Supporting information for:

**Supramolecular Chemistry of Metallogrids via Directed Hydrogen-bonding**

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Experimental

Reagents and solvents

Reagents (imidazole aldehydes and metal salts) obtained from Aldrich, Merck, Lancaster, Fluka, Acros or Alfa Aesar were used directly without further purification unless otherwise noted. DMSO solvates of various metal triflates were available from earlier work. 4,6-dihydrazino-2-phenylpyrimidine\(^7\) and 4,6-di(N-methylhydrazino)-2-phenylpyrimidine\(^8\) were prepared following literature methods.

Water was purified using a Millipore Elix 10 (reverse osmosis) system. Anhydrous DMSO, nitromethane, acetonitrile and absolute EtOH were purchased from Aldrich, and technical DCM (Aldrich) was bought with amylene as stabilizer. Diethyl ether and distilled DCM were dried by passage through a column of activated alumina and copper oxide under nitrogen. CDCl\(_3\) was filtered through basic alumina to remove traces of acid.

Instrumentation

\(^1\)H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz. Chemical shifts are given in ppm. The residual solvent proton peak was used as reference for calibration (CDCl\(_3\): 7.26 ppm, \([\text{D}_6]\)DMSO: 2.50 ppm, CD\(_3\)CN: 1.94 ppm, CD\(_3\)NO\(_2\): 4.33 ppm).\(^{23}\) The coupling constants J are given in Hz. Peaks are described as singlet (s), doublet (d), triplet (t), quartet (qt), quintuplet (quin), sextet (sxt), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet of doublets (td), multiplet (m) or broad (br). \(^{13}\)C NMR spectra were recorded on a Bruker Advance 400 spectrometer at 100 MHz. All spectra were measured under broadband decoupled conditions. Chemical shifts are given in ppm. The residual solvent peaks were taken as reference (CDCl\(_3\): 77.0 ppm, \([\text{D}_6]\)DMSO: 39.43).\(^{23}\) 2D NMR (COSY, NOESY) spectra were also recorded on a Bruker Avance 400 spectrometer. Unless otherwise noted, all spectra were recorded at 25°C.

LC/MS was performed using reverse phase HPLC (C\(_{18}\) solid phase, 5 \(\mu\)m particle size, 2.1 x 5 mm column, eluent: H\(_2\)O with 0.01% TFA→CH\(_3\)CN with 0.01% TFA, 0.7 mL/min flow, diode array detector) combined with a Thermo MSQ quadrupole electrospray mass spectrometer using the positive ion detection mode. The given value represents the largest peak. High Resolution Mass Spectrometry (HR-MS) analyses were performed on a Bruker Micro TOF mass spectrometer at the Service de Spectrométrie de Masse, Université de
MALDI-TOF analyses using a matrix incorporating Li(I) were performed on a Bruker AutoFlex II mass spectrometer at the Service de Spectrométrie de Masse, Université de Strasbourg. For the grid complexes, the concentration was adjusted to be approximately $5 \times 10^{-3}$ mol/L in acetonitrile solution.

Elemental analyses were obtained either from the “Service d’Analyses du CNRS” (Lyon) or from the Service de Microanalyse, Université de Strasbourg.

Magnetic measurements were performed by using a Quantum Design MPMS-XL SQUID magnetometer at the Institut de Physique et Chimie des Matériaux de Strasbourg. Susceptibility measurements were performed in the range 300-1.8 K with an applied field of 0.5 T. The temperature sweep rate was 5 K min$^{-1}$. Magnetization measurements at different fields at a given temperature were used to test for the presence of ferromagnetic impurities, although no significant levels were detected. Data were corrected for the diamagnetism of the sample holder and the ligands (as estimated from Pascal’s constants).

**Crystallography**

Single crystal, X-ray diffraction structure determinations for the ligands $L_2$, $L_4$ and $L_5$ and the complexes $[\text{Fe}_4(L_2)_4](\text{BF}_4)_8 \cdot 12\text{CH}_3\text{CN} \cdot 3.5\text{H}_2\text{O}$ and $[\text{Co}_4(L_5)_4](\text{CF}_3\text{SO}_3)_8 \cdot 6\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$ were performed by Dr Lydia Brelot at the Service de Radiocrystallographie, Université de Strasbourg, although all the structure solutions were ultimately refined at the University of Western Australia (Dr Alex Sobolev) or at ISIS, Strasbourg (Dr Augustin Madalan). The crystals were placed in oil and a single crystal was selected, mounted on a glass fibre and placed in a low-temperature nitrogen stream. The X-ray diffraction data were collected on a Nonius-Kappa-CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å), using a “phi-scan” type scan mode. Structures of the complexes $[\text{Zn}_4(L_2)_4](\text{ClO}_4)_8 \cdot 3.5\text{CH}_3\text{CN} \cdot 4\text{H}_2\text{O}$ and $[\text{Co}_4(L_2)_4]\text{Cl}(\text{PF}_6)_7 \cdot 4\text{CH}_3\text{CN}$ were determined at the University of Jyväskylä. Procedures were identical with those of Strasbourg except in that the diffraction data was collected on a Bruker-Nonius Kappa Apex-II diffractometer. Collect software$^{25}$ was used for the data measurement and DENZO-SMN$^{26}$ for the processing. The structures were solved by direct methods using the program SHELXS-97.$^{27}$ The refinement and all further calculations were carried out using SHELXL-97.$^{28}$ Full crystallographic data have been deposited with the Cambridge Crystallographic Data Base under CCDC 826148 – 826154.
**Synthesis**

### L1

![Structure of L1](image)

To a stirred solution of 4,6-dihydrazino-2-phenylpyrimidine (325.29 mg, 1.50 mmol) in EtOH (40 ml), 4(5)-imidazolecarboxaldehyde (288.94 mg, 3 mmol) was added. The clear mixture was stirred at reflux under nitrogen for 24 h. The white precipitate formed was collected by filtration, washed with EtOH and dried under high vacuum. Yield: 322 mg (0.86 mmol, 58%). $^1$H NMR ([D$_6$]DMSO, 400 MHz): $\delta$(ppm) = 6.85 (s, 2H, H$_6$), 7.33 (s, 2H, H$_1$), 7.49 (m, 3H, H$_{10}$ and H$_{11}$), 7.67 (s, 2H, H$_4$), 8.08 (s, 2H, H$_2$), 8.30 (m, 2H, H$_9$), 12.77 (s, 2H, NH$_{imid}$), 12.83 (s, 2H, NH$_{hydraz}$). $^{13}$C NMR ([D$_6$]DMSO, 100 MHz): 79.10, 120.05, 127.43, 128.13, 130.01, 130.52, 136.06, 136.16, 137.65, 162.28, 162.45. HR-MS (ES): calcd for C$_{18}$H$_{17}$N$_{10}$: $m$/z = 373.1632, found $m$/z = 373.1684 [M+H]$^+$. Microanalysis: calcd (%) for C$_{18}$H$_{16}$N$_{10}$·1H$_2$O: C 55.38, H 4.65, N 35.88; found C 55.20, H 4.64, N 37.49.

### N-C$_{16}$H$_{33}$L1

![Structure of N-C$_{16}$H$_{33}$L1](image)

Under a nitrogen atmosphere, 4(5)-imidazolecarboxaldehyde (123 mg, 1.22 mmol) was added to a suspension of NaH (60 % dispersion in mineral oil; 66.4 mg, 1.65 mmol) in dry, ice-cooled THF (12 mL). The mixture was then heated at reflux for 2 h before being cooled to room temperature and mixed with iodoheptadecane (3.99 mL, 12.7 mmol). Heating at reflux was resumed for 16 h and the cooled final mixture cooled before being filtered and diluted with water (50 mL). The resulting mixture was extracted with EtOAc (3x50 mL) and the combined extracts were washed with brine, dried over Na$_2$SO$_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (EtOAc/n-heptane = 6:4) to give the
product as a white solid. Yield: 150 mg (0.49 mmol, 39%). $^1$H NMR (CDCl$_3$, 400 MHz): $^\text{TM}(\text{ppm}) = 0.86$ (t, $J = 6.8$ Hz, 3H, H$_{\text{hexadecyl}}$), 1.24 (m, 26H, H$_{\text{hexadecyl}}$), 1.80 (quin, $J = 7.2$ Hz, 2H, H$_{\text{hexadecyl}}$), 3.97 (t, $J = 6.8$ Hz, 2H, H$_{\text{hexadecyl}}$), 7.53 (s, 1H, H$_2$ or H$_3$), 7.61 (d, $J = 1.2$ Hz, 1H, H$_2$ or H$_3$), 9.86 (s, 1H, H$_6$). $^{13}$C NMR (CDCl$_3$, 100 MHz): $^\text{TM} = 14.03, 22.60, 26.36, 28.90, 29.28, 29.40, 29.49, 29.54, 29.58, 30.75, 31.84, 47.67, 124.12, 138.59, 142.40, 186.19. HR-MS (ES): calcd for C$_{20}$H$_{36}$N$_2$Li$_1$O$_1$: $m/z$ = 327.2983, found $m/z$ = 327.2962 [$\text{M}+$Li]$^+$. 

$L2$

![Chemical structure of compound L2](image)

To a stirred solution of 4,6-di(N-methylhydrazino)-2-phenylpyrimidine (163.1 mg, 0.66 mmol) in EtOH (15 ml), 4(5)-imidazolecarboxaldehyde (128.2 mg, 1.32 mmol) was added. The solution was stirred under nitrogen at room temperature for 18 h. The white precipitate formed was collected by filtration and dried under high vacuum. Yield: 236 mg (0.59 mmol, 80%). $^1$H NMR ([D$_6$]DMSO, 400 MHz): $^\text{TM}(\text{ppm}) = 3.73$ (s, 6H, CH$_3$), 7.52 (m, 6H, H$_{11}$,H$_{12}$, H$_{7}$ and H$_1$), 7.79 (s, 2H, H$_2$), 7.95 (s, 2H, H$_4$), 8.43 (m, 2H, H$_{10}$), 12.37 (s, br, 2H, H$_{\text{imid}}$). $^{13}$C NMR ([D$_6$]DMSO, 100 MHz): 18.4, 29.4, 54.8, 55.9, 84.8, 127.5, 128.1, 130.1, 136.7, 137.6, 160.8, 162.3. HR-MS (ES): calcd for C$_{20}$H$_{20}$N$_{10}$Na: $m/z$ = 423.1765, found $m/z$ = 423.1821 [$\text{M}+$Na]$^+$ and calcd for C$_{20}$H$_{21}$N$_{10}$: $m/z$ = 401.1945, found $m/z$ = 401.1995 [$\text{M}+$H]$^+$. Microanalysis: calcd (%) for C$_{20}$H$_{20}$N$_{10}$·3H$_2$O: C 52.12, H 17.49, N 30.39; found C 52.56, H 17.31, N 30.70.

$L3$

![Chemical structure of compound L3](image)

To a stirred solution of 4,6-di(N-methylhydrazino)-2-phenylpyrimidine (83.76 mg, 0.34 mmol) in EtOH (7 ml), 5-methylimidazole-4-carboxaldehyde (75.50 mg, 0.68 mmol) and two
drops of AcOH were added. The mixture was stirred under nitrogen at room temperature for 24 h. The white precipitate formed was collected by filtration, washed with EtOH and dried under high vacuum. Yield: 131 mg (0.30 mmol, 88%). Due to the low solubility of this compound, no satisfactory NMR spectra could be obtained. HR-MS (ES): calcd for C_{22}H_{24}Li_{1}N_{10}: m/z = 435.2340, found m/z = 435.2311 \ [M + Li]^+ . Microanalysis: calcd (%) for C_{22}H_{24}N_{10}·2H_{2}O: C 56.88, H 6.08, N 30.15; found C 56.24, H 5.76, N 30.22.

To a stirred solution of 4,6-di(N-methylhydrazino)-2-phenylpyrimidine (72.73 mg, 0.29 mmol) in EtOH (7 ml), 2-methyl-1H-imidazole-4-carboxaldehyde (65.56 mg, 0.59 mmol) and two drops of AcOH were added. The mixture was stirred under nitrogen at room temperature for 24 h. The white precipitate formed was collected by filtration, washed with EtOH and dried under high vacuum. Yield: 110 mg (0.25 mmol, 88%). \(^{1}\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) = 2.37 (s, 6H, H\(_3\)), 3.66 (s, 6H, H\(_6\)), 6.96 (s, 2H, H\(_1\)), 7.35 (m, 3H, H\(_{12}\) and H\(_{13}\)), 7.60 (s, 2H, NH), 7.74 (brs, 1H, H\(_8\)), 8.35 (m, 2H, H\(_{11}\)). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta =\) 18.46, 29.70, 35.23, 57.43, 83.64, 122.23, 127.76, 128.69, 131.23, 135.81, 143.12, 161.45, 165.82. HR-MS (ES): calcd for C_{22}H_{25}N_{10} : m/z = 429.2258, found m/z = 429.2244 \[M + H]^+ . Microanalysis: calcd (%) for C_{22}H_{24}N_{10}·5H_{2}O: C 50.95, H 6.61, N 27.01; found C 51.19, H 6.79, N 27.37.

To a stirred solution of 4,6-di(N-methylhydrazino)-2-phenylpyrimidine (120.76 mg, 0.49 mmol) in EtOH (11 ml), 2-imidazolecarboxaldehyde (95.02 mg, 0.98 mmol) was added. The mixture was stirred under at reflux under nitrogen for 24 h. The white precipitate formed was
collected by filtration, washed with EtOH and dried under high vacuum. Yield: 145 mg (0.36 mmol, 73%). \(^1\)H NMR ([D\(_6\)]DMSO, 400 MHz): \(\tau^N(ppm) = 3.77 (s, 6H, CH\(_3\)), 7.12 (d, br, 2H, H\(_1\) or H\(_2\)), 7.34 (d, br, 2H, H\(_1\) or H\(_2\)), 7.53 (m, 3H, H\(_{11}\) and H\(_{12}\)), 7.71 (s, 1H, H\(_7\)), 7.89 (s, 2H, H\(_4\)), 8.46 (m, 2H, H\(_{10}\)), 12.55 (s, 2H, H\(_{\text{imid}}\)). \(^{13}\)C NMR ([D\(_6\)]DMSO, 100 MHz): 18.46, 29.70, 55.92, 85.63, 127.61, 128.30, 129.69, 130.42, 137.47, 143.92, 161.09, 162.43. HR-MS (ES): calcd for C\(_{20}\)H\(_{21}\)N\(_{10}\): \(m/z = 401.1945\), found \(m/z = 401.1921\) \([M+H]^+\). Microanalysis: calcd (%) for C\(_{20}\)H\(_{20}\)N\(_{10}\)·6H\(_2\)O: C 47.24, H 6.34, N 27.54; found C 46.98, H 6.53, N 27.79.

To a stirred solution of 4,6-di(N-methylhydrazino)-2-phenylpyrimidine (35.5 mg, 0.145 mmol) in EtOH abs (4 ml), 2-thiazole carboxaldehyde (32.8 mg, 0.29 mmol) was added. The mixture was stirred under nitrogen at room temperature for 24 h. The white precipitate formed was collected by filtration, washed with EtOH and dried under high vacuum. Yield: 60 mg (0.138 mmol, 95%). \(^1\)H NMR ([D\(_6\)]DMSO, 400 MHz): \(\tau^N(ppm) = 3.77 (s, 6H, CH\(_3\)), 7.54 (m, 3H, H\(_{11}\) and H\(_{12}\)), 7.60 (s, 1H, H\(_7\)), 7.80 (d, \(J = 3.2\) Hz, 2H, H\(_1\)), 7.95 (d, \(J = 3.2\) Hz, 2H, H\(_2\)), 8.16 (s, 2H, H\(_4\)), 8.46 (m, 2H, H\(_{10}\)). \(^{13}\)C NMR ([D\(_6\)]DMSO, 100 MHz): 30.07, 85.78, 120.52, 127.73, 128.36, 130.67, 132.43, 132.92, 137.05, 143.66, 162.23, 165.77. HR-MS (ES): calcd for C\(_{20}\)H\(_{18}\)N\(_8\)S\(_2\)Li: \(m/z = 441.1251\), found \(m/z = 441.1258\) \([M+Li]^+\). Microanalysis: calcd (%) for C\(_{20}\)H\(_{18}\)N\(_8\)S\(_2\)·7H\(_2\)O: C 42.85, H 5.75, N 19.99; found C 42.62, H 5.50, N 20.21.

\([\text{Fe}_4(L_1)_4(\text{OTf})_8]\)

To a suspension of ligand L\(_1\) (50.44 mg, 135 \(\mu\)mol) in CH\(_3\)NO\(_2\) (10 ml), [Fe(dmso)\(_6\)](OTf)\(_2\) (111.44 mg, 135 \(\mu\)mol) was added. The mixture was stirred at 120 °C for 24 h. The complex was isolated in quantitative yield as brown solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et\(_2\)O. \(^1\)H NMR (CD\(_3\)CN, 400 MHz): \(\tau^N(ppm) = -62.12, -40.82, -24.95, -7.80, 4.40, 19.89, 76.06, 88.25, 110.10, 187.69, 195.70\). Microanalysis: calcd (%) for C\(_{80}\)H\(_{64}\)F\(_{24}\)N\(_{40}\)O\(_{24}\)S\(_8\)Fe\(_4\)·21H\(_2\)O·5DMSO: C 29.42, H 3.73, N 15.25; found C 29.65, H 3.50, N 15.20.
[Fe₄(N-C₁₆H₃₃L₁)₄](BF₄)₈

[Fe(OH₂)₆](BF₄)₂ (3.4 mg, 10 μmol) was added to a stirred suspension of ligand N-C₁₆H₃₃L₁ (8 mg, 10 μmol) in CH₃CN (2 mL), a red solution slowly forming. After stirring the mixture at room temperature for 24 h to give a clear solution, the product was isolated by evaporation of the solvent. Sufficient material was obtained for SQUID magnetic measurements only.

[Zn₄(L₁)₄](OTf)₈

To a suspension of ligand L₁ (20.82 mg, 55.90 μmol) in CH₃NO₂ (4 ml), [Zn(dmso)₆](OTf)₂ (46.53 mg, 55.90 μmol) was added. The yellow solution was stirred at 100 °C for 24 h. The complex was isolated in quantitative yield as light brown solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et₂O. ¹H NMR (CD₃CN, 400 MHz): δ (ppm) = 5.86 (d, J = 6.8 Hz, 1H, H₉), 6.11 (s, 1H, H₆), 6.51 (d, J = 7.2 Hz, 1H, H₉), 7.08 (t, J = 8.0 Hz, 1H, H₁₀), 7.32 (s, 2H, H₁), 7.34 (d, J = 1.2 Hz, 2H, H₂), 7.56 (t, J = 7.2 Hz, 1H, H₁₀), 7.58 (s, 2H, H₄), 7.87 (t, J = 7.6 Hz, 1H, H₁₁), 10.80 (s, 2H, NH imid), 10.89 (s, 2H, NHhydr). HR-MS (ES): calcd for C₇₈H₆₄F₁₈N₄₀O₁₈S₆Zn₄: m/z = 1322.0232, found m/z = 1322.0236 [M - 2OTf]²⁺; calcd for C₇₇H₆₄F₁₅N₄₀O₁₅S₅Zn₄: m/z = 831.6979, found m/z = 831.6903 [M - 3OTf]³⁺. Microanalysis: calcd (%) for C₈₀H₆₄F₂₄N₄₀O₂₄S₈Zn₄·14H₂O·3DMSO: C 30.11, H 3.23, N 16.33; found C 30.37, H 3.21, N 16.31

[Zn₄(L₂)₄](OTf)₈

To a suspension of L₂ (14.8 mg, 37 μmol) in CH₃CN (2 ml), Zn(OTf)₂·H₂O (13.4 mg, 37 μmol) was added. The mixture was stirred at room temperature for 24 h. The complex was isolated as a dull yellow solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et₂O. Yield: 23 mg, 82%. ¹H NMR (CD₃CN, 400 MHz): δ (ppm) = 3.42 (s, 6H, CH₃), 5.73 (d, J = 7.6 Hz, 1H, H₁₀), 6.38 (s, 1H, H₂), 6.54 (d, J = 8 Hz, 1H, H₁₀), 7.08 (t, J = 8 Hz, 1H, H₁₁), 7.30 (s, 2H, H₁), 7.38 (d, J = 1.6 Hz, 2H, H₂), 7.48 (t, J = 7.6 Hz, 1H, H₁₁), 7.67 (s, 2H, H₄), 7.77 (t, J = 7.6 Hz, 1H, H₁₂), 10.93 (s, 2H, NH imid). HR-MS (ES): calcd for C₈₆H₈₀F₁₈N₄₀O₁₈S₆Zn₄: m/z = 1378.0859, found m/z = 1378.1067 [M - 2OTf]²⁺; calcd for C₈₅H₈₀F₁₅N₄₀O₁₅S₅Zn₄: m/z = 869.0731, found m/z = 869.0796 [M - 3OTf]³⁺; calcd for C₈₄H₈₀F₁₂N₄₀O₁₂S₄Zn₄: m/z = 614.5667, found m/z = 614.5768 [M - 4OTf]⁴⁺. Microanalysis: calcd (%) for C₈₀H₈₀Cl₈N₄₀O₃₂Zn₄·14H₂O: C 33.01, H 3.74, N 19.25; found C 32.89, H 3.84, N 19.71.
**[Co_4(L_2)_4(BF_4)_8]**

To a suspension of ligand **L_2** (29.7 mg, 74 µmol) in CH_3CN (4 ml), Co(BF_4)_2·6H_2O (25.3 mg, 74 µmol) was added. The mixture was stirred at room temperature for 24 h. The complex was isolated as dark red solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et_2O. Yield: 43 mg, 78%. ^1H NMR (CD_3CN, 400 MHz): δ (ppm) = -89.65, -75.59, -50.87, -17.45, 11.00, 43.55, 95.91, 124.58, 154.33, 224.22. HR-MS (ES): calcd for C_80H_80B_6F_24N_40Co_4: m/z = 1179.2517, found m/z = 1179.2451 [M – 2BF_4]^2+, calcd for C_80H_80B_5F_20N_40Co_4: m/z = 757.1644, found m/z = 757.1743 [M – 3BF_4]^3+, calcd for C_80H_80B_4F_16N_40Co_4: m/z = 546.1238, found m/z = 546.1494 [M – 4BF_4]^4+. Microanalysis: calcd (%) for C_80H_80B_8Co_4F_32N_40·12H_2O: C 34.96, H 3.81, N 20.39; found C 34.94, H 3.96, N 20.39. For an X-ray structure determination, the complex was converted to the hexafluorophosphate salt by addition of aqueous ammonium hexafluorophosphate to a solution of the tetrafluoroborate in acetonitrile.

**[Fe_4(L_2)_4(BF_4)_8]**

To a suspension of ligand **L_2** (29.3 mg, 73 µmol) in CH_3CN (4 ml), Fe(BF_4)_2·6H_2O (24.7 mg, 73 µmol) was added. The mixture was stirred at 60 °C for 24 h. A small amount of amorphous solid was filtered out and the complex was isolated as light orange solid by evaporation of the filtrate and crystallisation of the residue from MeCN by the addition of Et_2O. Yield: 40 mg, 74%. ^1H NMR (CD_3CN, 400 MHz): δ (ppm) = -81.03, -58.20, -37.13, -15.06, 3.06, 15.51, 37.71, 90.02, 96.90, 146.70, 176.13. HR-MS (ES): calcd for C_80H_80B_6F_24N_40Fe_4: m/z = 1173.2555, found m/z = 1173.2164 [M – 2BF_4]^2+, calcd for C_80H_80B_5F_20Fe_4N_40Co_4: m/z = 753.1690, found m/z = 752.1565 [M – 3BF_4]^3+, calcd for C_80H_80B_4F_16N_40Fe_4: m/z = 543.1257, found m/z = 543.0593 [M – 4BF_4]^4+. Microanalysis: calcd (%) for C_80H_80B_8F_32Fe_4N_40·9H_2O: C 35.83, H 3.68, N 21.89; found C 35.71, H 3.57, N 21.75.

**[Mn_4(L_2)_4(OTf)_8]**

To a suspension of ligand **L_2** (14.43 mg, 36,03 µmol) in CH_3CN (4 ml), [Mn(dmso)_6](OTf)_2 (29.61 mg, 36,03 µmol) was added. The mixture was stirred at 60 °C for 24 h to give a light yellow solution. The complex was isolated in quantitative yield as yellow crystals by precipitation with Et_2O. HR-MS (ES): calcd for C_80H_80Cl_6N_40O_24Cu_4: m/z = 1226.0766, found m/z = 1226.0815 [M – 2ClO_4]^2+, calcd for C_80H_80Cl_2N_40O_20Cu_4: m/z = 784.4015, found m/z = 784.4048 [M – 3ClO_4]^3+, calcd for C_80H_80Cl_4N_40O_16Cu_4: m/z = 562.0652, found m/z = 562.0664.
562.0639 \ [M – 4\text{ClO}_4]^{4+}. \text{Microanalysis: calcd (\%)} \text{ for } C_{88}H_{80}F_{24}Mn_4N_4O_{24}S_8\cdot11\text{H}_2\text{O}: \text{ C }32.90, \text{ H }3.20, \text{ N }17.44; \text{ found C }32.88, \text{ H }3.36, \text{ N }17.49.

\[\text{[Cu}_4\text{L}_2\text{]}\text{(ClO}_4\text{)}_8\]

To a suspension of ligand \textbf{L}_2 (37.6 mg, 94 \text{ µmol}) in CH$_3$CN (4 ml), Cu(ClO$_4$)$_2\cdot6\text{H}_2\text{O}$ (34.8 mg, 94 \text{ µmol}) was added. The mixture was stirred at room temperature for 24 h to give a dark brown solution. The complex was isolated as brown solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et$_2$O. Yield: 57 mg, 80%. $^1$H NMR (CD$_3$CN, 400 MHz): $^\text{TM}(\text{ppm}) = 3.24, 6.87, 7.00, 7.24, 10.05, 10.65, 27.38, 33.59$. HR-MS (ES): calcd for C$_{80}$H$_{80}$Cl$_6$N$_4$O$_{24}$Cu$_4$: m/z = 1226.0766, found m/z = 1226.0815 \ [M – 2\text{ClO}_4]^{2+}, \text{calcd for } C_{80}H_{80}Cl$_5$N$_4$O$_{20}$Cu$_4$: m/z = 784.4015, found m/z = 784.4048 \ [M – 3\text{ClO}_4]^{3+}, \text{calcd for } C_{80}H_{80}Cl$_4$N$_4$O$_{16}$Cu$_4$: m/z = 562.0652, found m/z = 562.0639 \ [M – 4\text{ClO}_4]^{4+}. \text{Microanalysis: calcd (\%)} \text{ for } C_{80}H_{80}Cl$_6$Cu$_4$N$_4$O$_{32}\cdot15\text{H}_2\text{O}: \text{ C }32.89, \text{ H }3.79, \text{ N }19.18; \text{ found C }32.79, \text{ H }3.57, \text{ N }19.35.

\[\text{[Zn}_4\text{L}_3\text{]}\text{(OTf)}_8\]

To a suspension of ligand \textbf{L}_3 (16.0 mg, 37.3 \text{ µmol}) in CH$_3$CN (3 ml), Zn(OTf)$_2\cdot\text{H}_2\text{O}$ (13.5 mg, 37.3 \text{ µmol}) was added. The yellow solution formed was stirred at room temperature for 24 h. The complex was isolated as yellow solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et$_2$O. Yield: 20 mg, 69%. $^1$H NMR (CD$_3$CN, 400 MHz): $^\text{TM}(\text{ppm}) = 2.28 (\text{s, 6H, } H_3), 3.41 (\text{s, 6H, } H_6), 5.71 (\text{d, } J = 7.6 \text{ Hz, } 1\text{H, } H_{11}), 6.32 (\text{s, 1H, } H_8), 6.53 (\text{d, } J = 7.2 \text{ Hz, 1H, } H_{11}), 7.02 (\text{t, } J = 7.6 \text{ Hz, 1H, } H_{12}), 7.15 (\text{s, 2H, } H_1), 7.46 (\text{t, } J = 7.6 \text{ Hz, 1H, } H_{12}), 7.60 (\text{s, 2H, } H_5), 7.75 (\text{t, } J = 7.6 \text{ Hz, 1H, } H_{13}), 10.87 (\text{s, 2H, NH}_{\text{imid}}). \text{HR-MS (ES): calcd for } C_{94}H_{96}F_{18}N_{40}O_{18}S_6Zn$_4$: \text{ m/z = 1434.1487, found m/z = 1434.0970 \ [M - 2\text{OTf}]^{2+}, calcd for } C_{93}H_{96}F_{18}N_{40}O_{16}S_5Zn$_4$: \text{ m/z = 906.4483, found m/z = 906.4374 \ [M - 3\text{OTf}]^{3+}, calcd for } C_{92}H_{96}F_{18}N_{40}O_{12}S_4Zn$_4$: \text{ m/z = 643.1031 \ [M - 4\text{OTf}]^{4+}. \text{Microanalysis: calcd (\%)} \text{ for } C_{96}H_{96}F_{24}N_{40}O_{24}S_8Zn$_4\cdot14\text{H}_2\text{O}: \text{ C }33.71, \text{ H }3.65, \text{ N }16.38; \text{ found C }33.74, \text{ H }3.70, \text{ N }16.19.

\[\text{[Co}_4\text{L}_3\text{]}\text{(OTf)}_8\]

To a suspension of ligand \textbf{L}_3 (29.47 mg, 68.77 \text{ µmol}) in CH$_3$CN (5 ml), [Co(dms)$_6$]_(OTf)$_2$ (56.78 mg, 68.77 \text{ µmol}) was added. The mixture was stirred at room temperature for 24 h. The complex was isolated as dark orange solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et$_2$O. Yield: 40 mg, 74%. $^1$H
NMR (CD$_3$CN, 400 MHz): $^\text{t}$(ppm) = -94.12, -77.87, -50.55, -16.67, -15.97, -15.73, 45.40, 95.36, 124.85, 154.69, 222.23. HR-MS (ES): calcd for C$_{94}$H$_{96}$F$_{18}$N$_{40}$O$_{18}$S$_6$Co$_4$: $m/z = 1421.1590$, found $m/z = 1421.1379 \ [M – 2OTf]^{2+}$, calcd for C$_{93}$H$_{96}$F$_{15}$N$_{40}$O$_{15}$S$_5$Co$_4$: $m/z = 898.1226$, found $m/z = 898.1194 \ [M – 3OTf]^{3+}$, calcd for C$_{92}$H$_{96}$F$_{12}$N$_{40}$O$_{12}$S$_4$Co$_4$: $m/z = 636.1032$, found $m/z = 636.1070 \ [M – 4OTf]^{4+}$. Microanalysis: calcd (%) for C$_{96}$H$_{96}$Co$_4$F$_{24}$N$_{40}$O$_{24}$S$_8$·12H$_2$O: C 34.33, H 3.60, N 16.68; found C 34.81, H 3.89, N 16.32.

[Fe$_4$(L$_3$)$_4$](OTf)$_8$

To a suspension of ligand L$_3$ (29.78 mg, 69.49 $\mu$mol) in CH$_3$CN (5 ml), [Fe(dmso)$_6$](OTf)$_2$ (57.18 mg, 69.49 $\mu$mol) was added. The mixture was stirred at 60 oC for 24 h. The complex was isolated as orange solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et$_2$O. Yield: 41 mg, 77%. $^1$H NMR (CD$_3$CN, 400 MHz): $^\text{t}$(ppm) = -75.87, -60.51, -36.62, -15.86, -9.30, 2.53, 36.71, 91.58, 98.89, 144.48, 171.65. Microanalysis: calcd (%) for C$_{96}$H$_{96}$Fe$_4$N$_{40}$O$_{24}$S$_8$·18H$_2$O: C 34.33, H 3.60, N 16.68; found C 33.20, H 3.68, N 16.47.

[Cu$_4$(L$_3$)$_4$](OTf)$_8$

To a suspension of ligand L$_3$ (40 mg, 82.90 $\mu$mol) in CH$_3$CN (4 ml), [Cu(dmso)$_6$](OTf)$_2$ (68.85 mg, 82.49 $\mu$mol) was added. The mixture was stirred at r.t. for 24 h. The complex was isolated as orange solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et$_2$O. Yield: 55 mg, 79%. $^1$H NMR (CD$_3$CN, 400 MHz): $^\text{t}$(ppm) = -3.26, -2.05, 2.95, 4.30, 6.76, 6.96, 7.13, 7.52, 10.80, 15.81, 32.51, 34.67, 51.77. Microanalysis: calcd (%) for C$_{96}$H$_{96}$Cu$_4$F$_{24}$N$_{40}$O$_{24}$S$_8$·33H$_2$O: C 30.70, H 4.35, N 14.92; found C 30.69, H 3.74, N 14.86.

[Mn$_4$(L$_3$)$_4$](OTf)$_8$

To a suspension of ligand L$_3$ (51.71 mg, 107.17 $\mu$mol) in CH$_3$NO$_2$ (5 ml), [Mn(dmso)$_6$](OTf)$_2$ (88.08 mg, 107.17 $\mu$mol) was added. The mixture was stirred at 60 oC under an atmosphere of N$_2$ for 24 h. The complex was isolated as yellow solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et$_2$O. Yield: 85 mg, 95%. $^1$H NMR (CD$_3$CN, 400 MHz): $^\text{t}$(ppm) = the spectra was broad and undefined. Microanalysis: calcd (%) for C$_{96}$H$_{96}$Mn$_4$F$_{24}$N$_{40}$O$_{24}$S$_8$·12H$_2$O: C 34.50, H 3.62, N 16.46; found C 34.14, H 3.62, N 16.60.
[Zn₄(L₄)₄](OTf)₈

To a suspension of ligand L₄ (21.0 mg, 49.0 μmol) in CH₃CN (4 ml), Zn(OTf)₂·H₂O (17.81 mg, 49.0 μmol) was added. The yellow solution was stirred at room temperature for 24 h. The complex was isolated as yellow solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et₂O. Yield: 29 mg, 76%. ¹H NMR (CD₃CN, 400 MHz): ⁴H (ppm) = 1.68 (s, 6H, H₃), 3.39 (s, 6H, H₆), 5.90 (d, J = 7.6 Hz, 1H, H₁₁), 6.41 (s, 1H, H₈), 6.46 (d, J = 7.2 Hz, 1H, H₁₂), 7.16 (t, J = 7.6 Hz, 1H, H₁₂), 7.36 (d, J = 2 Hz, 2H, H₁), 7.50 (t, J = 7.6 Hz, 1H, H₁₂), 7.65 (s, 2H, H₅), 7.80 (t, J = 7.6 Hz, 1H, H₁₃), 10.88 (s, 2H, NHimid). Microanalysis: calcld (%) for C₉₆H₉₆F₂₄N₄₀O₂₄S₈Zn₄·11H₂O: C 34.25, H 3.53, N 16.64; found C 34.00, H 3.65, N 16.54.

[Fe₄(L₄)₄](OTf)₈

To a suspension of ligand L₄ (18.44 mg, 43.03 μmol) in a CH₃CN/MeOH mixture (2:1, 6 ml), [Fe(dmso)₆](OTf)₂ (57.18 mg, 69.49 μmol) was added. The mixture was stirred at 60 °C for 24h. The complex was isolated as red solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et₂O. Yield: 21 mg, 63%. ¹H NMR (CD₃CN, 400 MHz): ⁴H (ppm) = -67.28, -61.79, -27.38, -5.56, 0.72, 2.22, 11.43, 35.81, 37.86, 86.76, 135.66, 177.32.

[Zn₄(L₅)₄](OTf)₈

To a suspension of ligand L₅ (19.3 mg, 48.1 μmol) in CH₃CN (4 ml), Zn(OTf)₂·H₂O (17.5 mg, 48.1 μmol) was added. The yellow solution was stirred at room temperature for 24 h. The complex was isolated as yellow solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et₂O. Yield: 30 mg, 81%. ¹H NMR (CD₃CN, 400 MHz): ⁴H (ppm) = 3.51 (s, 6H, H₅), 5.46 (d, J = 7.6 Hz, 1H, H₁₀), 6.49 (d, J = 7.6 Hz, 1H, H₁₀), 6.53 (s, 2H, H₂), 6.58 (s, 1H, H₃), 7.10 (dd, J = 2.2 Hz and 1.4 Hz, 2H, H₁), 7.24 (t, J = 7.2 Hz, 1H, H₁₁), 7.52 (t, J = 7.2 Hz, 1H, H₁₁), 7.74 (s, 2H, H₃), 7.86 (t, J = 7.6 Hz, 1H, H₁₂), 11.56 (s, 2H, NHimid). HR-MS (ES): calcld for C₈₆H₈₀F₁₈N₄₀O₁₈S₆Zn₄: m/z = 1378.0859, found m/z = 1378.1125 [M - 2OTf]²⁺, calcld for C₈₅H₈₀F₁₅N₄₀O₁₄S₅Zn₄: m/z = 869.0731, found m/z = 869.1080 [M - 3OTf]³⁺, calcld for C₈₄H₈₀F₁₂N₄₀O₁₂S₄Zn₄: m/z = 613.0831 [M - 4OTf]⁴⁺. Microanalysis: calcld (%) for C₈₃H₈₀F₂₄N₄₀O₂₄S₈Zn₄·10H₂O: C 32.66, H 3.11, N 17.31; found C 32.53, H 3.35, N 17.78.
**[Co₄(L₅)₄][OTf]₈**

To a suspension of ligand L₅ (16.58 mg, 41.4 μmol) in CH₃CN (4 ml), [Co(dmso)₆][OTf]₂ (34.18 mg, 41.4 μmol) was added. The red solution was stirred at room temperature for 24 h. The complex was isolated in quantitative yield as orange solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et₂O. ¹H NMR (CD₃CN, 400 MHz): δ (ppm) = -59.40, -46.04, -30.82, -24.88, -24.70, 28.11, 39.79, 83.95, 134.61, 157.68, 180.53. HR-MS (ES): calcd for C₈₆H₈₀F₁₈N₄₀O₁₈S₆Co₄: m/z = 1365.0964, found m/z = 1365.0743 [M – 2OTf]²⁺, calcd for C₈₅H₈₀F₁₅N₄₀O₁₅S₅Co₄: m/z = 860.7475, found m/z = 860.7434 [M – 3OTf]³⁺, calcd for C₈₄H₈₀F₁₂N₄₀O₁₂S₄Co₄: m/z = 608.0723, found m/z = 608.06 [M – 4OTf]⁴⁺. Microanalysis: calcd (%) for C₈₈H₈₀Co₄F₂₄N₄₀O₂₄S₈·12H₂O: C 32.56, H 3.23, N 17.26; found C 32.54, H 3.03, N 17.50.

**[Fe₄(L₅)₄][OTf]₈**

To a suspension of ligand L₅ (16.38 mg, 40.90 μmol) in CH₃CN (4 ml), [Fe(dmso)₆][OTf]₂ (33.65 mg, 40.90 μmol) was added. The mixture was stirred at 60 °C for 24 h. The complex was isolated in quantitative yield as red solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et₂O. ¹H NMR (CD₃CN, 400 MHz): δ (ppm) = -80.73, -60.79, -33.81, -10.16, 3.32, 42.58, 46.03, 58.44, 108.76, 147.31, 166.03. HR-MS (ES): calcd for C₈₆H₈₀F₁₈N₄₀O₁₈S₆Fe₄: m/z = 1359.6013, found m/z = 1359.6882 [M – 2OTf]²⁺, calcd for C₈₅H₈₀F₁₅N₄₀O₁₅S₅Fe₄: m/z = 856.7500, found m/z = 856.7995 [M – 3OTf]³⁺, calcd for C₈₄H₈₀F₁₂N₄₀O₁₂S₄Fe₄: m/z = 605.0740, found m/z = 605.0887 [M – 4OTf]⁴⁺. Microanalysis: calcd (%) for C₈₈H₈₀Fe₄F₂₄N₄₀O₂₄S₈·11H₂O: C 32.87, H 3.20, N 17.42; found C 32.58, H 3.21, N 17.78.

**[Mn₄(L₅)₄][OTf]₈**

To a suspension of ligand L₅ (9.86 mg, 24.62 μmol) in CH₃CN (4 ml), [Mn(dmso)₆][OTf]₂ (20.23 mg, 24.62 μmol) was added. The mixture was stirred at 60 °C for 24 h, giving a light yellow solution. The complex was isolated in quantitative yield as yellow crystals by precipitation with Et₂O. ¹H NMR (CD₃CN, 400 MHz): δ (ppm) = the spectra was broad and undefined. Microanalysis: calcd (%) for C₈₈H₈₀F₂₄Mn₄N₄₀O₂₄S₈·12H₂O: C 32.72, H 3.25, N 17.34; found C 32.54, H 3.33, N 17.68.

Electronic Supplementary Material (ESI) for Dalton Transactions
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To a suspension of ligand L6 (8.87 mg, 20.41 μmol) in CH3CN (3 ml), Zn(OTf)2·H2O (7.42 mg, 20.41 μmol) was added. The yellow solution was stirred at room temperature for 24 h. The slightly turbid solution was filtered and the complex was isolated as a yellow solid by evaporation of the filtrate and crystallisation of the residue from MeCN by the addition of Et2O. Yield: 14 mg, 85%. 1H NMR (CD3CN, 400 MHz): δ (ppm) = 3.63 (s, 6H, H5), 5.71 (d, J = 7.6 Hz, 1H, H10), 6.48 (d, J = 7.2 Hz, 1H, H10), 6.86 (s, 1H, H7), 7.28 (t, J = 7.6 Hz, 1H, H11), 7.37 (d, J = 3.2 Hz, 2H, H1 or H2), 7.61 (d, J = 3.2 Hz, 2H, H1 or H2), 7.75 (t, J = 7.2 Hz, 1H, H11), 7.97 (t, J = 7.6 Hz, 1H, H12), 8.07 (s, 2H, H4). HR-MS (ES): calcd for C86H72F18N32O18S14Zn4·nZn4: m/z = 1446.9295, found m/z = 1446.9081 [M - 2OTf]2+, calcd for C85H80F15N32O15S13Zn4: m/z = 914.9688, found m/z = 914.9824, [M - 3OTf]3+. Microanalysis: calcld (%) for C88H72F24N32O24S16Zn4·15H2O: C 30.53, H 2.97, N 12.94; found C 30.65, H 3.12, N 13.21.

To a suspension of ligand L6 (56.19 mg, 129.3 μmol) in CH3NO2 (4 ml), [Co(dmso)6](OTf)2 (106.76 mg, 129.3 μmol) was added. The red solution was stirred at room temperature for 24 h. Again, a small amount of insoluble, amorphous material was filtered out and the complex was isolated as a brown solid by evaporation of the filtrate and crystallisation of the residue from MeCN by the addition of Et2O. Yield: 88 mg, 86%. 1H NMR (CD3CN, 400 MHz): δ (ppm) = -74.19, -44.56, -38.29, -18.08, -16.19, 35.07, 75.86, 145.95, 149.15, 195.15. HR-MS (ES): calcd for C86H72Co4F18N32O18S14: m/z = 1433.9414, found m/z = 1433.9474 [M - 2OTf]2+, calcd for C85H80Co4F15N32O15S13: m/z = 906.3101, found m/z = 906.3137, [M - 3OTf]3+. Microanalysis: calcld (%) for C88H72F24N32O24S16Co4·8H2O: C 31.93, H 2.68, N 13.54; found C 31.80, H 2.89, N 13.88.

To a suspension of ligand L6 (10 mg, 23.01 μmol) in CH3NO2 (4 ml), [Fe(dmso)6](OTf)2 (18.93 mg, 23.01 μmol) was added. The red solution was stirred under N2 at 100 °C for 24 h. The complex was isolated as orange solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et2O. Yield: 22 mg, 75%. 1H NMR (CD3CN, 400 MHz): δ (ppm) = -86.76, -38.19, -36.33, -14.58, 9.43, 34.05, 55.70, 117.79, 151.18, 152.92. HR-MS (ES): calcd for C88H72Fe4N32O24S14: m/z = 1427.9452, found m/z =
1427.9291 \([M - 2OTf]^{2+}\), calcd for C\(_{85}\)H\(_{72}\)F\(_{15}\)Fe\(_4\)N\(_{32}\)O\(_{15}\)S\(_{13}\): \(m/z = 902.3126\), found \(m/z = 902.3003\), \([M - 3OTf]^{3+}\), calcd for C\(_{84}\)H\(_{72}\)F\(_{12}\)Fe\(_4\)N\(_{32}\)O\(_{12}\)S\(_{12}\): \(m/z = 638.9873\), found \(m/z = 638.9975\), \([M - 4OTf]^{4+}\). Microanalysis: calcd (%) for C\(_{88}\)H\(_{72}\)F\(_{24}\)N\(_{32}\)O\(_{24}\)S\(_{16}\)Fe\(_4\) · 29H\(_2\)O: C 28.75, H 3.56, N 12.19; found C 28.50, H 3.23, N 11.90.

\([\text{Cu}_4(\text{L}6)_4](\text{OTf})_8\)

To a suspension of ligand \(\text{L}6\) (43.62 mg, 100.38 \(\mu\)mol) in CH\(_3\)NO\(_2\) (4 ml), \([\text{Cu}(\text{dms0})_6](\text{OTf})_2\) (83.36 mg, 100.38 \(\mu\)mol) was added. The dark brown solution was stirred at room temperature for 24 h. The complex was isolated as brown solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et\(_2\)O. Yield: 22 mg, 75%. \(^1\)H NMR (CD\(_3\)CN, 400 MHz): \(\delta\) (ppm) = 2.59, 4.30, 7.13, 7.54, 10.63, 11.27, 37.77, 42.86. HR-MS (ES): calcd for C\(_{86}\)H\(_{72}\)Cu\(_4\)F\(_{18}\)N\(_{32}\)O\(_{18}\)S\(_{14}\): \(m/z = 1442.9301\), found \(m/z = 1442.9739\) \([M - 2OTf]^{2+}\), calcd for C\(_{84}\)H\(_{72}\)Cu\(_4\)F\(_{12}\)N\(_{32}\)O\(_{12}\)S\(_{12}\): \(m/z = 646.2353\), found \(m/z = 646.0146\), \([M - 4OTf]^{4+}\). Microanalysis: calcd (%) for C\(_{88}\)H\(_{72}\)Cu\(_4\)F\(_{24}\)N\(_{32}\)O\(_{24}\)S\(_{16}\) · 12H\(_2\)O: C 31.08, H 2.85, N 13.18; found C 30.88, H 2.59, N 13.13.
**Table 1:** General reaction conditions, yields and final product characteristics for grid complexes.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Metal salt</th>
<th>Solvent</th>
<th>Reaction conditions</th>
<th>Product</th>
<th>Yield</th>
</tr>
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<tbody>
<tr>
<td><strong>L2</strong></td>
<td>Zn(OTf)$_2$·xH$_2$O</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>diamagnetic</td>
<td>82%</td>
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<tr>
<td><strong>L2</strong></td>
<td>Co(BF$_4$)$_2$·6H$_2$O</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>paramagnetic</td>
<td>78%</td>
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<td><strong>L2</strong></td>
<td>Fe(BF$_4$)$_2$·6H$_2$O</td>
<td>MeCN</td>
<td>60°C, 24 h</td>
<td>paramagnetic</td>
<td>74%</td>
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<tr>
<td><strong>L2</strong></td>
<td>Cu(ClO$_4$)$_2$·6H$_2$O</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
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<td>80%</td>
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<td><strong>L2</strong></td>
<td><a href="OTf">Mn(dmso)$_6$</a>$_2$</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>paramagnetic</td>
<td>95%</td>
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<td><strong>L3</strong></td>
<td>Zn(OTf)$_2$·xH$_2$O</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>diamagnetic</td>
<td>69%</td>
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<tr>
<td><strong>L3</strong></td>
<td><a href="OTf">Co(dmso)$_6$</a>$_2$</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>paramagnetic</td>
<td>74%</td>
</tr>
<tr>
<td><strong>L3</strong></td>
<td><a href="OTf">Fe(dmso)$_6$</a>$_2$</td>
<td>MeCN</td>
<td>60°C, 24 h</td>
<td>paramagnetic</td>
<td>77%</td>
</tr>
<tr>
<td><strong>L3</strong></td>
<td><a href="OTf">Cu(dmso)$_6$</a>$_2$</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>paramagnetic</td>
<td>79%</td>
</tr>
<tr>
<td><strong>L3</strong></td>
<td><a href="OTf">Mn(dmso)$_6$</a>$_2$</td>
<td>MeNO$_2$</td>
<td>60°C, 24 h</td>
<td>paramagnetic</td>
<td>95%</td>
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<tr>
<td><strong>L4</strong></td>
<td>Zn(OTf)$_2$·xH$_2$O</td>
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<td>r.t., 24 h</td>
<td>diamagnetic</td>
<td>76%</td>
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<tr>
<td><strong>L4</strong></td>
<td><a href="OTf">Fe(dmso)$_6$</a>$_2$</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>diamagnetic</td>
<td>63%</td>
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<tr>
<td><strong>L5</strong></td>
<td>Zn(OTf)$_2$·xH$_2$O</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>diamagnetic</td>
<td>81%</td>
</tr>
<tr>
<td><strong>L5</strong></td>
<td><a href="OTf">Co(dmso)$_6$</a>$_2$</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>paramagnetic</td>
<td>quantitative</td>
</tr>
<tr>
<td><strong>L5</strong></td>
<td><a href="OTf">Fe(dmso)$_6$</a>$_2$</td>
<td>MeCN</td>
<td>60°C, 24 h</td>
<td>paramagnetic</td>
<td>quantitative</td>
</tr>
<tr>
<td><strong>L5</strong></td>
<td>Cu(OTf)$_2$·xH$_2$O</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>paramagnetic</td>
<td>no grid</td>
</tr>
<tr>
<td><strong>L5</strong></td>
<td><a href="OTf">Mn(dmso)$_6$</a>$_2$</td>
<td>MeCN</td>
<td>60°C, 24 h</td>
<td>paramagnetic</td>
<td>quantitative</td>
</tr>
<tr>
<td><strong>L6</strong></td>
<td>Zn(OTf)$_2$·xH$_2$O</td>
<td>MeCN</td>
<td>r.t., 24 h</td>
<td>diamagnetic</td>
<td>85%</td>
</tr>
<tr>
<td><strong>L6</strong></td>
<td><a href="OTf">Co(dmso)$_6$</a>$_2$</td>
<td>MeNO$_2$</td>
<td>r.t., 24 h</td>
<td>paramagnetic</td>
<td>86%</td>
</tr>
<tr>
<td><strong>L6</strong></td>
<td><a href="OTf">Fe(dmso)$_6$</a>$_2$</td>
<td>MeNO$_2$</td>
<td>reflux, 24 h</td>
<td>diamagnetic</td>
<td>quantitative</td>
</tr>
<tr>
<td><strong>L6</strong></td>
<td>Cu(dmso)$_6$</td>
<td>MeNO$_2$</td>
<td>reflux, 24 h</td>
<td>paramagnetic</td>
<td>75%</td>
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</table>
High resolution ESI mass spectrum of tetranuclear $[\text{Cu}_4(\text{L6})_4](\text{OTf})_4^{4+}$ and mononuclear $[\text{Cu}_1(\text{L6})_2](\text{OTf})_1^{1+}$
A set of 1-H NMR spectra of Fe(II) complexes with structurally different bis-hydrazone-type ligands.