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Ligand-controlled formation of covalently modified antimoniomolybdates and photochromic properties

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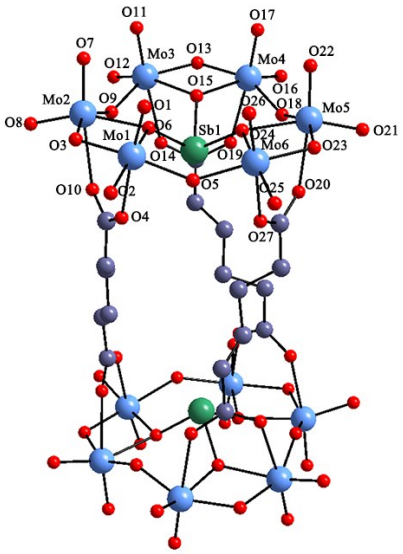

Bond	Bond length	Bond Valence	Valence Sum
Sb(1)-O(6)	1.945(4)	1.079	∑(Sb1) = 3.191
Sb(1)-O(15)	1.952(3)	1.059	
Sb(1)-O(24)	1.954(4)	1.053	

Bond	Bond length	Bond Valence	Valence Sum
Mo(1)-O(1)	1.701(4)	1.744	∑(Mo1) = 6.306
Mo(1)-O(2)	1.718(4)	1.666	
Mo(1)-O(3)	1.892(4)	1.041	
Mo(1)-O(5)	1.930(4)	0.939	
Mo(1)-O(6)	2.134(4)	0.541	
Mo(1)-O(4)	2.270(4)	0.375	

Bond	Bond length	Bond Valence	Valence Sum
Mo(2)-O(7)	1.701(4)	1.744	∑(Mo2) = 6.172
Mo(2)-O(8)	1.710(4)	1.702	
Mo(2)-O(9)	1.897(4)	1.027	
Mo(2)-O(3)	1.952(4)	0.885	
Mo(2)-O(6)	2.135(4)	0.540	
Mo(2)-O(10)	2.386(4)	0.274	

Bond	Bond length	Bond Valence	Valence Sum
Mo(3)-O(12)	1.694(4)	1.777	∑(Mo3) = 6.292
Mo(3)-O(11)	1.701(4)	1.744	
Mo(3)-O(9)	1.907(4)	0.999	
Mo(3)-O(13)	1.945(4)	0.902	
Mo(3)-O(15)	2.152(4)	0.515	
Mo(3)-O(14)	2.290(4)	0.355	

Bond	Bond length	Bond Valence	Valence Sum
Mo(4)-O(17)	1.704(4)	1.730	∑(Mo4) = 6.266
Mo(4)-O(16)	1.709(4)	1.707	
Mo(4)-O(13)	1.915(4)	0.978	
Mo(4)-O(18)	1.922(4)	0.960	
Mo(4)-O(15)	2.151(4)	0.517	
Mo(4)-O(19)	2.271(4)	0.374	

Bond	Bond length	Bond Valence	Valence Sum
Mo(5)-O(22)	1.688(4)	1.806	∑(Mo5) = 6.230
Mo(5)-O(21)	1.725(5)	1.634	
Mo(5)-O(18)	1.904(4)	1.008	
Mo(5)-O(23)	1.940(4)	0.914	
Mo(5)-O(24)	2.151(4)	0.517	
Mo(5)-O(20)	2.294(4)	0.351	

Bond	Bond length	Bond Valence	Valence Sum
Mo(6)-O(25)	1.697(4)	1.763	∑(Mo6) = 6.238
Mo(6)-O(26)	1.709(5)	1.706	
Mo(6)-O(5)	1.908(4)	0.997	
Mo(6)-O(23)	1.947(4)	0.897	
Mo(6)-O(24)	2.136(4)	0.538	
Mo(6)-O(27)	2.309(4)	0.337	

Table S1 Bond valence sum parameters for the Sb and Mo atoms in **1**. The bond valence sum parameters for the Sb and Mo atoms in **2**–**4** are almost the same as **1**, so they are omitted.

Fig. S1 Color variations of $(NH_4)_6Mo_7O_{24}·4H_2O$ at different time (in min) under the irradiation of xenon lamp.

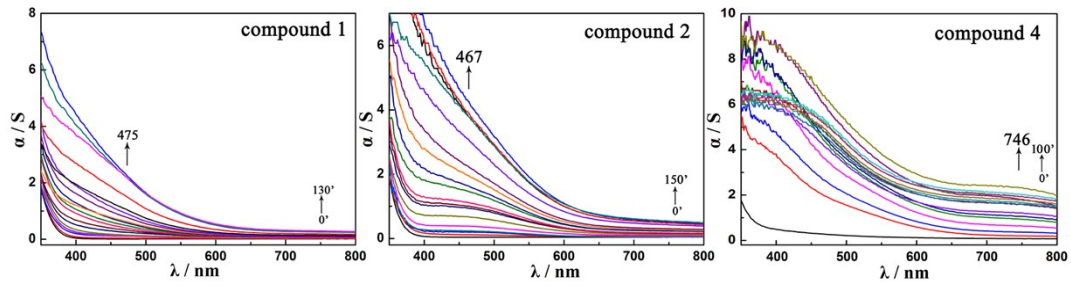

Fig. S2 Evolution of the Kubelka-Munk transformed reflectivity of compounds **1**, **2**, **4** vs wavelength for different irradiation durations during the coloration process.

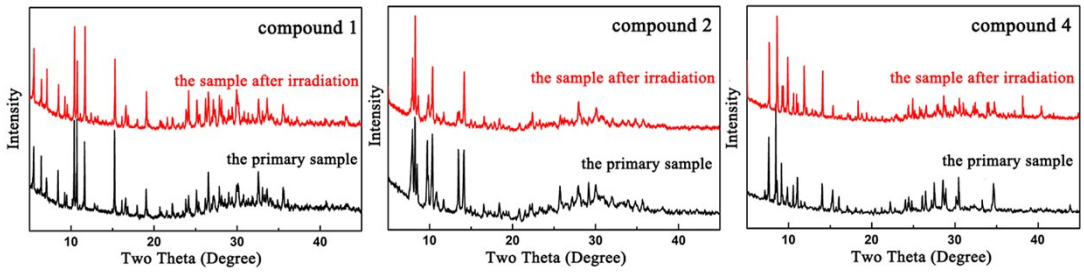

Fig. S3 The XRPD of compounds **1**, **2**, **4** before and after irradiation.

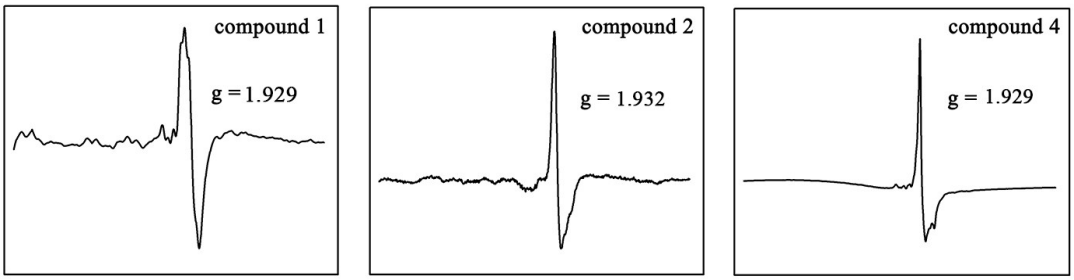

Fig. S4 EPR for compounds **1**, **2** and **4** after being irradiated for 120 min.

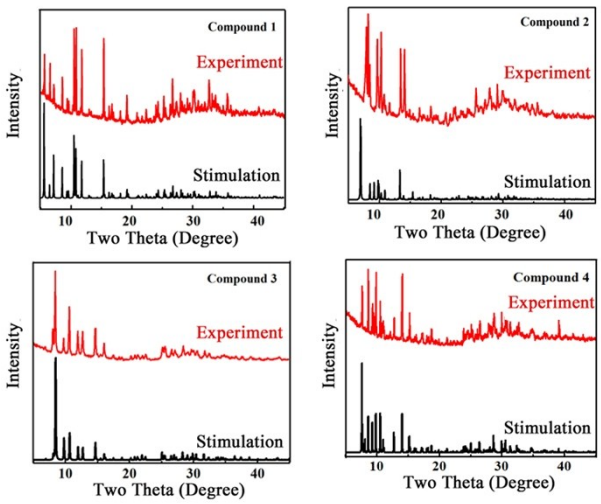

Fig. S5 X-ray powder diffraction patterns of compounds **1**−**4**. Black: the calculated patterns based on the single crystal X-ray diffraction data; Red: the experimental XPRD patterns for the samples.

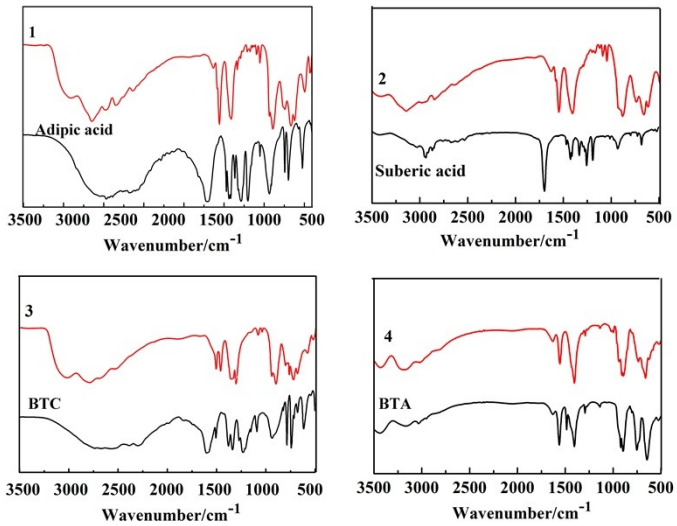

Fig. S6 IR spectra of compounds **1**-**4** and the corresponding carboxylic acids. Red: compounds **1**-**4**; Black: carboxylic acids.

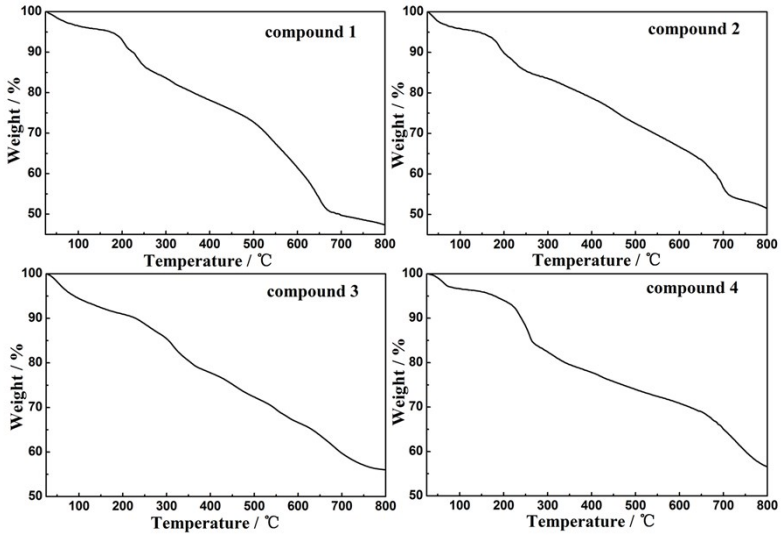

Fig. S7 TG curves of **1**−**4**.

Thermogravimetric analyses

The thermal decomposition processes of compounds **1**, **2** and **4** are similar (Fig. S5). The processes can be divided into two steps. The first weight losses of 4.35% (calc.4.23%) from 25 to 159 °C for **1,** 4.78% (calc.4.80%) from 25 to 140 °C for **2** and 3.85% (calc.3.74%) from 25 to 148 °C for **4** are assigned to the evaporation of seven, eight and three lattice water molecules respectively. The second weight losses between 159–800 °C for **1**, 140–800 °C for **2** are attributed to the release of dehydration protons, NH_3 molecules, imidazole molecules, multicarboxylic acid ligands and the sublimation of part of the metal oxides. While the second weight loss between 148–800 °C for compound **4** arises from the loss of six NH_3 molecules, one benzene-1,3,5-triacetic acid ligand and the sublimation of part of the metal oxides.

For compound **3** (Fig. S5), the TG curve shows a gradual decomposition giving a total

loss of 43.80% in the range of 25–800 °C, which can be attributed to the removal of eight lattice water molecules, twenty-four NH_3 molecules, four 1,3,5-benzenetricarboxylic acids and the sublimation of part of the metal oxides.

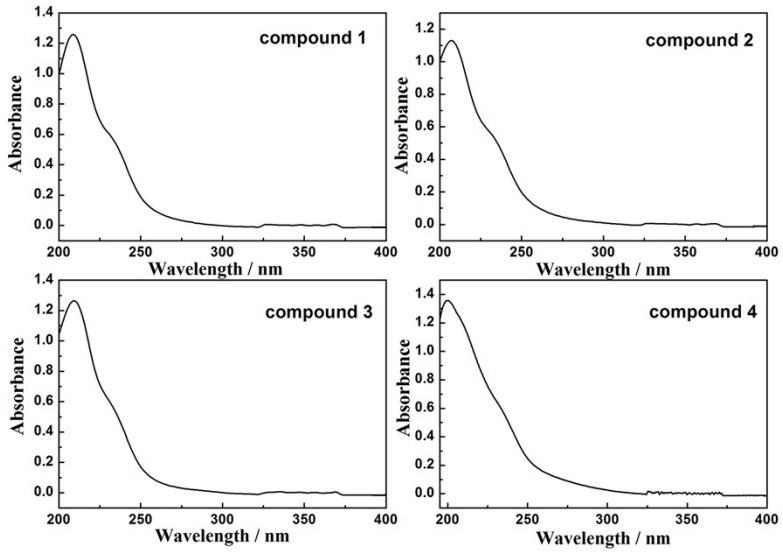

Fig. S8 UV spectra of compounds **1**−**4**.

UV Spectra.

UV spectra of compounds **1**−**4** in aqueous solution are shown in Fig. S6. The spectra are similar for **1**−**4** in the region 200–400 nm. They represent two characteristic peaks: the strong absorption bands centered at 208 nm for **1**, 207 nm for **2**, 209 nm for **3** and 200 nm for **4** are attributed to the pπ–dπ charge-transfer transitions of the O_t→Mo bonds.[S1] The weak absorption bands at about 234 nm for **1**−**4** are assigned to the pπ–dπ charge-transfer transitions of the $O_{b,c}$→Mo bonds.[S1]

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