

## Supporting Information

### Assembling the $[M(P_4Mo_6)_2]$ ( $M = Na, Mn, Na/Cu$ ) dimeric clusters via transition metal /sodium ions into 0D to 3D phospphosphomolybdates

Wei Li, Jian-Nan Zhu, Nan-Nan Shen, Wei-Wei Xiong\* and Xiao-Ying Huang\*

#### 1. Experimental

##### 1.1 Materials and physical measurements

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H, N) were carried out on a German Elementary Vario EL III instrument. Powder X-ray diffraction data were collected on a Rigaku Miniflex600 diffractometer using a graphite-monochromatized Cu- $K_\alpha$  radiation. IR spectra were recorded in the range of 400–4000  $\text{cm}^{-1}$  on a VERTEX70 FT/IR spectrophotometer with the pressed KBr pellets. Thermogravimetric analyses were performed on a NETZSCH STA 449F3 instrument in flowing  $\text{N}_2$ . Solid-state UV-Vis diffuse reflectance spectra were tested at room temperature on powder samples with a Perkin-Elmer Lambda 900 UV-vis spectrophotometer and  $\text{BaSO}_4$  plate was used as a standard (100% reflectance), whereas UV-vis spectra of solution samples were recorded on a SHIMADZU UV-1750 spectrophotometer. Rhodamine B (RhB) was chosen to judge the photocatalytic activity of compounds **1** and **5** under visible light irradiation. The typical process could be noted as follow: 10 mg crystals were dispersed in 50 mL RhB aqueous solution (10 mg/L), and stirred in darkness for 30 min to reach adsorption-desorption equilibrium. Then the suspension was irradiated by 300 W xenon lamp equipped with filter ( $\lambda > 420$  nm). During the degradation, the mixtures were kept stirring and 1 mL suspension was withdrawn for each 30 min. After removing the powder by centrifugation, the remained solution was tested by UV-vis spectrum.

##### 1.2. Synthesis

###### 1.2.1. $[H_3AEP]_4[Na(P_4Mo_6O_{31}H_{5.5})_2] \cdot 4H_2O$ (**1**)

A mixture of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.242 g, 1.00 mmol),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.170 g, 1.00 mmol),  $[\text{BMIm}]\text{Br}$  (1.064 g, 4.86 mmol), AEP (0.268 g, 2.07 mmol, 98%),  $\text{H}_3\text{PO}_4$  (0.5 mL, 85%), and  $\text{H}_2\text{O}$  (0.5 mL) was sealed in an autoclave equipped with a Teflon liner (25 mL). Then the autoclave was heated at 160 °C for 5 days. The product was filtrated and washed several times with distilled water. Orange flake-like crystals of **1** were obtained in a yield of 31.7% (80 mg, based on Mo). Elemental anal. Calculated values (%) for **1**: C, 9.52; H, 3.00; N, 5.56. Found: C, 9.11; H, 2.92; N, 5.16.

###### 1.2.2. $(Me_2NH_2)_7[NaMn(H_2O)][Mn(P_4Mo_6O_{31}H_6)_2] \cdot 5H_2O$ (**2**)

A mixture of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.242 g, 1.00 mmol),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.200 g, 1.01 mmol),  $\text{H}_3\text{PO}_4$  (0.2 mL, 85%),  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (0.05 mL, 85%),  $\text{H}_2\text{O}$  (1 mL), and DMF (0.5 mL) was sealed in an autoclave equipped with a Teflon liner (20 mL). Then the autoclave was heated at 140 °C for 5 days. The product was filtrated and washed several times with ethanol and distilled water. Orange strip-like crystals of **2** were obtained in a yield of 8.1% (20 mg, based on Mo). Elemental anal. Calculated values (%) for **2**: C, 5.67; H, 2.72; N, 3.30. Found(%): C, 5.66; H, 2.82; N, 3.31.

###### 1.2.3. $(H_4tpc)_{0.5}(H_4tpb)_{0.5}(H_{0.5}bpp)[Na_{2.5}(H_2O)][Na(Mo_6P_4O_{31}H_8)_2] \cdot 2H_2O$ (**3**)

A mixture of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.242 g, 1.00 mmol), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.170 g, 1.00 mmol), bpp (0.402 g, 2.03 mmol), [HMIm]Cl (1.004 g, 4.95 mmol), H<sub>3</sub>PO<sub>4</sub> (0.5 mL, 85%), and H<sub>2</sub>O (0.5 mL) was sealed in an autoclave equipped with a Teflon liner (25 mL). Then the autoclave was heated at 160 °C for 5 days. The product was filtrated and washed several times with distilled water. Brown yellow block-like crystals of **3** were obtained in a yield of 17.1% (45 mg, based on Mo). Elemental anal. Calculated values (%) for **3**: C, 14.87; H, 1.97; N, 2.67. Found(%): C, 15.16; H, 2.30; N, 2.71.

#### 1.2.4. (Me<sub>2</sub>NH<sub>2</sub>)<sub>6.5</sub>[Na<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>][Cu<sub>0.25</sub>Na<sub>0.75</sub>(Mo<sub>6</sub>P<sub>4</sub>O<sub>31</sub>H<sub>6.25</sub>)<sub>2</sub>] (**4**)

A mixture of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.244 g, 1.01 mmol), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.165 g, 0.97 mmol), 4,4'-bipy (0.154 g, 0.99 mmol), [HMIm]Cl (1.112 g, 5.48 mmol), H<sub>3</sub>PO<sub>4</sub> (0.5 mL, 85%), HF (0.1 mL), H<sub>2</sub>O (0.5 mL), and DMF (1 mL) was sealed in an autoclave equipped with a Teflon liner (25 mL). Then the autoclave was heated at 140 °C for 5 days. The product was filtrated and washed several times with distilled water. Orange flake-like crystals of **4** were obtained in a yield of 2.0% (5 mg, based on Mo). Elemental anal. Calculated values (%) for **4**: C, 5.25; H, 2.73; N, 3.06. Found(%): C, 5.53; H, 2.64; N, 2.97.

#### 1.2.5. (Me<sub>2</sub>NH<sub>2</sub>)<sub>1.5</sub>(NH<sub>4</sub>)<sub>4</sub>[Mn<sub>1.5</sub>Na<sub>4.5</sub>(H<sub>2</sub>O)<sub>7</sub>][Mn(P<sub>4</sub>Mo<sub>6</sub>O<sub>31</sub>H<sub>4.5</sub>)<sub>2</sub>]·3.5H<sub>2</sub>O (**5**)

Under the same reaction conditions as that for **2**, except that the amount of hydrazine was increased from 0.05 mL to 0.10 mL, red rhombic-like crystals of **5** were obtained in a yield of 12.1% (30 mg, based on Mo). Elemental anal. Calculated values (%) for **5**: C, 1.21; H, 1.97; N, 2.59. Found(%): C, 1.16; H, 1.98; N, 2.61.

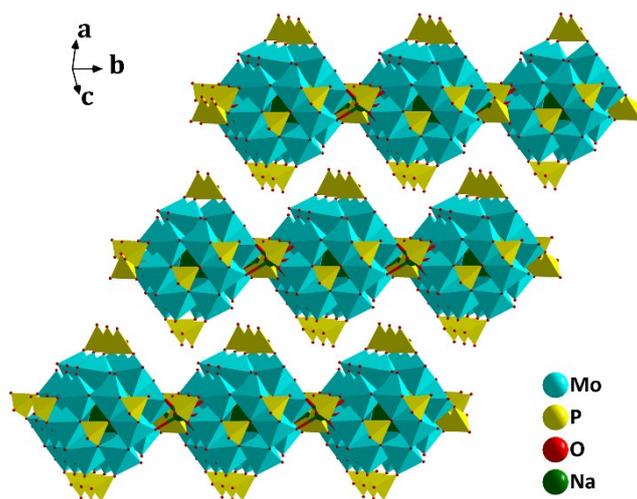
#### 1.2.6. (DMIm)<sub>4</sub>[Mn<sub>1.5</sub>Na<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>][Mn(P<sub>4</sub>Mo<sub>6</sub>O<sub>31</sub>H<sub>6.5</sub>)<sub>2</sub>]·1.5H<sub>2</sub>O (**6**)

A mixture of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.245 g, 1.01 mmol), MnCl<sub>2</sub>·4H<sub>2</sub>O (0.203 g, 1.03 mmol), [OMIm]Cl (1.221 g, 5.29 mmol), H<sub>3</sub>PO<sub>4</sub> (0.4 mL, 85%), H<sub>2</sub>O (0.5 mL), and methanol (1 mL) was sealed in an autoclave equipped with a Teflon liner (20 mL). Then the autoclave was heated at 150 °C for 5 days. The product was filtrated and washed several times with ethanol and distilled water, orange flake-like crystals of **6** were obtained in a yield of 3.8% (10 mg, based on Mo). Elemental anal. Calculated values (%) for **6**: C, 7.63; H, 2.18; N, 3.56. Found(%): C, 7.64, H, 2.16, N, 3.43.

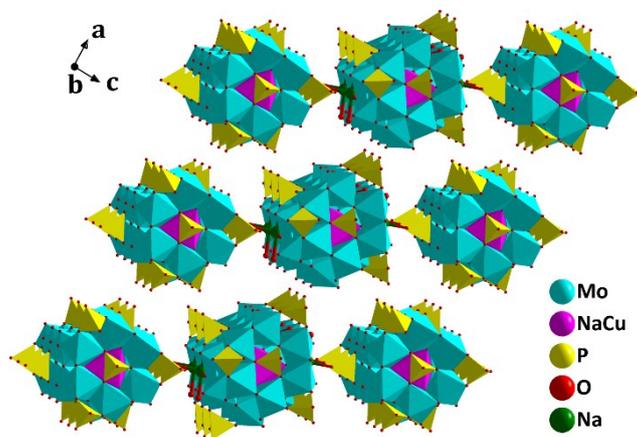
### 1.3. Single crystal X-ray crystallography

The crystal data of **1**, **5**, and **6** were collected on a Xcalibur Eos CCD diffractometer with MoK<sub>α</sub> radiation (λ = 0.71073 Å). The crystal data of **3** was collected on a SuperNova Dual CCD diffractometer with MoK<sub>α</sub> radiation (λ = 0.71073 Å). The crystal data of **2** and **4** were collected on a Bruker AXS Smart APEX II CCD diffractometer with MoK<sub>α</sub> radiation (λ = 0.71073 Å). The structures of **1-6** were solved by the direct methods and refined by the full-matrix least-squares cycles in SHELX-2016 program package. Anisotropic thermal parameters were used to refine the non-hydrogen atoms. Hydrogen atoms on C and N atoms of the organic ligands were included in their calculated positions. Hydrogen atoms attached to lattice water molecules were found from the difference Fourier maps. For compound **1**, one of the unique H<sub>3</sub>AEP cation displays a disorder on its terminal amine group over two positions (N6 and N6B with the SOF ratio of 0.5:0.5). In compound **2**, the cations and lattice solvent molecules are highly disordered and thus could not be rationally modeled. Instead, the SQUEEZE routine of the PLATON program was applied to remove the contributions to the scattering from the solvent molecules and cations. In compound **3**,

only a fraction of the cations and lattice water molecules were found from the difference-Fourier maps and included in the structure refinements, while the rest of cations and lattice water molecules were squeezed out by using the SQUEEZE routine of the PLATON program; two of the unique  $\text{PO}_4$  units in the asymmetric unit were treated as disordered ones during the refinements. The co-occupation of Na/Mn or half-occupation of Na also exist in the structure of **5**. While the cations and solvent molecules in **4-6** are generally disordered and thus it was not able to locate all of the H atoms attached to them. For all the six compounds, however, the structural formulas were determined with the aid of elemental analysis and EDS, etc.



**Fig. S1** The packing arrangement of compound **3**, the organic cations and solvent water molecules are omitted for clarity.



**Fig. S2** The packing arrangement of compound **4**, the  $[\text{Me}_2\text{NH}_2]^+$  cations and solvent water molecules are omitted for clarity.

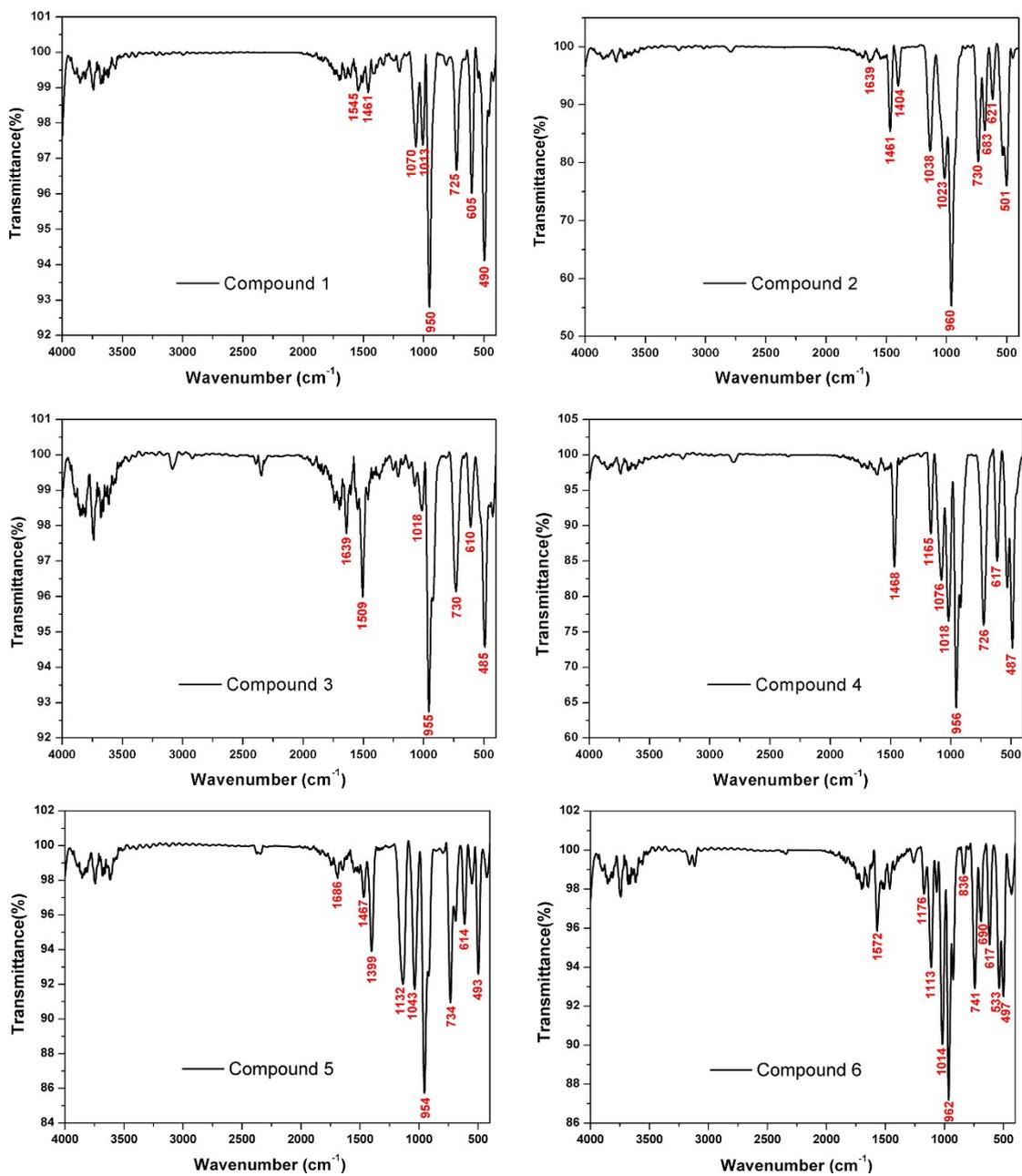


Fig. S3 IR spectra of compounds 1-6.

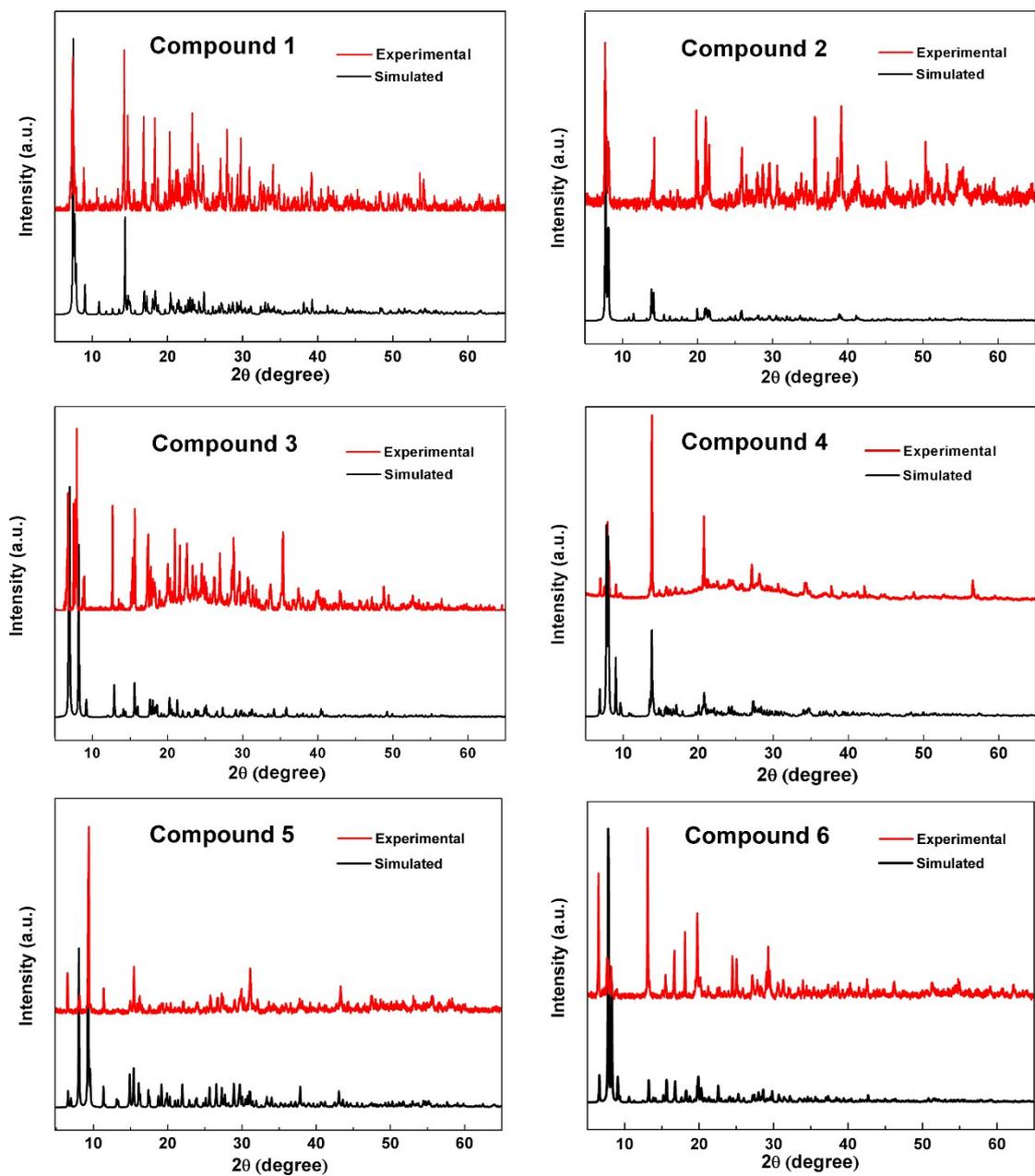
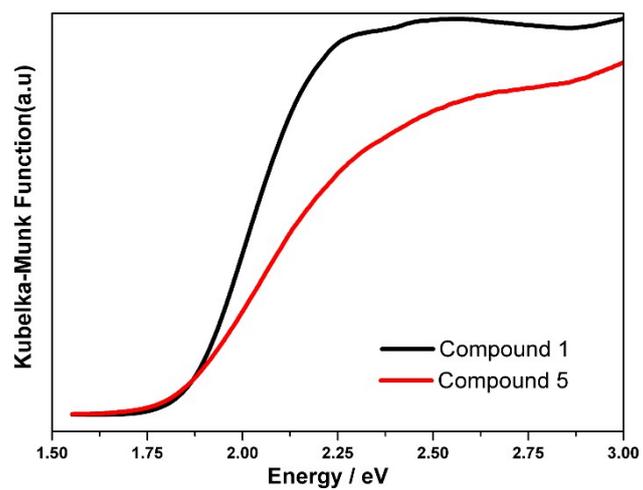


Fig. S4 The experimental (red) and simulated (black) PXR D patterns of compounds 1-6.



**Fig. S5** Solid state optical absorption spectra of compounds **1** and **5**.