Supplementary Information

A new Fe^{II} quaterpyridyl M_4L_6 tetrahedron exhibiting selective anion binding

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Section S1: Synthesis.

All products were freeze dried before microelemental and spectral analysis. Crystals employed for X-ray structural analysis were used directly after removal from the crystallizing solvent.

$[Fe_4L_6(BF_4)](BF_4)_7\cdot 4H_2O$. A solution of Fe^{II} tetrafluoroborate hexahydrate (47 mg, 0.14 mmol) and **L** (78 mg, 0.23 mmol) in dry degassed acetonitrile (10 cm^3) was heated at reflux (under nitrogen) for 5 h resulting in a characteristic deep red solution. The solvent was evaporated and the crude material was purified on Sephadex LH-20 using acetonitrile as the eluant affording the product (87 mg, 84 %) as a deep red solid. UV/Vis (CH_3CN, nm): $\lambda_{max}(\varepsilon)$ = 271 (82 049), 318 (288 680), 529 (21 768); ^1H NMR (300 MHz, $[D_3]$acetonitrile, 298 K): δ = 2.20 (s, 36H; CH_3), 7.05 (d, ^3J = 1.8 Hz, 12H; H-6’,6”), 7.31 (dd, ^3J = 8.4, 1.8 Hz, 12H; H-4’,4”), 7.37 (d, ^3J = 1.2 Hz, 12H; H-6,6”’), 7.97 (dd, ^3J = 8.4, 1.2 Hz, 12H; H-4,4”’), 8.41 (d, ^3J = 8.4 Hz, 12H; H-3’,3”), 8.53 (d, ^3J = 8.4 Hz, 12H; H-3,3”’); ^{13}C NMR (75 MHz, $[D_3]$acetonitrile, 298 K): δ = 18.79, 123.58, 125.27, 136.51, 139.95, 140.19, 140.58, 152.29, 155.60, 156.34, 160.38; ^{19}F NMR (282.4 MHz, $[D_3]$acetonitrile, 298 K): δ = -151.00 (s; B^{11}-F), -150.94 (s; B^{10}-F); HR-ESI-MS (acetonitrile/methanol): m/z calculated for $(C_{22}H_{18}N_4)_6Fe_4(BF_4)_8$: 2948.6819; found: 1387.3591 $[M - 2BF_4]^{2+}$; 895.8923 $[M - 3BF_4]^{3+}$; 650.1742 $[M - 4BF_4]^{4+}$; elemental analysis (%) calculated for $C_{132}H_{108}B_8F_{32}Fe_4N_{24}.4H_2O$ (3020.22 g mol^{-1}): C 52.44, H 3.87, N 11.13; found: C 52.26, H 3.78, N 11.08; X-ray quality crystals were obtained by diffusion of tetrahydrofuran into an acetonitrile solution of the product.

$[Fe_4L_6(PF_6)](PF_6)_7\cdot 2H_2O$. A solution of Fe^{II} bromide (21 mg, 0.14 mmol) and a suspension of **L** (78 mg, 0.23 mmol) in dry degassed acetonitrile (10 cm^3) was heated under reflux for 24 h (under nitrogen) resulting in a dark red solution. The solvent was evaporated and the deep red material remaining was taken up in water and excess KPF_6 (110 mg, 0.6 mmol) was added. the resulting red solid that formed was filtered off. This crude product was purified on Sephadex LH-20 using acetonitrile as the eluant to afford pure product (84 mg, 96 %) as a deep red solid. UV/Vis (CH_3CN, nm): $\lambda_{max}(\varepsilon)$ = 271 (80,948), 320 (340,147), 534 (25,756); ^1H NMR (300 MHz, $[D_3]$acetonitrile, 298 K): δ = 2.23 (s, 36H, CH_3), 6.77 (s, 12H, H-6’,6”), 7.23 (d, ^3J = 7.2 Hz, 12H; H-4’,4”), 7.55 (s, 12H; H-6,6”’), 7.97 (d, ^3J = 8.1 Hz, 12H; H-4,4”’), 8.42 (d, ^3J = 7.2 Hz, 12H; H-3’,3”), 8.49 (d, ^3J = 8.1 Hz, 12H; H-3,3”’); ^{13}C NMR (75 MHz, $[D_3]$acetonitrile, 298 K): δ = 18.78, 123.21, 125.06, 135.96, 138.73, 139.84, 140.54, 153.48, 155.80, 156.28, 159.78; ^{19}F NMR (282.4 MHz, $[D_3]$acetonitrile, 298 K): δ = 73.09 (d, ^1J = 707.1 Hz, 42F; $7PF_6$), -72.45 (d, ^1J = 717.3 Hz, 6F; $1PF_6$); HR-ESI-MS (acetonitrile/methanol): m/z calculated for $(C_{22}H_{18}N_4)_6Fe_4(PF_6)_8$: 3412.37205; found (%):1561.7274, $[M - 2PF_6]^{2+}$; 992.8323, $[M - 3PF_6]^{3+}$; 708.3785, $[M - 4PF_6]^{4+}$; elemental analysis (%) calculated for $C_{132}H_{108}F_{48}Fe_4N_{24}\ P_8.2H_2O$ (3449.47 g mol^{-}): C, 45.93; H, 3.27; N, 9.75; Found: C 45.75, H 3.23, N 9.81; FTIR (nujol mull) $\nu_{(P-F)}$, 835. X-ray quality crystals were obtained by diffusion of methanol into an acetonitrile solution of the product.

$[Fe_4L_6][ZnCl_4]_4\cdot CH_3CN\cdot 5.5THF\cdot 2.5H_2O$. L (50 mg, 0.148 mmol) and Fe^{II} chloride pentahydrate (21.5 mg, 0.099 mmol) were added to distilled water (10ml) and the resulting suspension placed in a microwave pressure vessel with both pressure and temperature sensors. The reaction mixture was irradiated (10% of 400W) with the temperature controlled at 120°C (the pressure did not exceed 140 kPa).

The reaction mixture was allowed to cool to room temperature and was filtered through celite. To this solution was added $ZnCl_2$ (68 mg, 0.5 mmol) in 1M HCl (1 ml), and the resulting 'instant' precipitate was filtered off and washed with a minimum of cold water. Thin layer chromatography on silica gel, eluted using a mixture of 7 parts CH_3CN, 1 part saturated KNO_3 (aq), and 0.5 part water, indicated the presence of one major product. ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, 298 K): $\delta = 2.16$ (s, 36H; CH_3), 7.18 (s, 12H: H-6’,6”), 7.32 (s, 12H; H-6,6”’), 7.55 (d, $^3J = 7.8$ Hz, 12H; H-4’,4”), 7.92 (d, $^3J = 7.5$ Hz, 12H; H-4,4”’), 8.54 (d, $^3J = 8.1$ Hz, 12H; H-3’,3”), 8.72 (d, $^3J = 8.4$ Hz, 12H; H-3,3”’); X-ray quality crystals were obtained by diffusion of THF into an acetonitrile solution of the above product.

Section S2: Characteristic UV/Vis spectrum.

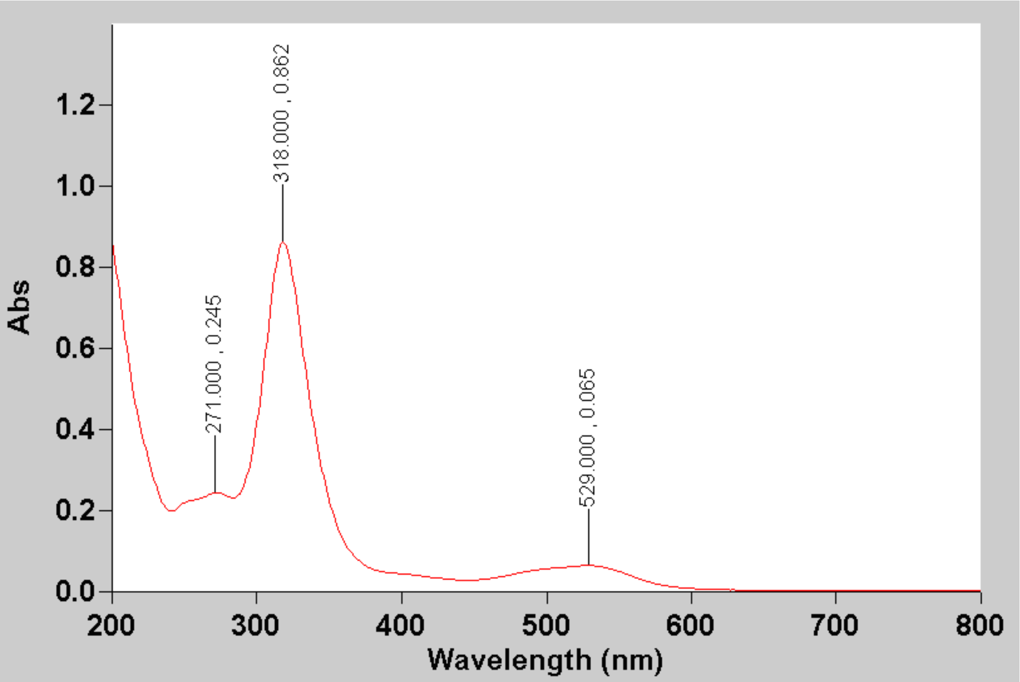
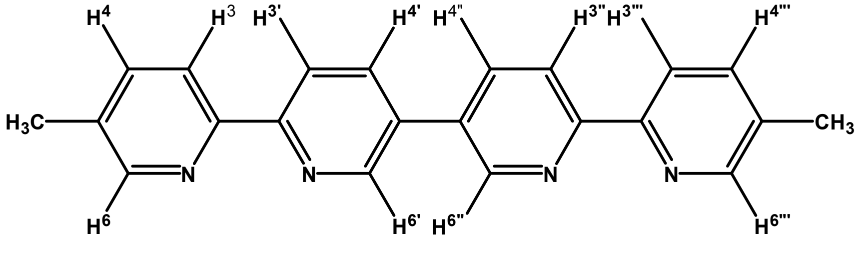


Figure S1. UV/Vis Spectrum of $[\mathrm{Fe}_4\mathbf{L}_6(\mathrm{BF}_4^{)}](\mathrm{BF}_4)_7$. This is characteristic of the spectra observed for the related inclusion complexes.

Section S3: Representative NMR spectrum.



L

Scheme S1. Quaterpyridyl numbering scheme.

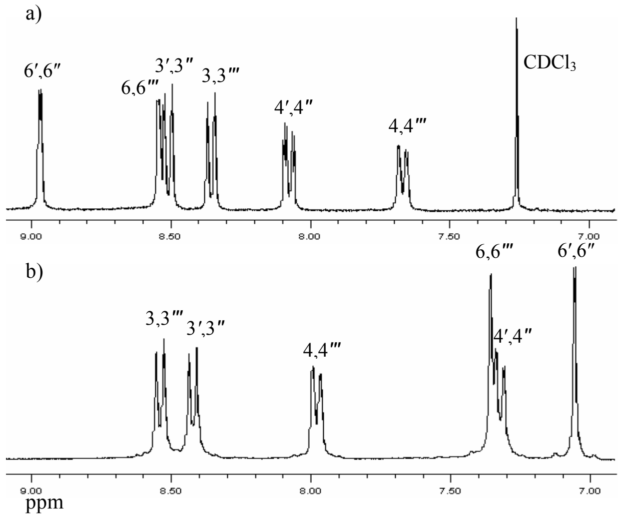


Figure S2. Partially assigned ^{1}H NMR spectra of, a) **L** in $CDCl_3$ and b) $[Fe_4\mathbf{L}_6(BF_4)](BF_4)_7$ in CD_3CN (spectrum is characteristic of the M_4L_6 topology).

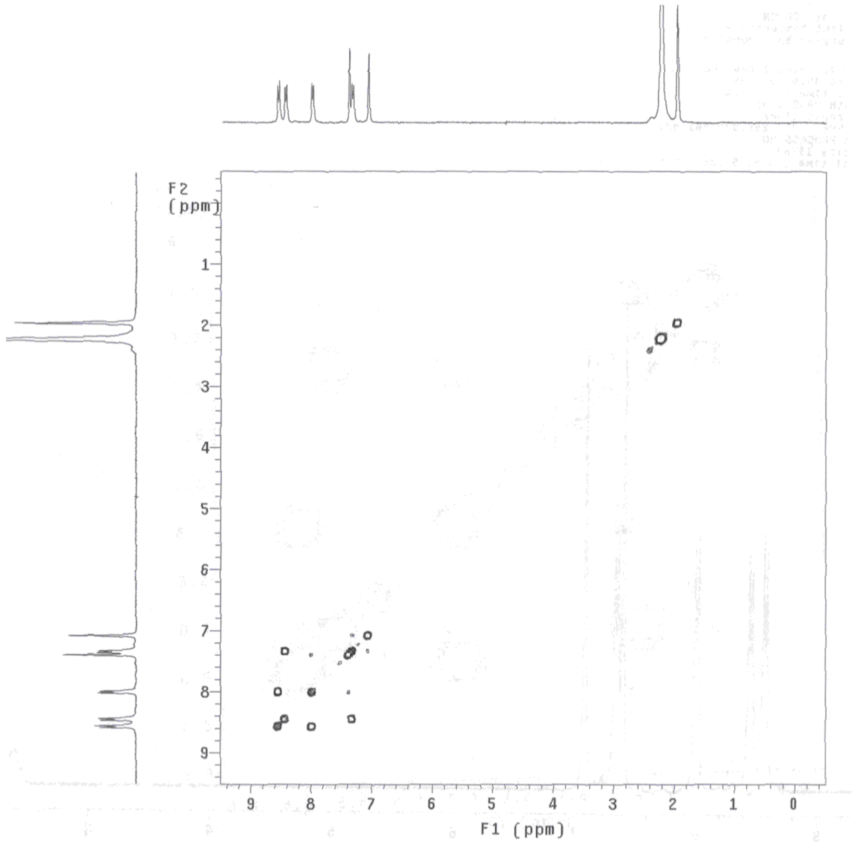


Figure S3. ^{1}H-^{1}H COSY spectrum of $[Fe_4\mathbf{L}_6(BF_4)](BF_4)_7$.

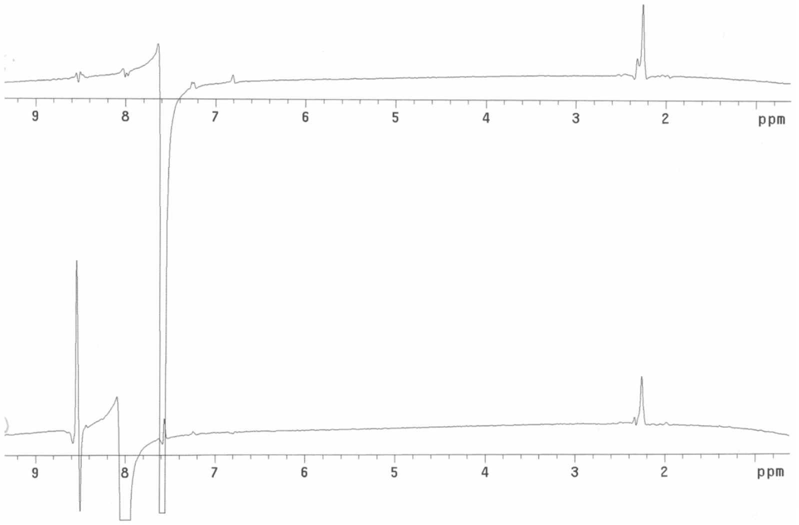


Figure S4. 1D slices through NOSEY spectrum of [Fe_4**L**$_6$(BF_4)](BF_4)$_7$; Correlation between protons in the 6,6'''-positions with the methyl protons (top); and correlation observed between protons in the 4,4'''-positions with the methyl protons (bottom).

Section S4: Selected HR-ESI-MS and theoretical isotopic distributions.

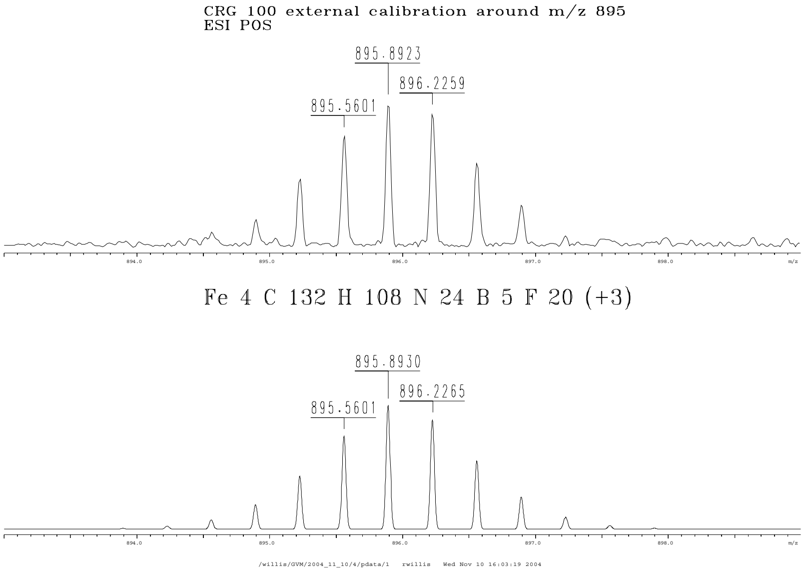


Figure S5. Portion of [Fe_4**L**$_6$(BF_4)](BF_4)$_7$ HR-ESI-MS spectrum (top) showing +3 charge state and corresponding theoretical Isotope distribution (bottom).

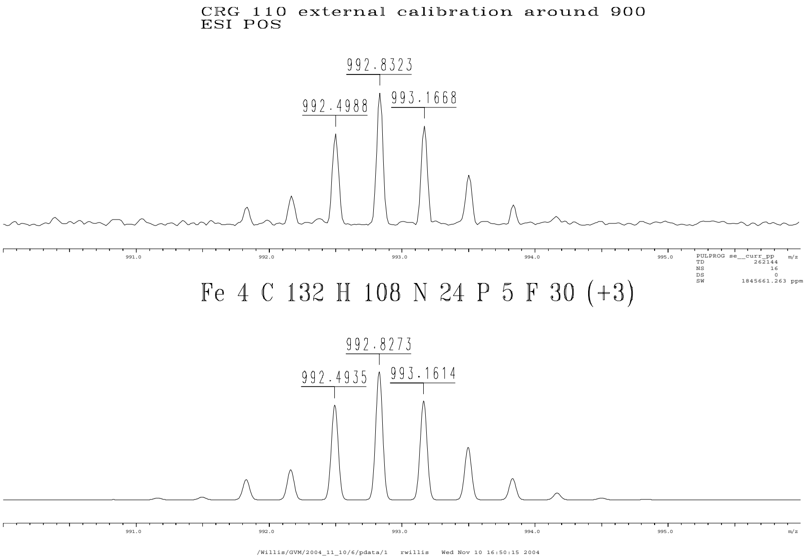


Figure S6. Portion of $[Fe_4L_6(PF_6)](PF_6)_7$ HR-ESI-MS spectrum (top) showing +3 charge state and corresponding theoretical Isotope distribution (bottom).

Section S5: X-ray structure data.

X-ray structural data for $[Fe_4L_6](BF_4)_8$·6THF·3MeCN·3.6H2O and $[Fe_4L_6][ZnCl_4]_4$MeCN·5.5THF·2.5H_2O were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å) with ω and ψ scans.[1] Data were collected at 150 K to approximately 56° 2θ. Data for $[Fe_4L_6](PF_6)_8$·9MeOH·6H_2O were collected using double diamond monochromated synchrotron radiation (0.48595 Å) with ω and ψ scans at the the ChemMatCARS beamline at the Advanced Photon Source at approximately 100 K. Data integration and reduction were undertaken with SAINT and XPREP[1] and subsequent computations were carried out using the WinGX-32 graphical user interface[2] The structures were solved by direct methods using SIR97.[3] Multi-scan empirical absorption corrections were applied to the data set using the program SADABS.[4] Data were refined and extended with SHELXL-97.[5] In general boron, carbon, nitrogen, oxygen and fluorine atoms with occupancies greater than 0.5, chlorine and phosphorus atoms with occupancies greater than or equal to 0.25 and iron and zinc atoms were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. The crystals employed in the study were unstable (due to rapid solvent loss) and in all cases rapid mounting (<1 min) at 200 K prior to quenching in the cryostream was required to enable data collection. Specific refinement details for each structure are given below.

$[Fe_4L_6](BF_4)_8$·6THF·3MeCN·3.6H_2O.

The crystal system is cubic with non-centrosymmetric space group symmetry $P\bar{4}3n$. The molecule lies around crystallographic 2-,3- and 4-fold axes. The asymmetric unit contains 1/12th of the complex cation, with the metal located on a three-fold axis and a two-fold axis bisecting each ligand. Encapsulated with in the complex cation, lying on the intersection of four three-fold axes and three two-fold axes, is a disordered BF_4^- anion (modelled with isotropic fluorines in two positions both on three-fold axes). The remaining charge is balanced by two BF_4^- anions, one of which is located on a four-fold special position (B(2)) and the other on a three-fold axis (B(1)). Also outside the cavity is a region of disordered solvent. The solvent site were modelled as comprising a THF molecule disordered over two positions with a total occupancy of 50 % occupancy, a 25 % occupancy acetonitrile molecule and three 10 % occupancy water molecules (the hydrogen atoms of which could not be located in the difference Fourier map and were not included in the model). Bond length restraints were applied to some atoms in the THF molecule to and one isotropic fluorine atom to facilitate realistic modelling. Isotropic fluorine atoms, atoms in the THF solvent and water molecules each were modelled with identical thermal parameters. Some bond length restraints were required to facilitate realistic modelling of the disordered solvent. The disorder solvent present and larger than ideal thermal parameters of some atoms are presumably due to solvent loss from the crystals during the mounting process. It was possible to determine reliably the absolute structure as indicated by the Flack parameter of -0.03(3).

Formula $C_{162}H_{172.2}B_8F_{32}Fe_4N_{27}O_{9.60}$, *M* 3569.47, cubic, space group $P\ \bar{4}_3n$(#218), *a* 22.0042(2), *b* 22.0042(2), *c* 22.0042(2) Å, *V* 10654.10(17) Å^3, D_c 1.113 g cm^{-3}, *Z* 2, crystal size 0.500 by 0.200 by 0.150 mm, colour red, habit prism, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.347 mm^{-1}, T(SADABS)$_{min,max}$ 0.800, 0.949, $2\theta_{max}$ 56.00, *hkl* range -29 28, -29 26, -29 26, *N* 81593, N_{ind} 4294(R_{merge} 0.0478), N_{obs} 3251(I > 2σ(I)), N_{var} 196, residuals* $R1(F)$ 0.0615, $wR2(F^2)$ 0.2027, GoF(all) 1.107, $\Delta\rho_{min,max}$ -0.598, 0.477 e$^-$ Å^{-3}.

$^*R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections
$w=1/[\sigma^2(F_o^2)+(0.1387P)^2+1.7003P]$ where $P=(F_o^2+2F_c^2)/3$

$[Fe_4L_6](PF_6)_8{\cdot}9MeOH{\cdot}6H_2O$

The material again crystallised in $P\bar{4}3n$ and is isostructural with complex A. The central anion containing P(1)) again is disordered and was modelled over two positions with the fluorine atoms located on three-fold axes (1/3rd and 1/6th occupancy). Large displacement parameters evident for the model atoms of the remaining anions are assumed to reflect unresolved disorder close to special positions. A number of constraints as well as bond length and rigid bond restraints were required to facilitate realistic modelling of the P(3) containing anion. Solvent atoms were modelled with a common isotropic displacement parameter. Disordered solvent regions were modelled with two methanol molecules, with one disordered over two sites of 50 % occupancy and the other at a second site of 25 % occupancy modelled overlapping with two disordered water molecules each having 25 % occupancy). The hydroxyl protons were modelled with a riding model and the water hydrogen atoms could not be located in the difference Fourier map and were not included in the model. Again the large thermal parameters and presence of disordered solvent is consistent with the observation of instability in the crystals during the mounting process.

It was possible to determine reliably the absolute structure as indicated by the refined Flack parameter of 0.09(5).

Formula $C_{141}H_{156}F_{48}Fe_4N_{24}O_{15}P_8$, *M* 3810.06, cubic, space group $P\ \bar{4}_3n$(#218), *a* 21.8735(2), *b* 21.8735(2), *c* 21.8735(2) Å, *V* 10465.38(17) Å^3, D_c 1.209 g cm^{-3}, *Z* 2, crystal size 0.080 by 0.070 by 0.060 mm, colour red, habit prism, temperature 100(2) Kelvin, λ(synchrotron) 0.48595 Å, μ(synchrotron) 0.227 mm^{-1}, T(SADABS)$_{min,max}$ 0.872, 0.986, $2\theta_{max}$ 34.96, *hkl* range -26 27, -27 26, -26 27, *N* 64646, N_{ind} 3459(R_{merge} 0.0541), N_{obs} 3095(I > 2σ(I)), N_{var} 194, residuals* $R1(F)$ 0.0601, $wR2(F^2)$ 0.1730, GoF(all) 1.136, $\Delta\rho_{min,max}$ -0.614, 0.593 e$^-$ Å^{-3}.

$^*R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections
$w=1/[\sigma^2(F_o^2)+(0.1107P)^2+4.6683P]$ where $P=(F_o^2+2F_c^2)/3$

$[Fe_4L_6][ZnCl_4]_4\cdot MeCN\cdot 5.5THF\cdot 2.5H_2O$

Crystals of this material rapidly lost solvent, and the diffraction quality was poor. Unlike the other complexes, this material crystallises in the monoclinic space group *P*2/n. Nevertheless each of the tetrahedra within the lattice is homochiral. The asymmetric unit consists of one half of the molecule such that there are two iron(II) centres and three ligands present with a the two-fold axis passing through the centre of the molecule. Adjacent molecules are generated via inversion symmetry and the crystal consists of a racemic mixture of the chiral molecules. Unlike the above structures, there is no anion present in the central cavity of the tetrahedron. Charge is balanced by a number of tetrachlorozincate anions. The Zn(1) containing anion is full occupancy and not disordered. The Zn(2) containing anion is 50 % occupancy and overlaps with 25 % occupancy Zn(4) containing anion and a number of disordered/low occupancy water molecules (modelled in four positions, the hydrogen ions of which could not be located in the difference Fourier map and were not included in the model). The remaining tetrachlorozincate anion (Zn(3)) was modelled with 25 % occupancy sites, with one of the chlorine atoms modelled over two positions with equal occupancy. Some bond length and ridged bond restraints and constraints were required to facilitate the realistic modelling of the disordered anions. The model also includes a 50 % occupancy THF molecule. Within the molecular cavity an acetonitrile molecule is disordered over two symmetry related locations. Attempts to model a significant region of residual electron density with solvate molecules were unsuccessful. The squeeze function of PLATON[6] was employed to remove the contribution of this electron density from the data. PLATON estimated the electron count associated with this region to be 373 per unit cell which corresponds to approximately nine tetrahydrofuran molecules per unit cell. Larger than ideal U_{eq} min/max ratios, some large thermal parameters and the presence of disordered anions and solvent is consistent with the observation of instability in the crystals during the mounting process.

Formula $C_{156}H_{160}Cl_{16}Fe_4N_{25}O_8Zn_4$, *M* 3565.17, monoclinic, space group *P*2/n(#13), *a* 17.7800(10), *b* 17.8806(10), *c* 31.0654(17) Å, β 94.113(4), *V* 9850.8(10) Å^3, D_c 1.202 g cm^{-3}, *Z* 2, crystal size 0.400 by 0.350 by 0.300 mm, colour red, habit prism, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 1.033 mm^{-1}, T(SADABS)$_{\mathrm{min,max}}$ 0.623, 0.734, $2\theta_{\mathrm{max}}$ 56.00, *hkl* range -23 23, -22 23, -41 41, *N* 152138, N_{ind} 23743(R_{merge} 0.0382), N_{obs} 15418(I > 2σ(I)), N_{var} 971, residuals* $R1(F)$ 0.0799, $wR2(F^2)$ 0.2685, GoF(all) 1.091, $\Delta\rho_{\mathrm{min,max}}$ -1.462, 1.185 e$^-$ Å^{-3}.

$^*R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections
$w=1/[\sigma^2(F_o^2)+(0.1787P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$

References

[1] Bruker-Nonius (2003). APEX v2.1, SAINT v.7 and XPREP v.6.14. Bruker AXS Inc. Madison, Wisconsin, USA.
[2] *WinGX-32: System of programs for solving, refining and analysing single crystal X-ray diffraction data for small molecules*, L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837.
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[5] G. M. Sheldrick, *SHELXL-97: Programs for Crystal Structure Analysis*, University of Göttingen, Germany, 1997.
[6] PLATON, A. L. Spek, *Acta Cryst.*, **1990**, *A46*, C-34.