Self-Assembly of Looped Triple-Stranded Helicates

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Supplementary Information

General experimental procedures

Reagents and starting materials

Compound $[(\mathrm{AuC{\equiv}Cbpyl})_2(\mu\text{-}\mathrm{Ph_2P(CH_2)_4PPh_2})]$ (**L**) was prepared as previously reported.[1] $Fe(ClO_4)_2\cdot 6.4H_2O$ and $Zn(ClO_4)_2\cdot 6H_2O$ were purchased from Aldrich. HPLC-grade acetonitrile (Baker) was used as received. Et_2O was distilled over sodium-benzophenone ketyl.

Physical measurements

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Spectrum 100 FT-IR spectrometer with KBr pellets. C, H, N and S analyses were carried out with a Carlo Erba 1108 analyzer. Melting points were determined on a Reichert apparatus in an air atmosphere. High resolution ESI-MS spectra were measured on a Agilent 6620 spectrometer; the exact masses have been calculated for the combination of the most abundant isotopes.

NMR spectra were measured on Bruker Avance 200, 300, 400 and 600 instruments. ^1H and $^{13}C\{^1H\}$ chemical shifts were referenced to residual CHD_2CN (1.94 ppm (H) and 1.32 ppm ($^{13}CD_3CN$)). $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4. NOESY measurements were carried out using a mixing time of 0.6 s. Diffusion NMR experiments were performed on 2.5 mM solutions of the complexes in CD_3CN using a Bruker Avance 400 spectrometer equiped with a BBO 5 mm probe. The measurements were carried out without spinning and with the airflow disconnected. The shape of the gradient was sinusoidal and its strengh was linearly increased in 32 steps from 2% to 95% of the maximum level. The standard ledbpgp2s pulse program supplied by Bruker was used (longitudinal eddy-current delay with bipolar gradient pulse pair and 2 spoil gradients[2]). The diffusion coeficients were calculated with the T_1/T_2 processing module of the Bruker Topspin 2.0 software using a one-component exponential fit to equation (1).

$$I = I_0\exp[-D(\gamma\delta G)^2(\Delta - \delta/3)] \qquad (1)$$

where D = diffusion coefficient, γ = magnetogyric ratio for hydrogen, G = gradient strength, Δ = diffusion time (100 ms), and δ = length of the bipolar diffusion gradient (2.4 ms for $[Fe_2\mathbf{L}_3](ClO_4)_4$ or 2.8 ms for $[Zn_2\mathbf{L}_3](ClO_4)_4$). In order to test the quality of the data, the signal intensity changes $\ln(I/I_0)$ were plotted against G^2. The plots were linear which confirmed that the data are suitable for the determination of D using equation (1). The experimental error was estimated as ±0.06.

Hydrodynamic radii were estimated via the Stokes–Einstein equation[3] (2) using a value of η = 0.341 cP for the viscosity of acetonitrile[4] at 298 K.

$$r_H = kT/6\pi\eta D \qquad (2)$$

Synthesis and characterization of the complexes

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantities and with caution.*

[Fe_2L_3](ClO_4)$_4$. A solution of $Fe(ClO_4)_2\cdot 6.4H_2O$ (0.036 mmol) in CH_3CN (8 mL) was added dropwise to a suspension of **L** (64 mg, 0.054 mmol) in CH_3CN (8 mL). The resulting suspension was stirred at room temperature for 2 h to give a red solution, which was concentrated under vacuum to ca. 1 mL. Addition of Et_2O (20 mL) gave a red precipitate which was filtered, washed with Et_2O (3 × 5 mL) and dried under vacuum. Yield: 60 mg, 83%. Mp: 246–249 ºC. Anal. Calcd. for $C_{156}H_{126}Au_6Cl_4Fe_2N_{12}O_{16}P_6$: C, 46.31; H, 3.14; N, 4.15. Found: 46.34; H, 3.14; N, 4.14. IR (Nujol, cm^{-1}): ν(C≡C) 2112; ν(ClO_4^-) 1089, 621. ^1H NMR (400.9 MHz, CD_3CN): δ 8.12 (d, 6 H, H3, $^3J_{HH}$ = 8.4 Hz), 8.01 (d, 6 H, H4, $^3J_{HH}$ = 8.4, $^4J_{HH}$ =1.7 Hz), 7.70 (m, 30 H, Ph^1), 7.51 (s, 6 H, H6), 7.20–7.08 (m, 30 H, H3', H6', *o*-Ph^2 and *p*-Ph^2), 6.90 (m, 12 H, H4' and H5'), 6.57 (m, 12 H, *m*-Ph^2), 2.90 (m, 6 H, $CH_2\mathit{CH_2}P$), 2.16–2.02 (two m, 12 H, $CH_2\mathit{CH_2}P$ and $\mathit{CH_2}CH_2P$), 1.84 (m, 6 H, $\mathit{CH_2}CH_2P$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ 160.0 (C2'), 157.0 (C6), 156.2 (C2), 155.4 (C6'), 152.7 (d, C≡*C*Au, $^2J_{PC}$ = 140.9 Hz), 142.7 (C4), 139.1 (C4'), 135.1 (d, *o*-Ph^2, $^2J_{PC}$ = 13.3 Hz), 134.9 (d, *o*-Ph^1, $^2J_{PC}$ = 13.8 Hz), 133.5 (d, *i*-Ph^1, $^1J_{PC}$ = 53.1 Hz), 133.3 (d, *p*-Ph^1, $^4J_{PC}$ = 2.2 Hz), 132.9 (d, *p*-Ph^2, $^4J_{PC}$ = 1.7 Hz), 130.9 (d, *m*-Ph^1, $^3J_{PC}$ = 11.1 Hz), 129.8 (d, *m*-Ph^2, $^3J_{PC}$ = 11.1 Hz), 129.4 (d, *i*-Ph^2, $^1J_{PC}$ = 54.7 Hz), 128.9 (d, C5, $^4J_{PC}$ = 2.8 Hz), 127.8 (C5'), 125.4 (C3), 124.0 (C3'), 102.3 (d, *C*≡CAu, $^3J_{PC}$ = 26.5 Hz), 26.9 (d, $CH_2\mathit{C}H_2P$, $^1J_{PC}$ = 34.3 Hz), 26.0 (m, $\mathit{C}H_2CH_2P$). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_3CN): δ 36.9 (s). ESI-MS (MeCN) *m/z*: 1923.2 ([Fe_2**L**$_3$](ClO_4)$_2^{2+}$), 1413.2, 1345.2, 1333.1 ([Fe**L**](ClO_4)$^+$), 1279.1, 1249.1 ([Fe_2**L**$_3$](ClO_4)$^{3+}$), 1206.7, 999.1 ([Au_2(C≡Cbpyl)(dppb)]$^+$), 911.9 ([Fe_2**L**$_3$]$^{4+}$), 855; exact *m/z* calcd. for [Fe_2**L**$_3$]$^{4+}$: 911.6331, found (ESI): 911,6340, Δ = 1 ppm.

[Zn_2L_3](ClO_4)$_4$. A solution of $Zn(ClO_4)_2\cdot 6H_2O$ (0.053 mmol) in CH_3CN (5 mL) was added dropwise to a suspension of **L** (93 mg, 0.079 mmol) in CH_3CN (8 mL). The resulting suspension was stirred at room temperature for 2 h to give a yellow solution, which was concentrated under vacuum to ca. 1 mL. Addition of Et_2O (20 mL) gave a cream precipitate which was filtered, washed with Et_2O (3 × 5 mL) and dried under vacuum. Yield: 100 mg, 93%. Mp: 183 ºC (dec). Anal. Calcd. for $C_{156}H_{126}N_{12}Au_6Cl_4O_{16}P_6Zn_2\cdot 4\ H_2O$: C, 45.29; H, 3.26; N, 4.06. Found: 45.00; H, 2.98; N, 4.03. Integration of the water signal in the ^1H NMR spectra (after substraction of the solvent contribution) was used to estimate the water content of the sample. IR (Nujol, cm^{-1}): ν(C≡C) 2117; ν(ClO_4^-) 1099, 623. ^1H NMR (400.9 MHz, CD_3CN): δ 8.30 (d, 6 H, H3, $^3J_{HH}$ = 8.5 Hz), 7.99 (dd, 6 H, H4,

$^3J_{HH}$ = 8.3, $^4J_{HH}$ =1.7 Hz), 7.88 (d, 6 H, H6, $^4J_{HH}$ = 1.5 Hz), 7.83 (ddd, 6 H, H6’, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 1.5, $^5J_{HH}$ = 0.6 Hz), 7.76 (d, 6 H, H3’, $^3J_{HH}$ = 7.9 Hz), 7.71–7.66 (m, 30 H, Ph^1), 7.29 (m, 6 H, *p*-Ph^2), 7.16 (m, 12 H, *o*-Ph^2), 7.01 (ddd, 6 H, H5’, $^3J_{HH}$ = 5.2, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.0 Hz), 6.83 (m, 18 H, H4’ and *m*-Ph^2), 2.83 (m, 6 H, CH_2CH_2P), 2.28 (m, 6 H, CH_2CH_2P), 2.05 (m, 6 H, CH_2CH_2P), 1.81 (m, 6 H, CH_2CH_2P). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_3CN): δ 151.3 (d, C≡*C*Au, $^2J_{PC}$ = 141.0 Hz), 150.7 (C6), 150.0 (C2 or C2'), 149.0 (C6’), 146.0 (C2 or C2'), 144.3 (C4), 141.8 (C4’), 134.8 (d, *o*-Ph^2, J_{PC} = 13.2 Hz), 134.3 (d, *o*-Ph^1, J_{PC} = 13.3 Hz), 132.9 (d, *i*-Ph, $^1J_{PC}$ = 51.8 Hz), 132.9 (d, *p*-Ph^1, $^4J_{PC}$ = 2.1 Hz), 132.6 (s, *p*-Ph^2), 130.5 (d, *m*-Ph^1, $^3J_{PC}$ = 10.8 Hz), 129.7 (d, *m*-Ph^2, $^3J_{PC}$ = 11.0 Hz), 129.3 (d, *i*-Ph, $^1J_{PC}$ = 54.7 Hz), 128.3 (d, C5, $^4J_{PC}$ = 3.0 Hz), 127.4 (C5’), 125.1 (C3), 123.8 (C3’), 101.5 (d, *C*≡CAu, $^3J_{PC}$ = 26.5 Hz), 26.6 (d, CH_2P, $^1J_{PC}$ = 33.9 Hz), 25.5 (m, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_3CN): δ 36.9 (s). ESI-MS (MeOH/MeCN) *m/z*: 3965 ($[Zn_2\mathbf{L}_3](ClO_4)_3^+$), 2521 ($[Zn\mathbf{L}_2](ClO_4)^+$), 1933 ($[Zn_2\mathbf{L}_3](ClO_4)_2^{2+}$), 1421 ($[Zn\{Au_2(C≡Cbpyl)_3(dppb)\}]^+$), 1355, 1341 ($[Zn\mathbf{L}](ClO_4)^+$), 1255 ($[Zn_2\mathbf{L}_3](ClO_4)^{3+}$), 1211 ($[Zn\mathbf{L}_2]^{2+}$), 999 ($[Au_2(C≡Cbpyl)(dppb)]^+$), 917 ($[Zn_2\mathbf{L}_3]^{4+}$), 855; exact *m/z* calcd. for $[Zn_2\mathbf{L}_3]^{4+}$: 915.6302, found (ESI): 915.6310, Δ = 0.9 ppm.

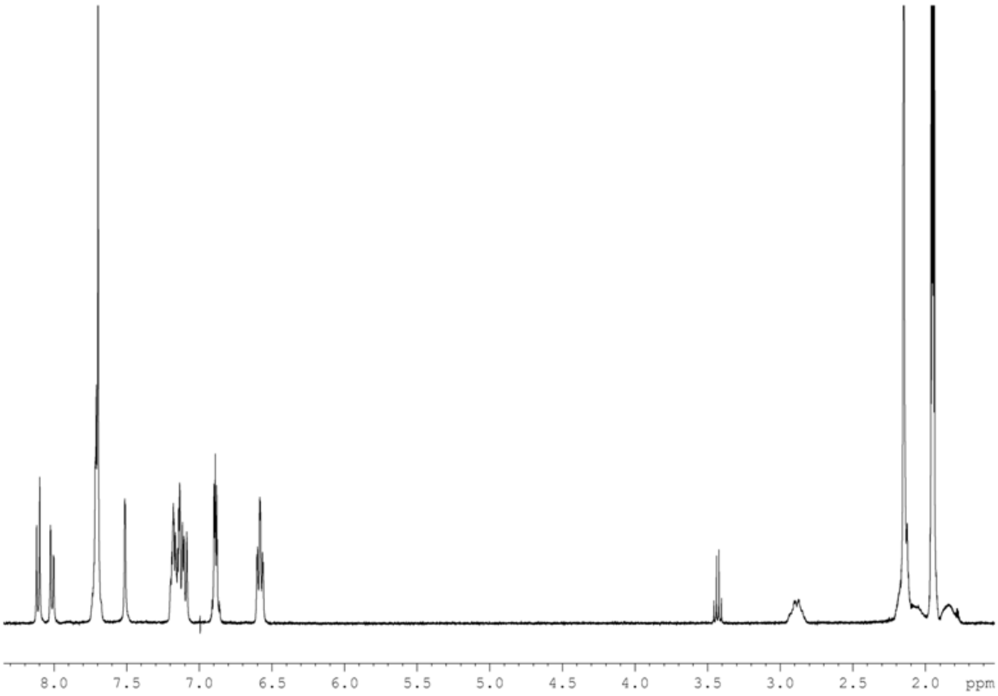


Fig. S1 ^{1}H NMR spectrum of [$Fe_2\mathbf{L}_3$](ClO_4)$_4$ (400.9 MHz, CD_3CN). The signals at 3.43, 2.15 and 1.95 correspond to Et_2O, H_2O and CHD_2CN, respectively. One the methylenic protons signals is overlaped with the H_2O signal, as observed in the HMQC spectra.

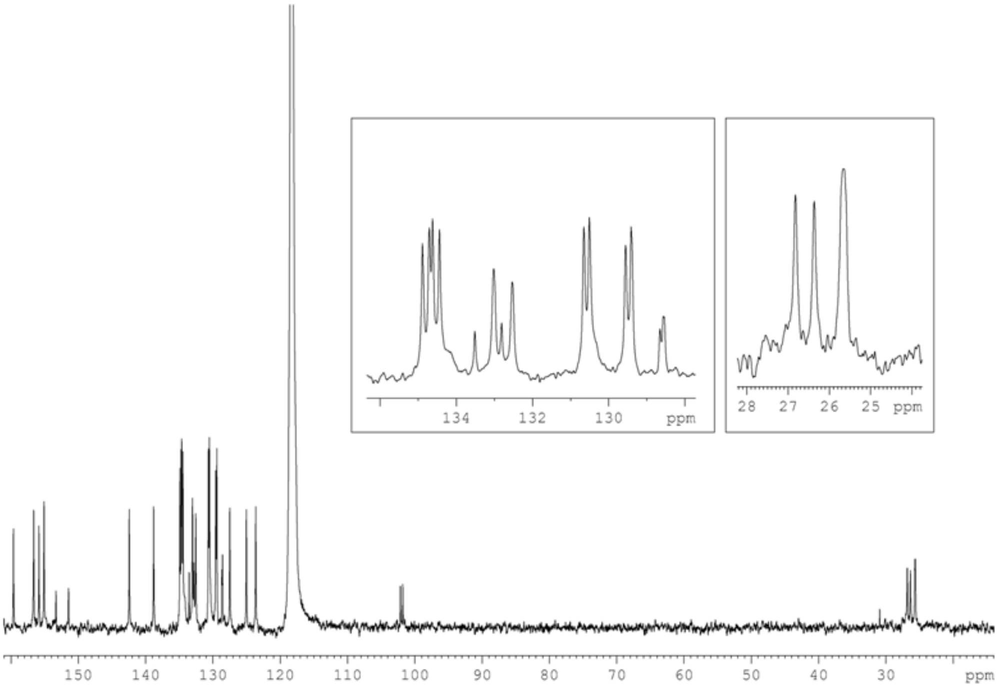


Fig. S2 ^{13}C{^{1}H} NMR spectrum of [$Fe_2\mathbf{L}_3$](ClO_4)$_4$ (75.5 MHz, CD_3CN)

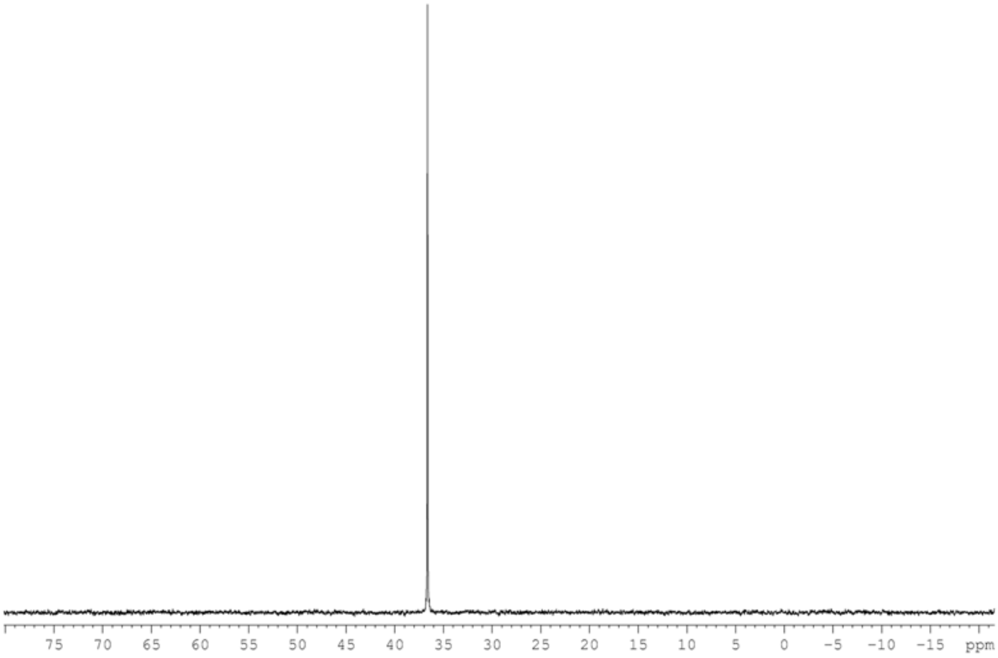


Fig. S3 $^{31}P\{^1H\}$ NMR spectrum of $[Fe_2\mathbf{L}_3](ClO_4)_4$ (81.0 MHz, CD_3CN)

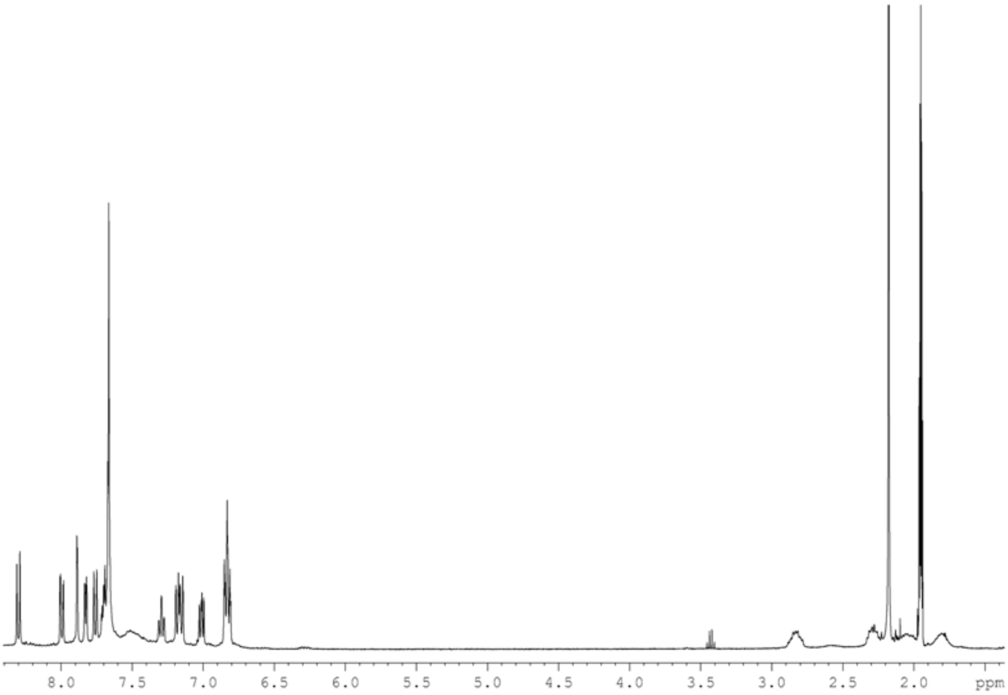


Fig. S4 ^1H NMR spectrum of $[Zn_2\mathbf{L}_3](ClO_4)_4$ (400.9 MHz, CD_3CN). The signals at 3.43, 2.15 and 1.95 correspond to Et_2O, H_2O and CHD_2CN, respectively.

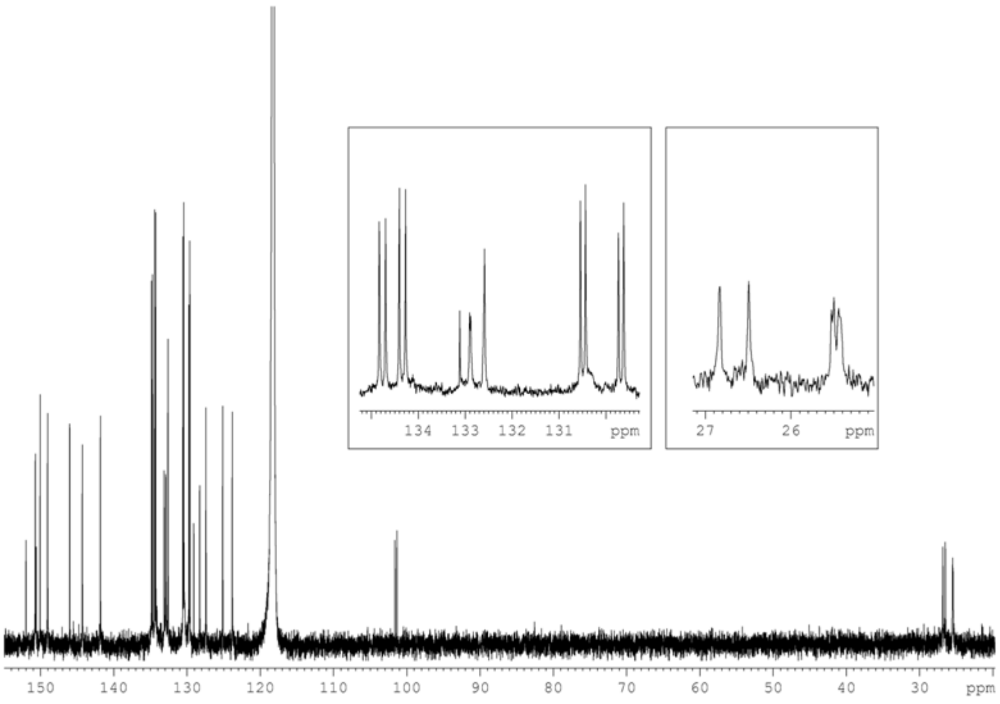


Fig. S5 $^{13}C\{^1H\}$ NMR spectrum of $[Zn_2\mathbf{L}_3](ClO_4)_4$ (100.8 MHz, CD_3CN)

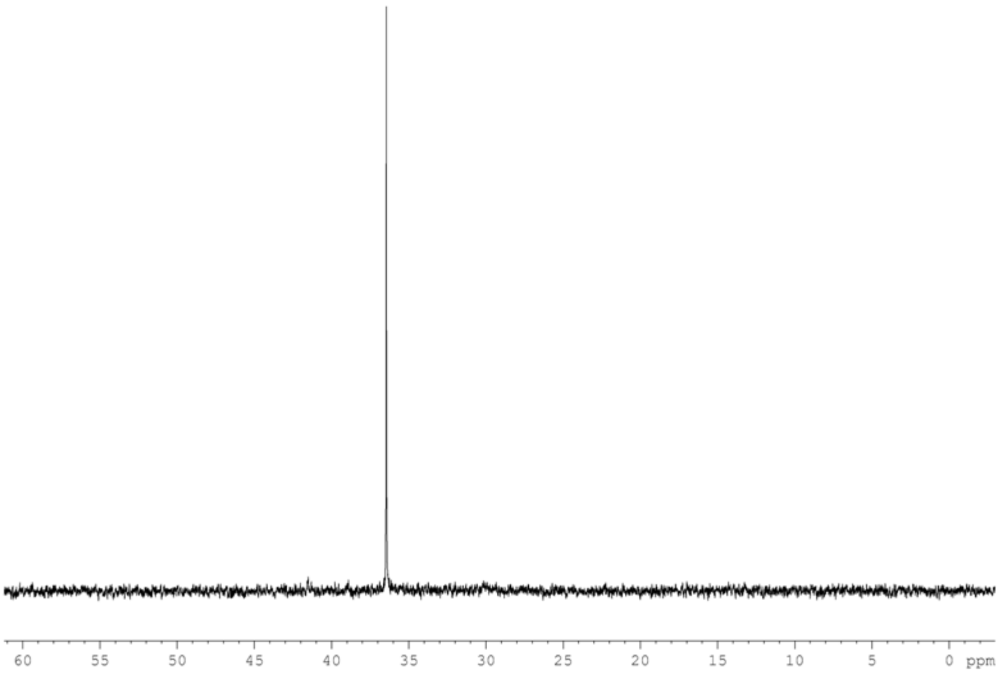
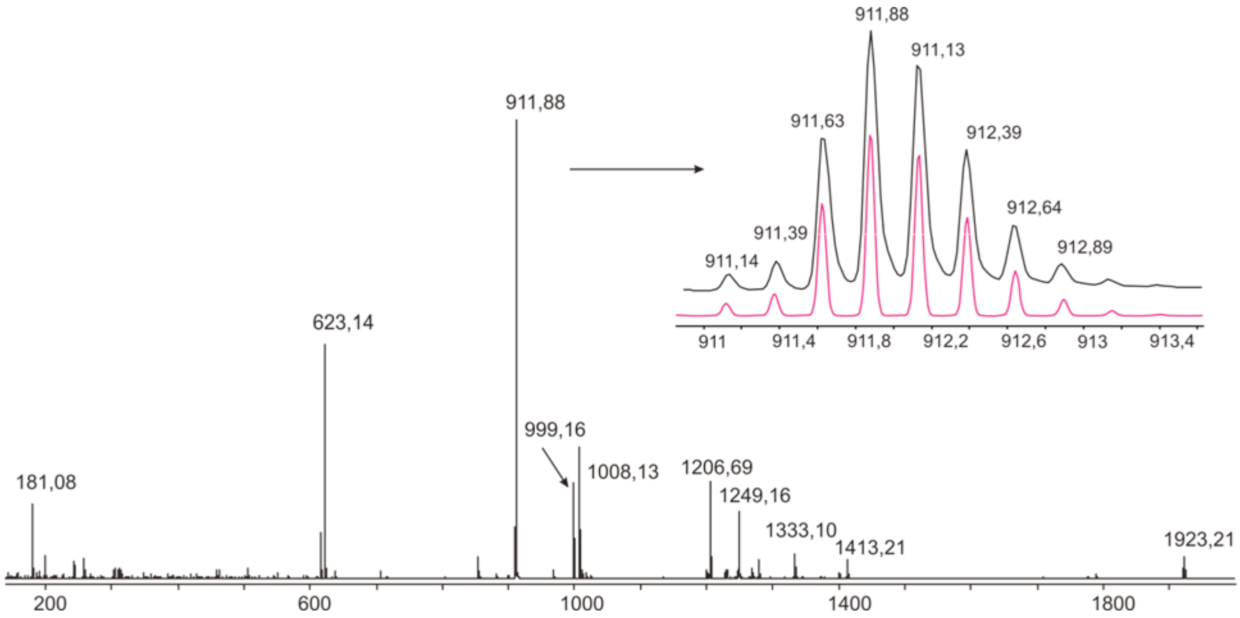


Fig. S6 $^{31}P\{^1H\}$ NMR spectrum of $[Zn_2\mathbf{L}_3](ClO_4)_4$ (81.0 MHz, CD_3CN)

Fe^{2+} + **L**



Zn^{2+} + **L**

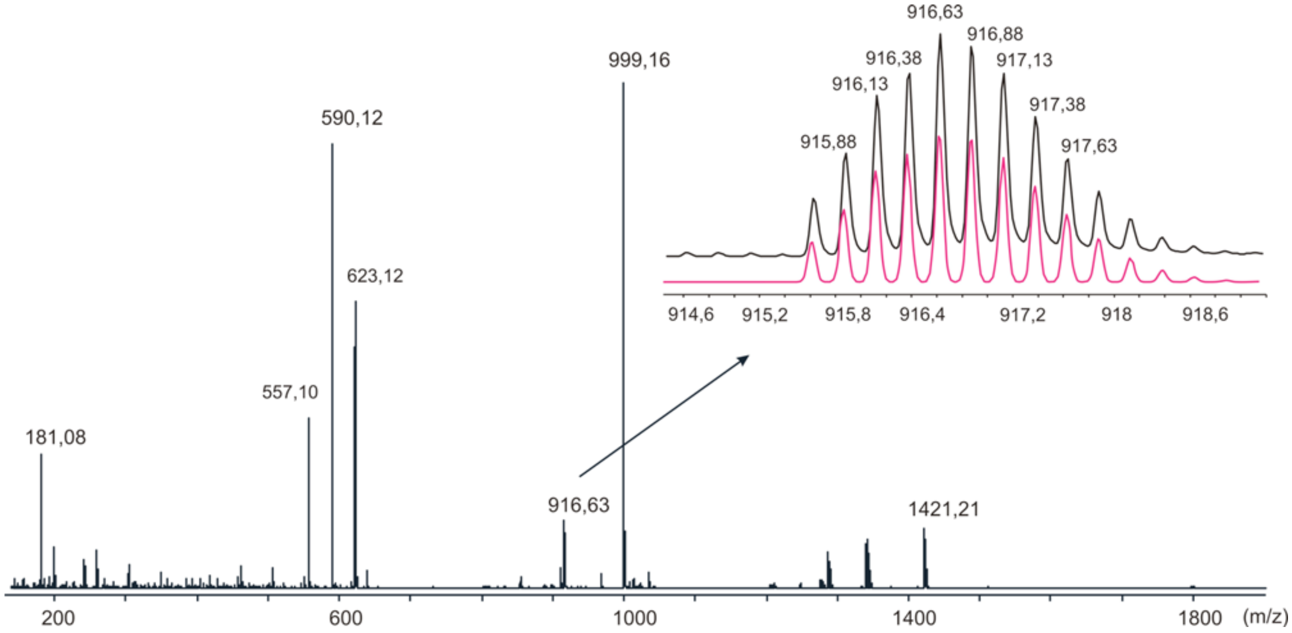


Fig. S7 ESI-MS spectra of the reaction mixtures of between M^{2+} and **L** (2:3 molar ratio) in acetonitrile. The isotope distributions of the $[M_2L_3]^{4+}$ cations are magnified (black) and compared with the calculated isotope distributions (magenta).

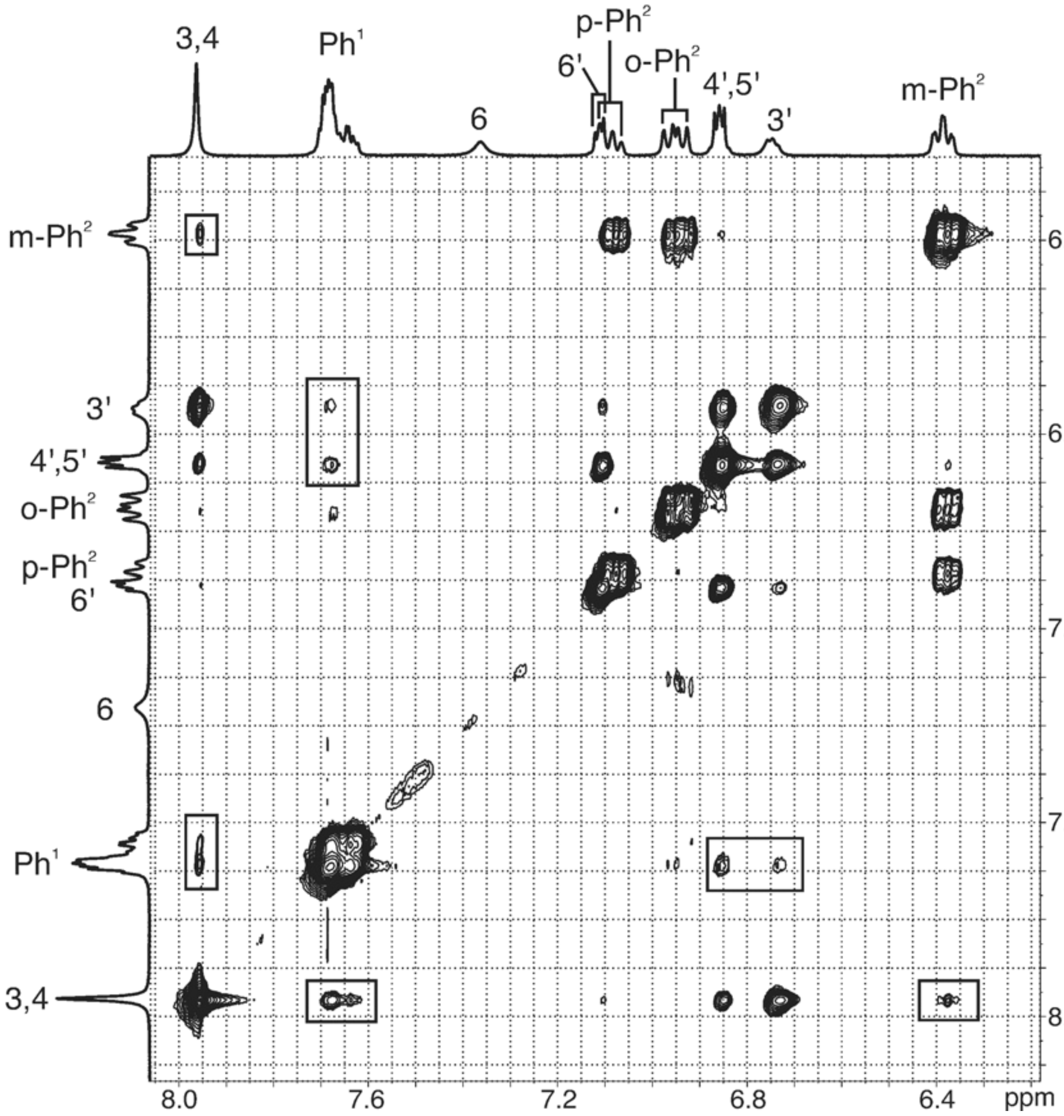


Fig. S8 NOESY spectrum of [$Fe_2\mathbf{L}_3$](ClO_4)$_4$ (400.9 MHz, CD_3CN, T = 243 K). The NOE peaks between phenylic and pyridinic hydrogens are indicated by rectangles.

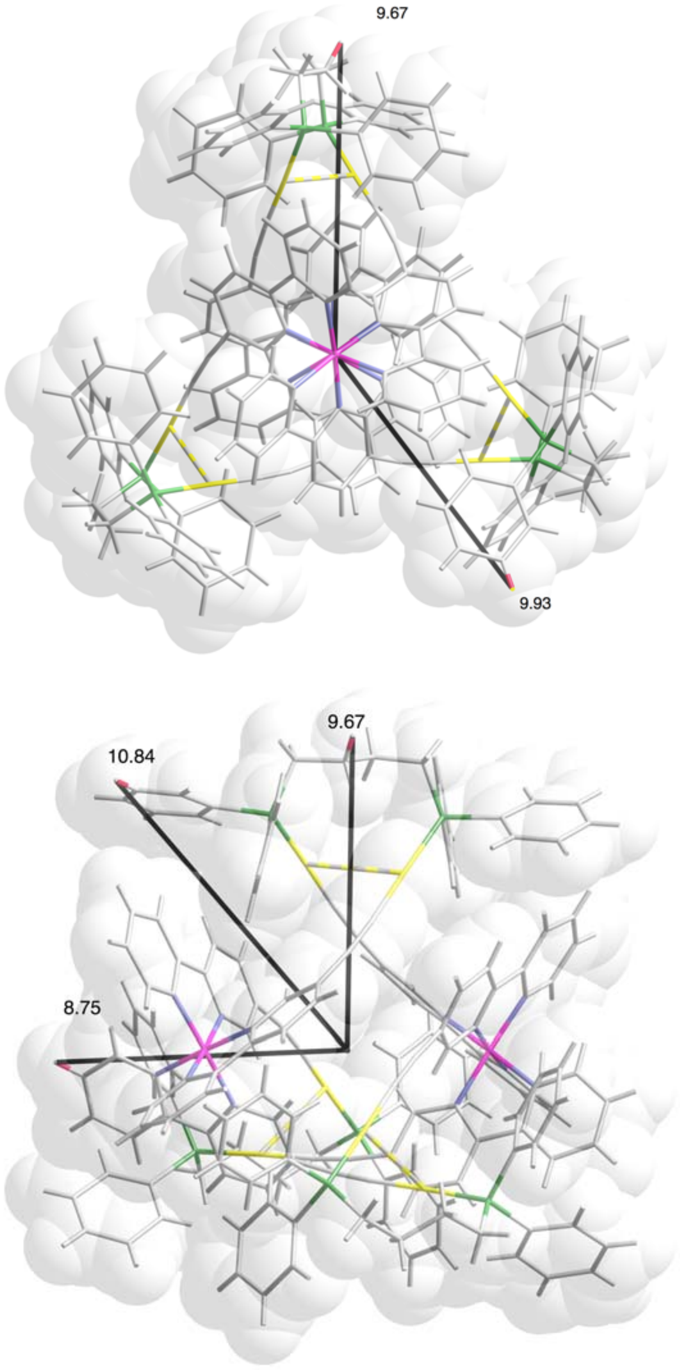


Figure S9 Space-filling plots (VdW surfaces) of the crystal structure of cation **$[Fe_2L_3]^{4+}$**. Views down the direction of the C_3 axis (up) and a side view (down). The distances from the centroid of the molecule to representative external hydrogen atoms are indicated for comparison with the spherical hydrodynamic radius (r_H = 11.0 Å) determined by diffusion NMR measurements.

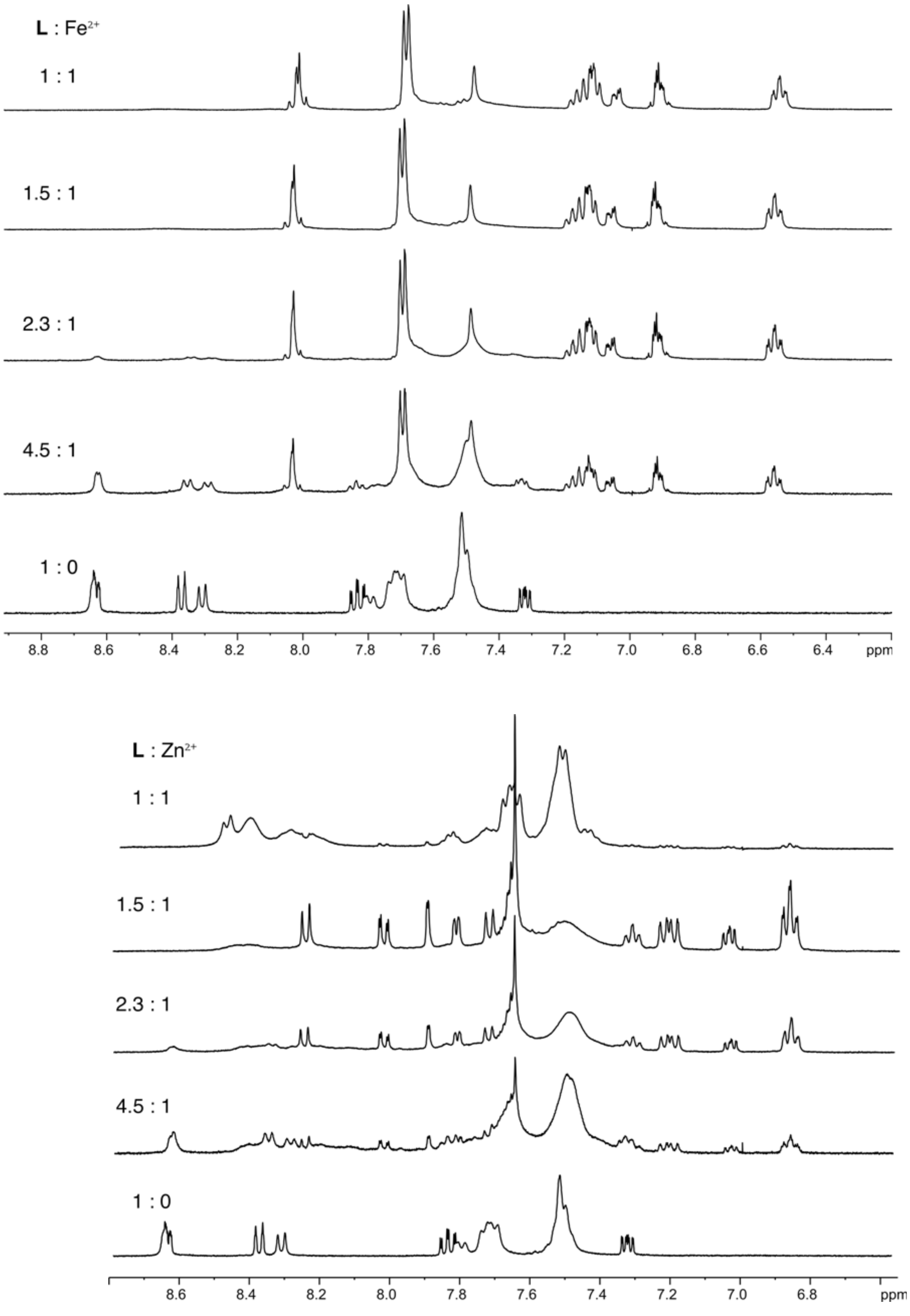
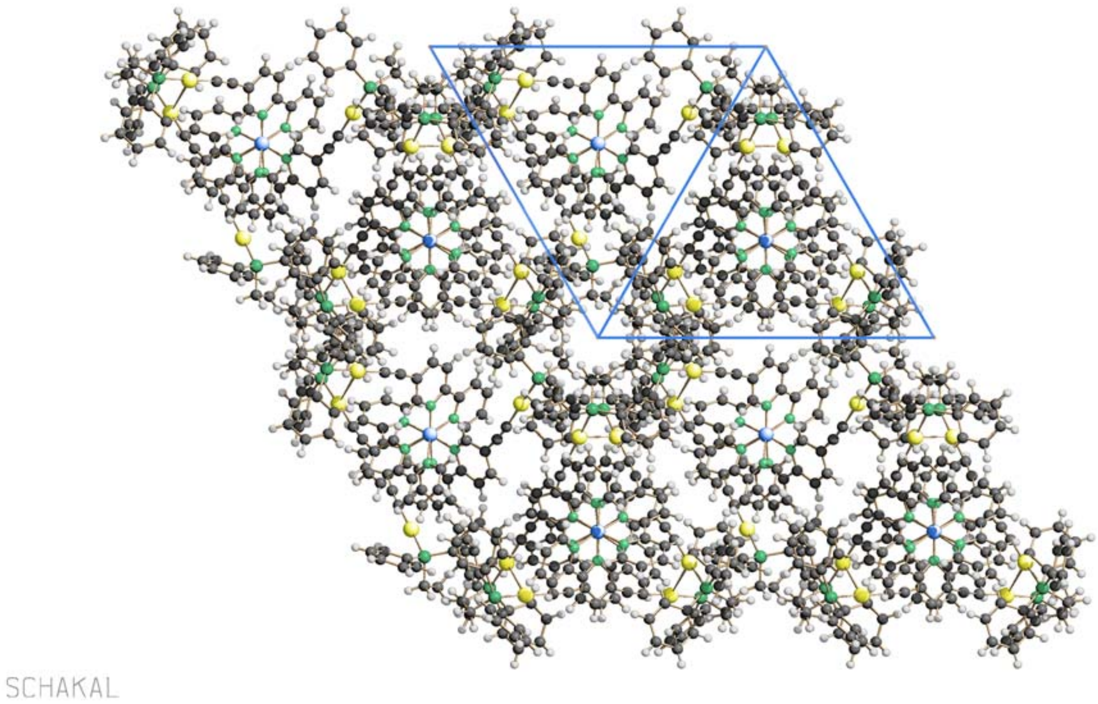


Fig. S10 ^{1}H NMR spectra (aromatic region) of the **L** + M^{2+} reaction mixtures (M = Fe (top), Zn) at different **L** : M^{2+} molar ratios.



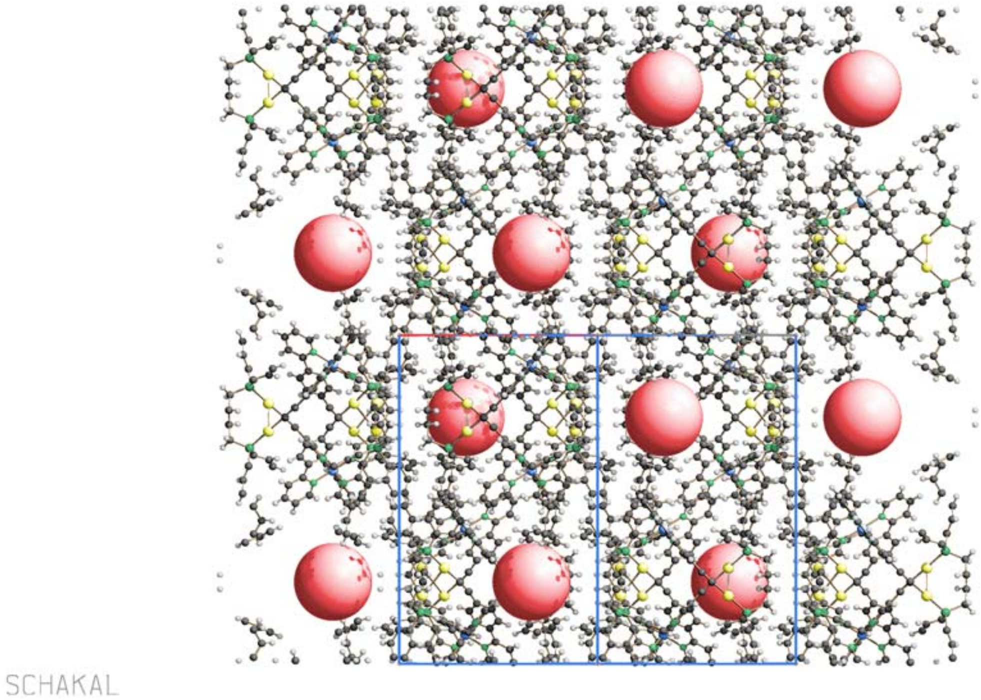


Fig. S11 Top: crystal packing of the $[Fe_2\mathbf{L}_3](ClO_4)_4$ species, viewed down the c axis of the trigonal space group, with disordered perchlorates and solvent molecules omitted for clarity. Au atoms in yellow, Fe atoms in blue and P atoms in green. Bottom: same crystal packing, viewed down a+b, highlighting, with red spheres, the empty space left by the packing of the large octametallic cations, normally occupied by the disordered anions and solvent molecules.

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