Electronic Supplementary Information

Facile assembly of hybrid materials containing polyoxometalates cluster anions and organic dye cations: crystal structures and initial spectral characterization

Jingli Xie,*[†,‡] Brendan F. Abrahams,[†] Anthony G. Wedd*[†,‡]

[†]School of Chemistry, The University of Melbourne, Parkville, Victoria 3052, Australia

[‡]Bio21 Molecular Science and Biotechnology Institute, The University of Melbourne, Parkville, Victoria 3052, Australia

E-mail: xij@unimelb.edu.au; agw@unimelb.edu.au

Synthesis and further description of crystal structures

(**1**) **$[C_{19}H_{18}N_3]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$**. $[n\text{-}(C_4H_9)_4N]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ (0.376 g; 0.1 mmol) was dissolved in CH_3CN (10 ml), solid $[C_{19}H_{18}N_3]Cl$ (0.133 g; 0.4 mmol) was added directly and the mixture allowed to stir at room temperature for 10 min. The resultant deep black-purple solution was filtered and undissolved solid was discarded. The solution was protected from light. Slow diffusion of Et_2O into this solution gave cuboid black-purple crystals of X-ray quality. Yield: 0.120 g (31 %). Anal. Calc. for $C_{76}H_{72}Mo_{18}N_{12}O_{62}S_2$ (3936.34): C 23.19, H1.84, N 4.27%; Found: C 22.88, H 1.66, N 4.23%. FTIR data (cm^{-1}): 3332(m, $\nu(NH_2)$), 3208(m, $\nu(NH_2)$), 1624(s, $\delta(C{=}C)$), 1580(vs, $\delta(C{=}C)$), 1365(s, $\delta(C{=}C)$), 1337(s, $\nu(NH_2)$), 1169(vs, $\nu(NH_2)$), 943(vs, ν(Mo-O)), 793(s, ν(Mo-O)), 727(s, ν(Mo-O)).

The two halves of the $[\alpha\text{-}S_2Mo_{18}O_{62}]^{4-}$ anion are related by a two-fold axis (Fig. S1a) and its dimensions are similar to those observed in other salts (eg, ref 5). In the central tetrahedral SO_4, the S-O distances [1.454(7) ~ 1.492(6) Å] and O-S-O angles [107.7(3) ~ 110.7(4)°] are within those values reported in the literature. The Mo-O bond distances fall into four categories: one short [1.671(7) ~ 1.697(6) Å], two in the range [1.802(6) ~

1.899(7) Å], two in the range [1.902(6) ~ 2.083(6) Å] and one long [2.443(6) ~ 2.511(6) Å]. This pattern is similar with those observed values in related molecules. There are two triarylcarbenium cations (central carbon atoms C7, C26) in the asymmetric unit, exhibiting the characteristic three-bladed propeller conformation. The packing of the pararosaniline cations provides cavities to accommodate the α-$[S_2Mo_{18}O_{62}]^{4-}$ anions and allows formation of multiple charge-assisted hydrogen bonds N-H···O exist between the cation $-NH_2$ functions and the anion oxygen atoms (Fig. S1c and d)

(2) $[C_{19}H_{18}N_3]_4[\beta$-$Mo_8O_{26}]$. A solution of $[C_{19}H_{18}N_3]Cl$ (0.066 g; 0.2 mmol) in water (10 ml) was added to a solution of $[n\text{-}(C_4H_9)_4N]_2[Mo_6O_{19}]$ (0.136 g; 0.1mmol) in CH_3CN (10 ml). The mixture was refluxed for 14 h. The black-purple precipitate was filtered and washed with water, CH_3CN and Et_2O before being dried under vacuum. Yield: 0.096 g (82 % based on $[C_{19}H_{18}N_3]^+$). FTIR data (cm^{-1}): 3342(m, $\nu(NH_2)$), 3216(m, $\nu(NH_2)$), 1629(s, δ(C=C)), 1574(vs, δ(C=C)), 1463(m, δ(C=C)), 1363(s, $\nu(NH_2)$), 1342(s, $\nu(NH_2)$), 1293(s, $\nu(NH_2)$), 1182(s, $\nu(NH_2)$), 943(vs, ν(Mo-O)), 905(s, δ(C-H)), 846(s, δ(C-H)), 797(s, ν(Mo-O)), 711(s, ν(Mo-O)). Anal. Calc. for $C_{76}H_{72}Mo_8N_{12}O_{26}$ (2336.93): C 39.06, H 3.11, N 7.19%; Found: C 38.82, H 3.20, N 7.33%. The product was dissolved in a minimum volume of DMF (~2 ml). Slow diffusion of CH_3CN into this solution afforded deep black-purple block crystals containing solvate DMF.

Special refinement details for single crystal structure of $[C_{19}H_{18}N_3]_4[\beta$-$Mo_8O_{26}]$·8.5DMF.

Although it was possible to assign the atomic positions of six DMF molecules in the asymmetric unit, analysis of the Fourier map revealed that there was additional disordered solvent within the unit cell. It was not possible to satisfactorily model this solvent and as a consequence the SQUEEZE routine within PLATON was used to determine the volume of this disordered region and the associated electron density. Analysis of the disordered region indicated 210 electrons corresponding to just over 5 molecules of DMF per unit cell, i.e. 2.5 molecules of DMF per formula unit. This extra solvent is included in the formula even though the atomic positions are not assigned. The structure was then refined using the modified reflection data.

The six-coordinate MoO_6 units containing Mo1, Mo2, Mo3, Mo5, Mo7 and Mo8 feature two short [1.692(5) ~ 1.718(5) Å], two medium [1.889(4) ~ 2.012(4) Å] and two long Mo-O [2.273(5) ~ 2.490(4) Å], consistent with dioxomolybdenum(VI) centres (Fig. S3b). The equivalent distances in the remaining two units containing Mo4, Mo6 vary somewhat [1.701(4) ~ 1.761(4) Å], [1.942(4) ~ 1.955 (5) Å], 2.155(4) Å for Mo4-O20, 2.164(4) Å for Mo6-O8, 2.346(4) Å for Mo4-O8 and 2.375(4) Å for Mo6-O20, respectively, but are still within the ranges found in similar species. There are four triarylcarbenium cations in the asymmetric unit, two of them (central carbon atoms C1, C39) are Λ enantiomers and the other two (C20, C58) are Δ enantiomers resulting in an overall achiral crystal. The cations exhibit the propeller blade conformation: for example, the phenyl rings of C2 ~ C7, C8 ~ C13, C14 ~ C19 exhibit dihedral angles of, respectively, 29.1, 33.2 and 30.7° with the reference plane defined by central carbons C1, C2, C8 and C14.

(3) $[C_{19}H_{18}N_3]_6[\alpha\text{-}CoW_{12}O_{40}]$. $Na_{12}[WCo_3(H_2O)_2(CoW_9O_{34})_2]\cdot 46H_2O$ (0.299 g, 0.05 mmol), $[C_{19}H_{18}N_3]Cl$ (0.033 g, 0.1mmol) and distilled water (15.0 g) were mixed in a Teflon-lined stainless steel autoclave (23 ml) and stirred for 15 min. The sealed vessel was heated at 165 °C for three days. After cooling to room temperature, black polyhedron crystals were obtained. Yield: 0.208 g (45 % based on $[C_{19}H_{18}N_3]Cl$). Anal. Calc. for $C_{114}H_{108}CoN_{18}O_{40}W_{12}$ (4635.34): C 29.54, H 2.35, N 5.44%; Found: C 29.16, H 2.40, N 5.41%. (Crystal of **3** contain solvent H_2O which is released at room temperature under vacuum. The elemental analyses were carried out on solvent-free samples). FTIR data (cm^{-1}): 3315(m, $\nu(NH_2)$), 3042(w, $\nu(NH_2)$), 1627(s, $\delta(C{=}C)$), 1575(vs, $\delta(C{=}C)$), 1367(vs, $\nu(NH_2)$), 1336(vs, $\nu(NH_2)$), 1282(s, $\nu(NH_2)$), 1162(vs, $\nu(NH_2)$), 932(vs, $\nu(W\text{-}O)$), 854(vs, $\delta(C\text{-}H)$), 729(vs, $\nu(W\text{-}O)$).

(4) $[(C_{19}H_{18}N_3)_6][\alpha\text{-}ZnW_{12}O_{40}]$. The procedure was similar to that of **3** with black-purple polyhedral crystals being obtained. Yield: 38%. Anal. Calc. for $C_{114}H_{108}N_{18}O_{40}W_{12}Zn$ (4641.80): C 29.50, H 2.35, N 5.43%; Found: C 29.05, H 2.30, N 5.45%. FTIR data (cm^{-1}): 3317(m, ν(NH_2)), 3028(w, ν(NH_2)), 1629(s, δ(C=C)), 1575(vs, δ(C=C)), 1366(vs, ν(NH_2)), 1337(vs, ν(NH_2)), 1282(s, ν(NH_2)), 1162(vs, ν(NH_2)), 932(vs, ν(W-O)), 854(vs, δ(C-H)), 715(vs, ν(W-O)).

Table S1. Selected hydrogen bonding parameters

$[C_{19}H_{18}N_3]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ (**1**)

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.86	2.53	126	3.123(18)	N1 [-x, -y+1, -z]
N1-H1A	0.86	2.58	133	3.236(12)	O19 [-x, -y+1, -z+1]
N1-H1B	0.86	2.19	159	3.009(12)	O18 [x, y, z-1]
N2-H2A	0.86	2.12	164	2.960(13)	O3 [-x+1/2, y+1/2, -z+3/2]
N2-H2B	0.86	2.56	166	3.404(13)	O2 [x, -y+1, z-1/2]
N3-H3A	0.86	2.41	148	3.176(12)	O3 [-x+1/2, -y+1/2, -z+1]
N3-H3B	0.86	2.36	146	3.112(13)	O23 [-x+1/2, -y+1/2, -z+1]
N4-H4A	0.86	2.31	149	3.076(13)	O3
N4-H4B	0.86	2.31	142	3.037(11)	O5 [-x+1/2, -y+1/2, -z+2]
N5-H5A	0.86	2.18	168	3.036(15)	O25 [-x+1/2, y+1/2, -z+3/2]
N6-H6A	0.86	2.19	161	3.018(14)	O17 [-x, y, -z+3/2]
N6-H6B	0.86	2.07	172	2.924(13)	O19 [x, -y+1, z-1/2]

$[C_{19}H_{18}N_3]_4[\beta\text{-}Mo_8O_{26}]\cdot 8.5DMF$ (**2**)

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.88	2.13	154	2.949(9)	O28 [x+1, y+1, z]
N1-H1B	0.88	2.35	124	2.929(8)	O2 [x, y+1, z]
N2-H2A	0.88	2.26	148	3.043(10)	O21 [x+1, y, z]
N2-H2B	0.88	2.09	163	2.944(11)	O30 [x+1, y, z-1]
N3-H3A	0.88	2.26	167	3.125(8)	O31 [x, y, z-1]
N3-H3B	0.88	2.42	145	3.181(7)	O12 [-x+1, -y+2, -z]
N3-H3B	0.88	2.56	139	3.275(7)	O19 [-x+1, -y+2, -z]
N4-H4A	0.88	2.12	176	3.000(7)	O19 [-x+1, -y+2, -z+1]
N4-H4B	0.88	2.10	168	2.963(7)	O31
N5-H5B	0.88	2.26	175	3.143(7)	O26 [x+1, y, z]
N6-H6A	0.88	2.22	160	3.060(7)	O9 [x, y+1, z]
N6-H6A	0.88	2.54	110	2.962(7)	O2 [x, y+1, z]
N6-H6B	0.88	2.16	164	3.020(8)	O28 [x+1, y+1, z]
N7-H7A	0.88	2.31	138	3.027(7)	O7 [-x+1, -y, -z+1]
N7-H7A	0.88	2.59	141	3.319(7)	O16 [-x+1, -y, -z+1]
N7-H7B	0.88	2.21	169	3.074(8)	O29
N8-H8A	0.88	2.28	138	2.993(8)	O10 [x, y-1, z]
N8-H8A	0.88	2.53	141	3.266(8)	O18 [x, y-1, z]
N8-H8B	0.88	2.15	154	2.961(8)	O32 [-x+1, -y, -z+1]
N9-H9A	0.88	2.09	154	2.902(7)	O27 [-x+1, -y+1, -z+1]
N9-H9B	0.88	2.38	132	3.036(7)	O23
N9-H9B	0.88	2.42	146	3.181(7)	O26
N10-H10A	0.88	2.36	160	3.199(8)	O4 [x, y-1, z]

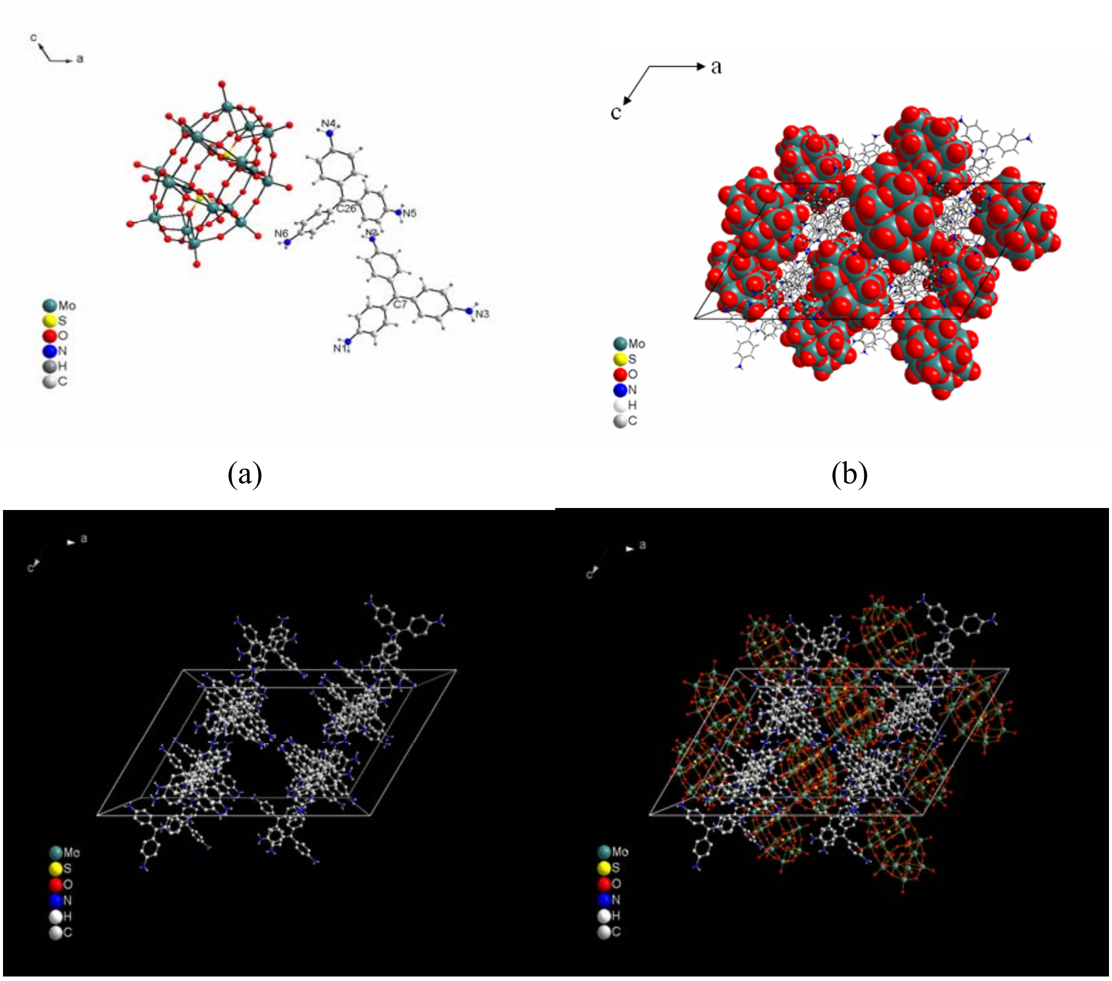
N10-H10A	0.88	2.50	132	3.157(7)	O3 [x, y-1, z]
N10-H10B	0.88	2.19	158	3.028(8)	O32 [-x+1, -y, -z+1]
N11-H11A	0.88	2.26	154	3.070(7)	O7 [-x+1, -y, -z]
N11-H11B	0.88	2.13	163	2.983(7)	O29 [x, y, z-1]
N12-H12A	0.88	2.22	161	3.061(7)	O14
N12-H12B	0.88	2.04	163	2.889(9)	O30 [x, y, z-1]

$[C_{19}H_{18}N_3]_6[\alpha\text{-}CoW_{12}O_{40}]\cdot H_2O$ (**3**)

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.86	2.01	177	2.870(13)	O2 [y-1/3, -x+y+1/3, -z+4/3]
N2-H2B	0.86	2.61	135	3.272(16)	O1 [-x+1, -y+2, -z]

$[C_{19}H_{18}N_3]_6[\alpha\text{-}ZnW_{12}O_{40}]\cdot H_2O$ (**4**)

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1B	0.88	1.97	177	2.851(17)	O2 [y-1/3, -x+y+1/3, -z+4/3]
N2-H2A	0.88	2.58	135	2.36(2)	O1 [-x+1, -y+2, -z]



(a) (b)

(c) (d)

Fig. S1 (a) Molecular structure of $[C_{19}H_{18}N_3]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ (**1**); (b) Packing structure of **1** (space-filling model for POM anions); (c) Three-dimensional network structure formed by pararosaniline cation in **1**; (d) Packing structure of **1**.

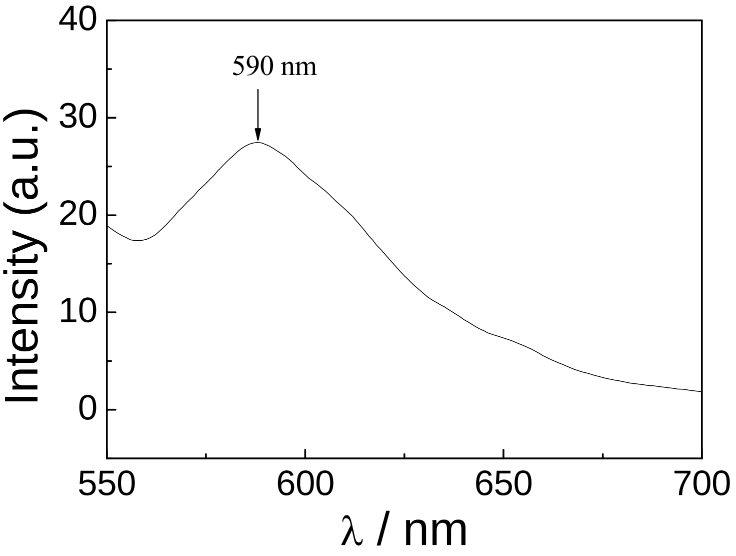
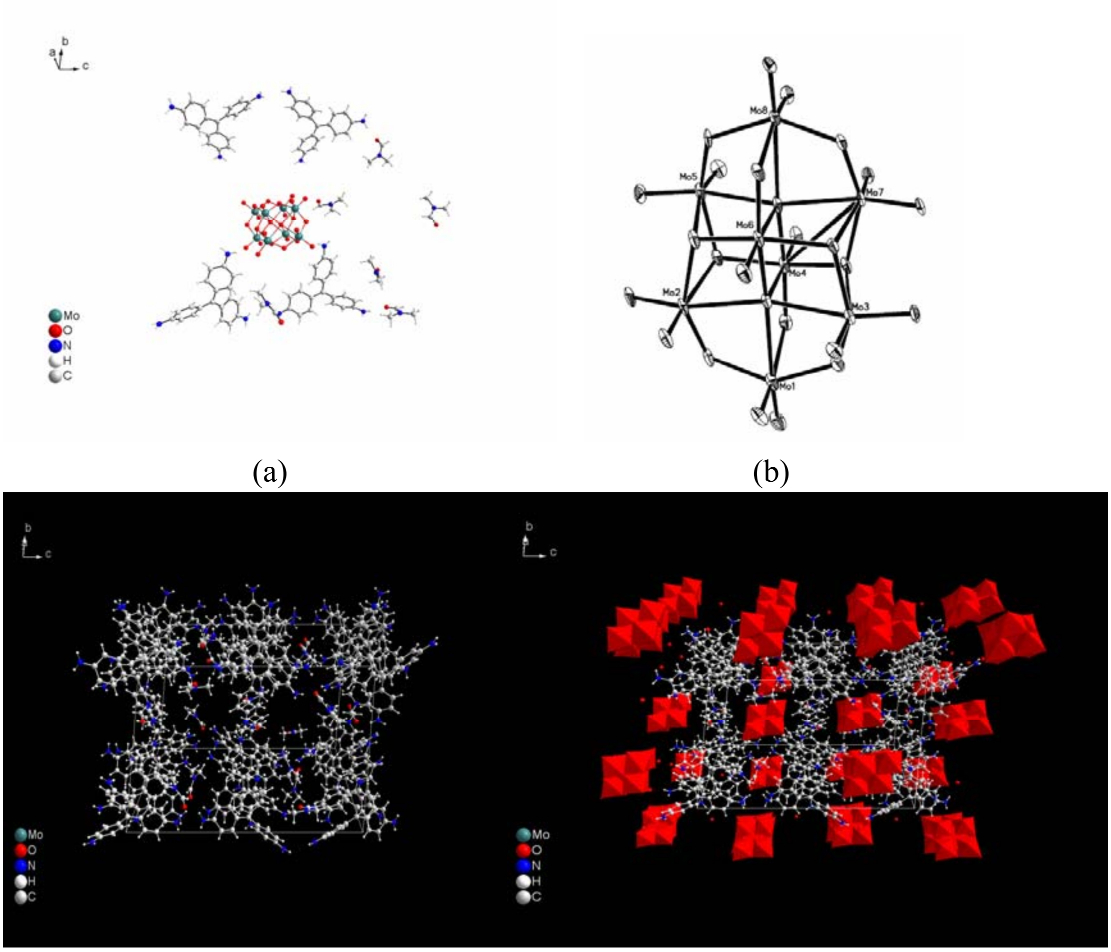


Fig. S2 Emission spectrum of $[C_{19}H_{18}N_3]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ (**1**) in DMF (2.5×10^{-5} M) excited at 320 nm.



(a) (b)

(c) (d)

Fig. S3 (a) Molecular structure of $[(C_{19}H_{18}N_3)_4][\beta\text{-}Mo_8O_{26}]\cdot 8.5DMF$ (**2**); (b) ORTEP diagram of the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion. Ellipsoids are at the 30% probability level; (c) Three-dimensional network structure formed by pararosaniline cation with solvent DMF in **2**; (d) Molecule packing of **2**.