Supporting information for:

Supramolecular Chemistry of Metallogrids *via* Directed Hydrogen-bonding

Artur R. Stefankiewicz,[a#] Guillaume Rogez,[b] Jack Harrowfield,[a] Alexandre N. Sobolev,[c] Augustin Madalan,[a†] Juhani Huuskonen,[d] Kari Rissanen[d] and Jean-Marie Lehn [a*]

[a]*Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg, 8, allée Gaspard Monge, 67083 Strasbourg, France*
 # Present address: University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom.
[b]*Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, 67034 Strasbourg, France*
[c]*Chemistry, M313, University of Western Australia, Crawley, WA 6009, Australia*
[d] *Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014 JYU, Finland*
† *Present address: Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie 23, 020464 Bucharest Romania.*

Email: lehn@unistra.fr; tel: +33 (0)3 68 85 51 45

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.[5] 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, [D_6]DMSO: 2.50 ppm, CD_3CN: 1.94 ppm, CD_3NO_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, [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^{o}C.

LC/MS was performed using reverse phase HPLC (C_{18} solid phase, 5 µm particle size, 2.1 x 5 mm column, eluent: H_2O with 0.01% TFA→CH_3CN 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

Strasbourg. 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 $5x10^{-3}$ 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.

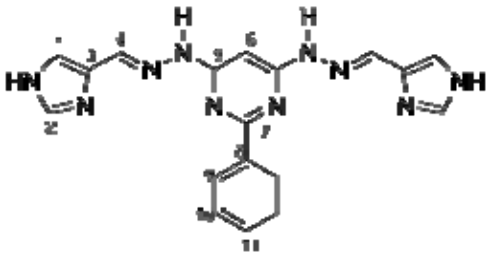
Magnetic measurements were performed by using a Quantum Design MPMS-XL SQUID magnetometer at the Instiut de Physique et Chimie des Matériaux de Strasbourg. Susceptibility measurements were performed in the range 300-1.8 K with an applied field of 0.5 T. The temperature sweep rate was 5 K min^{-1}. Magnetization 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 **L2**, **L4** and **L5** and the complexes $[Fe_4(\mathbf{L2})_4](BF_4)_8 \bullet 12CH_3CN \bullet 3.5H_2O$ and $[Co_4(\mathbf{L5})_4](CF_3SO_3)_8 \bullet 6CH_3CN \bullet 6H_2O$ were performed by Dr Lydia Brelot at the Service de Radiocristallographie, 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_α radiation (λ = 0.71073 Å), using a "phi-scan" type scan mode. Structures of the complexes $[Zn_4(\mathbf{L2})_4](ClO_4)_8 \bullet 3.5CH_3CN \bullet 4H_2O$ and $[Co_4(\mathbf{L2})_4]Cl(PF_6)_7 \bullet 4CH_3CN$ 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.

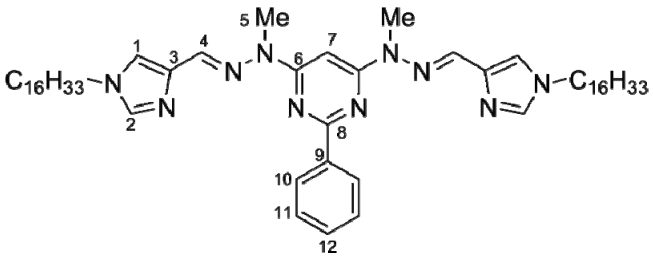
Synthesis

L1



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): ™(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.

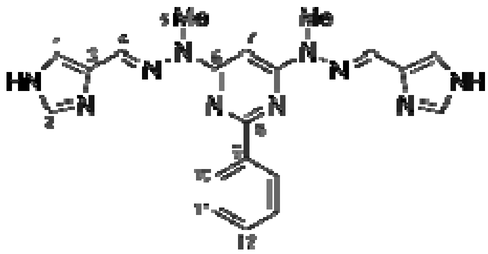
N-C$_{16}$H$_{33}$L1



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 iodohexadecane (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

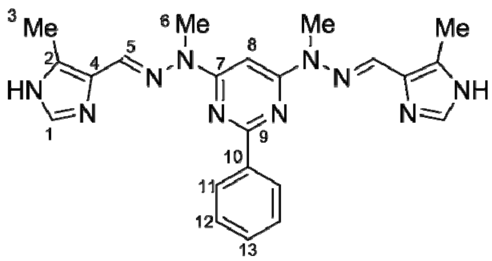
product as a white solid. Yield: 150 mg (0.49 mmol, 39%). ^{1}H NMR ($CDCl_3$, 400 MHz): ™(ppm) = 0.86 (t, J = 6.8 Hz, 3H, $H_{hexadecyl}$), 1.24 (m, 26H, $H_{hexadecyl}$), 1.80 (quin, J = 7.2 Hz, 2H, $H_{hexadecyl}$), 3.97 (t, J = 6.8 Hz, 2H, $H_{hexadecyl}$), 7.53 (s, 1H, H_2 or H_5), 7.61 (d, J = 1.2 Hz, 1H, H_2 or H_5), 9.86 (s, 1H, H_6). ^{13}C NMR ($CDCl_3$, 100 MHz): ™ = 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 $C_{20}H_{36}N_2Li_1O_1$: m/z = 327.2983, found m/z = 327.2962 $[M+Li]^+$.

L2



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): ™(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_{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 $[M+Na]^+$ and calcd for $C_{20}H_{21}N_{10}$: m/z = 401.1945, found m/z = 401.1995 $[M+H]^+$. Microanalysis: calcd (%) for $C_{20}H_{20}N_{10}\cdot 3H_2O$: C 52.12, H 17.49, N 30.39; found C 52.56, H 17.31, N 30.70.

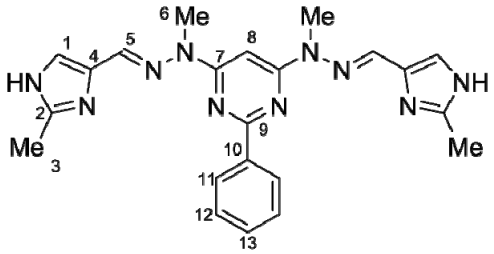
L3



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

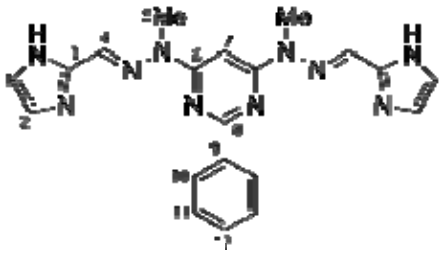
drops of AcOH were added. The mixture was stirred under nitrogen at room temperature for 24 h. The white precipitate formed was collected by filtration, washed with EtOH and dried under high vacuum. Yield: 131 mg (0.30 mmol, 88%). Due to the low solubility of this compound, no satisfactory NMR spectra could be obtained. HR-MS (ES): calcd for $C_{22}H_{24}Li_1N_{10}$: *m/z* = 435.2340, found *m/z* = 435.2311 $[M+Li]^+$. Microanalysis: calcd (%) for $C_{22}H_{24}N_{10}\cdot 2H_2O$: C 56.88, H 6.08, N 30.15; found C 56.24, H 5.76, N 30.22.

L4



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): ™(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, N*H*), 7.74 (brs, 1H, H_8), 8.35 (m, 2H, H_{11}). ^{13}C NMR ($CDCl_3$, 100 MHz): ™ = 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 C22H25N10 : *m/z* = 429.2258, found *m/z* = 429.2244 $[M + H]^+$. Microanalysis: calcd (%) for $C_{22}H_{24}N_{10}\cdot 5H_2O$: C 50.95, H 6.61, N 27.01; found C 51.19, H 6.79, N 27.37.

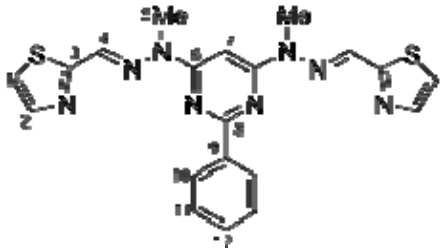
L5



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): ™(ppm) = 3.77 (s, 6H, C*H$_3$*), 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$_{imid}$). ^{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 $C_{20}H_{20}N_{10}\cdot 6H_2O$: C 47.24, H 6.34, N 27.54; found C 46.98, H 6.53, N 27.79.

L6



To a stirred solution of 4,6-di(*N*-methylhydrazino)-2-phenylpyrimidine (35.5 mg, 0.145 mmol) in EtOH$_{abs}$ (4 ml), 2-thiazolecarboxaldehyde (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): ™(ppm) = 3.77 (s, 6H, C*H$_3$*), 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 $C_{20}H_{18}N_8S_2Li$: *m/z* = 441.1251, found *m/z* = 441.1258 $[M+Li]^+$. Microanalysis: calcd (%) for $C_{20}H_{18}N_8S_2\cdot 7H_2O$: C 42.85, H 5.75, N 19.99; found C 42.62, H 5.50, N 20.21.

[Fe$_4$(L1)$_4$](OTf)$_8$

To a suspension of ligand **L1** (50.44 mg, 135 µmol) in CH_3NO_2 (10 ml), [Fe(dmso)$_6$](OTf)$_2$ (111.44 mg, 135 µmol) 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_2O. ^{1}H NMR (CD_3CN, 400 MHz): ™(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 $C_{80}H_{64}F_{24}N_{40}O_{24}S_8Fe_4\cdot 21H_2O\cdot 5DMSO$: C 29.42, H 3.73, N 15.25; found C 29.65, H 3.50, N 15.20.

[Fe_4(N-$C_{16}H_{33}$L1)$_4$](BF_4)$_8$

[$Fe(OH_2)_6$](BF_4)$_2$ (3.4 mg, 10 µmol) was added to a stirred suspension of ligand **N-$C_{16}H_{33}$L1** (8 mg, 10 µmol) in CH_3CN (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.

[Zn_4(L1)$_4$](OTf)$_8$

To a suspension of ligand **L1** (20.82 mg, 55.90 µmol) in CH_3NO_2 (4 ml), [Zn(dmso)$_6$](OTf)$_2$ (46.53 mg, 55.90 µmol) was added. The yellow solution was stirred at 100 ^oC 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 Et_2O. ^1H NMR (CD_3CN, 400 MHz): ™(ppm) = 5.86 (d, *J* = 6.8 Hz, 1H, H_9), 6.11 (s, 1H, H_6), 6.51 (d, *J* = 7.2 Hz, 1H, H_9), 7.08 (t, *J* = 8.0 Hz, 1H, H_{10}), 7.32 (s, 2H, H_1), 7.34 (d, *J* = 1.2 Hz, 2H, H_2), 7.56 (t, *J* = 7.2 Hz, 1H, H_{10}), 7.58 (s, 2H, H_4), 7.87 (t, *J* = 7.6 Hz, 1H, H_{11}), 10.80 (s, 2H, NH_{imid}), 10.89 (s, 2H, NH_{hydr}). HR-MS (ES): calcd for $C_{78}H_{64}F_{18}N_{40}O_{18}S_6Zn_4$: *m/z* = 1322.0232, found *m/z* = 1322.0236 [*M - 2OTf*]$^{2+}$, calcd for $C_{77}H_{64}F_{15}N_{40}O_{15}S_5Zn_4$: *m/z* = 831.6979, found *m/z* = 831.6903 [*M - 3OTf*]$^{3+}$. Microanalysis: calcd (%) for $C_{80}H_{64}F_{24}N_{40}O_{24}S_8Zn_4 \cdot 14H_2O \cdot 3DMSO$: C 30.11, H 3.23, N 16.33; found C 30.37, H 3.21, N 16.31

[Zn_4(L2)$_4$](OTf)$_8$

To a suspension of **L2** (14.8 mg, 37 µmol) in CH_3CN (2 ml), $Zn(OTf)_2 \cdot H_2O$ (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 Et_2O. Yield: 23 mg, 82%. ^1H NMR (CD_3CN, 400 MHz): ™(ppm) = 3.42 (s, 6H, C*H*$_3$), 5.73 (d, *J* = 7.6 Hz, 1H, H_{10}), 6.38 (s, 1H, H_7), 6.54 (d, *J* = 8 Hz, 1H, H_{10}), 7.08 (t, *J* = 8 Hz, 1H, H_{11}), 7.30 (s, 2H, H_1), 7.38 (d, *J* = 1.6 Hz, 2H, H_2), 7.48 (t, *J* = 7.6 Hz, 1H, H_{11}), 7.67 (s, 2H, H_4), 7.77 (t, *J* = 7.6 Hz, 1H, H_{12}), 10.93 (s, 2H, NH_{imid}). HR-MS (ES): calcd for $C_{86}H_{80}F_{18}N_{40}O_{18}S_6Zn_4$: *m/z* = 1378.0859, found *m/z* = 1378.1067 [*M - 2OTf*]$^{2+}$, calcd for $C_{85}H_{80}F_{15}N_{40}O_{15}S_5Zn_4$: *m/z* = 869.0731, found *m/z* = 869.0796 [*M - 3OTf*]$^{3+}$, calcd for $C_{84}H_{80}F_{12}N_{40}O_{12}S_4Zn_4$: *m/z* = 614.5667, found *m/z* = 614.5768 [*M - 4OTf*]$^{4+}$. Microanalysis: calcd (%) for $C_{80}H_{80}Cl_8N_{40}O_{32}Zn_4 \cdot 14H_2O$: C 33.01, H 3.74, N 19.25; found C 32.89, H 3.84, N 19.71.

[Co$_4$(L2)$_4$](BF$_4$)$_8$

To a suspension of ligand **L2** (29.7 mg, 74 µmol) in CH_3CN (4 ml), $Co(BF_4)_2 \cdot 6H_2O$ (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%. ^{1}H NMR (CD_3CN, 400 MHz): ™(ppm) = -89.65, -75.59, -50.87, -17.45, -16.47, 11.00, 43.55, 95.91, 124.58, 154.33, 224.22. HR-MS (ES): calcd for $C_{80}H_{80}B_6F_{24}N_{40}Co_4$: *m/z* = 1179.2517, found *m/z* = 1179.2451 $[M - 2BF_4]^{2+}$, calcd for $C_{80}H_{80}B_5F_{20}N_{40}Co_4$: *m/z* = 757.1664, found *m/z* = 757.1743 $[M - 3BF_4]^{3+}$, calcd for $C_{80}H_{80}B_4F_{16}N_{40}Co_4$: *m/z* = 546.1238, found *m/z* = 546.1494 $[M - 4BF_4]^{4+}$. Microanalysis: calcd (%) for $C_{80}H_{80}B_8Co_4F_{32}N_{40} \cdot 12H_2O$: 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$_4$(L2)$_4$](BF$_4$)$_8$

To a suspension of ligand **L2** (29.3 mg, 73 µmol) in CH_3CN (4 ml), $Fe(BF_4)_2 \cdot 6H_2O$ (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%. ^{1}H NMR (CD_3CN, 400 MHz): ™(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 $C_{80}H_{80}B_6F_{24}N_{40}Fe_4$: *m/z* = 1173.2555, found *m/z* = 1173.2164 $[M - 2BF_4]^{2+}$, calcd for $C_{80}H_{80}B_5F_{20}N_{40}Fe_4$: *m/z* = 753.1690, found *m/z* = 752.1565 $[M - 3BF_4]^{3+}$, calcd for $C_{80}H_{80}B_4F_{16}N_{40}Fe_4$: *m/z* = 543.1257, found *m/z* = 543.0593 $[M - 4BF_4]^{4+}$. Microanalysis: calcd (%) for $C_{80}H_{80}B_8F_{32}Fe_4N_{40} \cdot 9H_2O$: C 35.83, H 3.68, N 21.89; found C 35.71, H 3.57, N 21.75.

[Mn$_4$(L2)$_4$](OTf)$_8$

To a suspension of ligand **L2** (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 $C_{80}H_{80}Cl_6N_{40}O_{24}Cu_4$: *m/z* = 1226.0766, found *m/z* = 1226.0815 $[M - 2ClO_4]^{2+}$, calcd for $C_{80}H_{80}Cl_5N_{40}O_{20}Cu_4$: *m/z* = 784.4015, found *m/z* = 784.4048 $[M - 3ClO_4]^{3+}$, calcd for $C_{80}H_{80}Cl_4N_{40}O_{16}Cu_4$: *m/z* = 562.0652, found *m/z* =

562.0639 [*M* – *4ClO*$_4$]$^{4+}$. Microanalysis: calcd (%) for $C_{88}H_{80}F_{24}Mn_4N_{40}O_{24}S_8 \cdot 11H_2O$: C 32.90, H 3.20, N 17.44; found C 32.88, H 3.36, N 17.49.

[Cu$_4$(L2)$_4$](ClO$_4$)$_8$

To a suspension of ligand **L2** (37.6 mg, 94 μmol) in CH_3CN (4 ml), $Cu(ClO_4)_2 \cdot 6H_2O$ (34.8 mg, 94 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_2O. Yield: 57 mg, 80%. ^{1}H NMR (CD_3CN, 400 MHz): ™(ppm) = 3.24, 6.87, 7.00, 7.24, 10.05, 10.65, 27.38, 33.59. HR-MS (ES): calcd for $C_{80}H_{80}Cl_6N_{40}O_{24}Cu_4$: *m/z* = 1226.0766, found *m/z* = 1226.0815 [*M* – *2ClO*$_4$]$^{2+}$, calcd for $C_{80}H_{80}Cl_5N_{40}O_{20}Cu_4$: *m/z* = 784.4015, found *m/z* = 784.4048 [*M* – *3ClO*$_4$]$^{3+}$, calcd for $C_{80}H_{80}Cl_4N_{40}O_{16}Cu_4$: *m/z* = 562.0652, found *m/z* = 562.0639 [*M* – *4ClO*$_4$]$^{4+}$. Microanalysis: calcd (%) for $C_{80}H_{80}Cl_8Cu_4N_{40}O_{32} \cdot 15H_2O$: C 32.89, H 3.79, N 19.18; found C 32.79, H 3.57, N 19.35.

[Zn$_4$(L3)$_4$](OTf)$_8$

To a suspension of ligand **L3** (16.0 mg, 37.3 μmol) in CH_3CN (3 ml), $Zn(OTf)_2 \cdot H_2O$ (13.5 mg, 37.3 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_2O. Yield: 20 mg, 69%. ^{1}H NMR (CD_3CN, 400 MHz): ™(ppm) = 2.28 (s, 6H, H_3), 3.41 (s, 6H, H_6), 5.71 (d, *J* = 7.6 Hz, 1H, H_{11}), 6.32 (s, 1H, H_8), 6.53 (d, *J* = 7.2 Hz, 1H, H_{11}), 7.02 (t, *J* = 7.6 Hz, 1H, H_{12}), 7.15 (s, 2H, H_1), 7.46 (t, *J* = 7.6 Hz, 1H, H_{12}), 7.60 (s, 2H, H_5), 7.75 (t, *J* = 7.6 Hz, 1H, H_{13}), 10.87 (s, 2H, NH_{imid}). HR-MS (ES): calcd for $C_{94}H_{96}F_{18}N_{40}O_{18}S_6Zn_4$: *m/z* = 1434.1487, found *m/z* = 1434.0970 [*M* - *2OTf*]$^{2+}$, calcd for $C_{93}H_{96}F_{15}N_{40}O_{15}S_5Zn_4$: *m/z* = 906.4483, found *m/z* = 906.4374 [*M* - *3OTf*]$^{3+}$, calcd for $C_{92}H_{96}F_{12}N_{40}O_{12}S_4Zn_4$: *m/z* = 642.9663, found *m/z* = 643.1031 [*M* - *4OTf*]$^{4+}$. Microanalysis: calcd (%) for $C_{96}H_{96}F_{24}N_{40}O_{24}S_8Zn_4 \cdot 14H_2O$: C 33.71, H 3.65, N 16.38; found C 33.74, H 3.70, N 16.19.

[Co$_4$(L3)$_4$](OTf)$_8$

To a suspension of ligand **L3** (29.47 mg, 68.77 μmol) in CH_3CN (5 ml), $[Co(dmso)_6](OTf)_2$ (56.78 mg, 68.77 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_2O. Yield: 40 mg, 74%. ^{1}H

NMR (CD_3CN, 400 MHz): ™(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 $C_{94}H_{96}F_{18}N_{40}O_{18}S_6Co_4$: *m/z* = 1421.1590, found *m/z* = 1421.1379 $[M - 2OTf]^{2+}$, calcd for $C_{93}H_{96}F_{15}N_{40}O_{15}S_5Co_4$: *m/z* = 898.1226, found *m/z* = 898.1194 $[M - 3OTf]^{3+}$, calcd for $C_{92}H_{96}F_{12}N_{40}O_{12}S_4Co_4$: *m/z* = 636.1032, found *m/z* = 636.1070 $[M - 4OTf]^{4+}$. Microanalysis: calcd (%) for $C_{96}H_{96}Co_4F_{24}N_{40}O_{24}S_8 \cdot 12H_2O$: C 34.33, H 3.60, N 16.68; found C 34.81, H 3.89, N 16.32.

[Fe$_4$(L3)$_4$](OTf)$_8$

To a suspension of ligand **L3** (29.78 mg, 69.49 µmol) in CH_3CN (5 ml), $[Fe(dmso)_6](OTf)_2$ (57.18 mg, 69.49 µmol) was added. The mixture was stirred at 60 °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 Et_2O. Yield: 41 mg, 77%. ^{1}H NMR (CD_3CN, 400 MHz): ™(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 $C_{96}H_{96}F_{24}Fe_4N_{40}O_{24}S_8 \cdot 18H_2O$: C 33.38, H 3.85, N 16.22; found C 33.20, H 3.68, N 16.47.

[Cu$_4$(L3)$_4$](OTf)$_8$

To a suspension of ligand **L3** (40 mg, 82.90 µmol) in CH_3CN (4 ml), $[Cu(dmso)_6](OTf)_2$ (68.85 mg, 82.49 µmol) 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_2O. Yield: 55 mg, 79%. ^{1}H NMR (CD_3CN, 400 MHz): ™(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 $C_{96}H_{96}Cu_4F_{24}N_{40}O_{24}S_8 \cdot 33H_2O$: C 30.70, H 4.35, N 14.92; found C 30.69, H 3.74, N 14.86.

[Mn$_4$(L3)$_4$](OTf)$_8$

To a suspension of ligand **L3** (51.71 mg, 107.17 µmol) in CH_3NO_2 (5 ml), $[Mn(dmso)_6](OTf)_2$ (88.08 mg, 107.17 µmol) was added. The mixture was stirred at 60°C 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_2O. Yield: 85 mg, 95%. ^{1}H NMR (CD_3CN, 400 MHz): ™(ppm) = the spectra was broad and undefined. Microanalysis: calcd (%) for $C_{96}H_{96}F_{24}Mn_4N_{40}O_{24}S_8 \cdot 12H_2O$: C 34.50, H 3.62, N 16.46; found C 34.14, H 3.62, N 16.60.

[Zn$_4$(L4)$_4$](OTf)$_8$

To a suspension of ligand **L4** (21.0 mg, 49.0 µmol) in CH_3CN (4 ml), $Zn(OTf)_2 \cdot H_2O$ (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 Et_2O. Yield: 29 mg, 76%. ^{1}H NMR (CD_3CN, 400 MHz): ™(ppm) = 1.68 (s, 6H, H_3), 3.39 (s, 6H, H_6), 5.90 (d, *J* = 7.6 Hz, 1H, H_{11}), 6.41 (s, 1H, H_8), 6.46 (d, *J* = 7.2 Hz, 1H, H_{11}), 7.16 (t, *J* = 7.6 Hz, 1H, H_{12}), 7.36 (d, *J* = 2 Hz, 2H, H_1), 7.50 (t, *J* = 7.6 Hz, 1H, H_{12}), 7.65 (s, 2H, H_5), 7.80 (t, *J* = 7.6 Hz, 1H, H_{13}), 10.88 (s, 2H, NH_{imid}). Microanalysis: calcd (%) for $C_{96}H_{96}F_{24}N_{40}O_{24}S_8Zn_4 \cdot 11H_2O$: C 34.25, H 3.53, N 16.64; found C 34.00, H 3.65, N 16.54.

[Fe$_4$(L4)$_4$](OTf)$_8$

To a suspension of ligand **L4** (18.44 mg, 43.03 µmol) in a CH_3CN/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 24 h. The complex was isolated as red solid by evaporation of the solvent and crystallisation of the residue from MeCN by the addition of Et_2O. Yield: 21 mg, 63%. ^{1}H NMR (CD_3CN, 400 MHz): ™(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.

[Zn$_4$(L5)$_4$](OTf)$_8$

To a suspension of ligand **L5** (19.3 mg, 48.1 µmol) in CH_3CN (4 ml), $Zn(OTf)_2 \cdot H_2O$ (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 Et_2O. Yield: 30 mg, 81%. ^{1}H NMR (CD_3CN, 400 MHz): ™(ppm) = 3.51 (s, 6H, H_5), 5.46 (d, *J* = 7.6 Hz, 1H, H_{10}), 6.49 (d, *J* = 7.6 Hz, 1H, H_{10}), 6.53 (s, 2H, H_2), 6.58 (s, 1H, H_7), 7.10 (dd, *J* = 2.2 Hz and 1.4 Hz, 2H, H_1), 7.24 (t, *J* = 7.2 Hz, 1H, H_{11}), 7.52 (t, *J* = 7.2 Hz, 1H, H_{11}), 7.74 (s, 2H, H_4), 7.86 (t, *J* = 7.6 Hz, 1H, H_{12}), 11.56 (s, 2H, NH_{imid}). HR-MS (ES): calcd for $C_{86}H_{80}F_{18}N_{40}O_{18}S_6Zn_4$: *m/z* = 1378.0859, found *m/z* = 1378.1125 [*M - 2OTf*]$^{2+}$, calcd for $C_{85}H_{80}F_{15}N_{40}O_{15}S_5Zn_4$: *m/z* = 869.0731, found *m/z* = 869.1080 [*M - 3OTf*]$^{3+}$, calcd for $C_{84}H_{80}F_{12}N_{40}O_{12}S_4Zn_4$: *m/z* = 613.0675, found *m/z* = 613.0831 [*M - 4OTf*]$^{4+}$. Microanalysis: calcd (%) for $C_{88}H_{80}F_{24}N_{40}O_{24}S_8Zn_4 \cdot 10H_2O$: C 32.66, H 3.11, N 17.31; found C 32.53, H 3.35, N 17.78.

$[Co_4(L5)_4](OTf)_8$

To a suspension of ligand **L5** (16.58 mg, 41.4 μmol) in CH_3CN (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 Et_2O. ^1H NMR (CD_3CN, 400 MHz): ™(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 $C_{86}H_{80}F_{18}N_{40}O_{18}S_6Co_4$: *m/z* = 1365.0964, found *m/z* = 1365.0743 $[M - 2OTf]^{2+}$, calcd for $C_{85}H_{80}F_{15}N_{40}O_{15}S_5Co_4$: *m/z* = 860.7475, found *m/z* = 860.7434 $[M - 3OTf]^{3+}$, calcd for $C_{84}H_{80}F_{12}N_{40}O_{12}S_4Co_4$: *m/z* = 608.0723, found *m/z* = 608.06 $[M - 4OTf]^{4+}$. Microanalysis: calcd (%) for $C_{88}H_{80}Co_4F_{24}N_{40}O_{24}S_8 \cdot 12H_2O$: C 32.56, H 3.23, N 17.26; found C 32.54, H 3.03, N 17.50.

$[Fe_4(L5)_4](OTf)_8$

To a suspension of ligand **L5** (16.38 mg, 40.90 μmol) in CH_3CN (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 Et_2O. ^1H NMR (CD_3CN, 400 MHz): ™(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 $C_{86}H_{80}F_{18}N_{40}O_{18}S_6Fe_4$: *m/z* = 1359.6013, found *m/z* = 1359.6882 $[M - 2OTf]^{2+}$, calcd for $C_{85}H_{80}F_{15}N_{40}O_{15}S_5Fe_4$: *m/z* = 856.7500, found *m/z* = 856.7995 $[M - 3OTf]^{3+}$, calcd for $C_{84}H_{80}F_{12}N_{40}O_{12}S_4Fe_4$: *m/z* = 605.0740, found *m/z* = 605.0887 $[M - 4OTf]^{4+}$. Microanalysis: calcd (%) for $C_{88}H_{80}F_{24}Fe_4N_{40}O_{24}S_8 \cdot 11H_2O$: C 32.87, H 3.20, N 17.42; found C 32.58, H 3.21, N 17.78.

$[Mn_4(L5)_4](OTf)_8$

To a suspension of ligand **L5** (9.86 mg, 24,62 μmol) in CH_3CN (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 Et_2O. ^1H NMR (CD_3CN, 400 MHz): ™(ppm) = the spectra was broad and undefined. Microanalysis: calcd (%) for $C_{88}H_{80}F_{24}Mn_4N_{40}O_{24}S_8 \cdot 12H_2O$: C 32.72, H 3.25, N 17.34; found C 32.54, H 3.33, N 17.68.

[Zn_4(L6)$_4$](OTf)$_8$

To a suspension of ligand **L6** (8.87 mg, 20.41 μmol) in CH_3CN (3 ml), $Zn(OTf)_2 \cdot H_2O$ (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 Et_2O. Yield: 14mg, 85%. ^{1}H NMR (CD_3CN, 400 MHz): ™(ppm) = 3.63 (s, 6H, H_5), 5.71 (d, *J* = 7.6 Hz, 1H, H_{10}), 6.48 (d, *J* = 7.2 Hz, 1H, H_{10}), 6.86 (s, 1H, H_7), 7.28 (t, *J* = 7.6 Hz, 1H, H_{11}), 7.37 (d, *J* = 3.2 Hz, 2H, H_1 or H_2), 7.61 (d, *J* = 3.2 Hz, 2H, H_1 or H_2), 7.75 (t, *J* = 7.2 Hz, 1H, H_{11}), 7.97 (t, *J* = 7.6 Hz, 1H, H_{12}), 8.07 (s, 2H, H_4). HR-MS (ES): calcd for $C_{86}H_{72}F_{18}N_{32}O_{18}S_{14}Zn_4$: *m/z* = 1446.9295, found *m/z* = 1446.9081 [*M - 2OTf*]$^{2+}$, calcd for $C_{85}H_{80}F_{15}N_{32}O_{15}S_{13}Zn_4$: *m/z* = 914.9688, found *m/z* = 914.9824, [*M - 3OTf*]$^{3+}$. Microanalysis: calcd (%) for $C_{88}H_{72}F_{24}N_{32}O_{24}S_{16}Zn_4 \cdot 15H_2O$: C 30.53, H 2.97, N 12.94; found C 30.65, H 3.12, N 13.21.

[Co_4(L6)$_4$](OTf)$_8$

To a suspension of ligand **L6** (56.19 mg, 129.3 μmol) in CH_3NO_2 (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 flitered 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 Et_2O. Yield: 88 mg, 86%. ^{1}H NMR (CD_3CN, 400 MHz): ™(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 $C_{86}H_{72}Co_4F_{18}N_{32}O_{18}S_{14}$: *m/z* = 1433.9414, found *m/z* = 1433.9474 [*M - 2OTf*]$^{2+}$, calcd for $C_{85}H_{72}Co_4F_{15}N_{32}O_{15}S_{13}$: *m/z* = 906.3101, found *m/z* = 906.3137, [*M - 3OTf*]$^{3+}$. Microanalysis: calcd (%) for $C_{88}H_{72}F_{24}N_{32}O_{24}S_{16}Co_4 \cdot 8H_2O$: C 31.93, H 2.68, N 13.54; found C 31.80, H 2.89, N 13.88.

[Fe_4(L6)$_4$](OTf)$_8$

To a suspension of ligand **L6** (10 mg, 23.01 μmol) in CH_3NO_2 (4 ml), $[Fe(dmso)_6](OTf)_2$ (18.93 mg, 23.01 μmol) was added. The red solution was stirred under N_2 at 100 ^{o}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 Et_2O. Yield: 22 mg, 75%. ^{1}H NMR (CD_3CN, 400 MHz): ™(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 $C_{86}H_{72}F_{18}Fe_4N_{32}O_{18}S_{14}$: *m/z* = 1427.9452, found *m/z* =

1427.9291 [*M - 2OTf*]$^{2+}$, calcd for $C_{85}H_{72}F_{15}Fe_4N_{32}O_{15}S_{13}$: *m/z* = 902.3126, found *m/z* = 902.3003, [*M - 3OTf*]$^{3+}$, calcd for $C_{84}H_{72}F_{12}Fe_4N_{32}O_{12}S_{12}$: *m/z* = 638.9873, found *m/z* = 638.9975, [*M - 4OTf*]$^{4+}$. Microanalysis: calcd (%) for $C_{88}H_{72}F_{24}N_{32}O_{24}S_{16}Fe_4 \cdot 29H_2O$: C 28.75, H 3.56, N 12.19; found C 28.50, H 3.23, N 11.90.

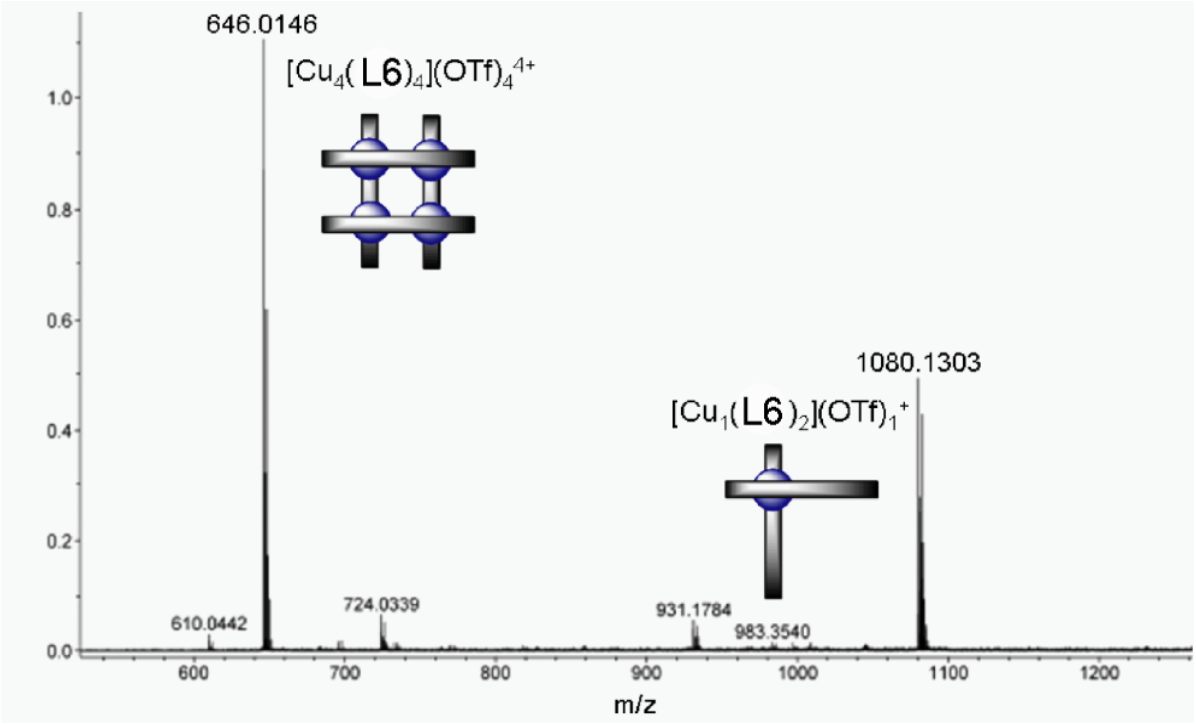
[Cu$_4$(L6)$_4$](OTf)$_8$

To a suspension of ligand **L6** (43.62mg, 100.38μmol) in CH_3NO_2 (4 ml), $[Cu(dmso)_6](OTf)_2$ (83.36 mg, 100.38 μmol) 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_2O. Yield: 22 mg, 75%. ^{1}H NMR (CD_3CN, 400 MHz): ™(ppm) = 2.59, 4.30, 7.13, 7.54, 10.63, 11.27, 37.77, 42.86. HR-MS (ES): calcd for $C_{86}H_{72}Cu_4F_{18}N_{32}O_{18}S_{14}$: *m/z* = 1442.9301, found *m/z* = 1442.9739 [*M - 2OTf*]$^{2+}$, calcd for $C_{84}H_{72}Cu_4F_{12}N_{32}O_{12}S_{12}$: *m/z* = 646.2353, found *m/z* = 646.0146, [*M - 4OTf*]$^{4+}$. Microanalysis: calcd (%) for $C_{88}H_{72}Cu_4F_{24}N_{32}O_{24}S_{16} \cdot 12H_2O$: 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.*

Ligand	Metal salt	Solvent	Reaction conditions	Product	Yield
L2	$Zn(OTf)_2 \cdot xH_2O$	MeCN	r.t., 24 h	diamagnetic	82%
L2	$Co(BF_4)_2 \cdot 6H_2O$	MeCN	r.t., 24 h	paramagnetic	78%
L2	$Fe(BF_4)_2 \cdot 6H_2O$	MeCN	60°C, 24 h	paramagnetic	74%
L2	$Cu(ClO_4)_2 \cdot 6H_2O$	MeCN	r.t., 24 h	paramagnetic	80%
L2	$[Mn(dmso)_6](OTf)_2$	MeCN	60°C, 24 h	paramagnetic	quantitative
L3	$Zn(OTf)_2 \cdot xH_2O$	MeCN	r.t., 24 h	diamagnetic	69%
L3	$[Co(dmso)_6](OTf)_2$	MeCN	r.t., 24 h	paramagnetic	74%
L3	$[Fe(dmso)_6](OTf)_2$	MeCN	60°C, 24 h	paramagnetic	77%
L3	$[Cu(dmso)_6](OTf)_2$	MeCN	r.t., 24 h	paramagnetic	79%
L3	$[Mn(dmso)_6](OTf)_2$	$MeNO_2$	60°C, 24 h	paramagnetic	95%
L4	$Zn(OTf)_2 \cdot xH_2O$	MeCN	r.t., 24 h	diamagnetic	76%
L4	$[Fe(dmso)_6](OTf)_2$	MeCN/MeOH	60°C, 24 h	paramagnetic	63%
L5	$Zn(OTf)_2 \cdot xH_2O$	MeCN	r.t., 24 h	diamagnetic	81%
L5	$[Co(dmso)_6](OTf)_2$	MeCN	r.t., 24 h	paramagnetic	quantitative
L5	$[Fe(dmso)_6](OTf)_2$	MeCN	60°C, 24 h	paramagnetic	quantitative
L5	$Cu(OTf)_2 \cdot xH_2O$	MeCN	r.t., 24 h	paramagnetic	no grid
L5	$[Mn(dmso)_6](OTf)_2$	MeCN	60°C, 24 h	paramagnetic	quantitative
L1	$[Zn(dmso)_6](OTf)_2$	$MeNO_2$	reflux, 24 h	diamagnetic	quantitative
L1	$[Fe(dmso)_6](OTf)_2$	$MeNO_2$	reflux, 24 h	paramagnetic	quantitative
L6	$Zn(OTf)_2 \cdot xH_2O$	MeCN	r.t., 24 h	diamagnetic	85%
L6	$[Co(dmso)_6](OTf)_2$	$MeNO_2$	r.t., 24 h	paramagnetic	86%
L6	$[Fe(dmso)_6](OTf)_2$	$MeNO_2$	reflux, 24 h	paramagnetic	75%
L6	$[Cu(dmso)_6](OTf)_2$	$MeNO_2$	reflux, 24 h	paramagnetic	75%

High resolution ESI mass spectrum of tetranuclear $[Cu_4(\mathbf{L6})_4](OTf)_4^{4+}$ and mononuclear $[Cu_1(\mathbf{L6})_2](OTf)_1^{1+}$



A set of 1-H NMR spectra of Fe(II) complexes with structurally different bis-hydrazone-type ligands.