Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A new fluorone-based bridging ligand for discrete and polymeric assemblies including Mo and W based [4+4] metallocycles

Ashley L. Sutton, Brendan F. Abrahams*, Timothy A. Hudson, Richard Robson*

School of Chemistry, University of Melbourne, Parkville, Victoria 3010, Australia. Email: bfa@unimelb.edu.au; r.robson@unimelb.edu.au; Fax: +61 3 9347 5180; Tel: +61 3 8344 0341

Electronic Supplementary Information

S1 Synthesis

General details

Elemental microanalyses were performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand.

Infrared spectra were collected on a Bruker Tensor 27 FT-IR using a pressed KBr disc.

^{1}H and ^{13}C NMR spectra were collected on a Varian 400 MHz NMR Spectrometer.

9-hydrogen-2,3,7-trihydroxyfluorone·HCl

To 1,2,4-triacetoxybenzene (9.97 g, 39.5 mmol) was added conc. hydrochloric acid (53 mL) and formic acid (53 mL, 1.41 mol). The mixture was stirred at room temperature until the solid dissolved (*ca.* 30 mins). Following dissolution, the clear solution was allowed to stand for five days, during which time a crystalline material formed. This intermediate was collected by vacuum filtration. The intermediate solid was dissolved in a mixture of methanol (60 mL) and conc. hydrochloric acid (50 mL). The mixture was gently heated with stirring to remove the methanol. After which time the reaction mixture was allowed to cool slowly to room temperature. The solid was collected by filtration, washed with acetone and dried under vacuum to yield 9-hydrogen-2,3,7-trihydroxyfluorone·HCl as a brown powder (3.03 g, 55 %). IR (KBr) ν: 3385 (broad), 3076 (broad), 1647, 1618, 1554, 1514, 1482, 1440, 1425, 1348, 1308, 1277, 1197, 1161, 1141, 867, 546, 458 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.24 (s, 2H), 7.32 (s, 2H), 8.98 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d$_6$): δ 102.0, 110.8, 117.7, 147.7, 147.9, 153.5.

General procedure for [4+4] metallocycles

An aqueous solution of either sodium molybdate or sodium tungstate was added to a solution of 9-hydrogen-2,3,7-trihydroxyfluorone·HCl and either PPh_4Br or $AsPh_4Cl$ in methanol (3.9 mL). The suspension was mixed before heating in a microwave reactor for 18 hours at 110 °C, without stirring. The reaction mixture was allowed to cool to room temperature over several hours undisturbed and red rods with green iridescence had formed amongst an amorphous precipitate. The red crystals were carefully separated from the amorphous solid - this was achieved by suspending the reaction mixture through careful agitation and allowing the denser crystals to settle and pipetting off the suspended amorphous solid. The solvent was replaced with an equal amount of methanol and the process repeated until only the crystalline product remained.

$(PPh_4)_4[(MoO_2)_4(9HL)_4]$: The reaction was carried out according to the general procedure for [4+4] metallocycles with sodium molybdate (15 mg, 0.07 mmol) in H_2O (0.1 mL), PPh_4Br (104.8 mg, 0.25 mmol), and 9-hydrogen-2,3,7-trihydroxyfluorone·HCl (17.4 mg, 0.06 mmol) to yield $(PPh_4)_4[(MoO_2)_4(9HL)_4]\cdot 4MeOH\cdot 3H_2O$ (8.8 mg, 20 %). Elemental analysis Calcd $(PPh_4)_4[(MoO_2)_4(9HL)_4]\cdot 20H_2O$, $C_{148}H_{140}Mo_4O_{48}P_4$: C, 55.65; H, 4.43; Found: C, 55.74; H, 3.35 %. IR (KBr) ν: 3435 (broad), 2924, 2853, 1627, 1580, 1529, 1479, 1437, 1387, 1319, 1252, 1213, 1181, 1108, 914, 888, 767, 724, 689, 653, 592, 528, 474 cm^{-1}.

$(PPh_4)_4[(WO_2)_4(9HL)_4]$: The reaction was carried out according to the general procedure for [4+4] metallocycles with sodium tungstate (18.2 mg, 0.07 mmol), PPh_4Br (104.8 mg, 0.25 mmol), and 9-hydrogen-2,3,7-trihydroxyfluorone·HCl (17.4 mg, 0.06 mmol) to yield $(PPh_4)_4[(WO_2)_4(9HL)_4]\cdot 4MeOH\cdot 3H_2O$ (8.4 mg, 16 %). Elemental analysis Calcd $(PPh_4)_4[(WO_2)_4(9HL)_4]\cdot 9H_2O$, $C_{148}H_{118}W_4O_{37}P_4$: C, 53.10; H, 3.56; Found: C, 52.67; H, 2.87 %. IR (KBr) ν: 3435 (broad), 2924, 2855, 1631, 1586, 1480, 1317, 1213, 1108, 939, 918, 890, 768, 723, 690, 661, 596, 527, 477 cm^{-1}.

$(AsPh_4)_4[(MoO_2)_4(9HL)_4]$: The reaction was carried out according to the general procedure for [4+4] metallocycles with sodium molybdate (15 mg, 0.07 mmol), $AsPh_4Cl$ (104.7 mg, 0.25 mmol), and 9-hydrogen-2,3,7-trihydroxy-fluorone·HCl (17.4 mg, 0.06 mmol) to yield $(AsPh_4)_4[(MoO_2)_4(9HL)_4]\cdot 3MeOH\cdot 4H_2O$ (13.8 mg, 29 %). IR (KBr) ν: 3443 (broad), 2920, 2851, 1625, 1580, 1479, 1440, 1385, 1320, 1252, 1211, 1180, 913, 889, 742, 688, 653 cm^{-1}.

$(AsPh_4)_4[(WO_2)_4(9HL)_4]$: The reaction was carried out according to the general procedure for [4+4] metallocycles with sodium tungstate (18.2 mg, 0.07 mmol) $AsPh_4Cl$ (104.7 mg, 0.25 mmol) and 9-hydrogen-2,3,7-trihydroxy-fluorone·HCl (17.4 mg, 0.06 mmol) to yield $(AsPh_4)_4[(WO_2)_4(9HL)_4]\cdot 4MeOH\cdot 4H_2O$ (5.9 mg, 11 %). IR (KBr) ν: 3442 (broad), 2919, 2851, 1630, 1585, 1482, 1385, 1318, 1211, 1178, 937, 918, 891, 769, 743, 688, 659 cm^{-1}.

S2 NMR spectra

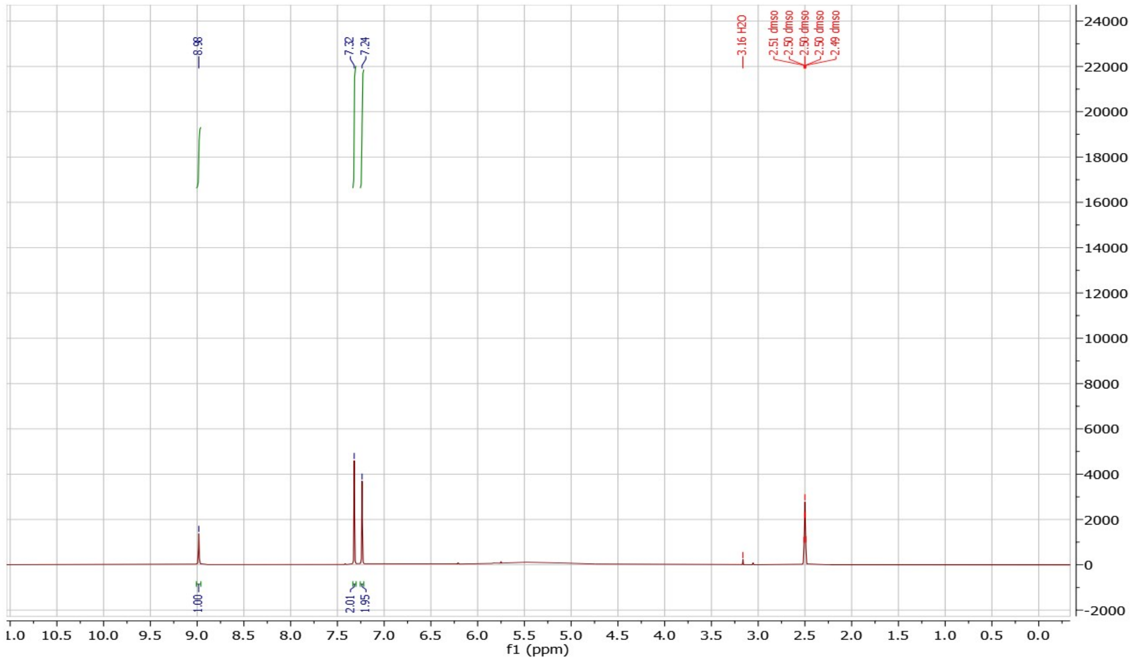


Figure S2.1 ^{1}H NMR of 9-hydrogen-2,3,7-trihydroxyfluorone·HCl.

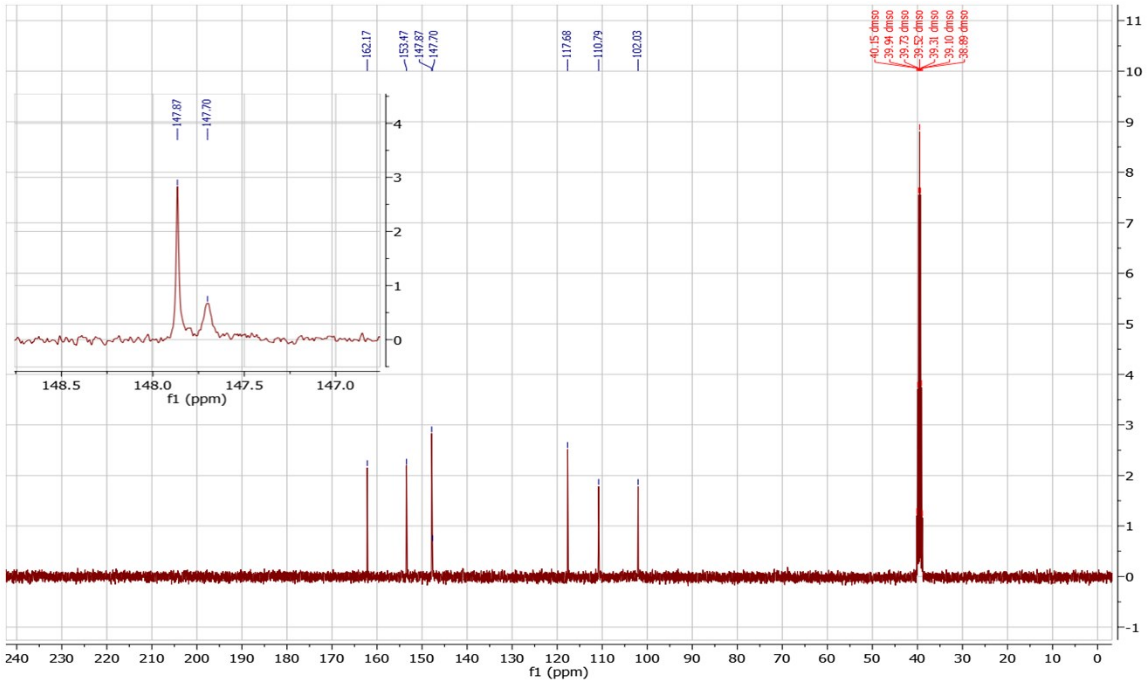


Figure S2.2 ^{13}C NMR of 9-hydrogen-2,3,7-trihydroxyfluorone·HCl.

S3 Single crystal X-ray diffraction

General procedures

Single crystal X-ray diffraction datasets were collected on either instrument based diffractometers or at the MX1 Beamline of the Australian Synchrotron.[1] Structures were solved using SHELX and refined using a full matrix least-squares procedure based on F^2.[2, 3]

All structures had some residual atoms of solvent molecules within the channels which were unable to be modelled successfully and as a consequence the MASK procedure within OLEX2[4] was used estimate the solvent within the channels based upon the void space and electron count.

$(PPh_4)_4[(MoO_2)_4(9HL)_4]$

Single crystal X-ray diffraction data was collected on the MX1 Beamline of the Australia Synchrotron with a monochromatic synchrotron radiation wavelength of 0.7109 Å. The phenyl ring of one of the PPh_4^+ cations (P3) is disordered and was modelled over two sites with complementary site occupation factors. A rigid bond restraint was applied to the two phenyl rings using the RIGU card. Three disagreeable reflections, (0 5 0), (0 3 1) and (2 2 0), were also excluded from the refinement with the OMIT card. The Flack parameter (-0.025(16)) which was refined with all other parameters, indicates the correct absolute configuration.

$(PPh_4)_4[(WO_2)_4(9HL)_4]$

Single crystal X-ray diffraction data was collected on a XtaLAB Synergy instrument fitted with a CuKα source. The phenyl ring of one of the PPh_4^+ cations (P3) is disordered and was modelled over two sites with complementary site occupation factors. A rigid bond restraint was applied to the phenyl rings using the RIGU card. The Flack parameter (-0.024(5)) which was refined with all other parameters, indicates the correct absolute configuration.

$(AsPh_4)_4[(MoO_2)_4(9HL)_4]$

Single crystal X-ray diffraction data was collected on the MX1 Beamline of the Australia Synchrotron with a monochromatic synchrotron radiation wavelength of 0.7107 Å. The phenyl ring of one of the $AsPh_4^+$ cations (As3) is disordered and was modelled over two sites with complementary site occupation factors. A rigid bond restraint was applied to the phenyl rings using the RIGU card. The Flack parameter (0.018(2)) which was refined with all other parameters, indicates the correct absolute configuration.

$(AsPh_4)_4[(WO_2)_4(9HL)_4]$

Single crystal X-ray diffraction data was collected on an Oxford Diffraction SuperNova instrument fitted with a CuKα source.The phenyl ring of one of the $AsPh_4^+$ cations (As3) is disordered and was modelled over two sites with complementary site occupation factors. A rigid bond restraint was applied to the phenyl rings using the RIGU card. The Flack parameter (-0.021(4)) which was refined with all other parameters, indicates the correct absolute configuration.

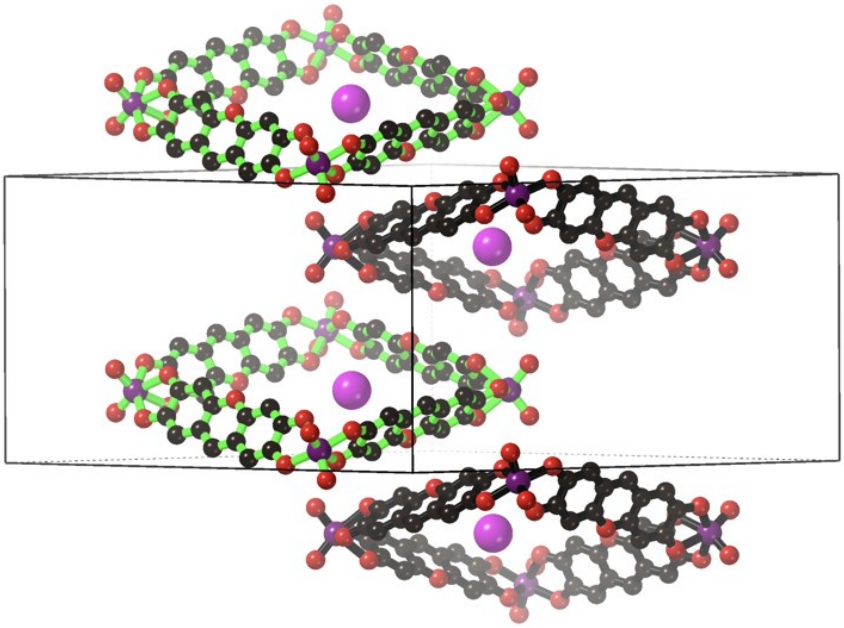


Figure S3.1 Part of a double stack (the double stack in represented by green and black metallocycles in Fig. 5) showing the location of the P atom (pink sphere) of the PPh_4^+ cation that sits within each square metallocycle. Note the location of the cation, which interacts with the MoO_2 cores of metallocycles sitting above and below. These electrostatic interactions appear to be responsible for the formation of the double stacks. The thin black lines represent the unit cell.

Table S3.1 Void volumes within each of compounds as estimated using Mercury. The structures for void volume calculations had their solvent molecules omitted and only one orientation of the disordered species.

Compound	**Cell volume (Å^3)**	**Void volume (Å^3)**	**Fraction (%)**
$(PPh_4)_4[(MoO_2)_4(9HL)_4]$	13386	1351.4	10
$(PPh_4)_4[(WO_2)_4(9HL)_4]$	13463	1146.8	8.5
$(AsPh_4)_4[(MoO_2)_4(9HL)_4]$	13448	983.24	7.3
$(AsPh_4)_4[(WO_2)_4(9HL)_4]$	13739	1487.1	11

Bond valence sum calculations

Bond valence sum (BVS) analysis[5] has been used for the determination of coordinated ion oxidation state. The sum of the valences of individual bonds is equal to the oxidation state, Z_j, and individual bond valences, S_{ij}, can be determined from equation 2 from observed bond lengths, r_{ij}. B is usually taken to be a constant of 0.37, whilst R_0 is to be considered a bond length of full valence.

$$Z_j = \sum_i S_{ij} \quad (1)$$

$$s_{ij} = \exp\,[(R_0 - r_{ij})/B] \quad (2)$$

Bond valence sum analyses were performed for all crystallographically unique metal centres in the reported compounds details are in Tables S3.2 and S3.3.

Table S3.2 Bond valence sum values for the Mo species using values, $R_0 = 1.907$ and B = 0.37. [5]

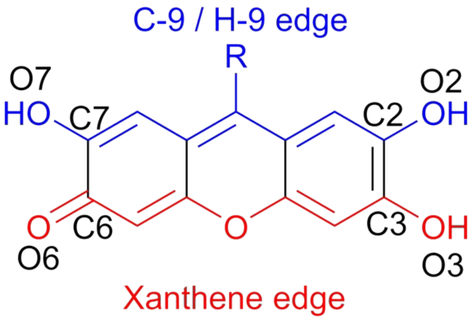
Compound	Species	M-O Bond lengths (Å)	Bond valence	BVS
$(PPh_4)_4[(MoO_2)_4(9HL)_4]$	Mo1	1.724	1.640	5.8
		1.724	1.640	
		2.002	0.774	
		2.002	0.774	
		2.181	0.477	
		2.181	0.477	
	Mo2	2.026	0.725	5.9
		2.189	0.467	
		1.716	1.676	
		1.692	1.788	
		1.977	0.828	
		2.209	0.442	
	Mo3	2.172	0.489	5.9
		2.172	0.489	
		1.991	0.797	
		1.991	0.797	
		1.716	1.676	
		1.716	1.676	
$(AsPh_4)_4[(MoO_2)_4(9HL)_4]$	Mo1	1.699	1.754	6.0
		1.699	1.754	
		2.039	0.700	
		2.039	0.700	
		2.147	0.523	
		2.147	0.523	
	Mo2	2.007	0.763	5.9
		2.176	0.483	
		1.715	1.680	
		1.696	1.769	
		2.217	0.433	
		1.980	0.821	
	Mo3	2.189	0.467	6.0
		2.189	0.467	
		1.997	0.784	
		1.997	0.784	
		1.701	1.745	
		1.701	1.745	

Table S3.3 Bond valence sum values for the W species using values, $R_0 = 1.917$ and B = 0.37.[5]

Compound	Species	M-O Bond lengths (Å)	Bond valence	BVS
$(PPh_4)_4[(WO_2)_4(9HL)_4]$	W1	2.179	0.493	6.0
		1.999	0.801	
		1.747	1.583	
		1.705	1.774	
		2.180	0.491	
		1.987	0.828	
	W2	2.011	0.776	5.9
		2.011	0.776	
		2.157	0.523	
		2.157	0.523	
		1.731	1.653	
		1.731	1.653	
	W3	2.152	0.530	6.1
		2.152	0.530	
		1.987	0.828	
		1.987	0.828	
		1.721	1.698	
		1.721	1.698	
$(AsPh_4)_4[(WO_2)_4(9HL)_4]$	W1	1.745	1.592	5.9
		1.745	1.592	
		1.985	0.832	
		1.985	0.832	
		2.152	0.530	
		2.152	0.530	
	W2	2.180	0.491	6.0
		2.006	0.786	
		1.719	1.708	
		1.732	1.649	
		1.990	0.821	
		2.169	0.506	
	W3	1.720	1.703	6.1
		1.720	1.703	
		1.995	0.810	
		1.995	0.810	
		2.143	0.543	
		2.143	0.543	

Table S3.4 Selected 2,3,7-trihydroxyfluorones based compounds depicting the difference in carbonyl bond length between the C9 and the xanthene edges.

Compound	**Substituent**	**C6 – O6 (Å)**	**C3 – O3 (Å)**	**C2 – O2 (Å)**	**C7 – O7 (Å)**	**Ref**
H_3(9PhL)	9-phenyl	1.281(5)	1.335(5)	1.362(5)	1.362(5)	6
K_3(9PhL)	9-phenyl	1.28(1)	1.29(1)	1.33(1)	1.30(1)	6
$(PPh_4)_2(NBu_4)_2[(MoO_2)_4(9PhL)_4]$	9-phenyl	1.299(8)	1.303(8)	1.328(9)	1.327(8)	7
		1.286(8)	1.283(8)	1.337(8)	1.354(8)	
		1.283(8)	1.304(9)	1.332(9)	1.349(8)	
		1.283(8)	1.310(9)	1.365(8)	1.349(8)	
$(AsPh_4)_2(NBu_4)_2[(WO_2)_4(9PhL)_4]$	9-phenyl	1.282(16)	1.310(17)	1.324(16)	1.357(15)	7
		1.270(18)	1.306(16)	1.323(17)	1.326(17)	
		1.274(16)	1.286(17)	1.320(18)	1.309(18)	
		1.299(17)	1.295(17)	1.322(16)	1.344(17)	
$(PPh_4)_4[(MoO_2)_4(9HL)_4]$	9-hydrogen	1.272(16)	1.305(16)	1.379(17)	1.364(16)	this work
		1.296(19)	1.318(18)	1.342(18)	1.353(18)	
$(PPh_4)_4[(WO_2)_4(9HL)_4]$	9-hydrogen	1.281(11)	1.284(9)	1.359(9)	1.351(10)	this work
		1.297(10)	1.319(10)	1.339(11)	1.334(10)	
$(AsPh_4)_4[(MoO_2)_4(9HL)_4]$	9-hydrogen	1.298(8)	1.305(7)	1.341(7)	1.359(7)	this work
		1.266(9)	1.297(8)	1.326(10)	1.351(8)	
$(AsPh_4)_4[(WO_2)_4(9HL)_4]$	9-hydrogen	1.294(13)	1.303(13)	1.345(12)	1.332(13)	this work
		1.281(14)	1.313(12)	1.350(12)	1.347(12)	



S4 Powder diffraction

The powder diffraction patterns were collected on either an Oxford Diffraction SuperNova diffractometer or a XtaLAB Synergy diffractometer. The diffraction patterns of the bulk products matched the calculated diffraction patterns obtained from the single crystal structure determinations.

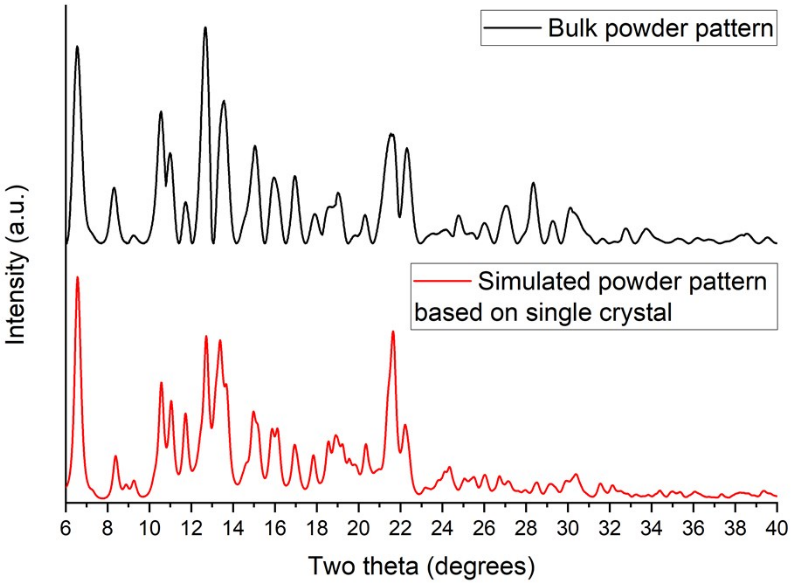


Figure S4.1 Bulk powder pattern and simulated powder pattern of $(PPh_4)_4[(MoO_2)_4(9HL)_4]$. Experimental data collected on an Oxford Diffraction SuperNova diffractometer at 130 K with CuKα radiation.

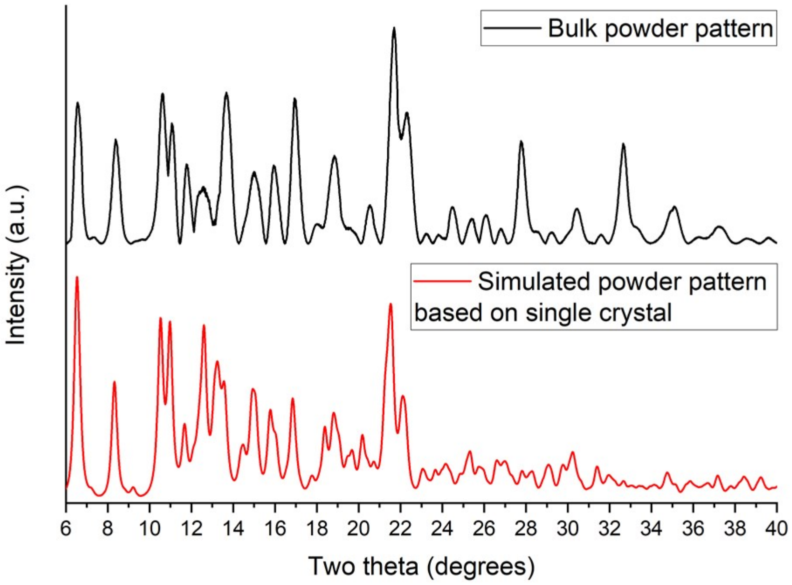


Figure S4.2 Bulk powder pattern and simulated powder pattern of $(PPh_4)_4[(WO_2)_4(9HL)_4]$. Experimental data collected on an Oxford Diffraction SuperNova diffractometer at 130 K with CuKα radiation.

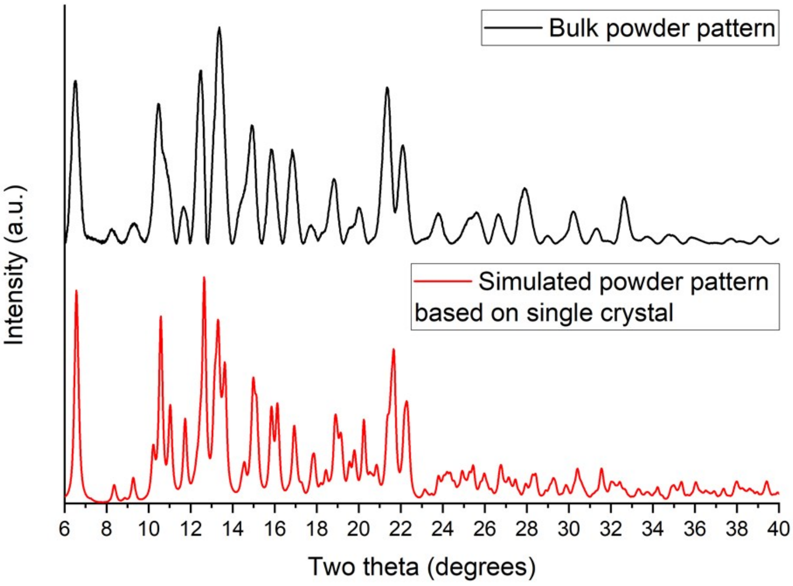


Figure S4.3 Bulk powder pattern and simulated powder pattern of $(AsPh_4)_4[(MoO_2)_4(9HL)_4]$. Experimental data collected on a XtaLAB Synergy diffractometer at 298 K with CuKα radiation.

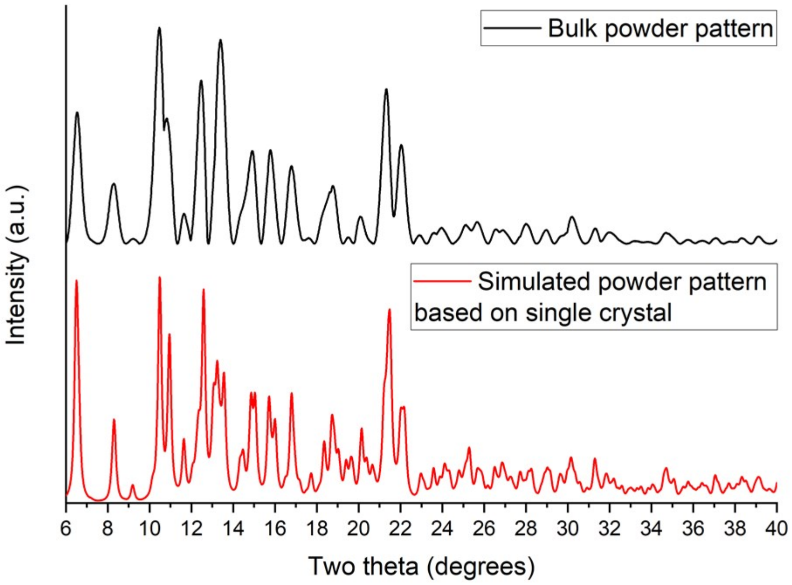


Figure S4.4 Bulk powder pattern and simulated powder pattern of $(AsPh_4)_4[(WO_2)_4(9HL)_4]$. Experimental data collected on an Oxford Diffraction SuperNova diffractometer at 293 K with CuKα radiation.

S5 References

1. N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjikar, J. R. Price, A. Riboldi-Tunnicliffe, R. Williamson and T. Caradoc-Davies, *J. Synchrotron Radiat.*, 2015, **22**, 187-190.
2. G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112-122.
3. G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3-8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
5. I. D. Brown and D. Altermatt, *Acta Crystallogr. B*, 1985, **41**, 244-247.
6. B. F. Abrahams, L. J. McCormick and R. Robson, *J. Mol. Struct.*, 2009, **920**, 466-471.
7. L. J. McCormick, B. F. Abrahams, B. A. Boughton, M. J. Grannas, T. A. Hudson and R. Robson, *Inorg. Chem.*, 2014, **53**, 1721-1728.