Electronic Supplementary Information (ESI)

Hybrid organic-inorganic compounds based on Lindqvist polyoxomolybdate and dioxomolybdenum(VI) complexes

Višnja Vrdoljak,* Biserka Prugovečki, Dubravka Matković-Čalogović and Jana Pisk

Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a,10000 Zagreb, Croatia

Contents:

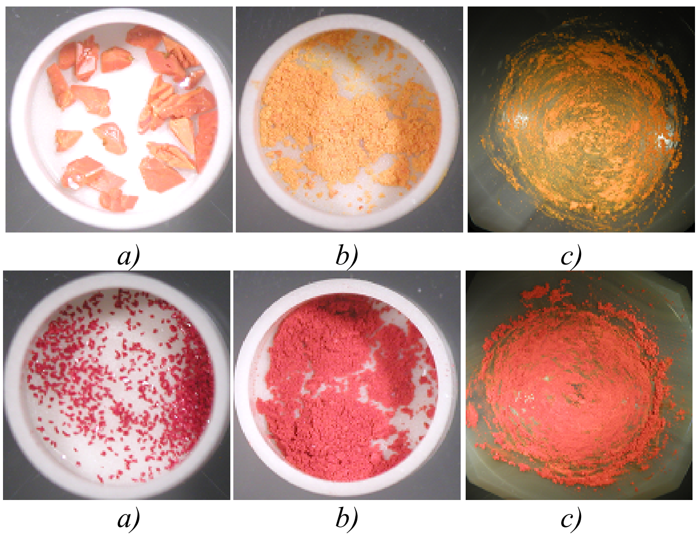


Fig. S1 Photos of **1a** (upper part) and **2a** (lower part): a) of single crystals; b) upon initial grinding; c) after 10 min of grinding by an agate mortar and pestle. Loss of the coordinated solvent molecules by grinding at room temperature was evident by a "wet" appearance of the sample.

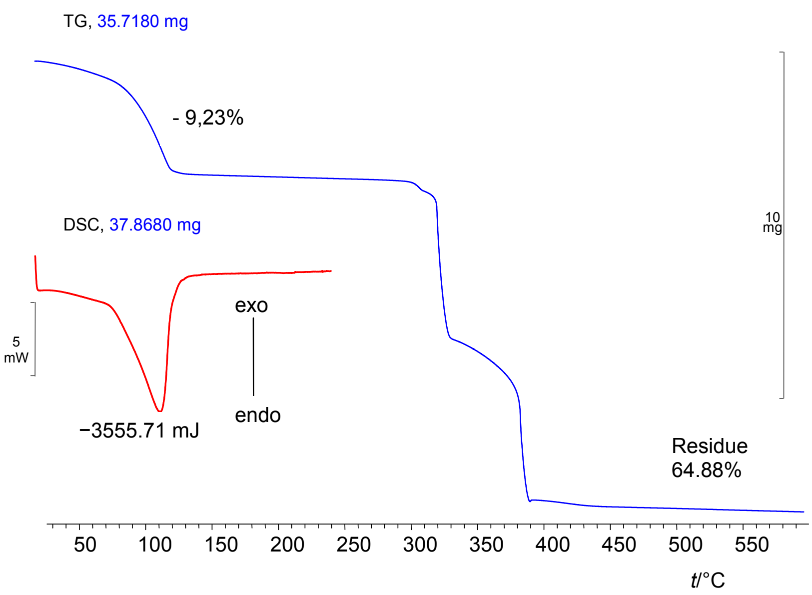


Fig. S2. TG and DSC curves of the crystalline sample **1a** under the O_2 atmosphere. Experiment was recorded with a heating rate of 5 °C min^{-1} in a dynamic atmosphere with a flow rate of 200 cm^3 min^{-1}.

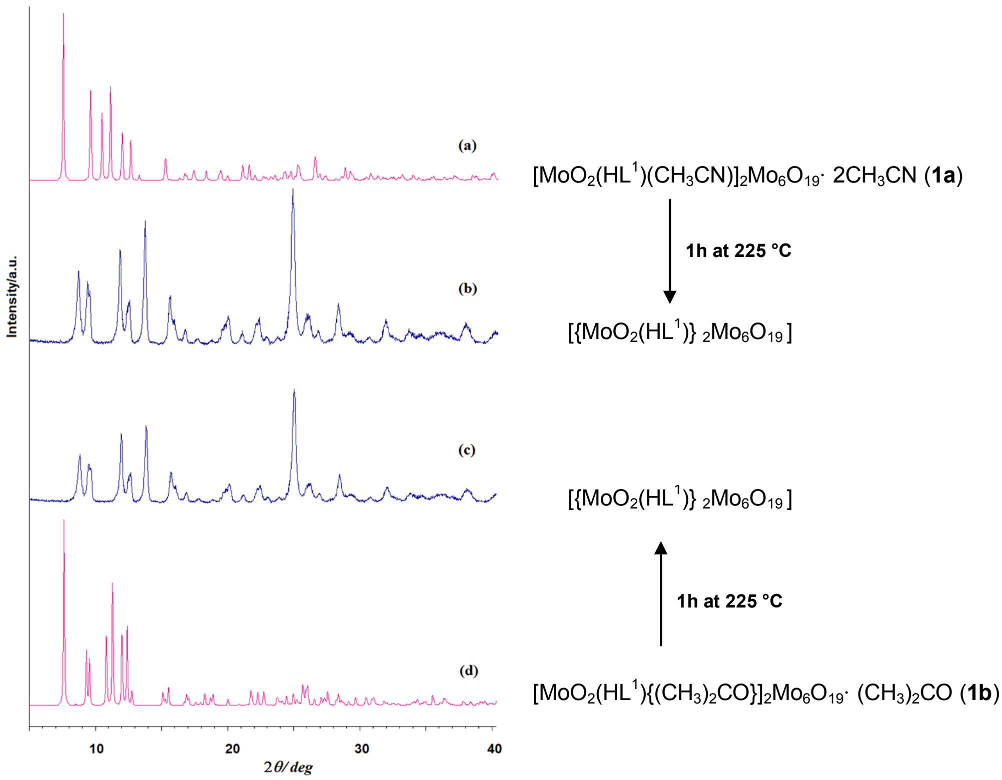


Fig. S3 Powder X-ray diffraction patterns of: (a) **1a** calculated from the X-ray single-crystal structure; (b) sample obtained after heating of **1a** at 225 °C for 1 h; (c) sample obtained after heating of **1b** at 225 °C for 1 h; (d) **1b** calculated from the X-ray single-crystal structure.

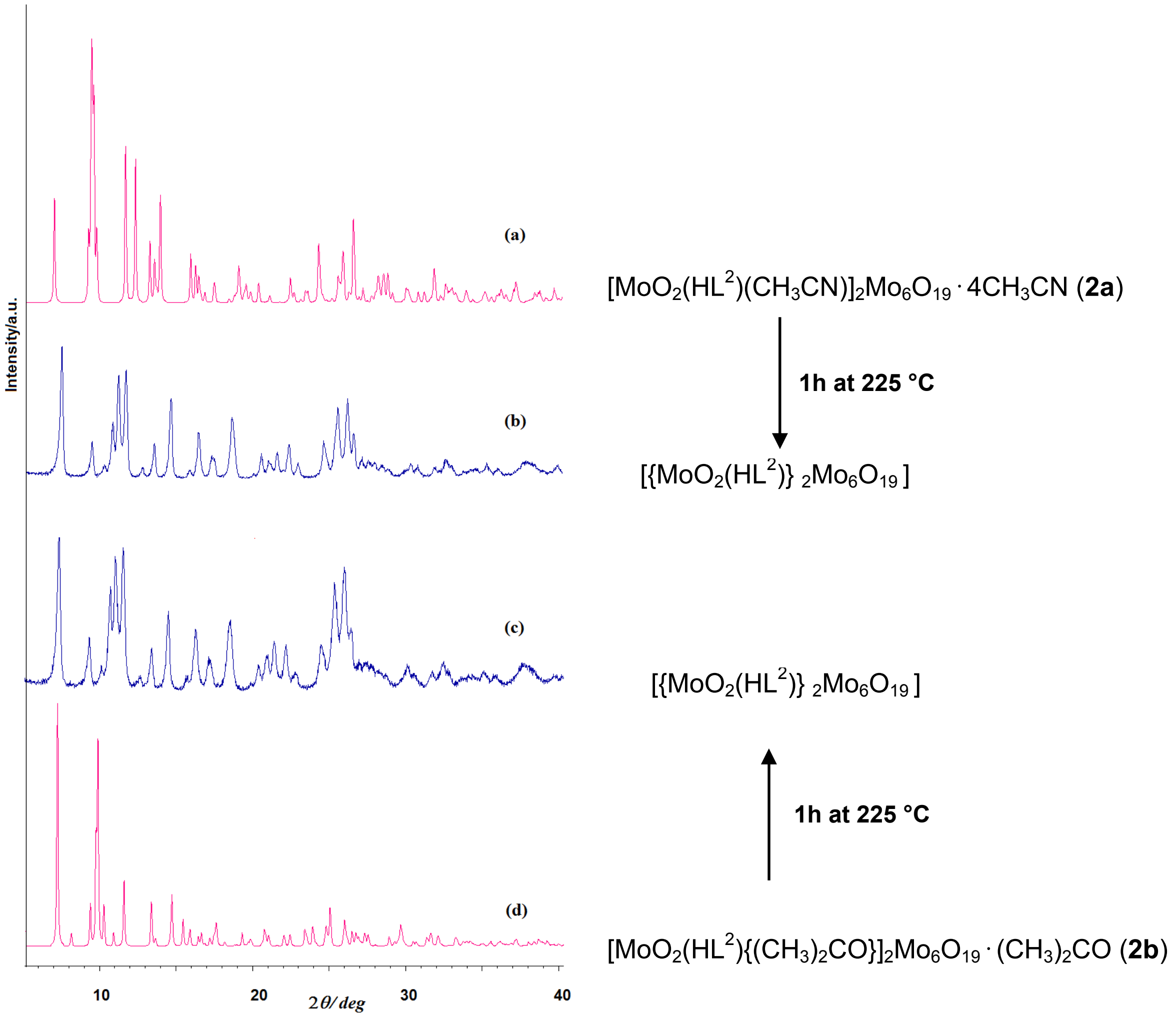


Fig. S4 Powder X-ray diffraction patterns of: (a) **2a** calculated from the X-ray single-crystal structure; (b) sample obtained after heating of **2a** at 225 °C for 1 h; (c) sample obtained after heating of 2**b** at 225 °C for 1 h; (d) **2b** calculated from the X-ray single-crystal structure.

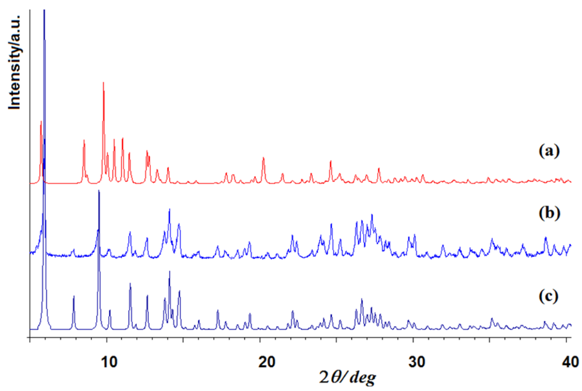
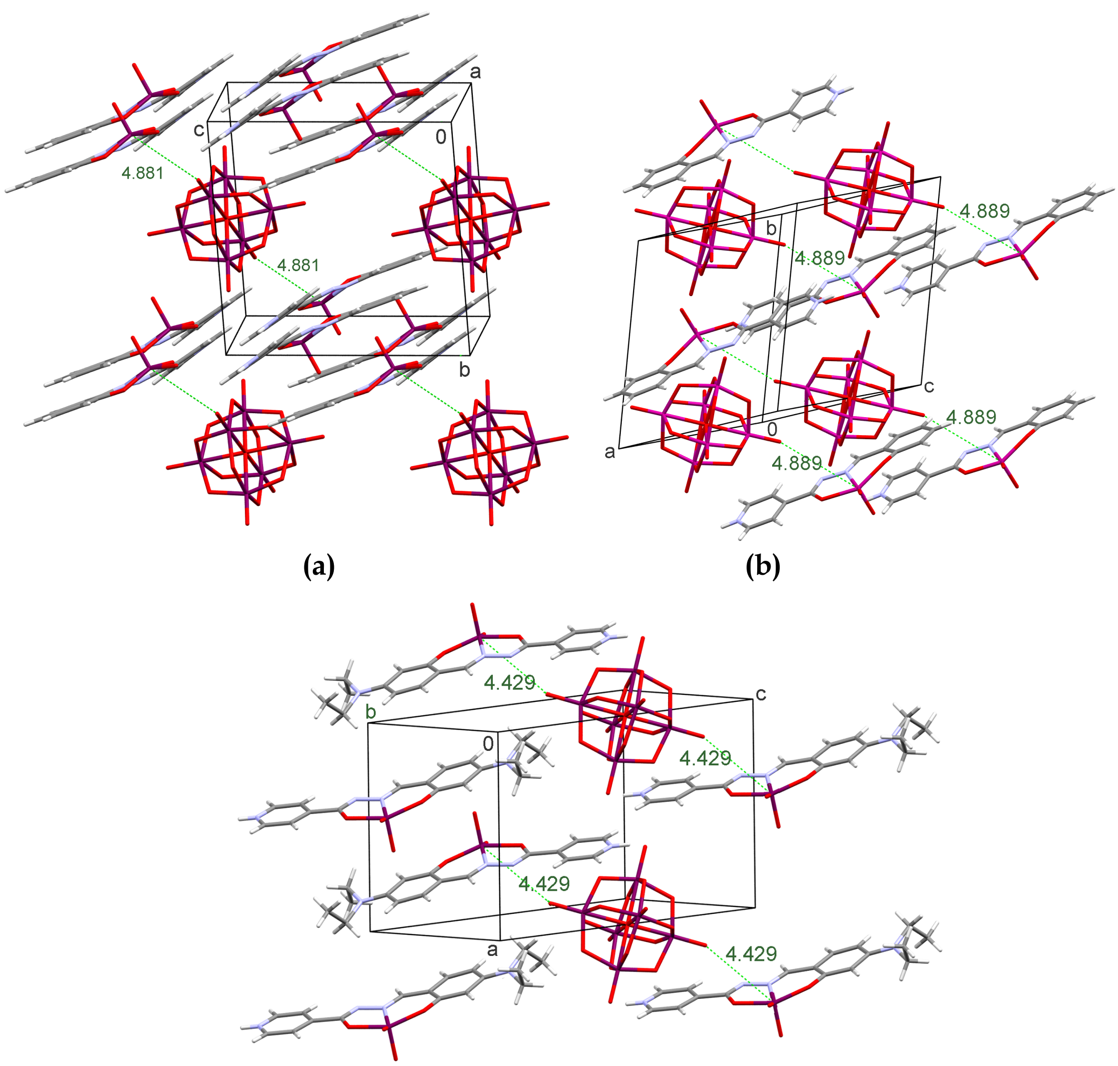


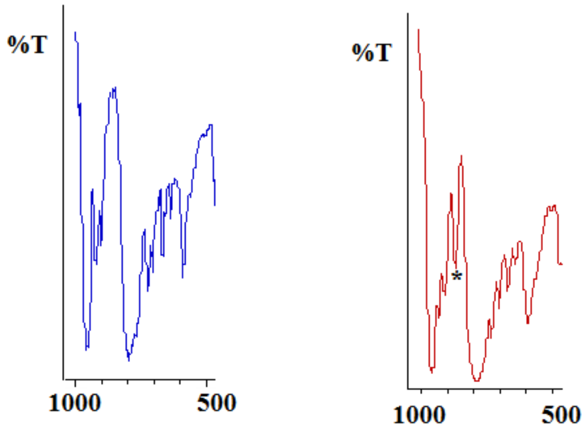
Fig. S5 XRPD patterns of: (a) **3b** calculated from the X-ray single-crystal structure; (b) product obtained upon heating of **3b** at 225 °C for 1 h; (c) **3·4H$_2$O** calculated from the X-ray single-crystal structure .



(a) **(b)**

(c)

Fig. S6 Packing of ions in the unit cell of (a) **1a**, (b) **1b** and (c) **3b** with the solvent molecule omitted; $Mo_{cation}\cdots O_{POM}$ atoms from neighboring ions are connected by green dashed lines (the Mo···O distance is 4.881(2) Å for **1a**, 4.889(2) for **1b**, 4.789(2) Å for **2a**, 4.967(2) Å **2b** and 4.429(2) Å for **3b**).



(a) (b)

Fig. S7 IR spectra of (a) $[MoO_2(HL^1)(CH_3CN)]_2Mo_6O_{19}$ (**1a**) and (b) $[\{MoO_2(HL^1)\}_2Mo_6O_{19}]$ obtained upon heating of the crystalline sample of **1a** for 1 hour at 225 °C. Appearance of a new band in the IR spectra is labelled with *.

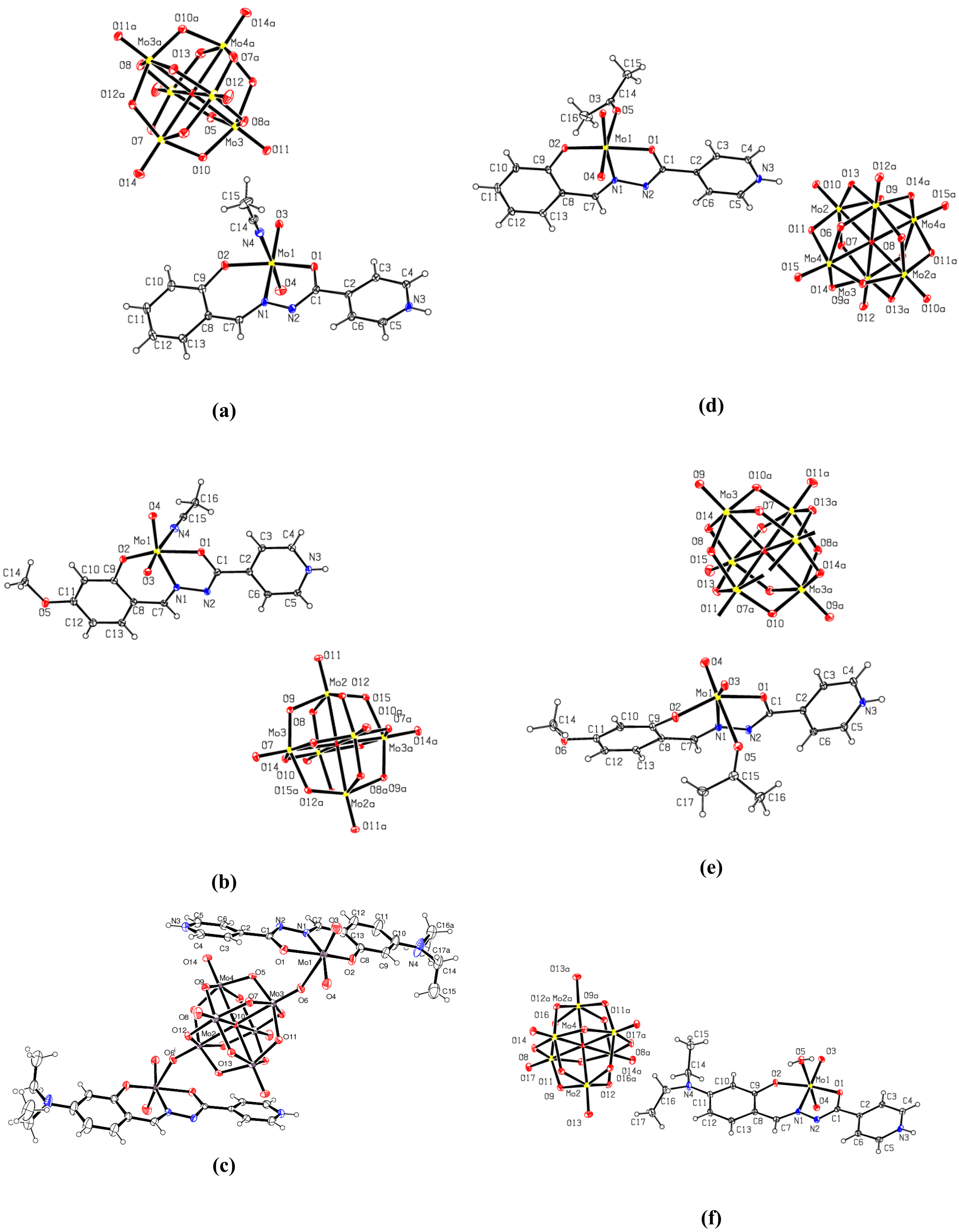
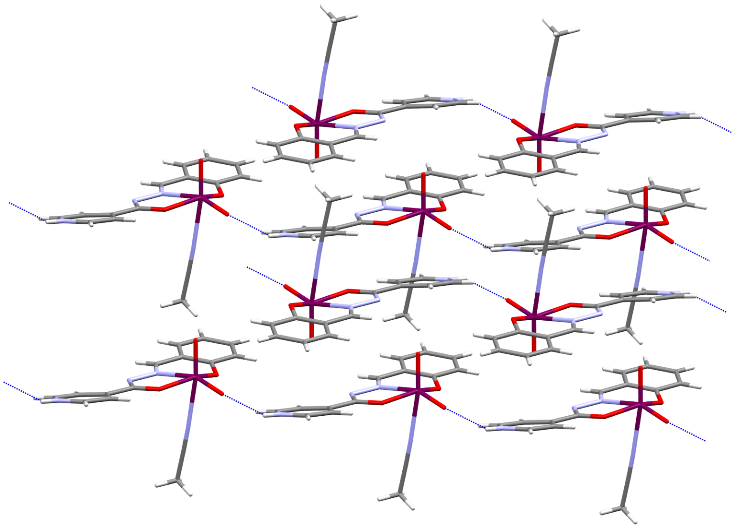
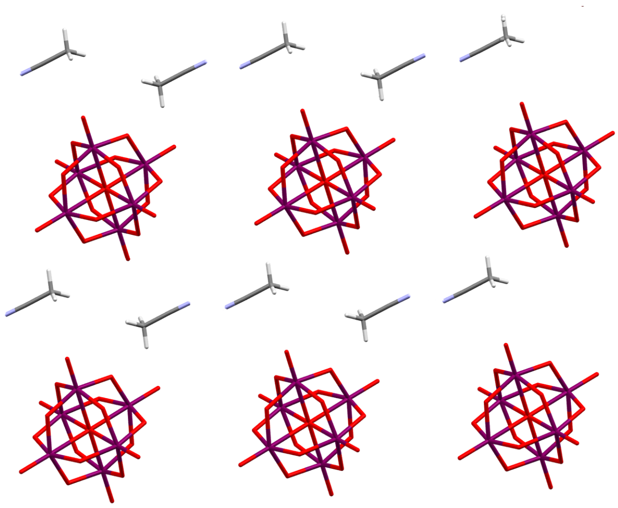


Fig. S8 ORTEP plots of the crystal structures of: (a) **1a**, (b) **2a**, (c) **3·4H$_2$O** (d) **1b**, (e) **2b**, and (f) **3b**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level, the solvent molecules are omitted for clarity.

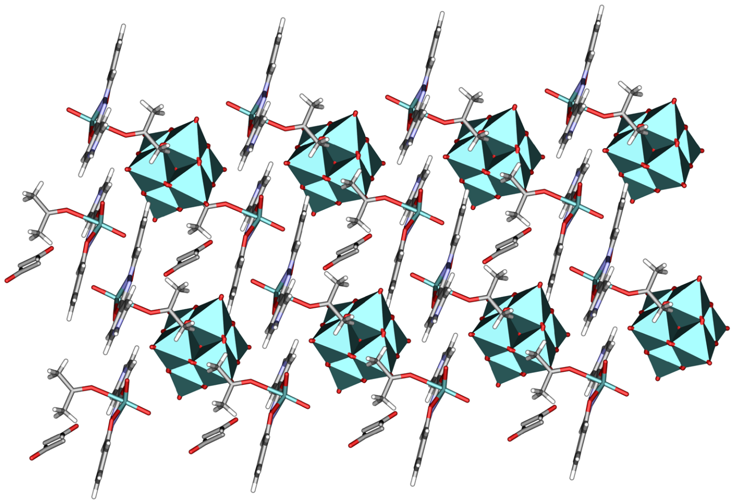


(a)

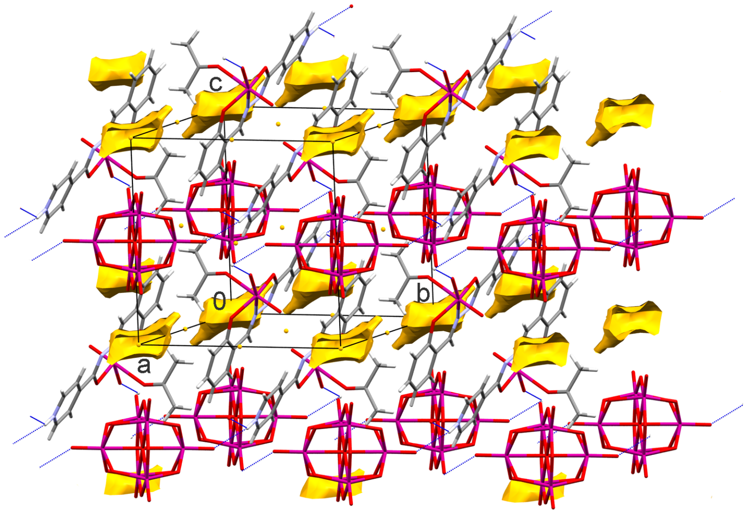


(b)

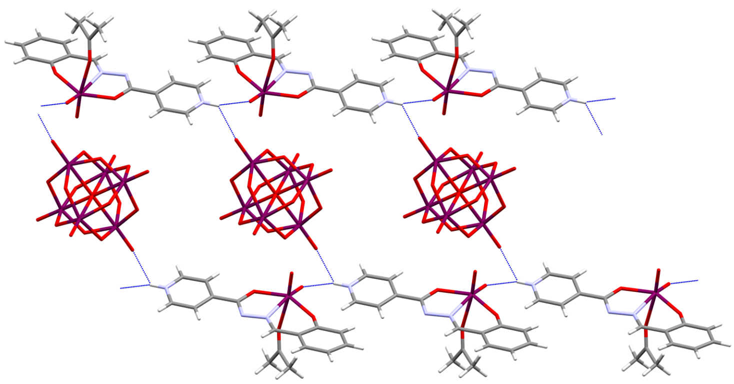
Fig. S9 (a) Metal-organic layer of **1a**; complex cations are connected by blue dashed lines representing hydrogen bonds; (b) POM/solv layer with only one part of the disordered acetonitrile molecule shown. Its occupancy is 0.5.



(a)

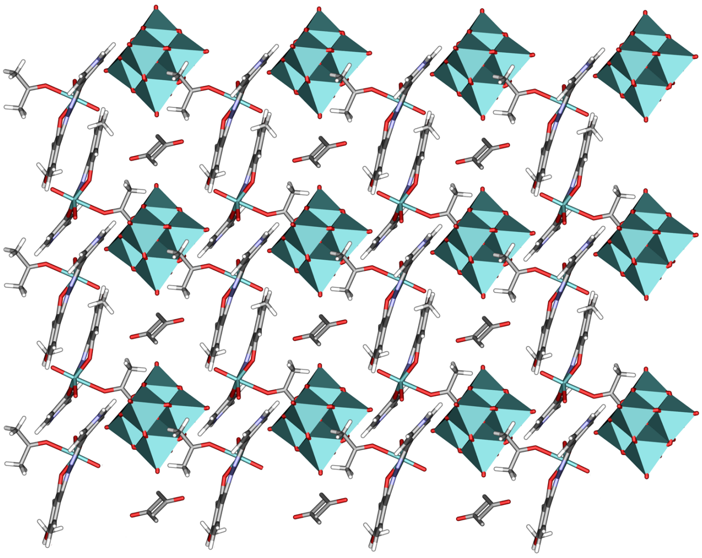


(b)

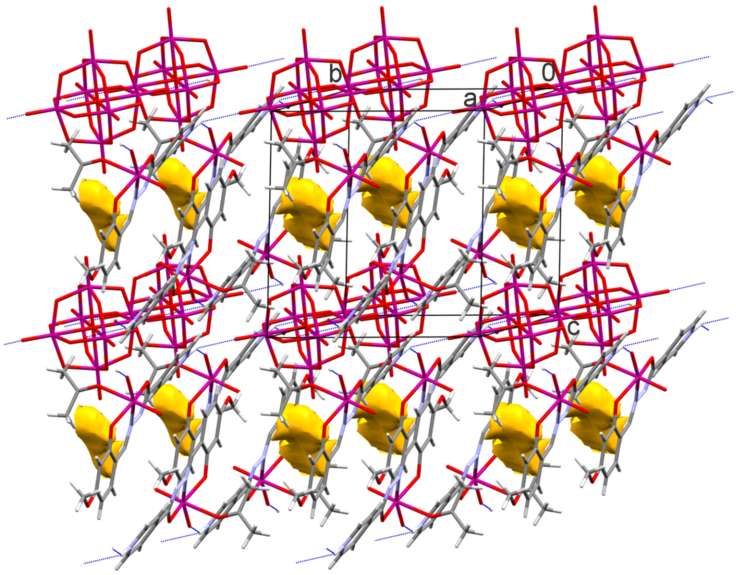


(c)

Fig. S10 (a) Structure of **1b** shown along the *a* axis. Lindqvist polyoxomolybdate anions are represented as blue-green polyhedra. The alternating metal-organic and POM/solv layers can be seen. (b) Packing of the ions in the unit cell. The solvent acetone molecules are omitted and the void channels are shown in yellow (the search sphere was 1.2 Å). (c) Hydrogen bond pattern (blue dashed lines) interconnecting the organic and POM/solv layers.

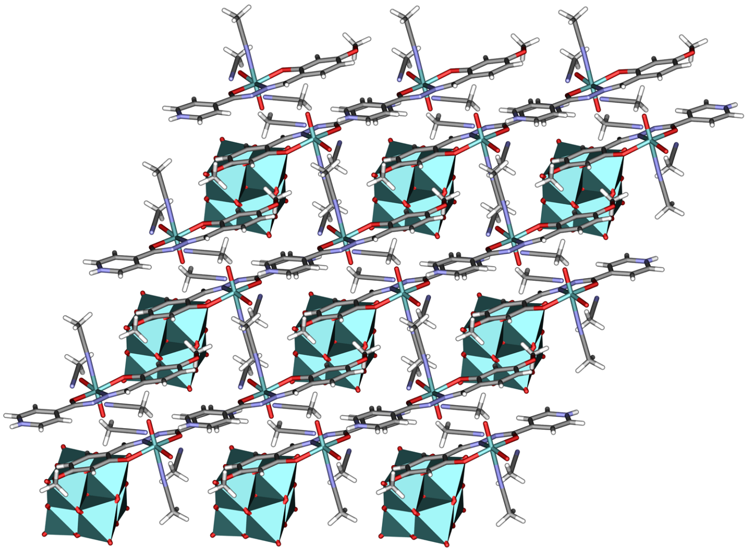


(a)

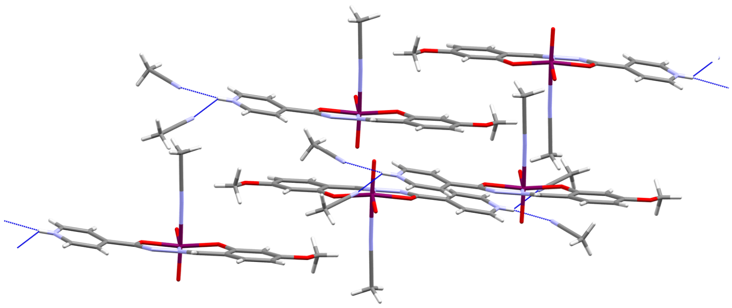


(b)

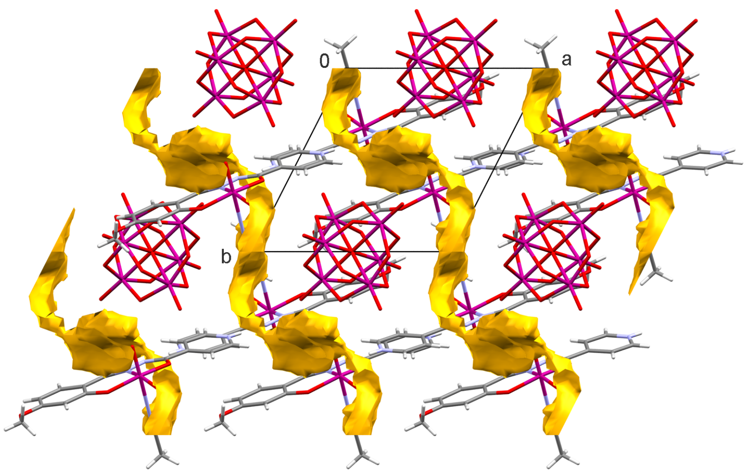
Fig. S11 (a) Structure of **2b** shown along the *a* axis. Lindqvist polyoxomolybdate anions are represented as blue-green polyhedra. The alternating metal-organic and POM/solv layers can be seen. (b) Packing of the ions in the unit cell. The solvent acetone molecules are omitted and the void channels are shown in yellow (the search sphere was 1.2 Å).



(a)



(b)



(c)

Fig. S12 (a) Structure of **2a** shown along the *c* axis. Lindqvist polyoxomolybdate anions are represented as blue-green polyhedra. The alternating metal-organic and POM/solv layers can be seen. (b) Hydrogen bond pattern (blue dashed lines) in the organic/solv layer of **2a**. (c) Packing of the ions in the unit cell. The solvent acetonitrile is omitted and the void channels are shown in yellow (the search sphere was 1.2 Å).

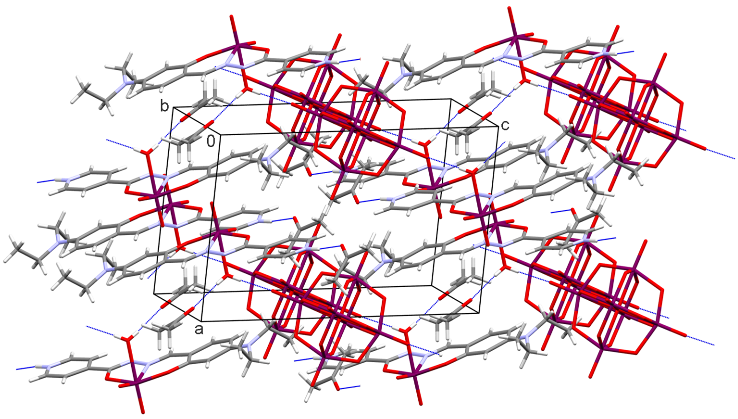


Fig. 13 Packing diagram of **3b** with hydrogen bonds shown as blue dashed lines.

Table S1. Selected bond lengths (Å) and angles (°) for **1a**, **2a**, **3·4H$_2$O**, **1b**, **2b** and **3b**

	1a	**2a**	**3·4H$_2$O**	**1b**	**2b**	**3b**
Mo1-O1	2.0094(16)	2.0217(16)	1.991(3)	2.0161(15)	2.0091(17)	2.0208(16)
Mo1-O2	1.9228(16)	1.9305(18)	1.916(3)	1.9339(14)	1.9425(17)	1.9146(17)
Mo1-O3	1.7192(15)	1.6975(18)	1.707(4)	1.7092(14)	1.7163(17)	1.7060(17)
Mo1-O4	1.6803(15)	1.6970(15)	1.690(4)	1.6847(14)	1.6879(16)	1.6955(19)
Mo1-N1	2.2343(18)	2.2365(19)	2.197(4)	2.2356(16)	2.227(2)	2.218(2)
Mo1-X[b]	2.4227(18)	2.397(2)	2.573(3)	2.4026(14)	2.3751(16)	2.413(2)
N1-N2	1.397(3)	1.403(3)	1.394(5)	1.396(2)	1.392(3)	1.390(3)
N1-C7	1.289(3)	1.295(3)	1.313(6)	1.291(2)	1.291(3)	1.306(3)
N2-C1	1.294(3)	1.297(3)	1.290(6)	1.293(2)	1.290(3)	1.292(3)
O1-Mo1-O2	148.70(6)	151.46(6)	149.41(14)	147.85(6)	150.01(7)	150.16(7)
O1-Mo1-O3	97.28(7)	94.61(8)	94.74(15)	100.35(6)	99.80(7)	94.70(7)
O1-Mo1-O4	98.47(8)	95.90(7)	99.56(16)	99.29(7)	97.93(8)	97.16(8)
O1-Mo1-N1	72.21(6)	72.05(7)	72.50(14)	72.24(6)	72.00(7)	72.37(7)
O2-Mo1-O3	101.55(7)	104.86(8)	101.19(17)	99.15(6)	99.99(8)	103.66(8)
O2-Mo1-O4	99.50(7)	99.17(8)	100.58(17)	99.05(6)	97.90(8)	100.48(8)
O2-Mo1-N1	81.06(7)	81.88(7)	81.24(15)	80.73(6)	81.41(7)	81.41(7)
O3-Mo1-O4	107.25(7)	104.34(8)	106.7(2)	107.15(7)	106.24(8)	104.95(9)
O3-Mo1-N1	157.35(6)	154.96(7)	151.21(15)	159.81(6)	158.36(7)	154.85(8)
O4-Mo1-N1	94.32(7)	98.18(7)	100.91(18)	92.72(6)	94.86(8)	98.15(8)
O4-Mo1-X	170.07(8)	171.92(7)	171.87(17)	171.58(7)	171.20(8)	172.94(8)

[b]X = N4 in **1a** and **2a**; X = O6 in **3**; X = O5 in **1b**, **2b** and **3b**

Table S2. Geometry of hydrogen bonds (Å, °) for **1a**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
N3-H3···O3[a]	0.86	2.16	2.810(3)	132
N3-H3···O11[b]	0.86	2.50	3.023(2)	120
C5-H5···O2[a]	0.93	2.55	3.302(3)	139
C11-H11···O12[c]	0.93	2.50	3.365(3)	155
C13-H13···O13[d]	0.93	2.51	3.429(3)	168
C15-H15b···O8[e]	0.96	2.40	3.360(4)	173

[a] 1+x,y,z; [b] x,-1+y,z; [c]-x,1-y,1-z; [d]1-x,1-y,1-z; [e]-x,1-y,-z

Table S3. Geometry of hydrogen bonds (Å, °) for **2a**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
N3-H31··· N5[a]	0.75(2)	2.23(2)	2.856(3)	143(2)
N3-H31··· N6[a]	0.75(2)	2.68(2)	3.186(3)	156.92(18)
C3- H3···O1	0.89(2)	2.43(2)	2.791(3)	104.5(19)
C4-H4···O4[a]	0.87(3)	2.41(3)	3.188(3)	148.4(19)
C5-H5···O11[b]	0.81(2)	2.54(2)	3.256(3)	149(2)
C5-H5···N6[a]	0.81(2)	2.62(2)	3.197(3)	129(2)
C7-H7···O4[c]	0.95(2)	2.41(2)	2.978(3)	118.0(17)
C14-H14B···O11[d]	1.00(3)	2.56(3)	3.520(3)	161(2)
C16-H16A···O3[e]	1.03(4)	2.59(3)	2.941(3)	100(2)
C17-H17B···O9[d]	0.96(3)	2.57(3)	3.417(4)	146(2)

[a]-x,1-y,1-z; [b]1-x,2-y,1-z; [c] 1-x,1-y,1-z; [d] x,-1+y,z; [e] -x,-y,1-z

Table S4. Geometry of hydrogen bonds (Å, °) for **3·4H$_2$O**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
O1W-H11W···O2W	0.89	2.15	2.886(11)	140
O1W-H12W···O2W [a]	0.88	2.25	3.090(10)	159
O2W-H21W···O3	0.85	2.24	3.071(10)	168
N3-H3···O1W[b]	0.86	1.91	2.762(6)	171
C4-H4···O3[c]	0.93	2.52	3.259(7)	137
C6-H6···O8[d]	0.93	2.59	3.189(7)	122
C7 -H7···O11[d]	0.93	2.49	3.313(6)	148
C3-H31···O8[e]	0.93	2.54	3.270(6)	135

[a]2-x,-1/2+y,1/2-z; [b] x,1/2-y,-1/2+z; [c] 2-x,1-y,-z; [d] x,-1+y,-1+z; [e] 2-x,1-y,1-z

Table S5. Geometry of hydrogen bonds (Å, °) for **1b**.

D-H…A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
C4-H4···O5[a]	0.95	2.45	3.398(2)	178
C5-H5···O2[b]	0.95	2.47	3.385(3)	161
C7-H7···O12[c]	0.95	2.40	3.269(2)	152
C10-H10···O16	0.95	2.49	2.967(5)	112
C11-H11···O4[d]	0.95	2.59	3.182(3)	121
C12-H12···O11[e]	0.95	2.56	3.231(2)	128
C13-H13···O12[c]	0.95	2.47	3.312(3)	148
C15-H15A···O11[f]	0.98	2.58	3.478(4)	152
C15-H15C···O13[a]	0.98	2.48	3.206(3)	131
C16-H16A···O2	0.98	2.54	3.346(3)	139
C18-H18C···O14[e]	0.98	2.49	3.376(5)	150
N3-H3···O3[b]	0.88	2.25	2.917(2)	132
N3-H3···O10	0.88	2.28	2.932(2)	130

[a]1-x,1-y,1-z; [b]-1+x,y,z; [c]-x,1-y,-z; [d] 2-x,1-y,-z; [e]1-x,1-y,-z; [f] x,-1+y,z

Table S6. Geometry of hydrogen bonds (Å, °) for **2b**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
N3-H3···O3[a]	0.88	2.21	2.923(3)	138
N3-H3···O11[a]	0.88	2.28	2.847(3)	122
C3-H3A···O9[b]	0.95	2.43	3.201(3)	138
C5-H5···O2[a]	0.95	2.56	3.363(3)	143
C6- H6···O17[a]	0.95	2.31	3.240(4)	168
C13-H13···O7[c]	0.95	2.50	3.088(3)	126
C14-H14A···O4[d]	0.98	2.45	3.114(4)	125
C14- H14A···O13[d]	0.98	2.56	3.444(4)	149
C14-H14C···O17	0.98	2.22	3.190(5)	173
C19-H19B···O15[d]	0.98	2.56	3.460(5)	153

[a]1+x,y,z; [b]1-x,2-y,2-z; [c]1+x,-1+y,-1+z; [d]1-x,1-y,1-z

Table S7. Geometry of hydrogen bonds (Å, °) for **3b**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
O5-HW1···O17[a]	0.78(4)	2.09(4)	2.873(3)	177(5)
O5-HW2···O6	0.74(3)	2.04(3)	2.776(4)	176(3)
N3-H30···O7[b]	0.86	1.91	2.756(3)	169
C4-H4···O14	0.93	2.49	3.117(3)	125
C5-H5···O3[b]	0.93	2.26	3.116(3)	153
C6-H6···O4[c]	0.93	2.49	3.319(3)	149
C10-H10···O4[d]	0.93	2.56	3.463(3)	163
C12-H12···O11[c]	0.93	2.47	3.331(3)	153
C16-H16A···O13[c]	0.97	2.57	3.325(4)	134
C16-H16B···O16[d]	0.97	2.52	3.294(3)	137

[a] 1+x,y,z; [b]x,-1+y,z; [c] 1-x,-y,-z; [d]1-x,1-y,-z

Table S8. *π···π* interactions in the crystal structures of compounds **1a**, **1b**, **3·4H_2O** and **3b**

	CgX	CgY	CgX-CgY (Å)	Slippage (Å)
1a	Cg3 (N3, C2-C6)	Cg4 (C8-C13)	3.6773(12)^{i}	1.23
1b	Cg3 (N3, C2-C6)	Cg4 (C8-C13)	3.6865(13)^{ii}	1.55
3·4H_2O	Cg1 (Mo1-O1-C1-N2-N1)	Cg3 (N3, C2-C6)	3.660(3)^{iii}	1.58
3b	Cg3 (N3, C2-C6)	Cg4 (C8-C13)	3.7125(14)^{iv}	1.17

^{i}-x,-y,1-z; ^{ii} 1-x, 1-y, -z; ^{iii}2-x,-y,-z; ^{iv}1-x,-y,-z