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Supplementary Materials: New photomagnetic ionic salts based on $[Mo^{IV}(CN)_8]^{4-}$ and $[W^{IV}(CN)_8]^{4-}$ anions

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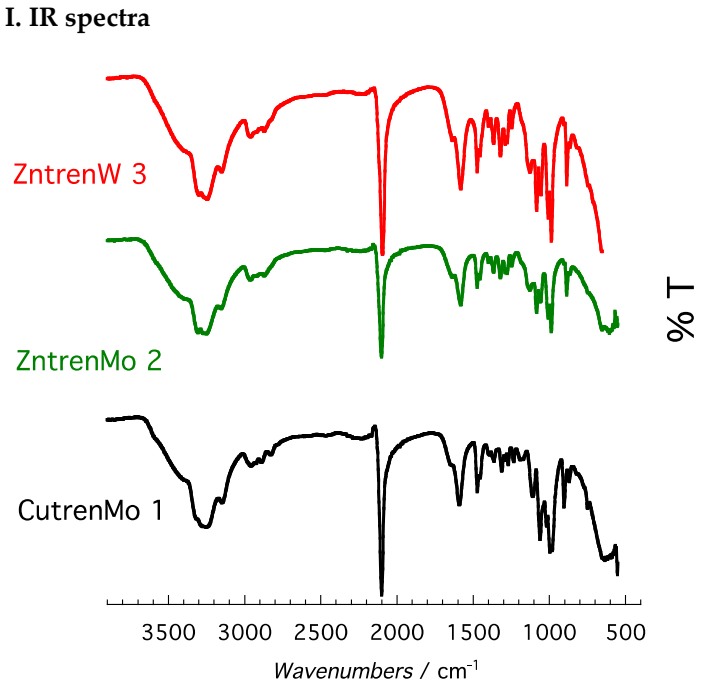


Figure S1. FT-IR spectra of **1**, **2** and **3**.

Table S1. Possible attributions of IR vibrations according to the literature.[1]

Region	Assignment
Broad peaks in the 3700 – 3000 cm^{-1}	ν(O–H) stretching bands of water molecules
Sharp peaks in the 3000 – 2750 cm^{-1}	ν(C–H) and ν(N–H) vibrations of the tren ligand
2200 – 2100 cm^{-1}	Stretching bands ν(C≡N) of cyanide group
1700 – 600 cm^{-1}	δ(O–H) bending bands of water and several other bands from the tren ligand: δ(H–C–H), ν(N–C) and ν(C–C)

Table S2. Summary of CN stretching bands observed for **1**, **2**, **3** and their precursors used during their synthesis involved in this work.

Compounds	CN stretching bands / cm^{-1}
$K_4Mo(CN)_8.2H_2O$	2160, 2123, 2100, 2059
$[\{Cu(tren)\}_3(\mu\text{-tren})]_4[Mo(CN)_8]_6\cdot$solv **1**	2098
$[\{Zn(tren)\}_3(\mu\text{-tren})]_2[Mo(CN)_8]_3\cdot$solv **2**	2098
$K_4W(CN)_8.2H_2O$	2168, 2125, 2093, 2056
$[\{Zn(tren)\}_3(\mu\text{-tren})]_2[W(CN)_8]_3\cdot$solv **3**	2091

II. UV-Visible Spectra

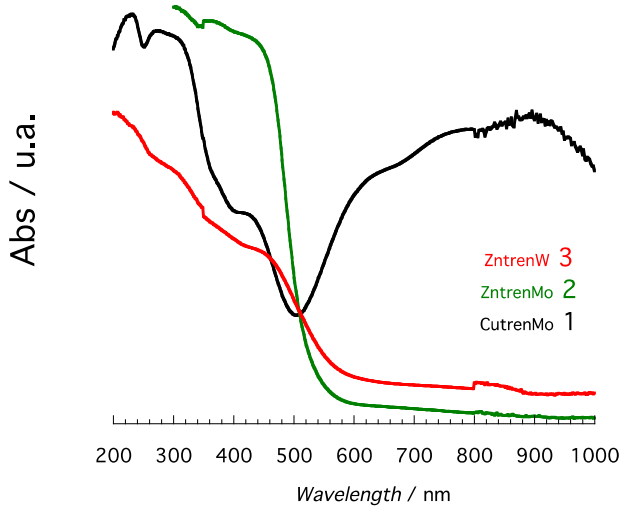


Figure S2. : Solid State UV-Visible spectra of **1**, **2** and **3**.

Table S3. Optical absorptions observed in **1**, **2**, **3**, their precursors and reported $[Cu(tren)(NH_3)][ClO_4]_2$.

Compounds	**λ / nm**
$K_4Mo(CN)_8 \cdot 2H_2O$[2]	430, 368, 308 (Mo ligand field transitions)
$[Cu(tren)(NH_3)][ClO_4]_2$[3]	872, 643
$[\{Cu(tren)\}_3(\mu\text{-tren})]_4[Mo(CN)_8]_6 \cdot$solv **1**	877, 657, 430, 306
$[\{Zn(tren)\}_3(\mu\text{-tren})]_2[Mo(CN)_8]_3 \cdot$solv **2**	430, 356
$K_4W(CN)_8.2H_2O$[2]	435, 370, 303 (W ligand field transitions)
$[\{Zn(tren)\}_3(\mu\text{-tren})]_2[W(CN)_8]_3 \cdot$solv **3**	445, 300

III. Additional crystallographic tables and figures

Table S4. Selected bond lengths and angles for $[Mo^{IV}(CN)_8]^{4-}$ anion in **1**.

Atoms		Length/Å	Atoms		Length/Å	Atoms			Angle/°
Mo1	C1	2.166(10)	N1	C1	1.176(15)	N1	C1	Mo1	177.8(9)
Mo1	C2	2.192(9)	N2	C2	1.143(14)	N2	C2	Mo1	174.4(10)
Mo1	C3	2.187(8)	N3	C3	1.131(14)	N3	C3	Mo1	177.8(10)
Mo1	C4	2.175(11)	N4	C4	1.139(15)	N4	C4	Mo1	178.5(9)
Mo1	C5	2.185(9)	N5	C5	1.139(14)	N5	C5	Mo1	175.7(9)
Mo1	C6	2.165(11)	N6	C6	1.153(14)	N6	C6	Mo1	177.0(10)
Mo1	C7	2.185(9)	N7	C7	1.131(14)	N7	C7	Mo1	178.4(9)
Mo1	C8	2.178(9)	N8	C8	1.145(14)	N8	C8	Mo1	176.7(10)
Average		2.179(10)	Average		1.145(14)	Average			177.0(10)
Mo2	C9	2.178(10)	N9	C9	1.118(15)	N9	C9	Mo2	177.5(11)
Mo2	C10	2.169(10)	N10	C10	1.140(14)	N10	C10	Mo2	179.0(9)
Mo2	C11	2.158(10)	N11	C11	1.153(14)	N11	C11	Mo2	175.4(8)
Mo2	C12	2.169(9)	N12	C12	1.137(13)	N12	C12	Mo2	176.2(9)
Mo2	C13	2.173(9)	N13	C13	1.147(13)	N13	C13	Mo2	177.1(10)
Mo2	C14	2.154(10)	C14	N14	1.152(16)	N14	C14	Mo2	177.8(11)
Mo2	C15	2.194(9)	N15	C15	1.138(14)	N15	C15	Mo2	174.9(9)
Mo2	C16	2.165(9)	N16	C16	1.145(14)	N16	C16	Mo2	175.7(9)
Average		2.170(10)	Average		1.141(14)	Average			176.7(10)
Mo3	C17	2.196(14)	C17	N17	1.11(2)	N17	C17	Mo3	177.6(14)
Mo3	C18	2.184(13)	C18	N18	1.14(2)	N18	C18	Mo3	176.0(14)
Mo3	C19	2.169(13)	N19	C19	1.107(18)	N19	C19	Mo3	177.2(13)
Mo3	C20	2.186(14)	N20	C20	1.12(2)	N20	C20	Mo3	177.1(15)
Mo3	C21	2.173(16)	C21	N21	1.11(2)	N21	C21	Mo3	175.4(19)
Mo3	C22	2.166(14)	N22	C22	1.17(2)	N22	C22	Mo3	173(2)
Mo3	C23	2.153(14)	N23	C23	1.194(19)	N23	C23	Mo3	177.7(14)
Mo3	C24	2.177(15)	C24	N24	1.13(2)	N24	C24	Mo3	173(2)
Average		2.176(14)	Average		1.135(6)	Average			175.9(12)
Mo4	C25	2.147(13)	C25	N25	1.162(18)	N25	C25	Mo4	176.2(11)
Mo4	C26	2.204(10)	N26	C26	1.121(14)	N26	C26	Mo4	174.8(9)
Mo4	C27	2.176(9)	N27	C27	1.154(14)	N27	C27	Mo4	178.0(9)
Mo4	C28	2.163(10)	N28	C28	1.152(14)	N28	C28	Mo4	178.4(9)
Mo4	C29	2.174(10)	N29	C29	1.136(14)	N29	C29	Mo4	179.1(10)
Mo4	C30	2.161(8)	N30	C30	1.145(14)	N30	C30	Mo4	179.7(10)
Mo4	C31	2.196(14)	C31	N31	1.11(2)	N31	C31	Mo4	178(2)
Mo4	C32	2.198(9)	N32	C32	1.119(15)	N32	C32	Mo4	175.7(12)
Average		2.177(10)	Average		1.137(13)	Average			177.5(9)
Mo5	C33	2.137(14)	C33	N33	1.18(2)	N33	C33	Mo5	175.5(18)
Mo5	C34	2.160(14)	N34	C34	1.16(2)	N34	C34	Mo5	177.7(15)
Mo5	C35	2.127(11)	N35	C35	1.170(17)	N35	C35	Mo5	178.0(13)
Mo5	C36	2.176(12)	N36	C36	1.122(17)	N36	C36	Mo5	176.6(14)
Mo5	C37	2.114(14)	N37	C37	1.181(18)	N37	C37	Mo5	177.0(10)
Mo5	C38	2.194(13)	N38	C38	1.13(2)	N38	C38	Mo5	177.8(15)
Mo5	C39	2.172(10)	N39	C39	1.162(17)	N39	C39	Mo5	178.5(13)
Mo5	C40	2.144(13)	C40	N40	1.15(2)	N40	C40	Mo5	173(3)
Average		2.153(13)	Average		1.157(10)	Average			176.8(13)
Mo6	C41	2.175(10)	N41	C41	1.134(14)	N41	C41	Mo6	177.8(11)
Mo6	C42	2.160(10)	C42	N42	1.149(16)	N42	C42	Mo6	178.6(13)
Mo6	C43	2.172(9)	N43	C43	1.129(14)	N43	C43	Mo6	176.3(9)
Mo6	C44	2.172(10)	N44	C44	1.146(13)	N44	C44	Mo6	174.9(9)
Mo6	C45	2.174(9)	N45	C45	1.134(14)	N45	C45	Mo6	179.2(11)
Mo6	C46	2.176(11)	N46	C46	1.131(15)	N46	C46	Mo6	178.2(10)
Mo6	C47	2.154(10)	N47	C47	1.140(14)	N47	C47	Mo6	175.7(8)
Mo6	C48	2.170(10)	N48	C48	1.138(14)	N48	C48	Mo6	177.7(9)
Average		2.169(10)	Average		1.138(14)	Average			177.3(10)

Table S5. Selected bond lengths and angles for $[Mo^{IV}(CN)_8]^{4-}$ anion in **2**.

Atoms		Length/Å	Atoms		Length/Å		Atoms		Angle/°
Mo1	C1	2.168(14)	N1	C1	1.164(19)	N1	C1	Mo1	176.6(12)
Mo1	C2	2.180(11)	N2	C2	1.112(16)	N2	C2	Mo1	176.2(13)
Mo1	C3	2.181(13)	N3	C3	1.129(18)	N3	C3	Mo1	175.2(13)
Mo1	C4	2.178(16)	N4	C4	1.14(2)	N4	C4	Mo1	175.2(16)
Mo1	C5	2.157(12)	N5	C5	1.136(17)	N5	C5	Mo1	179.8(16)
Mo1	C6	2.206(14)	N6	C6	1.11(2)	N6	C6	Mo1	178(2)
Mo1	C7	2.175(12)	N7	C7	1.144(17)	N7	C7	Mo1	178.7(12)
Mo1	C8	2.144(13)	N8	C8	1.18(2)	N8	C8	Mo1	176.6(15)
Average		2.174 (13)	Average		1.139(12)		Average		177.0(12)
Mo2	C9	2.153(13)	N9	C9	1.150(18)	N9	C9	Mo2	177.1(11)
Mo2	C10	2.199(9)	N10	C10	1.126(16)	N10	C10	Mo2	177.2(13)
Mo2	C11	2.146(14)	N11	C11	1.14(2)	N11	C11	Mo2	178.8(17)
Mo2	C12	2.200(10)	N12	C12	1.156(19)	N12	C12	Mo2	178.9(16)
Mo2	C13	2.147(14)	N13	C13	1.18(2)	N13	C13	Mo2	177.9(18)
Mo2	C14	2.160(12)	N14	C14	1.148(19)	N14	C14	Mo2	176.9(14)
Mo2	C15	2.187(12)	N15	C15	1.116(19)	N15	C15	Mo2	178.2(14)
Mo2	C16	2.133(14)	N16	C16	1.18(2)	N16	C16	Mo2	176.3(17)
Average		2.166(12)	Average		1.150(12)		Average		177.7(15)
Mo3	C17	2.164(12)	N17	C17	1.177(19)	N17	C17	Mo3	175.8(13)
Mo3	C18	2.176(16)	N18	C18	1.13(2)	N18	C18	Mo3	178.1(14)
Mo3	C19	2.178(13)	N19	C19	1.128(19)	N19	C19	Mo3	175.0(14)
Mo3	C20	2.146(14)	N20	C20	1.151(19)	N20	C20	Mo3	178.3(13)
Mo3	C21	2.21(2)	N21	C21	1.10(3)	N21	C21	Mo3	176(2)
Mo3	C22	2.216(12)	N22	C22	1.075(19)	N22	C22	Mo3	177.9(19)
Mo3	C23	2.160(14)	N23	C23	1.20(2)	N23	C23	Mo3	174.2(13)
Mo3	C24	2.178(12)	N24	C24	1.095(19)	N24	C24	Mo3	177.6(14)
Average		2.179(12)	Average		1.132(12)		Average		176.6(13)

Table S6. Selected bond lengths and angles for $[W^{IV}(CN)_8]^{4-}$ anions in **3**.

Atoms		Length/Å	Atoms		Length/Å		Atoms		Angle/°
W1	C1	2.144(11)	N1	C1	1.158(14)	N1	C1	W1	177.8(10)
W1	C7	2.166(11)	N7	C7	1.139(13)	N7	C7	W1	177.7(9)
W1	C6	2.150(11)	N6	C6	1.167(14)	N6	C6	W1	177.7(10)
W1	C2	2.172(12)	N2	C2	1.154(14)	N2	C2	W1	179.1(10)
W1	C3	2.161(11)	C3	N3	1.137(14)	N3	C3	W1	179.3(11)
W1	C4	2.200(12)	N4	C4	1.117(14)	N4	C4	W1	179.0(12)
W1	C8	2.198(12)	N8	C8	1.133(14)	N8	C8	W1	174.8(10)
W1	C5	2.155(13)	N5	C5	1.155(15)	N5	C5	W1	175.8(14)
Average		2.168(12)	Average		1.145(14)		Average		177.7(11)
W2	C10	2.151(11)	C10	N10	1.134(13)	N10	C10	W2	178.3(9)
W2	C9	2.162(11)	N9	C9	1.146(13)	N9	C9	W2	178.0(10)
W2	C13	2.176(12)	N13	C13	1.153(14)	N13	C13	W2	175.3(9)
W2	C15	2.149(12)	N15	C15	1.169(14)	N15	C15	W2	176.4(9)
W2	C11	2.143(11)	N11	C11	1.163(13)	N11	C11	W2	178.0(11)
W2	C16	2.179(12)	N16	C16	1.151(13)	N16	C16	W2	175.3(10)
W2	C14	2.168(12)	C14	N14	1.163(14)	N14	C14	W2	178.8(11)
W2	C12	2.192(11)	N12	C12	1.143(14)	N12	C12	W2	178.3(10)
Average		2.165(12)	Average		1.153(14)		Average		177.3(10)
W3	C20	2.163(11)	C20	N20	1.119(13)	N20	C20	W3	179.5(10)
W3	C22	2.176(13)	N22	C22	1.158(15)	N22	C22	W3	179.0(10)
W3	C18	2.117(12)	C18	N18	1.174(14)	N18	C18	W3	177.8(11)
W3	C23	2.155(12)	N23	C23	1.192(15)	N23	C23	W3	177.2(12)
W3	C19	2.193(11)	N19	C19	1.147(13)	N19	C19	W3	177.5(9)
W3	C21	2.202(13)	N21	C21	1.113(14)	N21	C21	W3	177.3(11)
W3	C17	2.179(12)	N17	C17	1.144(14)	N17	C17	W3	179.6(12)

W3	C24	2.188(13)	N24	C24	1.127(15)	N24	C24	W3	178.0(12)
Average		2.172(12)	Average		1.147(14)	Average			178.2(11)

Table S7. Selected bond lengths for $[\{Cu(tren)\}_3(\mu\text{-tren})]^{6+}$ cation in **1**.

Atoms		**Length/Å**	**Atoms**		**Length/Å**		**Atoms**	**Length/Å**
Cu1	N64	2.045(8)	Cu2	N50	1.993(9)	Cu3	N55	2.022(9)
Cu1	N60	1.984(9)	Cu2	N54	2.068(12)	Cu3	N57	2.148(9)
Cu1	N62	2.104(9)	Cu2	N52	2.129(11)	Cu3	N56	2.046(9)
Cu1	N61	2.091(9)	Cu2	N51	2.059(11)	Cu3	N59	2.082(10)
Cu1	N63	2.120(8)	Cu2	N53	2.101(12)	Cu3	N58	2.066(10)
Average		2.069(9)	Average		2.070(11)	Average		2.073(9)
Cu4	N66	2.020(9)	Cu5	N80	2.027(14)	Cu6	N72	2.020(8)
Cu4	N75	2.082(9)	Cu5	N79	2.170(16)	Cu6	N68	2.000(10)
Cu4	N74	2.113(10)	Cu5	N78	2.024(19)	Cu6	N69	2.067(12)
Cu4	N76	2.064(10)	Cu5	N67	1.998(14)	Cu6	N71	2.171(10)
Cu4	N73	2.048(18)	Cu5	N77	2.060(18)	Cu6	N70	2.024(12)
Average		2.065(11)	Average		2.056(16)	Average		2.056(10)
Cu7	N10	2.034(8)	Cu8	N95	2.000(10)	Cu9	N94	2.027(9)
Cu7	N98	2.099(10)	Cu8	N10	2.076(10)	Cu9	N108	2.096(9)
Cu7	N96	2.008(9)	Cu8	N10	2.117(10)	Cu9	N107	2.136(11)
Cu7	N97	2.105(9)	Cu8	N10	2.085(12)	Cu9	N105	2.035(12)
Cu7	N99	2.131(11)	Cu8	N10	2.066(13)	Cu9	N106	2.027(11)
Average		2.075(9)	Average		2.069(11)	Average		2.064(10)
Cu10	N84	2.014(11)	Cu11	N83	1.981(8)	Cu12	N82	2.000(10)
Cu10	N11	2.049(10)	Cu11	N85	2.116(8)	Cu12	N90	2.140(9)
Cu10	N11	2.076(12)	Cu11	N86	2.104(10)	Cu12	N92	2.076(10)
Cu10	N10	2.117(16)	Cu11	N88	2.048(9)	Cu12	N89	2.073(9)
Cu10	N11	2.093(14)	Cu11	N87	2.081(16)	Cu12	N91	2.058(13)
Average		2.070(13)	Average		2.066(10)	Average		2.069(10)

Table S8. Selected bond lengths for $[\{Zn(tren)\}_3(\mu\text{-tren})]^{6+}$ cation in **2**.

Atoms		**Length/Å**	**Atoms**		**Length/Å**		**Atoms**	**Length/Å**
Zn1	N25	2.095(14)	Zn2	N30	2.081(11)	Zn3	N34	2.015(19)
Zn1	N26	2.075(14)	Zn2	N31	2.081(13)	Zn3	N35	2.02(2)
Zn1	N27	2.084(11)	Zn2	N32	2.065(13)	Zn3	N36	2.055(16)
Zn1	N28	2.294(12)	Zn2	N33	2.119(10)	Zn3	N37	2.272(16)
Zn1	N29	2.101(11)	Zn2	N39	2.315(13)	Zn3	N40	2.193(19)
Average		2.130(12)	Average		2.132(12)	Average		2.111(14)
Zn4	N41	2.070(11)	Zn5	N46	2.077(11)	Zn6	N51	2.113(12)
Zn4	N42	2.077(11)	Zn5	N47	2.082(11)	Zn6	N52	2.102(11)
Zn4	N43	2.103(12)	Zn5	N48	2.073(10)	Zn6	N53	2.063(12)
Zn4	N44	2.259(12)	Zn5	N49	2.301(12)	Zn6	N54	2.311(11)
Zn4	N45	2.110(12)	Zn5	N50	2.105(10)	Zn6	N55	2.101(10)
Average		2.124(12)	Average		2.128(11)	Average		2.138(11)

Table S9. Selected bond lengths for $[\{Zn(tren)\}_3(\mu\text{-tren})]^{6+}$ cation in **3**.

Atoms		**Length/Å**	**Atoms**		**Length/Å**		**Atoms**	**Length/Å**
Zn1	N28	2.113(8)	Zn2	N36	2.308(8)	Zn3	N56	2.299(9)
Zn1	N51	2.061(8)	Zn2	N33	2.081(9)	Zn3	N54	2.083(9)
Zn1	N49	2.081(8)	Zn2	N35	2.042(9)	Zn3	N53	2.076(8)
Zn1	N52	2.283(9)	Zn2	N27	2.080(8)	Zn3	N26	2.110(8)
Zn1	N50	2.080(9)	Zn2	N34	2.063(8)	Zn3	N55	2.070(9)
Average		2.124(8)	Average		2.115(8)	Average		2.128(9)
Zn4	N48	2.295(12)	Zn5	N57	2.107(8)	Zn6	N61	2.295(9)
Zn4	N45	2.097(11)	Zn5	N43	2.060(9)	Zn6	N59	2.060(8)
Zn4	N47	2.020(14)	Zn5	N42	2.090(9)	Zn6	N38	2.122(8)

Zn4	N39	2.146(12)	Zn5	N44	2.351(9)	Zn6	N58	2.034(10)
Zn4	N46	2.028(13)	Zn5	N41	2.067(10)	Zn6	N60	2.095(10)
Average		2.117(12)	Average		2.135(9)	Average		2.121(9)

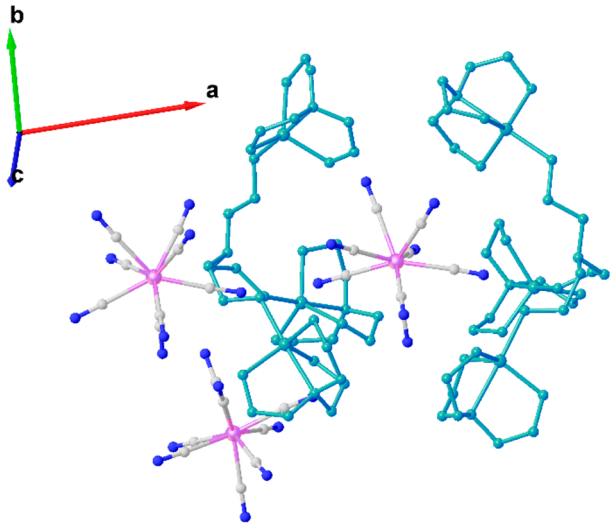


Figure S3. Asymmetric unit of **3** in *ab* plane with $[\{Zn(tren)\}_3(\mu\text{-tren})]^{6+}$ units in green, with *a, b, c* indicating crystallographic axes.

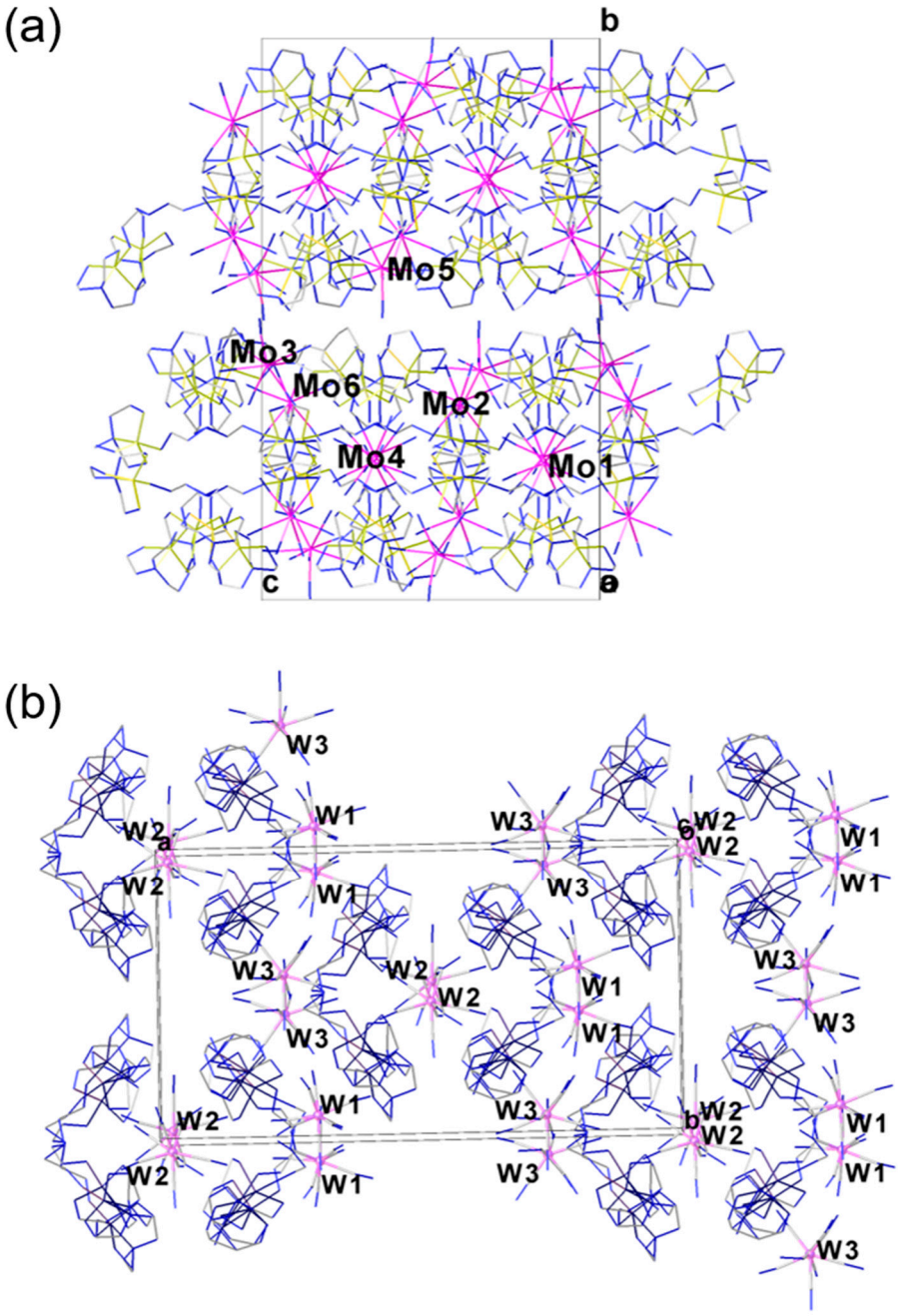
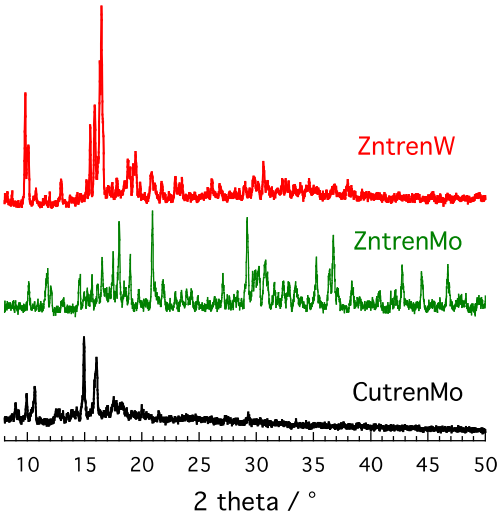
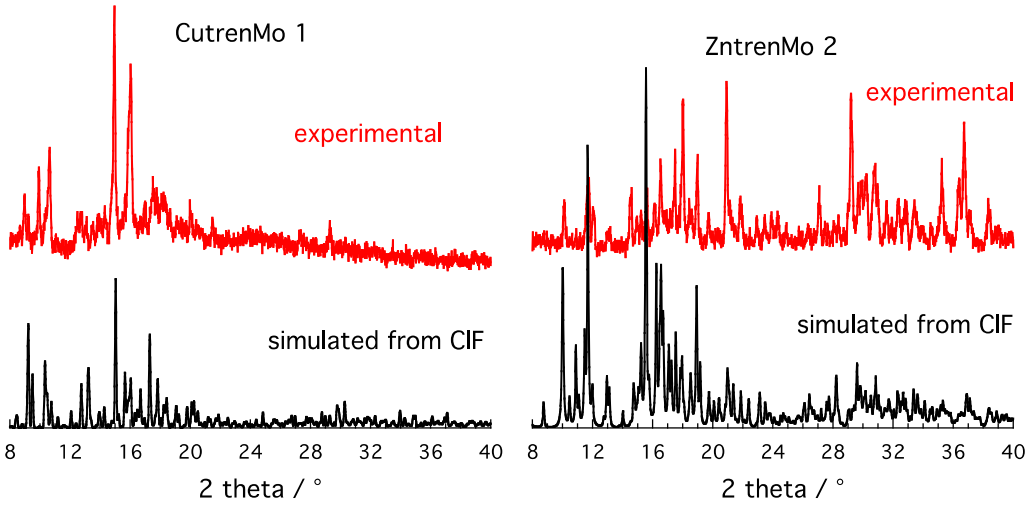


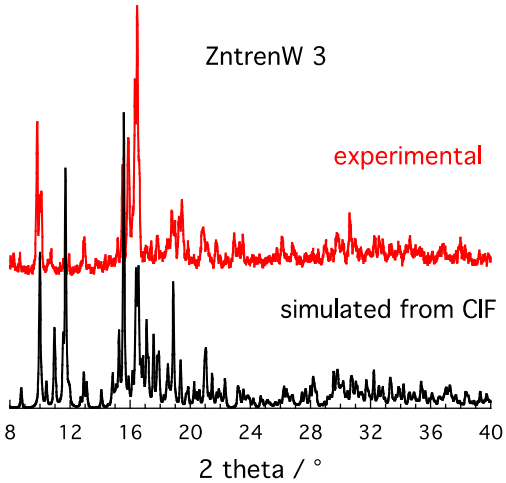
Figure S4. Packing diagrams of **1** (**a**) and **3** (**b**), where the solvent molecules and hydrogen atoms are omitted for clarity.

Figure S5. PXRD patterns for the three compounds.



Experimental PXRD patterns compared with simulated ones from CIF.





IV. Additional magnetic measurements.

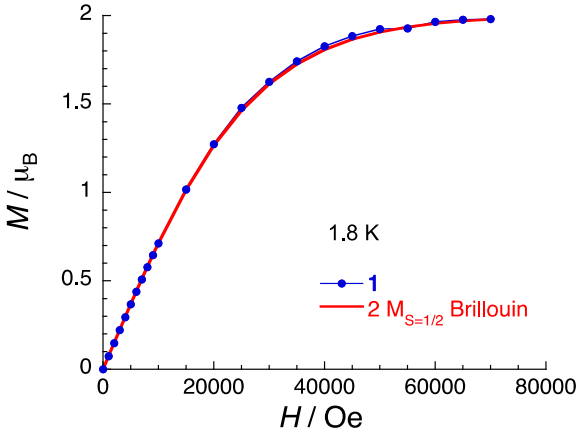


Figure S6. Fit of the magnetization of **1** at 1.8 K using Brillouin functions with $g = 2$.

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