Self-assembly of a Heteroleptic One-Dimensional Chains Comprising Different Dinuclear *Meso*-Helicates.

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Electronic Supplementary Information

X-ray Crystallography.

Single crystal X-ray diffraction data was collected at 150(2) K on a Bruker Apex Duo diffractometer equipped with a graphite monochromated Mo(Kα) radiation source and a cold stream of N_2 gas. Solutions were generated by conventional heavy atom Patterson or direct methods and refined by full-matrix least squares on all F^2 data, using SHELXS-97 and SHELXL software respectively.[1] Absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS.[2]

$[Cd_2(\mathbf{L^2})_2](ClO_4)_5 0.86(CH_3NO_2)\cdot 4(CH_2Cl_2)\cdot H_2O$. This structure contained substitutional disorder comprising nitromethane and dichloromethane molecules and a molecule of dichloromethane and these were modelled in two positions using the part instruction. The bond lengths of the dichloromethane molecule were constrained using SADI and the thermal ellipsoids of the nitromethane solvent using DELU and SIMU in the least-squares refinement.

$[[Cd_2(\mathbf{L^1})_2][Cd_2(\mathbf{L^2}\text{-}H)_2]](ClO_4)_{10}$. Crystals of this species diffracted poorly at high angles hence data was limited to 2theta = 50. The glycol chain was refined isotropically as a satisfactory anisotropic disordered model could not be found. The majority of the solvent water positions, one CH_2Cl_2 and two ClO_4 anions were refined isotropically. The C-Cl distances of one CH_2Cl_2 and the Cl-O distances of one ClO_4 were restrained to be chemically reasonable.

Compound	$[Fe_2(\mathbf{L^1})_2](ClO_4)_4\cdot 4(CHCl_3)\cdot 2(CH_3CN)$	$[Cd_2(\mathbf{L^2})_2](ClO_4)_5\cdot 0.86(CH_3NO_2)\cdot 4(CH_2Cl_2)\cdot H_2O$	$[[Cd_2(\mathbf{L^1})_2][Cd_2(\mathbf{L^2}\text{-}H)_2]](ClO_4)_{10}\cdot CH_2Cl_2\cdot 10.5H_2$

			O
Formula	$C_{108}H_{90}Cl_{16}Fe_2N_{14}O_{22}S_4$	$C_{94.86}H_{75.57}Cd_2Cl_{13}N_{14.86}O_{22.71}S_4$	$C_{98}H_{93}Cd_2Cl_{10}N_{13}O_{30}S_4$
M	2743.08	2600.83	2639.39
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/c
a (Å)	11.7211 (6)	13.8209(7)	13.3018(3)
b (Å)	13.4503 (8)	18.3351(9)	20.7598(4)
c (Å)	21.2922 (12)	21.5994(10)	44.2313(9)
α (˚)	104.0930 (10)	95.0080(10)	90
β (˚)	96.2950 (10)	92.1730(10)	91.2640(10)
γ (˚)	110.1670 (10)	107.4850(10)	90
V (Å^3)	2986.2 (3)	5188.8(4)	12211.2(4)
Z	1	2	4
ρ_{calc} (Mg cm^{-1})	1.525	1.665	1.436
F(000)	1400	2622.8	5364
Crystal dimensions (mm)	0.50×0.26×0.03	0.40×0.3×0.01	0.50×0.18×0.07
Reflections measured	55213	118786	104867
Range	$1.69 \leq \theta \leq 28.72$ ˚	$1.43 \leq \theta \leq 30.51$ ˚	$1.35 \leq \theta \leq 25.00$ ˚
hkl range indices	$-15 \leq h \leq 14$, $-17 \leq k \leq 17$, $-28 \leq l \leq 28$	$-19 \leq h \leq 19$, $-26 \leq k \leq 26$, $-30 \leq l \leq 30$	$-15 \leq h \leq 15$, $-24 \leq k \leq 24$, $-52 \leq l \leq 52$
N^o independent reflections	14883	31560	21329
Reflections with $I > 2\sigma(I)$	8603	20025	13700
R_{int}	0.0774	0.0580	0.0686
Final R_1 values	0.0596	0.0588	0.1218
Final $wR(F^2)$ values	0.1324	0.1514	0.3489
Final R_1 values (all data)	0.1243	0.1070	0.1708

Final $wR(F^2)$ values (all data)	0.1594	0.1784	0.4018
GOF	1.016	1.045	1.516
Refined parameters	751	1401	1304
Restraints	0	52	6
Largest peak and hole (e $Å^{-3}$)	1.518, -1.128	1.888, -1.980	2.368, -1.571
CCDC Number	958173	958174	958175

1. SHELXTL Program System, Vers. 5.1, Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.

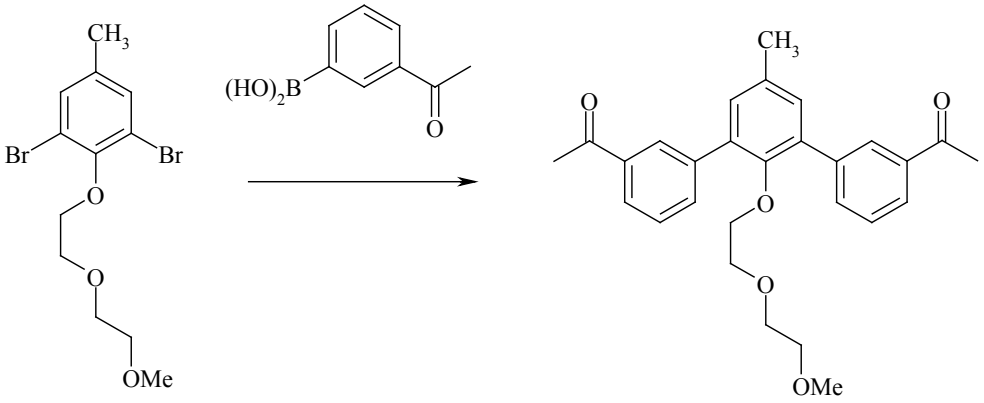
2. G. M. Sheldrick, SADABS: A Program for Absorption Correction with the Siemens SMART System, University of Göttingen (Germany), 1996.

Synthetic Details

Chemicals were purchased and used without further purification. ^{1}H NMR spectra were recorded on a 400MHz Bruker Avance DP X400. Mass spectra were obtained on a Bruker MicroTOF LC. *Great care should be taken with perchlorate salts as they are potentially explosive, in all cases they are used in small quantities (<5 mgs).*

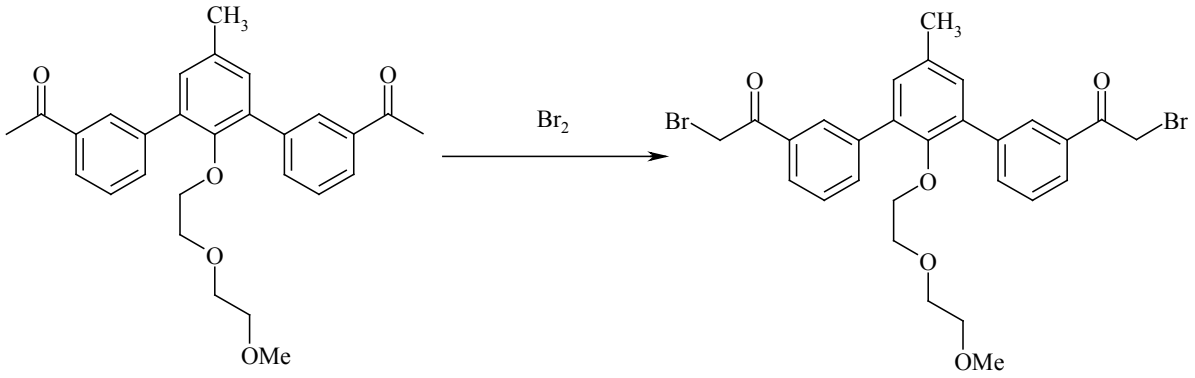
1

Synthesis of 1,3-dibromo-2-[2-(2-methoxyethoxy)ethoxy]-5-methyl-benzene (1): A two necked round bottom flask charged with 2,6-dibromo-4-methylphenol (1.36 g, 5.1 mmol) and sodium hydride (0.12 g, 5.1 mmol) was placed under an atmosphere of dinitrogen, to this was added anhydrous THF (35 ml). This was left to stir at room temperature for 1h. After this time 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (0.71 g, 2.6 mmol) was added to the reaction and set to stir at 80˚C. The reaction was monitored *via* TLC (SiO_2, 2 % MeOH in DCM) and once all the benzenesulfonate was consumed methanol was added to the reaction whilst under $N_{2(g)}$ (to remove any unreacted sodium hydride). The reaction was concentrated and $NaHCO_{3(aq)}$ (50 ml) added to the reaction and extracted into ether (3 x 30 ml). The combined organic layers were dried ($MgSO_4$) and the solvent removed by rotary evaporation. Separation and purification *via* column chromatography (SiO_2, 2 % MeOH in DCM) gave **1** as a pale green oil (0.52 g, 56 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 7.31 (s, 2H, Ph), 4.18 (t, *J*= 5.0, 2H, -C*H*$_2$), 3.94 (t, *J*= 5.2, 2H, -C*H*$_2$), 3.78 (t, *J*= 4.5, 2H, -C*H*$_2$), 3.60 (t, *J*= 4.5 Hz, 2H, -C*H*$_2$), 3.41 (s, 3H, -C*H*$_3$), 2.28 (s, 3H, -ArC*H*$_3$). ESI-MS *m/z* 388 (M + Na^+), HR ESI-MS found 388.9358 $C_{12}H_{16}Br_2NaO_3$ requires 388.9358 (error 1.09 ppm).



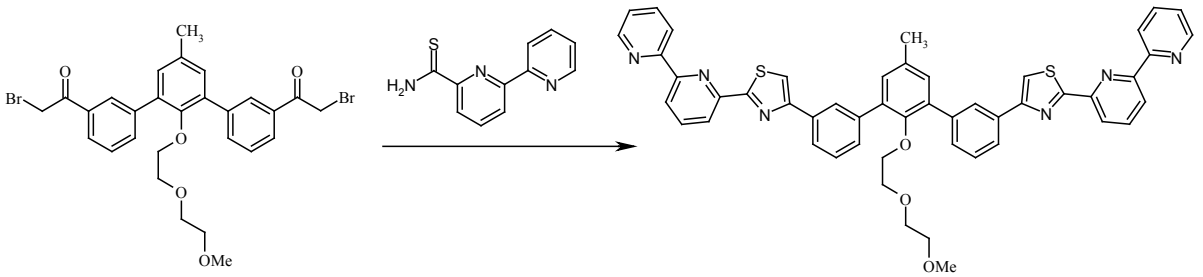
1 **2**

Synthesis of (2): In a 50 ml round bottom flask **1** (0.20 g, 0.54 mmol), 3-acetyl phenylboronic acid (0.27 g, 1.63 mmol), sodium carbonate (0.06 g, 0.54 mmol), $Bu^n{}_4NBr$ (0.17 g, 0.54 mmol) and bis (triphenylphosphine) palladium chloride (0.008 g, 2 mol %) was suspended in deionised water (10 ml) and ethanol (10 ml). The reaction was left to stir at 70˚C for 20 h, and was monitored *via* TLC (SiO_2, 1:1 ethyl acetate: petroleum ether 40-60). The ethanol was removed by rotary evaporation to allow extraction into DCM (3 x 30ml); the combined organic layers dried over $MgSO_4$. Filtration and evaporation provided a crude product that was purified *via* column chromatography (SiO_2, 1:1 ethyl acetate: petroleum ether 40-60), producing the desired product, **2**, as a yellow oil (0.21 g, 89 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.21 (s, 2H, Ph), 7.95 (d, *J*= 7.7, 2H, Ph), 7.89 (d, *J*= 7.6, 2H, Ph), 7.53 (t, *J*= 7.7, 2H, Ph), 7.22 (s, 2H, Ph^{cent}), 3.35 (t, *J*= 5.0 Hz, 2H, -C*H*$_2$), 3.28-3.26 (m, overlap, 5H, -C*H*$_2$, -C*H*$_3$), 3.18-3.14 (m, overlap, 4H, 2 x -C*H*$_2$), 2.68 (s, 6H, -C*H*$_3$), 2.43 (s, 3H, -ArC*H*$_3$). ESI-MS *m/z* 469 (M + Na^+), HR ESI-MS found 469.2001 $C_{28}H_{30}NaO_5$ requires 469.1985 (error 3.32 ppm).



2 **3**

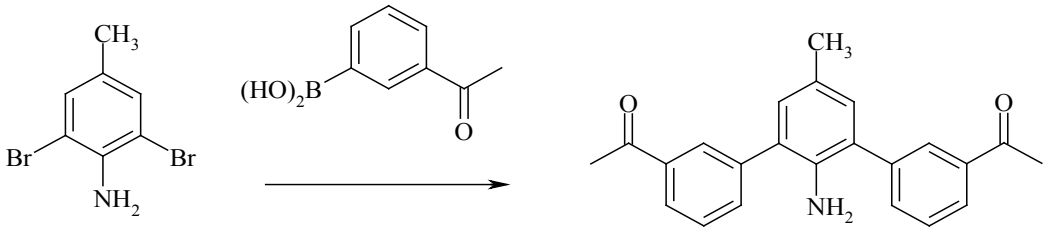
Synthesis of (3): Compound **2** (0.21 g, 0.47 mmol) was dissolved in acetic acid (25 ml) and set to stir at 80 ˚C under an atmosphere of dinitrogen. Bromine (0.15 g, 0.94 mmol) was diluted using acetic acid to give approximately 1 ml (approx. 0.9 ml acetic acid) to allow slow addition to the reaction over 1 h. The reaction was monitored *via* TLC (SiO_2, 1:1 ethyl acetate: petroleum ether 40-60); once the starting material was consumed the reaction was allowed to cool then poured over deionised water (30 ml) and $NaHCO_3$ (0.1 g) was added to neutralise the reaction. The product was extracted into DCM (3 x 30 ml) and the combined organic layers dried ($MgSO_4$). Removal of solvent left a crude product as a yellow-orange oil. Purification *via* column chromatography (SiO_2, 1:1 ethyl acetate: petroleum ether 40-60) gave **3** as a yellow oil (0.13 g, 46 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.25 (s, 2H, Ph), 7.99 (d, *J*= 7.8, 2H, Ph), 7.92 (d, *J*= 7.7, 2H, Ph), 7.57 (t, *J*= 7.7, 2H, Ph), 7.22 (s, 2H, Ph^{cent}), 4.55 (s, 4H, -C*H*$_2$Br), 3.36 (t, *J*= 4.8 Hz, 2H, -C*H*$_2$), 3.29-3.26 (m, overlap, 5H, -C*H*$_2$, -C*H*$_3$), 3.19-3.15 (m, overlap, 4H, 2 x -C*H*$_2$), 2.43 (s, 3H, -ArC*H*$_3$). ESI-MS *m/z* 625 ($M + Na^+$), HR ESI-MS found 625.0206 $C_{28}H_{28}Br_2NaO_5$ requires 625.0196 (error 1.60 ppm).



3 **L^1**

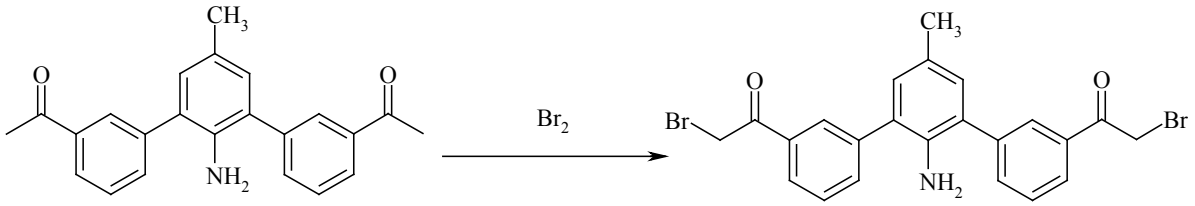
Synthesis of ligand L^1: To a solution of 2,2'-bipyridine-6-thioamide (0.098 g, 0.46 mmol) in ethanol (25 ml) was added **3** (0.125 g, 0.21 mmol) and the reaction refluxed for 8 h; the reaction was monitored *via* TLC (Al_2O_3, 1 % MeOH in DCM). Upon completion the solvent was removed by rotary evaporation followed by purification *via* column chromatography (Al_2O_3, 1 % MeOH in DCM) giving the final ligand, **L^1**, as a fine white solid once completely dry (0.09 g, 51 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.72 (dt, *J*= 4.8, 0.8, 2H, Py^{term}), 8.61 (d, *J*= 8.0, 2H, Py^{term}), 8.50 (dd, *J*= 7.8, 0.9, 2H, Py), 8.37 (dd, *J*= 7.8, 0.9, 2H, Py), 8.28 (t, *J*= 1.5, 2H, Ph), 8.05 (dt, *J*= 7.7, 1.4, 2H, Ph), 7.97 (t, *J*= 7.8, 2H, Py), 7.90 (dt, *J*= 7.7, 1.7, 2H, Py^{term}), 7.73 (s, 2H, Tz), 7.69 (dt, *J*= 7.8, 1.3, 2H, Ph), 7.54 (t, *J*= 7.7, 2H,

Ph), 7.36 (ddd, *J*= 7.8, 4.8, 1.1, 2H, Py^{term}), 7.31 (s, 2H, Ph^{cent}), 3.53 (t, *J*= 4.8, 2H, -CH_2), 3.28 (t, *J*= 4.8 Hz, 2H, -CH_2), 3.21-3.16 (m, overlap, 7H, 2 x -CH_2, -CH_3), 2.48 (s, 3H, -ArCH_3). ^{13}C NMR [500 MHz, $CDCl_3$/CD_3OD]: δ_C = 169.1 (quaternary, Q), 156.7 (Q), 155.5 (Q), 155.3 (Q) 151.9 (Q), 150.7 (Q), 149.1 (CH), 139.3 (Q), 138.1 (CH), 137.2 (CH), 135.5 (Q), 134.5 (Q), 133.8 (Q), 131.1 (CH), 129.6 (CH), 128.6 (CH), 127.4 (CH), 125.2 (CH), 124.1 (CH), 121.8 (CH), 121.4 (CH), 119.8 (CH), 115.6 (CH), 72.1 (OCH_2), 71.7 (OCH_2), 69.9 (OCH_2), 69.8 (OCH_2), 58.9 (OCH_3), 20.9 ($ArCH_3$). ESI-MS *m/z* 837 (M + H^+), HR ESI-MS found 837.2661 $C_{50}H_{41}N_6O_3S_2$ requires 837.2676 (error 1.75 ppm).



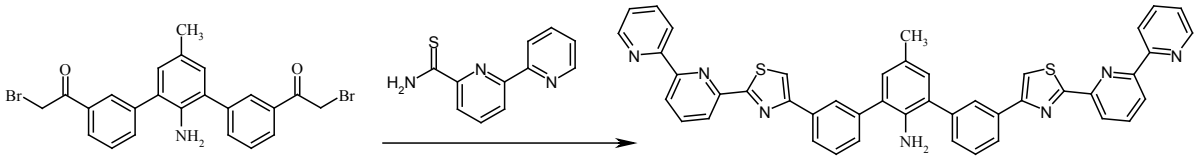
4

Synthesis of (4): This compound was produced in an identical manner to compound **2**, except 2,6-dibromo-p-toluidine was used in place of **1**. The reaction was monitored *via* TLC (SiO_2, 3:7 ethyl acetate: petroleum ether 40-60). Purification *via* column chromatography (SiO_2, 1:2 ethyl acetate : petroleum ether 40-60) gave the desired product as a yellow oil (49 % yield).^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.10 (s, 2H, Ph), 7.97 (d, *J*= 7.8, 2H, Ph), 7.74 (d, *J*= 7.7, 2H, Ph), 7.57 (t, *J*= 7.7 Hz, 2H, Ph), 7.00 (s, 2H, Ph^{cent}), 3.64 (br s, 2H, -NH_2), 2.66 (s, 6H,-CH_3), 2.34 (s, 3H, -ArCH_3). ESI-MS *m/z* 366 (M + Na^+), HR ESI-MS found 366.1465 $C_{23}H_{21}NNaO_2$ requires 366.1465 (error 0.24 ppm).



4 **5**

Synthesis of (5): This compound was produced in an identical manner to compound **3**, except compound **4** was used in place of compound **2**. The reaction was monitored *via* TLC (SiO_2, 3:7 ethyl acetate: petroleum ether 40-60), purification *via* column chromatography (SiO_2, 3:7 ethyl acetate: petroleum ether 40-60) gave the desired product, **5**, as a dark yellow oil (38 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.22 (s, 2H, Ph), 8.00 (d, *J*=7.3, 2H, Ph), 7.79 (d, *J*=7.0, 2H, Ph), 7.61 (t, *J*=7.7 Hz, 2H, Ph), 7.01 (s, 2H, Ph^{cent}), 4.50 (s, 4H, -CH_2Br), 3.69 (br s, 2H, -NH_2), 2.34 (s, 3H, -ArCH_3). ESI-MS *m/z* 499 (M + H^+), HR ESI-MS found 499.9854 $C_{23}H_{20}Br_2NO_2$ requires 499.9855 (error 0.33 ppm).



5 **L²**

Synthesis of L^2 : To a solution of 2,2'-bipyridine-6-thioamide (0.052 g, 0.24 mmol) in ethanol (25 ml) was added the α-bromoacetyl (**5**) (0.06 g, 0.12 mmol) and the reaction refluxed for 8 h, during which time a precipitate was produced. This was isolated by filtration, whilst hot, followed by washing with EtOH and Et_2O (2 x 2 ml). The compound was isolated as the HBr salt; to obtain the free ligand the product was suspended in concentrated ammonia (0.88 S.G., 10 ml) for 24 h. Filtration and washing with H_2O, EtOH and Et_2O (2 x 2 ml) gave the ligand, L^2, as an off white powder (0.026 g, 30 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.72 (dd, *J*= 4.8, 0.8, 2H, Py^{term}), 8.61 (d, *J*= 8.6, 2H, Py^{term}), 8.50 (dd, *J*= 7.8, 0.9, 2H, Py), 8.35 (dd, *J*= 7.8, 0.9, 2H, Py), 8.19 (s, 2H, Ph), 8.04 (dt, *J*= 7.0, 1.8, 2H, Ph), 7.97 (t, *J*= 7.8, 2H, Py), 7.90 (dt, *J*= 7.8, 1.8, 2H, Py^{term}), 7.70 (s, 2H, Tz), 7.60-7.53 (m, overlap, 4H, Ph), 7.37 (ddd, *J*= 7.4, 4.8, 1.2 Hz, 2H, Py^{term}), 7.10 (s, 2H, Ph^{cent}), 3.84 (br s, 2H, -N*H*$_2$), 2.39 (s, 3H, -ArC*H*$_3$). 13C NMR [500 MHz, $CDCl_3$/CD_3OD]: δC = 168.7 (quaternary, Q), 156.1 (Q), 155.7 (Q), 154.7 (Q), 150.5 (Q), 149.9 (CH), 140.5 (Q), 139.5 (CH), 138.0 (CH), 135.0 (Q), 130.8 (CH), 130.7 (Q), 129.8 (CH), 129.4 (CH), 128.0 (Q), 127.2 (CH), 125.9 (Q), 125.4 (CH), 125.1 (CH), 122.2 (CH), 121.1 (CH), 120.0 (CH), 118.0 (CH), 20.5 (CH_3). ESI-MS *m/z* 734 ($M + H^+$), HR ESI-MS found 734.2150 $C_{45}H_{32}N_7S_2$ requires 734.2155 (error 0.66 ppm).

Synthesis of Complexes

$[Fe_2(L^1)_2](ClO_4)_4$. The ligand L^1 (5 mg, 6.0 x 10^{-3} mmol) was suspended in CD_3CN (1 ml) and a solution of $Fe(ClO_4)_2{\cdot}6H_2O$ (2.2 mg, 6.0 x 10^{-3} mmol) in CH_3CN was added giving a dark purple solution. Slow diffusion of $CHCl_3$ resulted in dark purple crystals which were filtered, washed with $CHCl_3$ (1 ml) and Et_2O (1 ml) and dried under vacuum (75% yield). $[Fe_2(L^1)_2](ClO_4)_4{\cdot}(CHCl_3)$ Found: C, 52.5; H, 3.2; N, 6.8%. Calculated for $C_{101}H_{81}Cl_7Fe_2N_{12}O_{22}S_4$: C, 52.7; H, 3.6; N, 7.3%.

$[Cd_2(L^2)(L^2{+}H)](ClO_4)_5$. The ligand L^2 (5 mg, 6.8 x 10^{-3} mmol) was suspended in CH_3NO_2 (2 ml) to which was added $Cd(ClO_4)_2{\cdot}6H_2O$ (2.9 mg, 6.8 x 10^{-3} mmol) and the reaction sonicated until complete dissolution of the ligand and metal ion giving a colourless solution. To this was added camphorsulfonic acid* (1.57 mg, 6.8 x 10^{-3} mmol) and slow diffusion of CH_2Cl_2 resulted in pale yellow crystals which were filtered, washed with CH_2Cl_2 (1 ml) and Et_2O (1 ml) and dried under vacuum (48% yield). $[Cd_2(L^2)(L^2{+}H)](ClO_4)_5$ Found: C, 49.0; H, 2.7; N, 8.7 %. Calculated for $C_{90}H_{63}Cd_2Cl_5N_{14}O_{20}S_4$: C, 49.3; H, 2.9; N, 9.0%.

$[[Cd_2(\mathbf{L^1})_2][Cd_2(\mathbf{L^2}\text{-}H)_2]](ClO_4)_{10}$. To a suspension of $\mathbf{L^1}$ (5 mg, 6.0 x 10^{-3} mmol) and $\mathbf{L^2}$ (4.4 mg, 6.0 x 10^{-3} mmol) in $MeNO_2$ was added $Cd(ClO_4)_2 \cdot 6H_2O$ (5.1 mg, 1.2 x 10^{-2} mmol) and the reaction sonicated until complete dissolution of the ligand and metal ion giving a colourless solution. To this was added camphorsulfonic acid* (1.39 mg, 6.0 x 10^{-3} mmol) and slow diffusion of CH_2Cl_2 resulted in pale yellow crystals which were filtered, washed with CH_2Cl_2 (1 ml) and Et_2O (1 ml) and dried under vacuum (62 % yield). $[[Cd_2(\mathbf{L^1})_2][Cd_2(\mathbf{L^2}\text{-}H)_2]](ClO_4)_{10} \cdot 2H_2O$ Found: C, 48.8; H, 2.9; N, 7.5%. Calculated for $C_{190}H_{148}Cd_4Cl_{10}N_{26}O_{48}S_8$: C, 49.3; H, 3.2; N, 7.9%.

* Camphorsulfonic acid is used as it's a non-hygroscopic solid which is easy to weigh accurately and is soluble in a wide variety of solvents.