407	O	2.949849	2.601295	5.393152
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C	-5.665720	-5.913581	-1.890439	C	4.851921	-0.493348	-5.367753
C	-0.463080	-0.984606	-4.946061	C	5.029630	0.035738	-4.067364
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C	-4.851968	0.490022	5.368030	C	8.290449	-5.626225	-1.782105

C	8.120206	-6.096114	-0.471114	H	-2.747220	0.996041	3.737387
C	7.306896	-5.381490	0.420580	H	-1.498445	0.976015	1.573830
C	6.623854	-4.208060	0.027589	H	7.184885	-5.726155	1.448539
C	0.450633	1.016201	2.501658	H	8.627472	-7.006801	-0.130004
C	-0.956003	1.001845	2.523499	H	8.930990	-6.163041	-2.492380
C	-1.654212	1.005850	3.739346	H	7.806482	-4.052588	-3.193775
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C	0.461513	0.984062	4.945191	H	4.321626	-0.121833	-7.430947
C	1.171182	1.026422	3.725803	H	3.849149	2.326765	-7.044913
C	5.619095	3.065870	4.185494	H	4.126797	3.280420	-4.753413
C	5.407032	4.157515	5.062570	H	1.958995	0.445272	1.163829
C	6.460105	5.011390	5.423801	H	2.457183	1.323142	-0.835677
C	7.745522	4.818878	4.889753	H	4.383917	-2.087739	2.384182
C	7.967428	3.756021	4.002302	H	5.793610	-2.454644	0.829523
C	6.933150	2.863233	3.656813	H	5.960427	-1.846030	-0.926424
C	9.259720	-0.965926	1.591831	H	4.906761	-0.496524	-2.060835
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C	11.423046	-2.050164	1.939870	H	5.091104	2.741919	-0.235510
C	11.152054	-2.937823	0.875215	H	3.041087	0.556168	2.896150
C	9.937083	-2.843554	0.158016	H	4.682609	1.824482	2.809573
C	9.016336	-1.866317	0.510964	H	6.458600	1.612958	2.024592
C	6.102255	7.079620	1.219861	H	7.375264	-0.185782	1.317125
C	6.261899	7.080466	-0.183424	H	-4.406148	-4.320103	-5.453959
C	5.997018	5.929624	-0.922428	H	-12.365413	2.145054	-2.485392
C	5.386696	4.770284	1.150799	H	-8.083334	1.775784	0.047533
C	5.658424	5.914909	1.887486	H	-9.717109	3.538450	0.662116
C	5.561748	4.738918	-0.267266	H	-10.702747	0.406272	-3.126824
C	4.783120	1.431387	-3.857242	H	-3.850239	-2.331329	7.043745
H	5.539591	5.910222	2.973695	H	-4.128466	-3.283738	4.751777
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H	6.127274	5.930282	-2.003888	H	-1.031244	-0.961438	-5.879709
H	6.600029	7.990282	-0.686738	H	-5.551330	-5.907196	-2.977117
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N	12.129152	-3.946137	0.512720	H	-8.573462	-5.489111	-5.152674
H	12.368446	-2.133320	2.482720	H	-6.268054	-5.839719	-6.112445
H	10.704199	-0.395776	3.123361	H	1.482716	-0.958153	-5.907621
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H	8.567891	5.496321	5.148268	H	1.497381	-0.977557	-1.574993
H	6.262390	5.845038	6.108502	H	-6.117923	-5.935005	2.002893
H	4.401845	4.323226	5.451222	H	-6.590068	-7.994808	0.685309
H	1.029567	0.961229	5.878918	H	-7.803367	4.052773	3.196592
H	-1.484383	0.957066	5.906488	H	-4.321575	0.117301	7.430971

H	-7.182536	5.727802	-1.445275	H	1.686273	-1.557385	4.520206
H	-8.623483	7.008880	0.134423	H	4.011374	-4.312003	4.348344
H	-8.926579	6.164378	2.496591	H	3.810912	-2.571785	4.728811
N	-6.397603	-8.279324	-1.982507	H	-2.519517	-2.929661	2.449571
H	-7.376181	0.188966	-1.317284	H	-1.990820	-4.129046	1.228885
H	-6.461061	-1.609835	-2.026316	C	-2.242870	3.381022	-3.487754
H	-4.684979	-1.822674	-2.811054	C	-1.790100	4.399347	-2.621878
H	-3.042168	-0.556121	-2.896329	C	-0.492334	4.352937	-2.090451
H	-4.384440	2.087914	-2.383647	C	0.381327	3.291996	-2.404169
H	-5.793168	2.455059	-0.828129	C	-0.052248	2.306205	-3.311408
H	-5.960022	1.845739	0.927519	C	-1.351153	2.351953	-3.843992
H	-4.907566	0.494633	2.061076	C	-3.694055	3.338286	-3.939589
H	-5.094215	-2.742416	0.234151	C	1.734053	3.165676	-1.713733
H	-4.580718	-1.376679	1.769028	H	-2.477122	5.206574	-2.340515
H	-1.959886	-0.446334	-1.164254	H	-0.157403	5.128223	-1.390471
H	-2.457901	-1.324426	0.834965	H	0.611292	1.474173	-3.571756
P	4.626293	0.106478	0.613623	H	-1.687444	1.557363	-4.520202
P	-4.627462	-0.106839	-0.613681	H	-4.011985	4.312487	-4.347485
C	2.242386	-3.380911	3.487900	H	-3.811960	2.572261	-4.728204
C	1.790104	-4.399294	2.621838	H	2.519104	2.928412	-2.450304
C	0.492429	-4.353231	2.090151	H	1.990987	4.127930	-1.229512
C	-0.381611	-3.292565	2.403755	O	-6.805788	-9.294894	-1.376893
C	0.051527	-2.306640	3.311057	O	-6.235809	-8.261730	-3.221587
C	1.350331	-2.352055	3.843910	O	13.177933	-4.042438	1.187511
C	3.693415	-3.337906	3.940225	O	11.895026	-4.687803	-0.465165
C	-1.734277	-3.166697	1.713126	O	6.229935	8.262969	3.218239
H	2.477400	-5.206329	2.340586	O	6.810320	9.292336	1.374682
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H	-0.612272	-1.474759	3.571247	O	-11.892274	4.693676	0.467641

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