

**Self-assembled Co(II) and Co(III) [M₂L₃] helicates and [M₄L₆]
tetrahedra from an unsymmetrical quaterpyridine ligand**

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ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental

General

All reagents were purchased from commercial sources used without further purification. Solvents were dried using Innovative Technologies Pure Solv solvent purification system. NMR spectra were recorded on Bruker ASCEND 500MHz spectrometer. Mass spectrometry was performed on Bruker MicroTOFQ, Bruker HCT and Thermo LCQ Fleet mass spectrometers. **L** was prepared as previously reported.¹

Synthesis of [Co₂L₃](ClO₄)₄ and [Co₄L₆](ClO₄)₈

The helical and tetrahedral self-assemblies of cobalt (II) were obtained by reacting cobalt(II) perchlorate (13.7 mg, 0.0373 mmol) with ligand **L** (23 mg, 0.0556 mmol) in acetonitrile (5 mL) under microwave conditions (130 °C for 30 minutes). The resulting orange solution contains both assemblies and the overall yield of both products was quantitative by NMR. Long range ¹H NMR (500MHz, CD₃CN, -60 to 230 ppm) of [Co₂(**L**)₃](ClO₄)₄ and [Co₄(**L**)₆](ClO₄)₈: 118-134 (broad singlets for protons a, a', m and g), 80-86 (broad and poorly resolved region), 75.7-77.5 (four peaks), 72.60-73.3 (four peaks), 48-48.5 and 49-49.5 (four peaks), 8.95-9.4 (four peaks), 3.8-4.8 (four peaks for proton p of C₃ and C_l helical species), 1-3.6 (bunch of singlets), 75-75.7, 71-72.6, 49-48.5, 48-47.6, 43.45-47, 15.20-11.2 (broader peaks). Positive ion ESI-HRMS: m/z (M= [Co₂(**L**)₃](ClO₄)₄ in acetonitrile); calculated (M-2ClO₄)²⁺ m/z = 774.11, found m/z = 774.11; calculated (M-3ClO₄)³⁺ m/z = 482.42, found m/z = 482.42. Positive ion ESI-HRMS: m/z (M= [Co₄(**L**)₆](ClO₄)₈ in acetonitrile); calculated (M-2ClO₄)²⁺ m/z = 1647.17, found m/z = 1647.17; calculated (M-3ClO₄)³⁺ m/z = 1065.13, found m/z = 1065.13; calculated (M-4ClO₄)⁴⁺ m/z = 773.86, found m/z = 773.86; calculated (M-5ClO₄)⁵⁺ m/z = 599.29, found m/z = 599.29, calculated (M-6ClO₄)⁶⁺ m/z = 482.75, found m/z = 482.75; calculated (M-7ClO₄)⁷⁺ m/z = 399.65, found m/z = 399.65; calculated (M-8ClO₄)⁸⁺ m/z = 337.20, found m/z = 337.20.

Diffraction quality crystals were grown by slow diffusion of diisopropyl ether into solution of the complex.

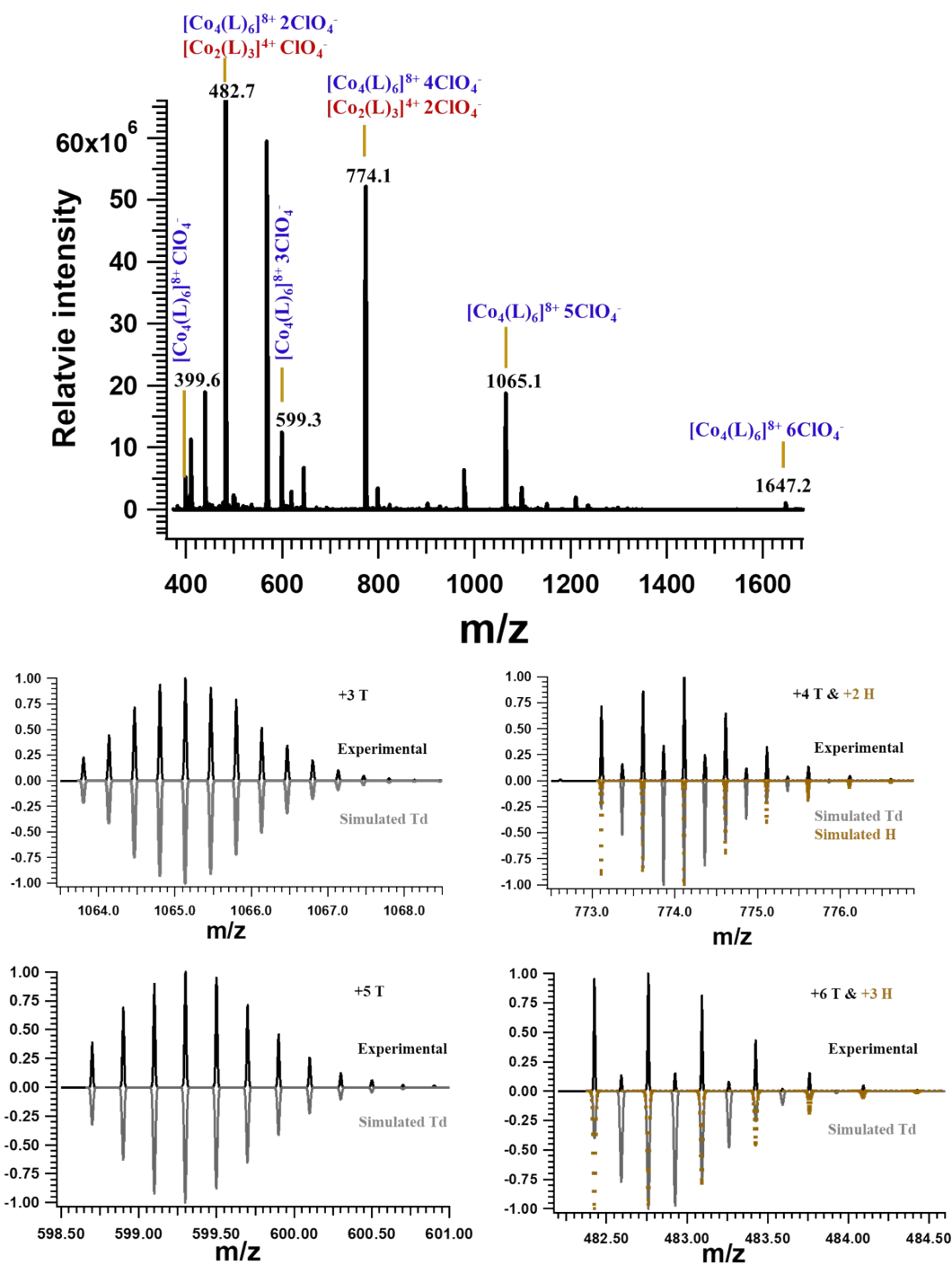


Figure S1: ESI-MS of tetrahedral +3, +4, +5 and +6 assembly ions of formula $[\text{Co}_4\text{L}_6](\text{ClO}_4)_8$ that correspond to successive losses of ClO_4^- ions from an $[\text{Co}_4\text{L}_6]^{8+}$ and overlapping peaks for +2 and +3 ions that corresponds to successive losses of ClO_4^- ions from an $[\text{Co}_4\text{L}_6](\text{ClO}_4)_4$ helicate formula.

Synthesis of $[\text{Co}_2\text{L}_3](\text{PF}_6)_6$ and $[\text{Co}_4\text{L}_6](\text{PF}_6)_{12}$

The Co(II) assemblies were then oxidized by adding a solution of ammonium cerium(IV) nitrate (22mg, 0.04 mmol, 8mL acetonitrile). The resulting mixture was stirred overnight and the precipitates were collected and washed with acetonitrile. The precipitates were then re-dissolved in the 2:1 mixture of water and acetonitrile (6 ml). The addition of saturated solution of KPF_6 to the above assembly solution resulted the formation of precipitates, which were collected and washed with water. The orange product was then dried under high vac.

^1H NMR (500MHz, CD_3CN , δ/ppm) of $[\text{Co}_2(\text{L})_3](\text{PF}_6)_4$ and $[\text{Co}_4(\text{L})_6](\text{PF}_6)_{12}$: 3.4-3.5 (four peaks for proton **p** of C_3 and C_I helical assembly), 3.0-3.36 (32 peaks for proton **p** of $4C_I$ and $4C_3$ tetrahedral assembly). ^1H DOSY NMR: 12.4 Å and 15.9 Å hydrodynamic radius for helical and tetrahedral assemblies respectively. The ^{19}F NMR (500MHz, CD_3CN , δ/ppm): -72.5. Positive ion ESI-HRMS: m/z ($M = [\text{Co}_2(\text{L})_3](\text{PF}_6)_6$ in acetonitrile); calculated $(M-\text{PF}_6)^{1+}$ $m/z = 2073.14$, found $m/z = 2073.14$; calculated $(M-2\text{PF}_6)^{2+}$ $m/z = 964.09$, found $m/z = 964.09$; calculated $(M-3\text{PF}_6)^{3+}$ $m/z = 594.40$, found $m/z = 594.40$.

Positive ion ESI-HRMS: m/z ($M = [\text{Co}_4(\text{S})_6](\text{PF}_6)_{12}$ in acetonitrile); calculated $(M-2\text{PF}_6)^{2+}$ $m/z = 2073.14$, found $m/z = 2073.14$; calculated $(M-3\text{PF}_6)^{3+}$ $m/z = 1334.10$, found $m/z = 1334.10$; calculated $(M-4\text{PF}_6)^{4+}$ $m/z = 964.34$, found $m/z = 964.34$; calculated $(M-5\text{PF}_6)^{5+}$ $m/z = 742.48$, found $m/z = 742.48$; calculated $(M-6\text{PF}_6)^{6+}$ $m/z = 594.57$, found $m/z = 594.57$; calculated $(M-7\text{PF}_6)^{7+}$ $m/z = 488.92$, found $m/z = 488.92$.

Diffraction quality crystals were grown by slow diffusion of diisopropyl ether into solution of the complex.

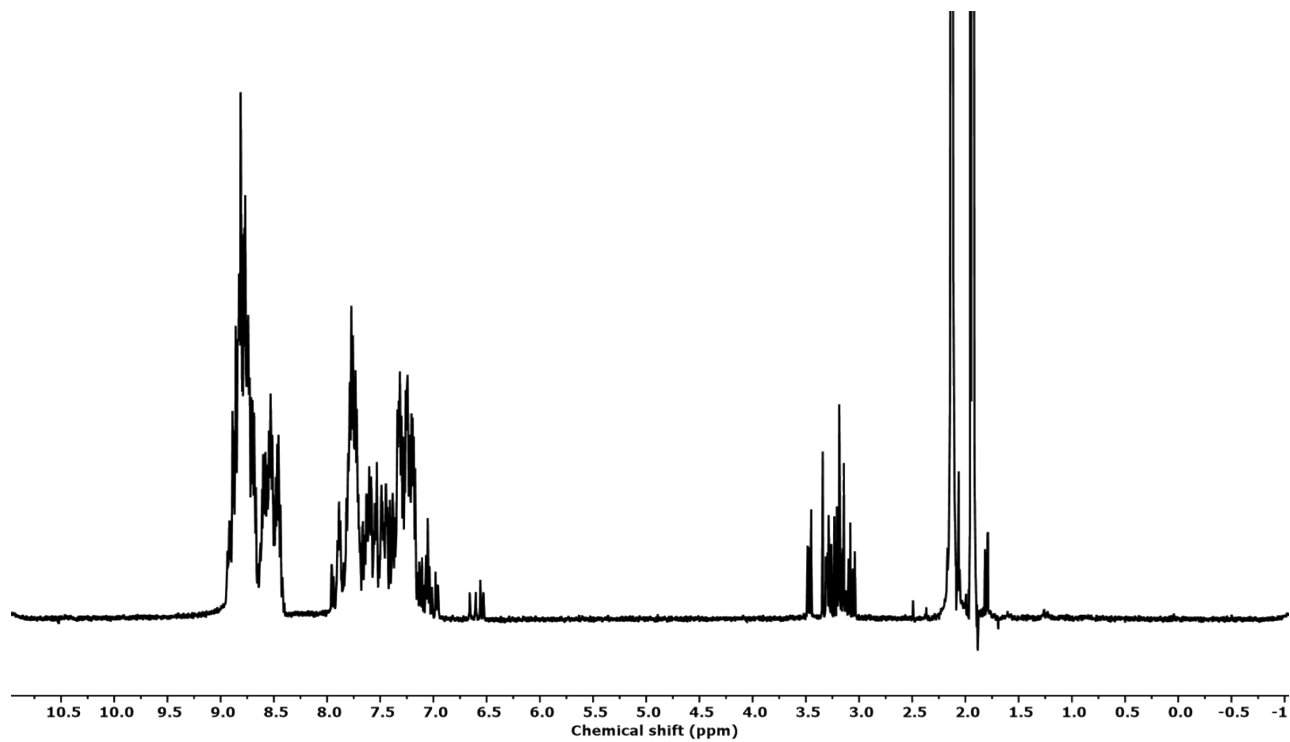


Figure S2: ^1H NMR spectrum of the $[\text{Co}_2\text{L}_3]^{6+}$ helicate and $[\text{Co}_4\text{L}_6]^{12+}$ in CD_3CN , 500 MHz, 298 K

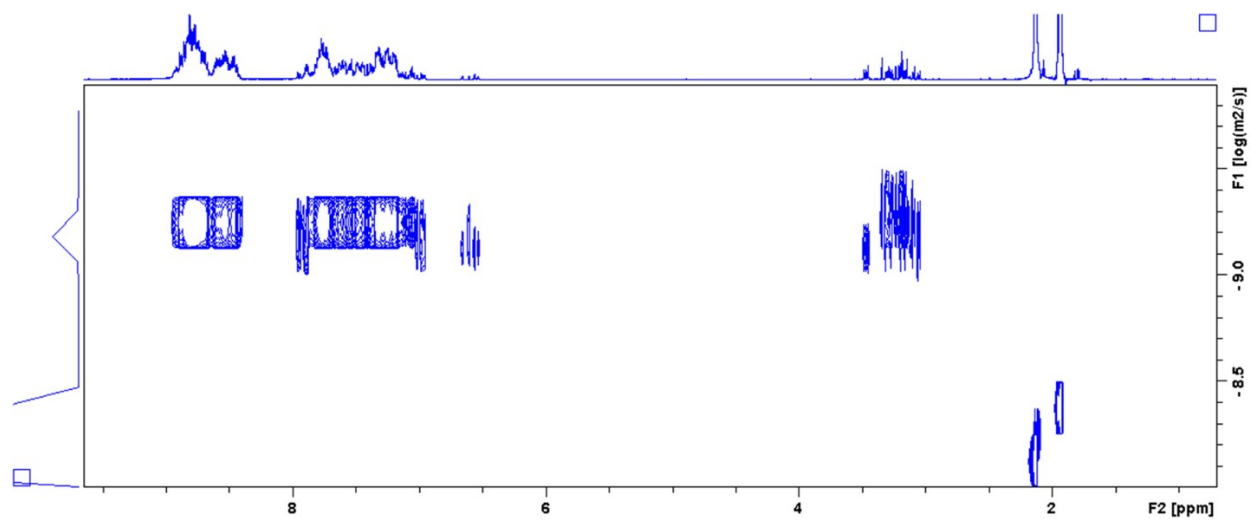


Figure S3: 2D DOSY NMR of helical $[\text{Co}_2\text{L}_3](\text{PF}_6)_6$ and tetrahedral $[\text{Co}_4\text{L}_6](\text{PF}_6)_{12}$ assemblies in CD_3CN , 500 MHz, 298 K

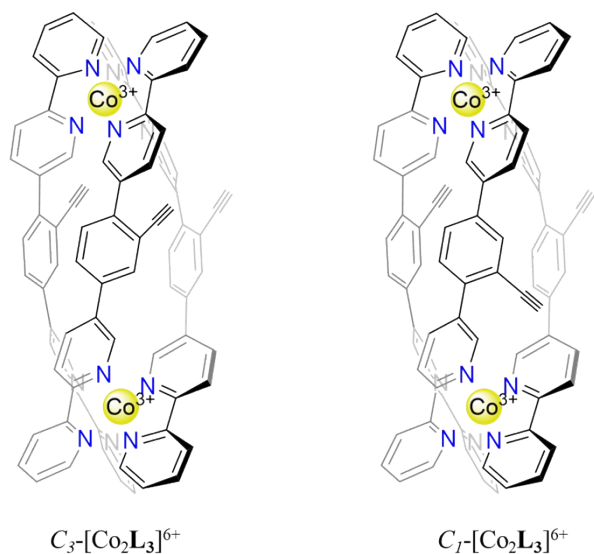


Figure S4: The two observed diastereomers of the [Co₂L₃]⁶⁺ helicate.

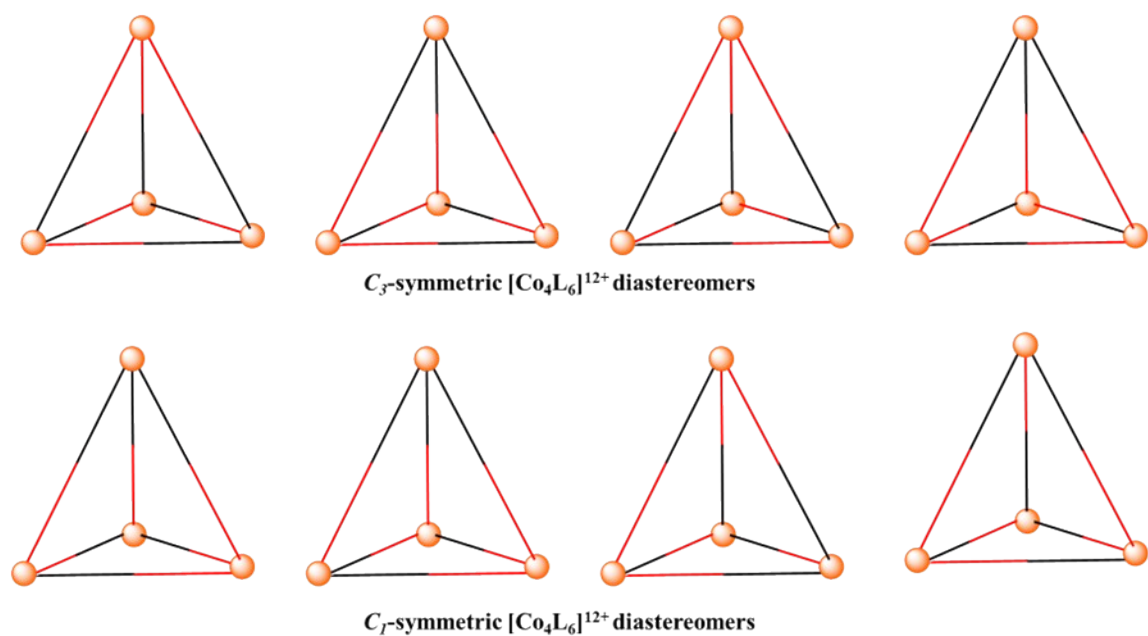


Figure S5. Schematic representations of the observed diastereomers of the [Co₄L₆]¹²⁺ tetrahedral cage. Different colored lines represent ligands arranged such that the acetylenes point towards different metals.

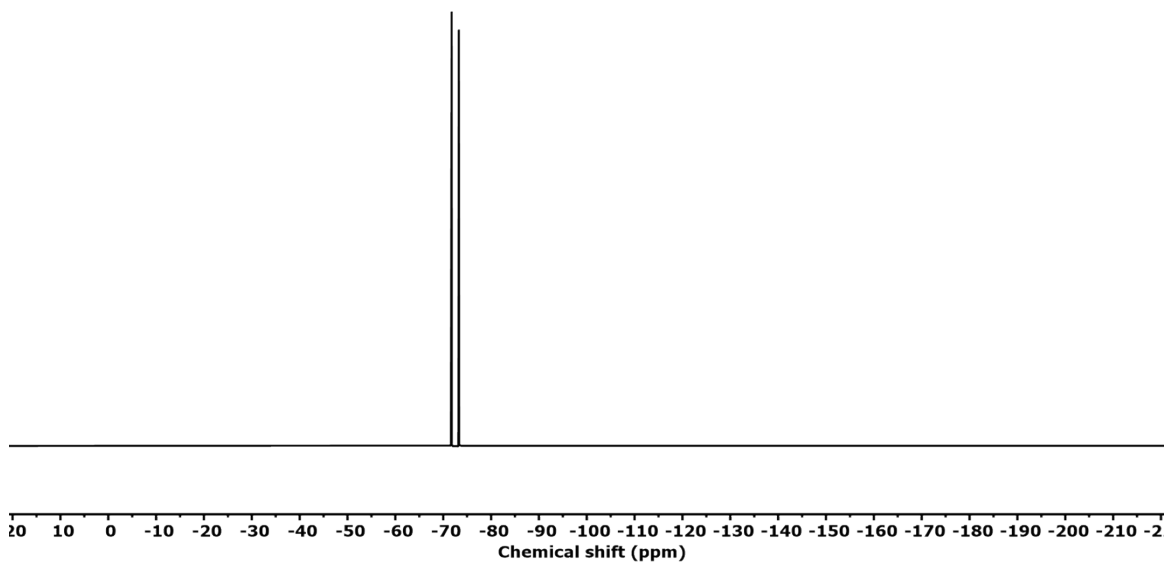


Figure S6: ^{19}F NMR spectrum (CD_3CN , 470 MHz, 298 K) for $[\text{Co}_2\text{L}_3](\text{PF}_6)_6$ and $[\text{Co}_4\text{L}_6](\text{PF}_6)_{12}$.

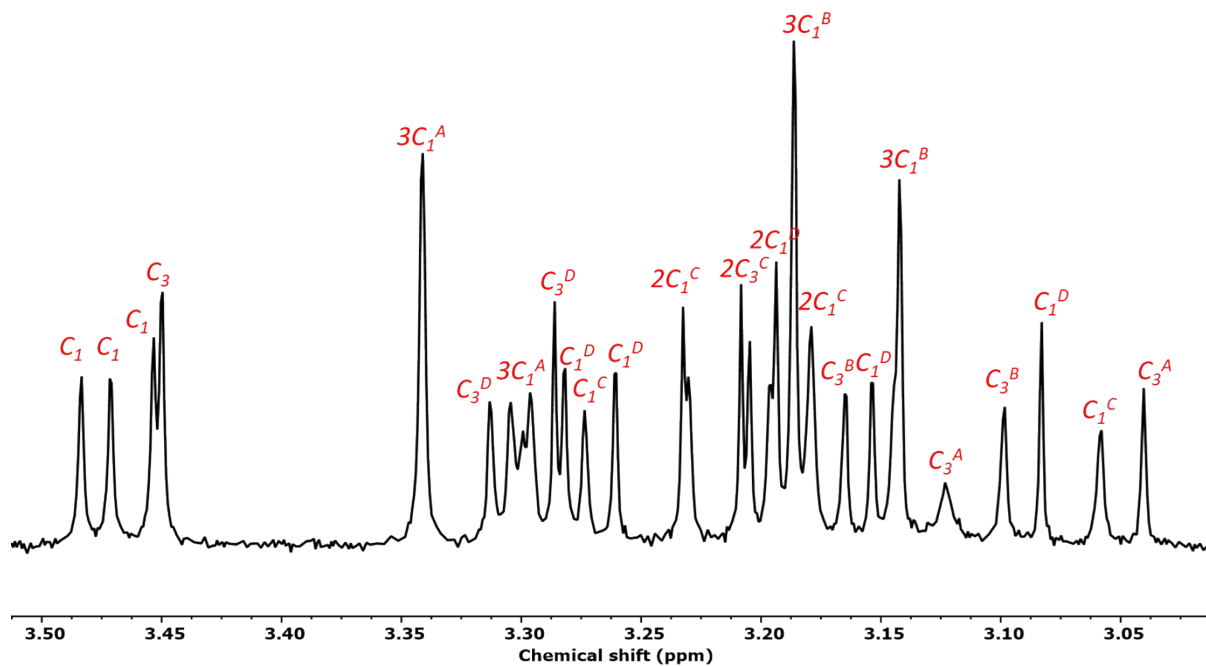


Figure S7. Expanded view of ^1H NMR spectrum (CD_3CN , 500 MHz, 298K) of two protons (**q** and **r**) in the aliphatic region of helical $[\text{Co}_2\text{L}_3](\text{PF}_6)_6$ and tetrahedral $[\text{Co}_4\text{L}_6](\text{PF}_6)_{12}$.

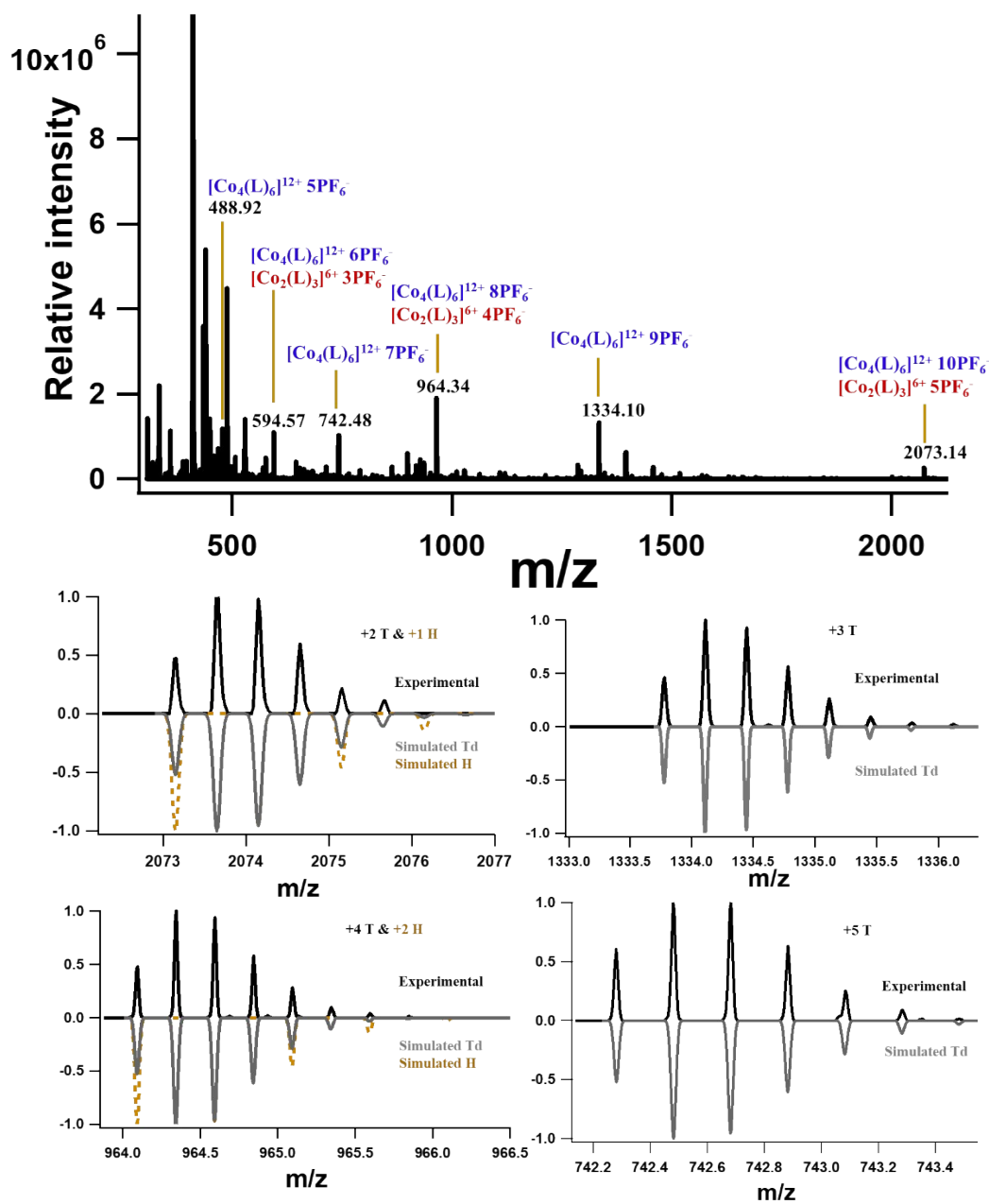


Figure S8: ESI-MS of tetrahedral $[\text{Co}_4\text{L}_6](\text{PF}_6)_{12}$ assembly showed +2, +3, +4, +5, +6 and +7 ions that correspond to successive losses of PF_6^- ions from an $[\text{Co}_4\text{L}_6]^{12+}$ and overlapping peaks for +1, +2 and +3 ions that corresponds to successive losses of PF_6^- ions from an $[\text{Co}_4\text{L}_6](\text{PF}_6)_6$ helicate formula

Crystallography

Data were collected using an Oxford Rigaku Synergy-S employing confocal mirror monochromated Mo-K α radiation generated from a microfocus source (0.71073 Å) with ω and ψ scans at 100(2) K.² Data integration and reduction were undertaken with CrysAlisPro². Subsequent computations were carried out using Olex2.³ Structures were solved with ShelXT⁴ and refined and extended with ShelXL.⁵ Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Generally, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. In both structures there are regions of significantly disordered anions and solvents and so the SQUEEZE⁶ function of PLATON^{7, 8} was employed when necessary. Both structures also showed some disorder in the ligands and so a variety of restraints and constraints (including rigid bodies) were required to facilitate realistic modelling. The disorder also resulted in lower than ideal diffraction patterns, particularly in [Co₄L₆](ClO₄)₈·6MeCN in which no diffraction was observed at better than 1.0 Å resolution. Nevertheless, the connectivity is unambiguous in both cases. Crystallographic data for each refinement are given below.

[Co₄L₆](ClO₄)₈·6MeCN

Crystal Data for C₁₆₈H₁₀₈Cl₂Co₄N₂₄O₈ ($M=2897.40$ g/mol): triclinic, space group P-1 (no. 2), $a = 17.0436(6)$ Å, $b = 22.9283(9)$ Å, $c = 25.8861(10)$ Å, $\alpha = 83.289(3)^\circ$, $\beta = 84.512(3)^\circ$, $\gamma = 73.500(3)^\circ$, $V = 9612.0(7)$ Å³, $Z = 2$, $T = 100(2)$ K, $\mu(\text{Mo K}\alpha) = 0.419$ mm⁻¹, $D_{\text{calc}} = 1.001$ g/cm³, 104725 reflections measured ($4.166^\circ \leq 2\theta \leq 41.632^\circ$), 20090 unique ($R_{\text{int}} = 0.0516$, $R_{\text{sigma}} = 0.0370$) which were used in all calculations. The final R_1 was 0.1368 ($I > 2\sigma(I)$) and wR_2 was 0.3897 (all data).

[Co₄L₆](PF₆)₁₂·10MeCN

Crystal Data for C₁₉₈H₁₅₃Co₄F₇₂N₃₉P₁₂ ($M=5053.95$ g/mol): triclinic, space group P-1 (no. 2), $a = 21.0998(4)$ Å, $b = 21.1425(4)$ Å, $c = 34.7365(5)$ Å, $\alpha = 97.0320(10)^\circ$, $\beta = 98.7350(10)^\circ$, $\gamma = 119.772(2)^\circ$, $V = 12936.4(5)$ Å³, $Z = 2$, $T = 99.99(10)$ K, $\mu(\text{Mo K}\alpha) = 0.430$ mm⁻¹, $D_{\text{calc}} = 1.297$ g/cm³, 109873 reflections measured ($3.702^\circ \leq 2\theta \leq 50.44^\circ$), 44207 unique ($R_{\text{int}} = 0.0576$, $R_{\text{sigma}} = 0.0643$) which were used in all calculations. The final R_1 was 0.1215 ($I > 2\sigma(I)$) and wR_2 was 0.3167 (all data).

References

1. R. G. Siddique, K. S. A. Arachchige, H. A. AL-Fayaad, J. D. Thoburn, J. C. McMurtrie and J. K. Clegg, *Angew. Chem., Int. Ed.*, 2022, **61**, e202115555.
2. Rigaku OD CrysAlisPro, 2009-2024
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
4. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.
5. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
6. P. van der Sluis and A. L. Spek, *Acta Cryst.*, 1990, **46**, 194-201.
7. A. Spek, *Acta Cryst.*, 2015, **C71**, 9-18.
8. Utrecht University, PLATON: A Multipurpose Crystallographic Tool, 2008