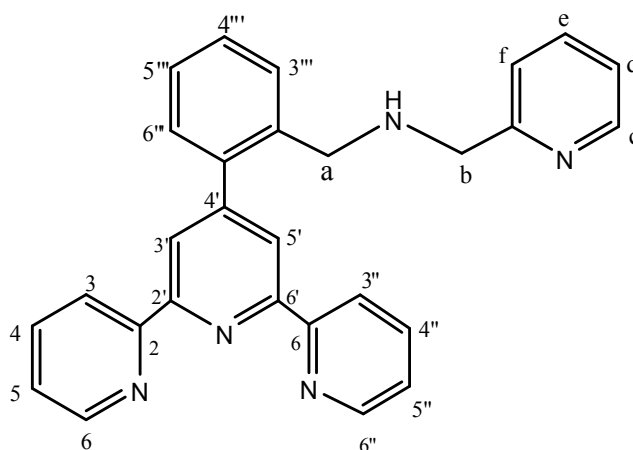


Supplementary Information

4'-[2'''-{2-(pyridylmethyl)amine}-N-methylphenyl]2,2':6,2''-terpyridine, L: In 30 ml of dry acetonitrile solution of **ottpbr** (3 g, 7.4 mmol) a solution of picolylamine (0.80 g, 7.4 mmol) in 30 mL of dry acetonitrile was added, while stirring. An equivalent of K_2CO_3 (0.74 g, 7.4 mmol) was also added. The resulting mixture was heated to 60-65°C for 3 days, filtered and the filtrate was taken up to dryness under vacuum. The residual oil was a mixture of required ligand and unreacted picolylamine. Purification by



column chromatography (Alumina, 1-2% CH_3OH in DCM) afforded orange oil as the ligand L. Yield 1.9 g, 63%. M.P. 185 – 187°C. 1H NMR (500 MHz, $CDCl_3$): δ = 8.68 (d, $J=8$, 2H, 3,3''), 8.65 (d, $J=4$, 2H, 6,6''), 8.54 (s, 2H, 3', 5'), 8.34 (d, $J=5$, 1H, c), 7.86 (td, 2H, 4, 4''), 7.65 (d, $J=8$, 1H, 3'''), 7.42-7.38 (m, 4H, 5''', 6''', 4''', e), 7.34 (td, 2H, 5, 5''), 7.23 (d, $J=8$, 1H, f), 6.98 (t, $J=5$, 1H, d), 3.85 (d, 4H, a, b). ^{13}C NMR (500MHz) 158.3 (C2'''), 156.1 (2C, 2, 2''), 155.3 (2C, 2', 6'), 150.9 (4'), 149.2 (2C, 6, 6''), 149.0 (6'''), 139.9 (1'''), 136.8 (2C, 4, 4''), 136.3 (c), 135.9 (g), 129.9-129.8 (2C, f, 4'''), 128.7 (d), 127.5 (e), 123.8 (2C, 5, 5''), 122.3 (3'''), 121.9 (5'''), 121.6 (2C, 3', 5'), 121.3 (2C, 3', 3''), 53.9 (b), 50.5 (a). MS(EI) m/z : 430.2026 ($[M+H^+]$), 215.6051 ($[M+2H^{2+}]$), 859.3961 ($[2M+H^+]$). Anal. Calcd. $C_{28}H_{23}N_5$ (429.20): C 78.3, H 5.4, N 16.3; Found C 78.0, H 4.6, N 15.6, Br 3.9. IR (KBr, cm^{-1}) 3140 m, 3055 m, 2925 m, 2854 m, 1585 s, 1567 ssh, 1541 msh, 1466 s, 1393 w, 1335 m, 1264 m, 1131 w, 992 m, 907 w, 851 m, 762 s, 652 w, 627 m, 508 w, 467 w.

$[Ni_{10}(L)_{10}Br_4(H_2O)_6]Br_{16} \cdot 68H_2O$: A 10 ml of aqueous solution of $NiBr_2 \cdot 3H_2O$ (0.008 g, 0.029 mmol) was added to L (0.006 g, 0.014 mmol) in methanol, heated to reflux for $\frac{1}{2}$ h. The pale green of the complex reduced to 1 ml under vacuum. Pale green crystals were produced due to evaporation of the solvent. Yield 0.009 g. IR (KBr, cm^{-1}) 3645 w, 3190 s, 1605 s, 1550 w, 1470 m, 1417 w, 1302 w, 1247 m, 1162 w, 1055 w, 1016 s, 890 w, 772 s, 645 w, 598 w, 548 w, 516 w, 499 w, 481 w, 465 w. Anal. Calc. for

$C_{280}H_{230}N_{50}Ni_{10}Br_{20} \cdot 68H_2O$ (7705.196): C 43.65, H 4.79, N 9.09%; found: C 43.91, H 4.86, N 9.18.

$[Ni_{10}(L)_{10}Cl_4(H_2O)_6]Cl_{16} \cdot 88H_2O$: A methanolic solution of L (0.006 g, 0.014 mmol) was mixed with 10 ml aqueous solution of $NiCl_2 \cdot 6H_2O$ (0.003 g, 0.014 mmol). To the resulting mixture an excess of NaCl in water was added and heated to reflux for 1 h, then reduced to 1 ml by rotary evaporation. Within a period of 3 weeks rectangular blocks of pale green crystals were formed. Yield 0.004 g. IR (KBr, cm^{-1}) 3628 w, 3199 s, 3050 w, 1604 s, 1550 w, 1460 s, 1416 m, 1300 w, 1245 m, 1162 w, 1053 w, 1017 s, 891 w, 795 w, 770 s, 739 msh, 645 w, 598 w, 548 w, 516 w, 499 w, 465 w. Anal. Calc. for $C_{280}H_{230}N_{50}Ni_{10}Cl_{20} \cdot 88H_2O$ (7155.61): C 46.86, H 5.71, N 9.76%; found: C 47.16, H 5.83, N 9.97%.

$[Zn_4(L)_4(CH_3COO)_2](PF_6)_6 \cdot 2CH_3CN$: A methanolic solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.01 g, 0.046 mmol) mixed with a methanolic solution of L (0.010 g, 0.023 mmol) resulting in a pale yellow solution. The solution was then treated with a concentrated methanolic solution of ammonium hexafluoridophosphate. Later addition of an excess of cold water resulted in formation of the white precipitates. The precipitates were collected by centrifugation, and washed with methanol and ether. An undisturbed slow diffusion of di-isopropyl ether into acetonitrile solution of the white precipitates produced colourless blocks of x-ray quality crystals within two days. Yield 0.012 g, 63%. M.P. 248 °C. UV-vis (CH_3CN): λ_{max} (ϵ) = 275 (111208), 287 (96801), 322 (63446), 561 (668) nm ($L \text{ mol}^{-1} \text{ cm}^{-1}$). IR (KBr, cm^{-1}) 3675 w, 3340 s, 2542 w, 1866 w, 1603 s, 1575 w, 1549 w, 1478 s, 1419 w, 1371 w, 1325 w, 1248 m, 794 s, 764 w, 739 w, 658 w, 559 s, 469 w. Anal. Calc. for $C_{116}H_{98}N_{20}Zn_4O_4P_6F_{36} \cdot 2H_2O$ (2296.33): C 46.40, H 3.43, N 9.34%; found: C 46.17, H 3.34, N 9.37%.

$[Fe_2Zn_2(L)_4Cl_2](PF_6)_6 \cdot 4H_2O$: $FeCl_2 \cdot 2H_2O$ (0.05 g, 0.025 mmol) in methanol was added to a solution of L (0.02 g, 0.05 mmol) in methanol to give a soluble purple solution, immediately. The resulting purple complex solution was treated with an excess of methanolic $ZnCl_2 \cdot 2H_2O$. The mixture was heated for 1h while stirring and then cooled to room temperature, followed by addition of few drops of concentrated methanolic solution of ammonium hexafluoridophosphate. An excess of cold water was also added to enhance the precipitation of complex. The complex was collected by centrifugation from the aqueous solution, washed with ether: methanol (2:1) solution, dried under N_2 stream. The x-ray quality single crystals as purple fragile plates were collected by slow evaporation of acetonitrile solution of the complex. Yield 0.056 g, 60%. M.P. > 280 °C. UV-vis (CH_3CN): λ_{max} (ϵ) = 275 (88851), 287

(95819), 322 (73242), 561 (28724), nm (L mol⁻¹ cm⁻¹). Anal. Calc. for C₁₁₂H₉₂N₂₀Zn₄Br₂P₆F₃₆·4H₂O (2968.27): C 45.27, H 3.39, N 9.43%; found: C 45.49, H 3.40, N 9.40%. IR (KBr, cm⁻¹) 3340 s, 2368 w, 1844 w, 1611 m, 1535 w, 1468 w, 1368 w, 1040 w, 794 s, 626 w, 558 m, 497 w, 458 w.

[Fe₂Zn₂(L)₄C₈H₄O₄](PF₆)₄(NO₃)₂: To a methanolic solution of L (30 mg, 0.070 mM) methanolic (NH₄)₂Fe(SO₄)₂·6H₂O (9 mg, 0.035 mM) was added to produce a soluble purple solution, immediately. A solution of an excess of sodium terephthalate in methanol was added. After stirring for 30 mins, a methanolic solution of Zn(NO₃)₂·6H₂O (20 mg, 0.070 mM) was added. The mixture was heated at reflux for 8 hrs and then cooled to room temperature, followed by addition of few drops of concentrated methanolic solution of ammonium hexafluoridophosphate. An excess of cold water was also added to enhance the precipitation of the complex. The precipitate was collected by centrifugation from the aqueous solution, washed with ether:methanol (2:1) solution, dried under N₂ stream. The x-ray quality single crystals as purple square shaped plates were collected by slow diffusion of ethyl acetate into acetonitrile solution of the complex over a period of 3 weeks. Yield 0.056 g, 60%. M.P. > 280 °C. UV-vis (CH₃CN): λ_{max} (ε) = 275 (88300), 287 (94830), 322 (71800), 561 (24720) nm (L mol⁻¹ cm⁻¹). IR (KBr, cm⁻¹) 3340 s, 2368 w, 1844 w, 1698 w, 1557 s, 1551 m, 1504 w, 1381 w, 1020 w, 823 s, 789 s, 653 w, 556 m, 447 w. Anal. Calc. for C₁₁₂H₉₂N₂₀Fe₂Zn₂C₈H₄O₄P₆F₃₆·3H₂O (%): C 47.28, H 3.37, N 9.19; found (%): C 47.42, H 3.72, N 8.89.

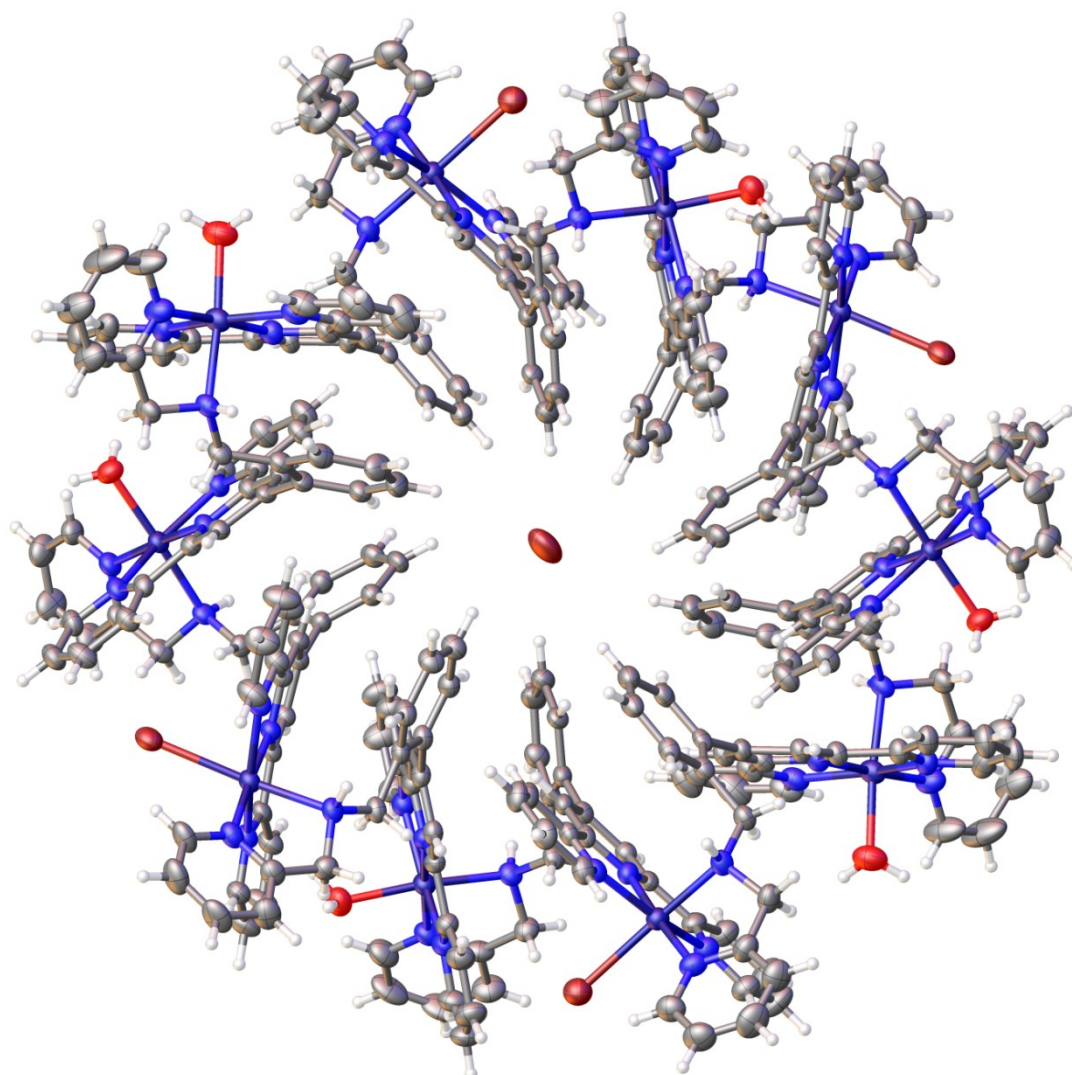


Figure S1: Molecular structure for $[\text{Ni}_{10}(\text{L})_{10}\text{Br}_4(\text{H}_2\text{O})_6](\text{Br})_{16}\cdot 130\text{H}_2\text{O}$. The water molecules and the uncoordinated bromide ions omitted for clarity.

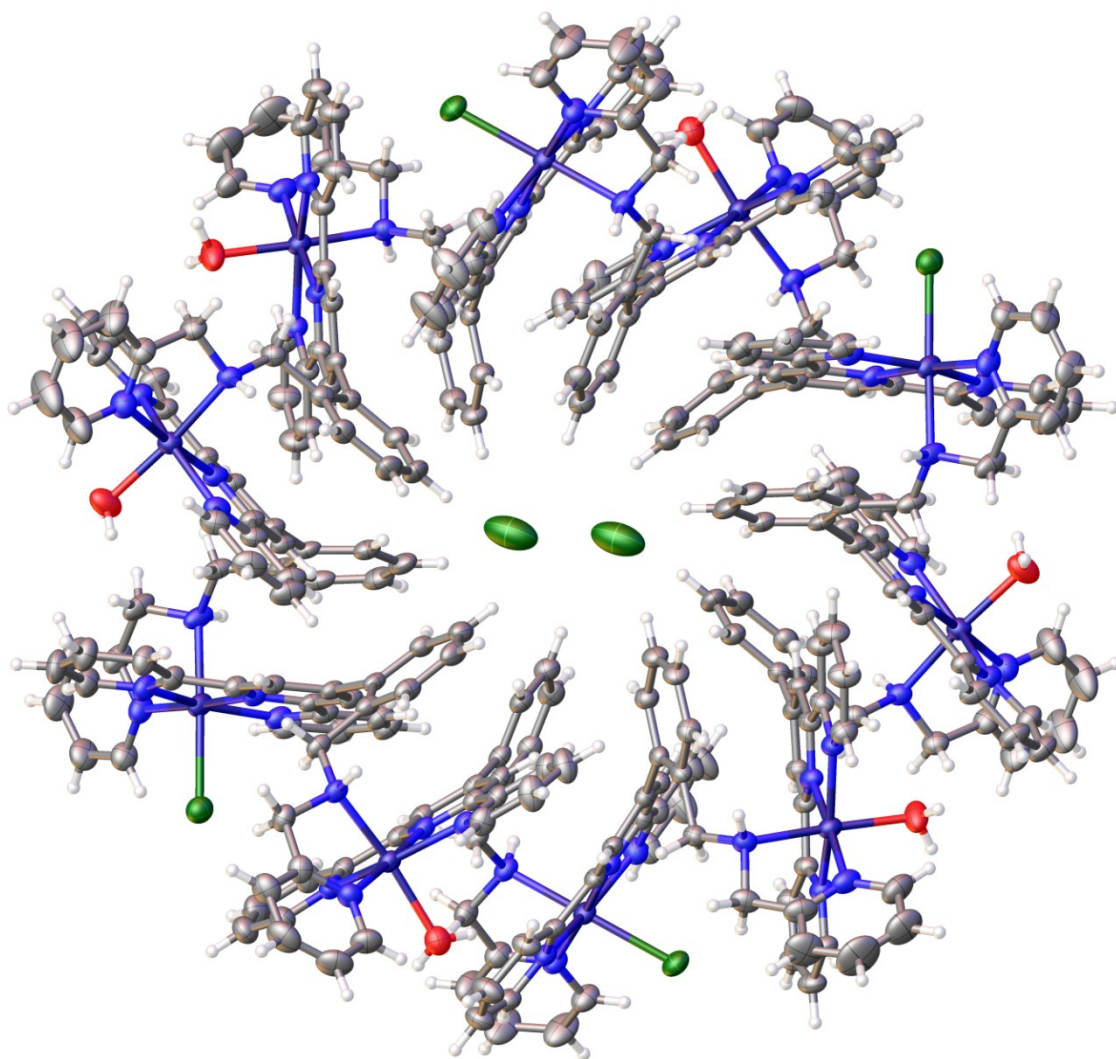


Figure S2: oblique view of molecular structure for $[\text{Ni}_{10}(\text{L})_{10}\text{Cl}_4(\text{H}_2\text{O})_6](\text{Cl})_{16}\cdot 130\text{H}_2\text{O}$. The water molecules and the uncoordinated chloride ions omitted for clarity.

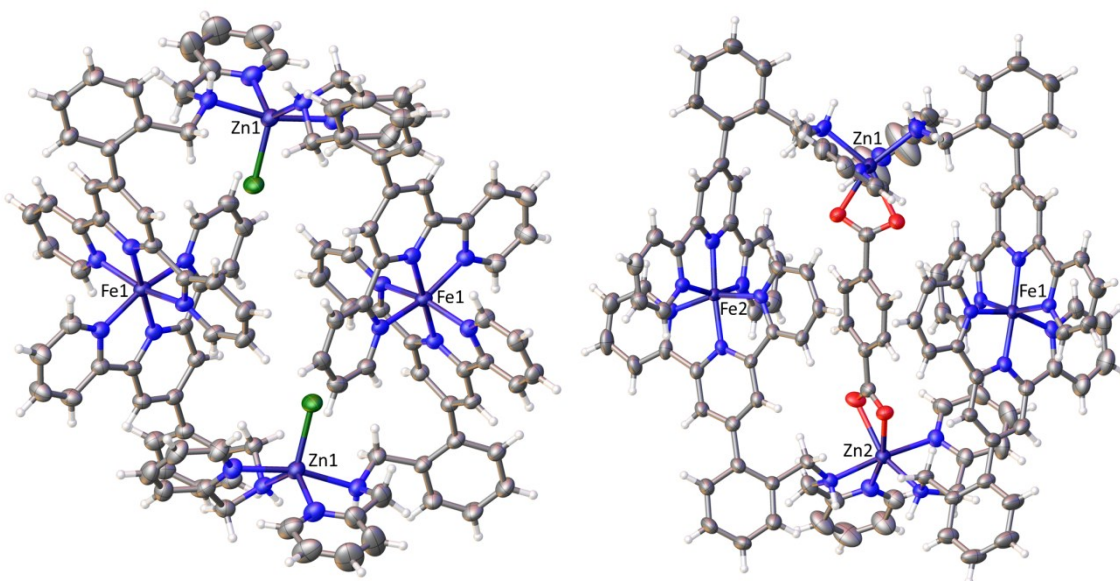
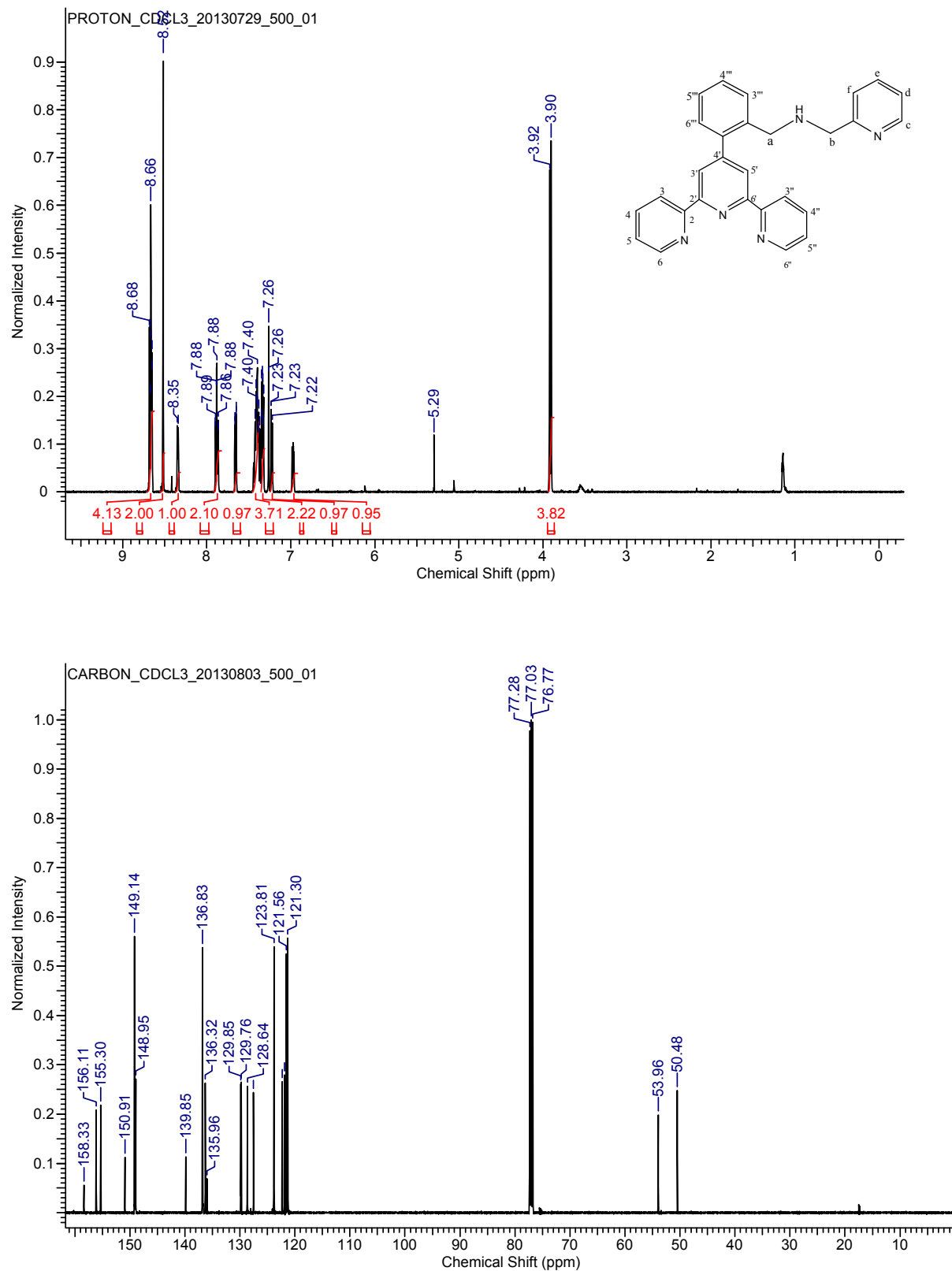


Figure S3: A side by side view of X-ray crystal structures of $[\text{Fe}_2\text{Zn}_2(\text{L})_4\text{Cl}_2]6\text{PF}_6 \cdot 4\text{H}_2\text{O}$ and $[\text{Fe}_2\text{Zn}_2(\text{L})_4\text{C}_8\text{H}_4\text{O}_4](\text{NO}_3)_2(\text{PF}_6)_4$. The PF_6 and NO_3 ions and H_2O molecules have been omitted for clarity.



Crystallography

Table 1 Crystal data and structure refinement.

Identification code	[Fe ₂ Zn ₂ (L) ₄ (tpt)] ⁶⁺	[Ni ₁₀ L ₁₀ Cl ₄ (H ₂ O) ₆] ¹⁶⁺	[Ni ₁₀ L ₁₀ Br ₄ (H ₂ O) ₆] ¹⁶⁺
Empirical formula	C ₁₂₂ H ₉₉ F ₃₀ Fe ₂ N ₂₂ O ₇ P ₅ Zn ₂	C ₂₈₀ H ₂₄₅ Cl ₂₀ N ₅₀ Ni ₁₀ O ₅₂	C ₂₈₀ H ₂₄₆ Br ₂₀ N ₅₀ Ni ₁₀ O ₅₄
Formula weight	2952.52	6428.54	7358.75
Temperature/K	120.00(10)	120.02(10)	120.00(10)
Crystal system	monoclinic	triclinic	triclinic
Space group	P2 ₁ /n	P-1	P-1
a/Å	20.9518(10)	16.7862(2)	16.9013(4)
b/Å	19.8601(6)	24.9108(4)	25.0753(7)
c/Å	36.0894(12)	26.1281(5)	26.0861(7)
α/°	90	64.9465(18)	65.062(3)
β/°	101.626(4)	85.1949(14)	85.547(2)
γ/°	90	81.8728(13)	82.033(2)
Volume/Å ³	14708.9(10)	9794.8(3)	9925.6(5)
Z	4	1	1
ρ _{calc} /mg/mm ³	1.333	1.090	1.231
m/mm ⁻¹	3.260	2.267	3.365
F(000)	5992.0	3306.0	3687.0
Crystal size/mm ³	0.1981 × 0.1494 × 0.0135	0.3677 × 0.211 × 0.1418	0.3128 × 0.1667 × 0.0883
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection	5.398 to 148.856°	6.24 to 147.732°	5.28 to 147°
Index ranges	-26 ≤ h ≤ 25, -24 ≤ k ≤ 22, -29 ≤ l ≤ 44	-20 ≤ h ≤ 19, -31 ≤ k ≤ 31, -32 ≤ l ≤ 32	-15 ≤ h ≤ 20, -31 ≤ k ≤ 29, -32 ≤ l ≤ 30
Reflections collected	62630	111735	89188
Independent reflections	28900 [R _{int} = 0.0582, R _{sigma} = 0.0798]	38593 [R _{int} = 0.0367, R _{sigma} = 0.0401]	38714 [R _{int} = 0.0378, R _{sigma} = 0.0396]
Data/restraints/ parameters	28900/4/1712	38593/0/1800	38714/0/1828
Goodness-of-fit on F ²	0.993	1.092	1.366
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0707, wR ₂ = 0.1861	R ₁ = 0.0801, wR ₂ = 0.2399	R ₁ = 0.1000, wR ₂ = 0.3087
Final R indexes [all data]	R ₁ = 0.1124, wR ₂ = 0.2075	R ₁ = 0.0928, wR ₂ = 0.2548	R ₁ = 0.1149, wR ₂ = 0.3323
Largest diff. peak/hole / e Å ⁻³	0.80/-0.99	3.48/-0.79	5.59/-2.16

Identification code	[Fe ₂ Zn ₂ (L) ₄ Cl ₂] ⁶⁺	[Zn ₄ (L) ₄ (Ac) ₂] ⁶⁺
Empirical formula	C ₅₈ H ₅₀ ClF ₁₈ FeN ₁₀ O ₂ P ₃ Zn	C ₆₀ H ₅₂ F ₁₈ N ₁₁ O ₂ P ₃ Zn ₂

Formula weight	3021.31	1524.77
Temperature/K	120.00(10)	120.01(10)
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a/Å	12.8625(5)	35.189(2)
b/Å	14.2811(7)	14.8680(6)
c/Å	18.9563(9)	26.4641(16)
α /°	76.066(4)	90
β /°	83.142(4)	109.638(7)
γ /°	82.373(4)	90
Volume/Å ³	3335.9(3)	13040.6(14)
Z	1	8
ρ_{calc} /mg/mm ³	1.504	1.553
m/mm ⁻¹	4.120	2.523
F(000)	1528.0	6176.0
Crystal size/mm ³	0.1988 × 0.0519 × 0.0309	0.05 × 0.03 × 0.01
Radiation	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
2 θ range for data collection	6.414 to 147.964°	5.332 to 130.992
Index ranges	-12 ≤ h ≤ 15, -16 ≤ k ≤ 17, -23 ≤ l ≤ 23	-43 ≤ h ≤ 31, -9 ≤ k ≤ 17, -30 ≤ l ≤ 32
Reflections collected	33745	25940
Independent reflections	13087 [R _{int} = 0.0417, R _{sigma} = 0.0504]	11241 [R _{int} = 0.0882, R _{sigma} = 0.1372]
Data/restraints/ parameters	13087/8/933	11241/0/867
Goodness-of-fit on F ²	1.030	1.097
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0536, wR ₂ = 0.1394	R ₁ = 0.0702, wR ₂ = 0.1821
Final R indexes [all data]	R ₁ = 0.0788, wR ₂ = 0.1595	R ₁ = 0.1272, wR ₂ = 0.2280
Largest diff. peak/hole / e Å ⁻³	0.70/-0.56	0.86/-0.89

Refinement special details

The $[\text{Fe}_2\text{Zn}_2\text{L}_4(\text{tpt})]^{6+}$ $[\text{Ni}_{10}\text{L}_{10}\text{Br}_4(\text{H}_2\text{O})_6]^+$ and $[\text{Ni}_{10}\text{L}_{10}\text{Cl}_4(\text{H}_2\text{O})_6]$ structures contained significant amounts of disordered solvent molecules. This was handled systematically for the two wheel structures. First, a phase solution was found and the structure of interest was determined and refined anisotropically for all non-hydrogen atoms. Hydrogen atoms were calculated as riding atoms with thermal parameters dependant on the riding atom for all carbon atoms. For all non-carbon atoms with hydrogens except for solvent molecules, the hydrogens were located in the electron difference map, and allowed to refine at a fixed distance from the heteroatom, with a thermal parameter dependant on the riding atom. Solvent water atoms and counterions were inserted into the model as isolated, isotropic atoms where there was sufficient electron density, sufficiently distant from other solvent waters/counterions, and their occupancies were allowed to refine. This used about 60 water molecules of some occupancy in the asymmetric unit of $[\text{Ni}_{10}\text{L}_{10}\text{Br}_4(\text{H}_2\text{O})_6]^{16+}$ and $[\text{Ni}_{10}\text{L}_{10}\text{Cl}_4(\text{H}_2\text{O})_6]^{16+}$. Estimates of these numbers were included in the formula used for the final absorption correction, but not in the final atom count. Counterions were distinguished from solvent waters by the electron density, and were refined anisotropically. No attempt was made to model co-occupancy of a partial counterion with a solvent water. Once a stable refinement had been achieved, water molecules with an occupancy of less than one were deleted from the model and the OLEX2 solvent mask was used to correct for these poorly refined water molecules and the additional, highly disordered regions occupied by solvent water which had not been modelled. The remaining water molecules were refined as isotropic oxygen atoms, without hydrogens, due to the lack of electron density to indicate the position of the hydrogen atoms for most of the solvent waters. The total number of waters from the model and electrons corrected for in the mask (180 waters) approximately agrees with the results from TGA experiments (>160 waters)

$[\text{Fe}_2\text{Zn}_2\text{L}_4(\text{tpt})]^{6+}$ was solved and refined with the complex of interest, four well-ordered PF_6 anions and one acetonitrile solvent molecule in the asymmetric unit as above. The final PF_6 anion and a single nitrate anion were poorly ordered, with the PF_6 anion being rotationally disordered about the phosphorous atom, occupying at least two closely spaced sites. The nitrate anion is involved in hydrogen bonding to the nitrogen atoms coordinated to the zinc atoms, and is disordered over two sites. This was modelled as disordered over two equal occupancy sites, with isotropic thermal parameters fixed at the value of the central phosphorous atom. The OLEX2 solvent mask was used to correct for the remaining unidentified solvent molecules as above. $[\text{Fe}_2\text{Zn}_2\text{L}_4\text{Cl}_2]^{6+}$ was solved and refined with the complex of interest, three independent PF_6 anions, two half occupancy water molecules and two partial occupancy ethyl acetate molecules (0.2 and 0.3 occupancy) in the asymmetric unit. No mask was required for this structure.

Voids

$[\text{Fe}_2\text{Zn}_2\text{L}_4(\text{tpt})]^{6+}$ Volume = 3397.7 Å³, electrons = 1182.1 e

$[\text{Ni}_{10}\text{L}_{10}\text{Br}_4(\text{H}_2\text{O})_6]^{16+}$ total for three voids; Volume = 2274.8 Å³, electrons = 585.5 e

$[\text{Ni}_{10}\text{L}_{10}\text{Cl}_4(\text{H}_2\text{O})_6]^{16+}$; Volume = 2695.3 Å³, electrons = 587.7 e

Experimental

Single crystals were mounted in perfluorinated oil on a nylon loop. A suitable crystal was selected and data were collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 120.0(1) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation. A solvent mask [4] was applied for the relevant structures using Olex2 [1]

[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.

[2] Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.

[3] Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.

[4] Rees, B., Jenner, L., and Yusupov, M. (2005), *Acta Cryst. D*, 61(9), 1299-1301

Crystal structure determination of [GKA26A][Fe₂Zn₂L₄Cl₂]⁶⁺

Crystal Data for C₅₈H₅₀ClF₁₈FeN₁₀O₂P₃Zn (M = 1510.66): triclinic, space group P-1 (no. 2), a = 12.863 Å, b = 14.281 Å, c = 18.956 Å, α = 76.07°, β = 83.14°, γ = 82.37°, V = 3335.9 Å³, Z = 2, T = 293(2) K, μ(CuKα) = 4.120 mm⁻¹, D_{calc} = 1.504 g/mm³, 33745 reflections measured (6.414 ≤ 2θ ≤ 147.964), 13091 unique (R_{int} = 0.0418, R_{sigma} = 0.0504) which were used in all calculations. The final R1 was 0.0536 (I > 2σ(I)) and wR2 was 0.1609 (all data).

Crystal structure determination of [GKA116A][Fe₂Zn₂L₄(tpt)]⁶⁺

Crystal Data for C₁₂₂H₉₉F₂₄Fe₂N₂₂O₇P₄Zn₂ (M = 2807.55): monoclinic, space group P21/n (no. 14), a = 20.9518(10) Å, b = 19.8601(6) Å, c = 36.0894(12) Å, β = 101.626(4)°, V = 14708.9(10) Å³, Z = 4, T = 173.35(10) K, μ(CuKα) = 3.073 mm⁻¹, D_{calc} = 1.268 g/mm³, 62630 reflections measured (5.398 ≤ 2θ ≤ 148.856), 28897 unique (R_{int} = 0.0582, R_{sigma} = 0.0798) which were used in all calculations. The final R1 was 0.0604 (I > 2σ(I)) and wR2 was 0.1701 (all data).

Crystal structure determination of [GKA39a][Ni₁₀L₁₀Br₄(H₂O)₆]¹⁶⁺

Crystal Data for C₂₈₀H_{245.8}Br₂₀N₅₀Ni₁₀O_{53.9} (M = 7358.75): triclinic, space group P-1 (no. 2), a = 16.9013(4) Å, b = 25.0753(7) Å, c = 26.0861(7) Å, α = 65.062(3)°, β = 85.547(2)°, γ = 82.033(2)°, V = 9925.6(5) Å³, Z = 1, T = 286.13(10) K, μ(CuKα) = 3.365 mm⁻¹, D_{calc} = 1.231 g/mm³, 89188 reflections measured (5.28 ≤ 2θ ≤ 147), 38714 unique (R_{int} = 0.0378, R_{sigma} = 0.0396) which were used in all calculations. The final R1 was 0.1000 (I > 2σ(I)) and wR2 was 0.3323 (all data).

Crystal structure determination of [GKA57a][Ni₁₀L₁₀Cl₄(H₂O)₆]¹⁶⁺

Crystal Data for C₂₈₀H_{244.8}Cl₂₀N₅₀Ni₁₀O_{51.4} (M = 6428.54): triclinic, space group P-1 (no. 2), a = 16.7862(2) Å, b = 24.9108(4) Å, c = 26.1281(5) Å, α = 64.9465(18)°, β = 85.1949(14)°, γ = 81.8728(13)°, V = 9794.8(3) Å³, Z = 1, T = 120.02(10) K, μ(CuKα) = 2.267 mm⁻¹, D_{calc} = 1.090 g/mm³, 111735 reflections measured (6.24 ≤

$2\Theta \leq 147.732$), 38593 unique ($R_{\text{int}} = 0.0367$, $R_{\text{sigma}} = 0.0401$) which were used in all calculations. The final R1 was 0.0801 ($I > 2\sigma(I)$) and wR2 was 0.2548 (all data).