

Supplementary information

Controllable assembly of multicarboxylic acids functionalized heteropolyoxomolybdates and allochroic properties

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UV spectra

The UV spectra of compounds **1–3** in aqueous solution are shown in Fig. S1. Being consistent with the results of single crystal X-ray diffraction analyses, the spectra of **1–3** are almost the same in the range of 400–200 nm. They all have two characteristic peaks: the strong absorption bands at 208 nm for **1**, 208 nm for **2** and 210 nm for **3** can be assigned to the $p\pi-d\pi$ charge-transfer transition of the $O_t \rightarrow Mo$ bond.^{s1} The weak ones at 230–240 nm for the three compounds are attributed to the $p\pi-d\pi$ charge-transfer transition of the $O_{b,c} \rightarrow Mo$ bond.^{s1}

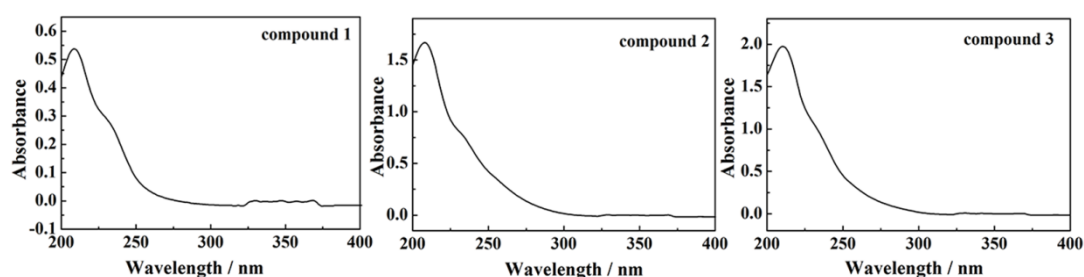


Fig. S1 UV spectra of compounds **1–3**.



Fig. S2 Color of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at different temperatures.

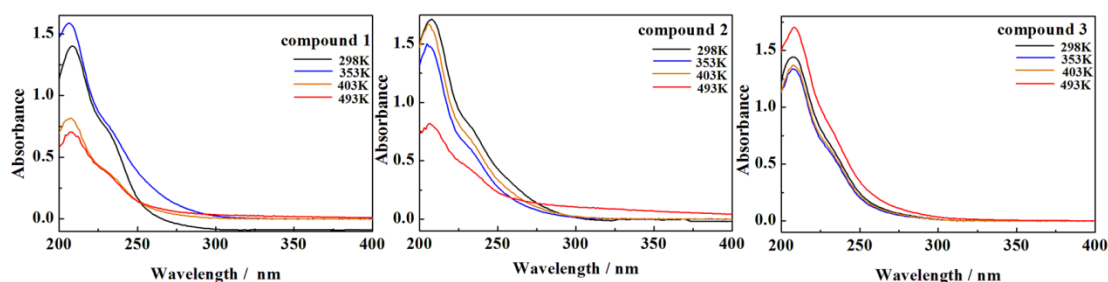


Fig. S3 UV spectra of compounds 1–3 after being heated at different temperatures.

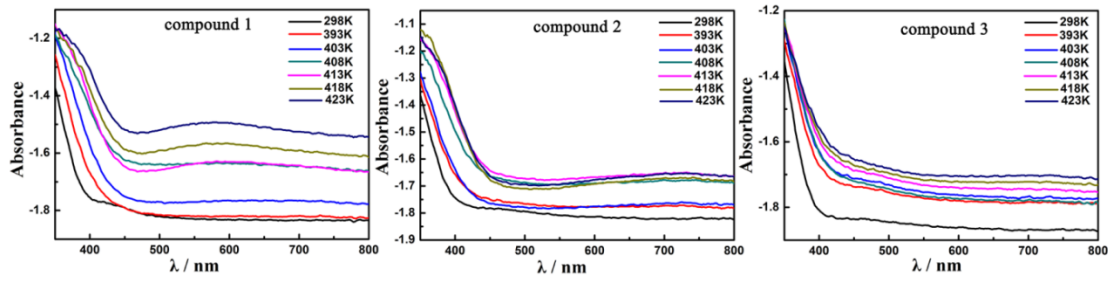


Fig. S4 The UV-vis diffuse reflectance spectra of compounds 1–3 at different temperatures.

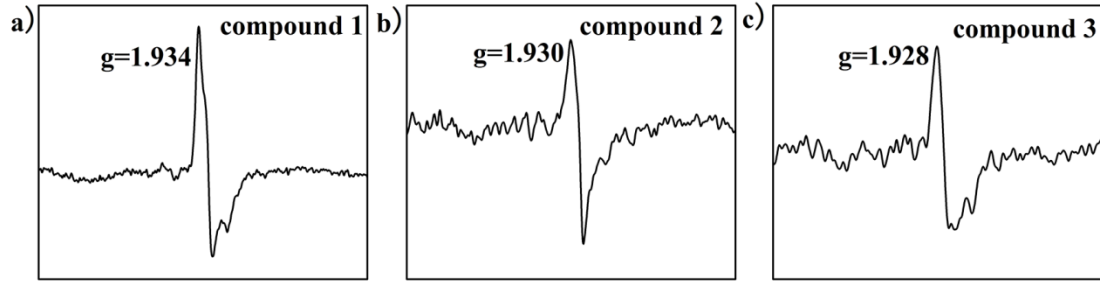


Fig. S5 EPR spectra of compounds 1–3 after being heated.

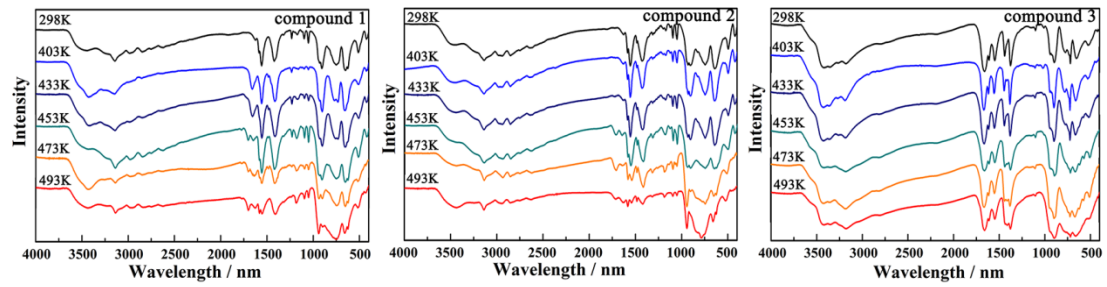


Fig. S6 VT IR spectra of compounds 1–3.

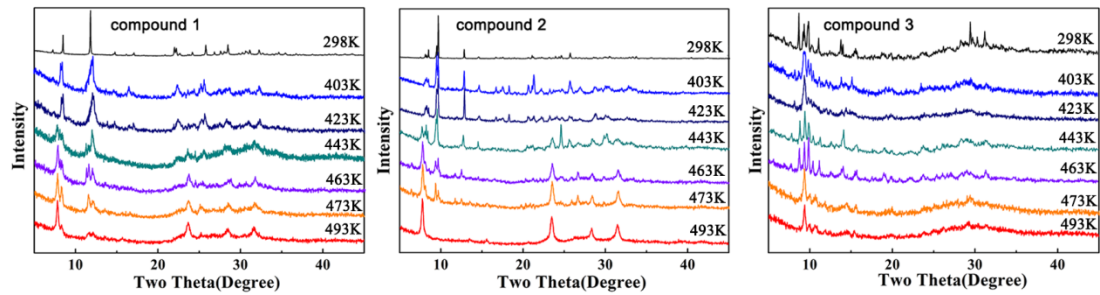


Fig. S7 VT XPRD of compounds 1–3.

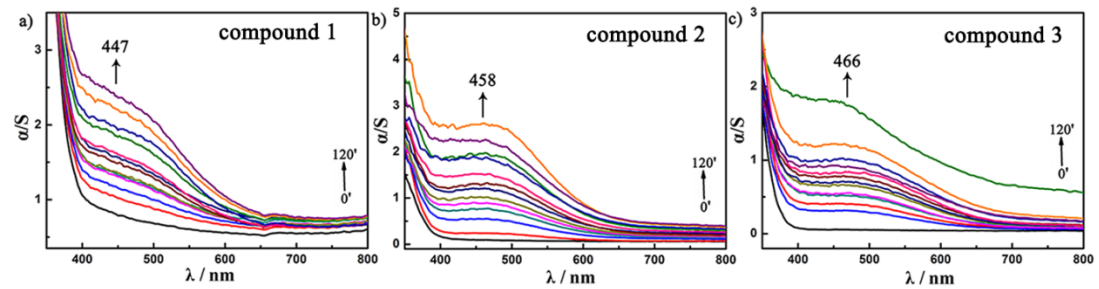


Fig. S8 Kubelka–Munk transformed reflectivity of compounds 1–3 vs irradiation times of 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, 100 and 120 min.

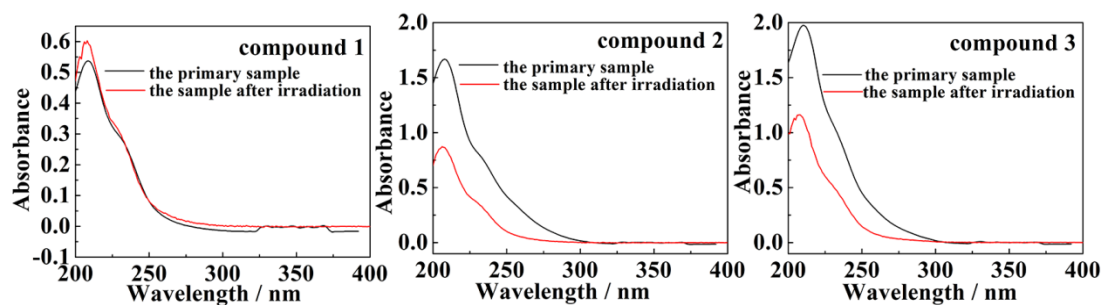


Fig. S9 UV spectra of compounds 1–3 before and after irradiation.

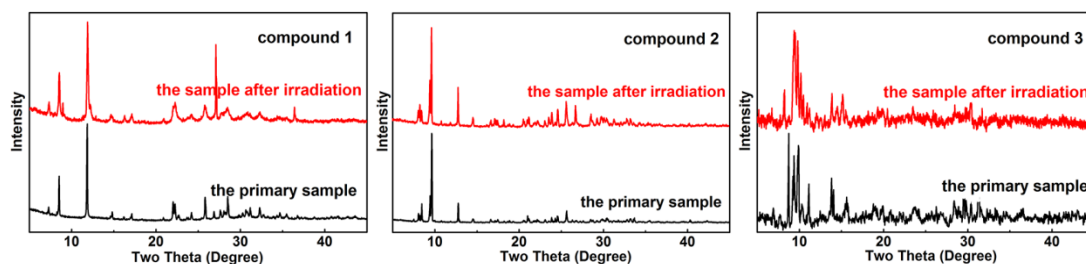


Fig. S10 X-ray powder diffraction patterns of compounds 1–3. Black: Experiment XPRD patterns of pure primary samples; Red: Samples after irradiation.

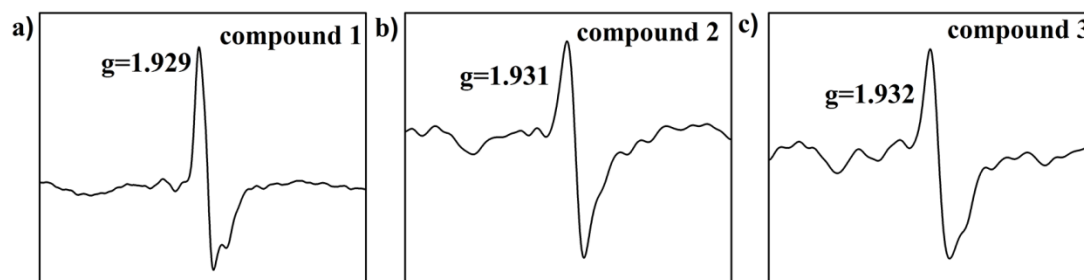


Fig. S11 EPR spectra of compounds 1–3 after irradiation.



Fig. S12 Color of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ after certain minutes irradiation by xenon lamp.

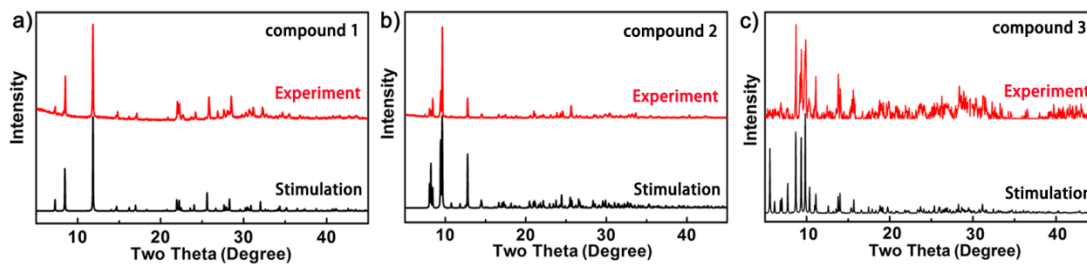


Fig. S13 X-ray powder diffraction patterns of compounds 1–3. Black, the calculated patterns based on the single-crystal X-ray diffraction data. Red, the experimental XPRD patterns for the samples.

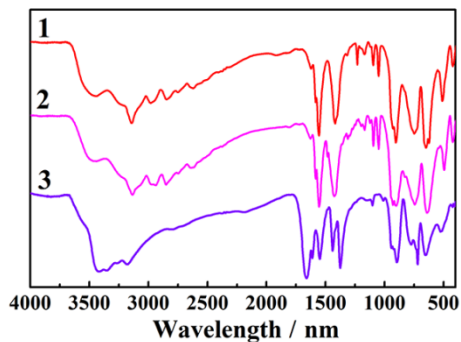


Fig. S14 IR spectra of 1–3.

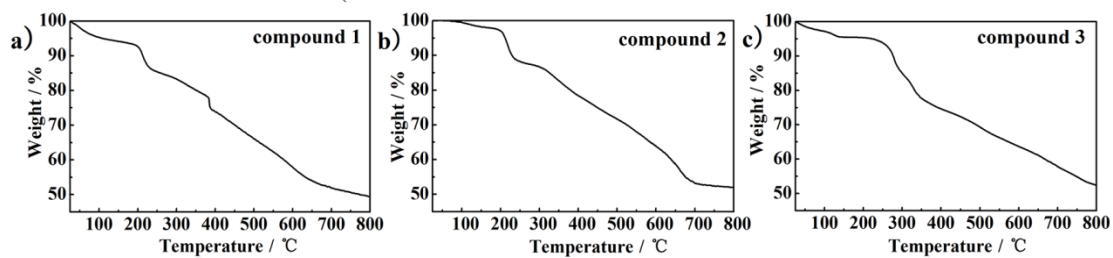
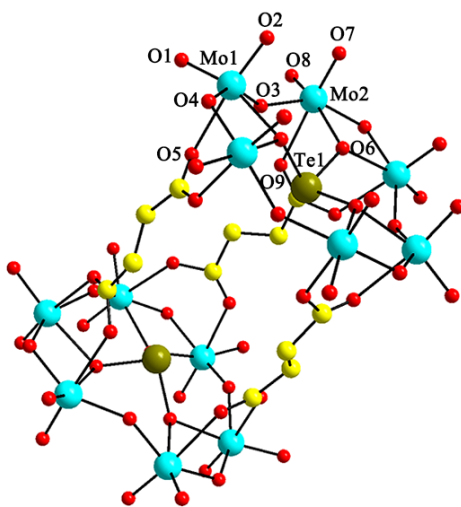


Fig. S15 TG curve of 1–3.



Bond	Bond length	Bond Valence	Valence Sum
Mo(1)–O1	1.715(9)	1.680	$\Sigma(\text{Mo1}) = 6.037$
Mo(1)–O2	1.697(8)	1.764	
Mo(1)–O3	1.928(8)	0.945	
Mo(1)–O4	1.941(8)	0.912	
Mo(1)–O5	2.331(8)	0.318	
Mo(1)–O6	2.230(7)	0.418	

Bond	Bond length	Bond Valence	Valence Sum
Mo(2)–O3	1.922(8)	0.960	
Mo(2)–O4	1.936(8)	0.925	

Mo(2)–O6	2.216(7)	0.434	
Mo(2)–O7	1.702(8)	1.740	
Mo(2)–O8	1.724(9)	1.640	
Mo(2)–O9	2.360(10)	0.294	

Bond	Bond length	Bond Valence	Valence Sum
Te(1)–O6	1.882(7)	1.293	$\Sigma(\text{Te1}) = 3.879$
Te(1)–O6	1.882(7)	1.293	
Te(1)–O6	1.882(7)	1.293	

Table S1 Bond valence sum parameters for the Mo (1), Mo (2) and Te (1) in **1**. The bond valence sum parameters for other Mo and Te atoms for compound **1** as well as compound **2** and **3** are almost the same, so they are omitted.

D–H···A	$d(\text{H}\cdots\text{A})$	$\angle\text{DHA}$	$d(\text{D}\cdots\text{A})$
N(1)–H(1A)···O(4)	1.89	164	2.7277

D–H···A	$d(\text{H}\cdots\text{A})$	$\angle\text{DHA}$	$d(\text{D}\cdots\text{A})$
N(1)–H(1A)···O(3)	2.01	174	2.868
N(2)–H(2A)···O(6)	1.98	169	2.826
N(3)–H(3A)···O(5)	2.09	152	2.875
N(4)–H(4A)···O(2)	2.55	123	3.102
N(4)–H(4A)···O(15)	2.17	159	2.993
N(5)–H(5A)···O(11)	2.35	162	3.176
N(6)–H(6A)···O(23)	2.40	175	3.25
N(6)–H(6A)···O(27)	2.39	109	2.79
N(8)–H(8A)···O(1)	2.54	122	3.09
N(8)–H(8A)···O(17)	2.43	124	3.00
N(9)–H(9A)···O(1W)	2.03	162	2.86
N(10)–H(10A)···O(14)	2.07	161	2.90

D–H···A	$d(\text{H}\cdots\text{A})$	$\angle\text{DHA}$	$d(\text{D}\cdots\text{A})$
N(1)–H(1B)···O(5)	2.58	142	3.335
N(2)–H(2A)···O(1)	2.07	147	2.870
N(2)–H(2B)···O(11)	2.03	178	2.926
N(3)–H(3A)···O(52)	2.49	138	3.220
N(3)–H(3A)···O(54)	2.14	147	2.938
N(3)–H(3B)···O(12)	2.04	163	2.913
N(4)–H(4A)···O(12)	2.40	150	3.209
N(4)–H(4B)···O(50)	2.20	146	2.984
N(5)–H(5A)···O(13)	2.00	159	2.859
N(5)–H(5B)···O(34)	1.98	156	2.822
N(6)–H(6A)···O(35)	2.29	160	3.151
N(6)–H(6B)···O(1W)	1.92	167	2.801
N(8)–H(8A)···O(7)	2.04	148	2.847

N(8)–H(8B)···O(25)	2.07	176	2.969
N(9)–H(9A)···O(29)	2.07	148	2.880
N(9)–H(9B)···O(26)	2.06	167	2.939
N(10)–H(10A)···O(17)	2.13	143	2.901
N(11)–H(11A)···O(17)	2.27	140	3.013
N(11)–H(11B)···O(34)	2.57	106	2.954
N(11)–H(11B)···O(38)	2.24	164	3.110
N(12)–H(12A)···O(21)	2.16	141	2.915
N(13)–H(13A)···O(21)	2.09	143	2.860
N(13)–H(13B)···O(48)	2.20	150	3.019
N(13)–H(13B)···O(50)	2.56	107	2.945
N(14)–H(14A)···O(8)	2.01	175	2.909
N(14)–H(14B)···O(53)	2.12	167	3.003
N(15)–H(15B)···O(20)	2.22	157	3.067
N(16)–H(16A)···O(15)	2.54	124	3.129
N(16)–H(16B)···O(2W)	2.28	154	3.115
N(16)–H(16B)···O(16)	2.52	122	3.095
N(17)–H(17A)···O(4W)	2.13	151	2.95
N(17)–H(17B)···O(6W)	2.21	159	3.06
N(18)–H(18A)···O(7W)	2.14	162	3.01
N(18)–H(18B)···O(36)	2.25	160	3.114
N(19)–H(19A)···O(4W)	2.57	137	3.28
N(19)–H(19B)···O(40)	2.29	170	3.18
N(21)–H(21A)···O(40)	2.35	140	3.09
N(21)–H(21B)···O(1)	2.41	128	3.06
N(22)–H(22A)···O(36)	2.22	161	3.08
N(22)–H(22B)···O(4W)	2.58	121	3.05
N(23)–H(23A)···O(1W)	2.48	145	3.25
N(24)–H(24B)···O(54)	2.38	139	3.12
N(25)–H(25B)···O(54)	2.17	149	2.99
N(28)–H(28B)···O(2)	2.23	140	2.973
N(28)–H(28B)···O(26)	2.38	134	3.074
N(29)–H(29A)···O(28)	2.38	126	3.002
N(29)–H(29B)···O(16)	2.42	152	3.242
N(29)–H(29B)···O(17)	2.26	138	2.989
N(30)–H(30A)···O(26)	2.43	137	3.150
N(30)–H(30B)···O(16)	2.27	162	3.138

Table S2 Selected hydrogen-bond lengths (Å) and angles (°) for compounds **1–3**.

	$\nu_{\text{as}}(\text{COO})$			$\nu_{\text{s}}(\text{COO})$	
1	1625	1552		1417	
2	1625	1552		1429	
3	1661	1602	1547	1440	1373

Table S3 Carboxyl stretching frequencies in **1–3** (cm^{-1}).

S1 J. Y. Niu, J. A. Hua, X. Ma and J. P. Wang, *CrystEngComm.*, 2012, **14**, 4060.