

**Electronic supplementary information (ESI)**

**pH-Dependent assembly of two inorganic-organic hybrid compounds based on octamolybdates: an unusual intercalated layer and a 3D 4-connected framework**

Hai-Yan Liu,<sup>a,b</sup> Jin Yang,\*<sup>a</sup> Ying-Ying Liu<sup>a</sup> and Jian-Fang Ma\*<sup>a</sup>

<sup>a</sup>*Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China*

<sup>b</sup>*Department of Chemistry and Pharmaceutical Engineering, Suihua University, Suihua 152061, People's Republic of China*

\* Correspondence authors

E-mail: yangjinnenu@yahoo.com.cn (J. Yang)

E-mail: jianfangma@yahoo.com.cn (J.-F. Ma)

Fax: +86-431-85098620 (J.-F. Ma)

**Table S1.** Selected bond lengths [Å] and angles [°] for **1** and **2**<sup>[a]</sup>

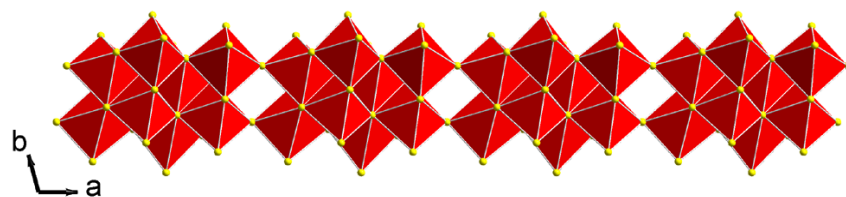
| Compound 1           |           |                      |           |
|----------------------|-----------|----------------------|-----------|
| Cu(1)-O(12)#1        | 1.935(3)  | Cu(1)-O(12)          | 1.935(3)  |
| Cu(1)-N(3)           | 1.959(5)  | Cu(1)-N(3)#1         | 1.959(5)  |
| O(12)#1-Cu(1)-O(12)  | 180       | O(12)#1-Cu(1)-N(3)   | 88.95(18) |
| O(12)-Cu(1)-N(3)     | 91.05(18) | O(12)#1-Cu(1)-N(3)#1 | 91.05(18) |
| O(12)-Cu(1)-N(3)#1   | 88.95(18) | N(3)-Cu(1)-N(3)#1    | 180       |
| Compound 2           |           |                      |           |
| Cu(1)-O(1W)          | 1.931(5)  | Cu(1)-O(1W)#1        | 1.931(5)  |
| Cu(1)-N(1)#1         | 1.997(5)  | Cu(1)-N(1)           | 1.997(5)  |
| Cu(1)-O(2)           | 2.572(5)  | Cu(1)-O(2)#1         | 2.572(5)  |
| O(1W)-Cu(1)-O(1W)#1  | 180       | O(1W)-Cu(1)-N(1)#1   | 89.0(2)   |
| O(1W)#1-Cu(1)-N(1)#1 | 91.0(2)   | O(1W)-Cu(1)-N(1)     | 91.0(2)   |
| O(1W)#1-Cu(1)-N(1)   | 89.0(2)   | N(1)#1-Cu(1)-N(1)    | 180       |
| O(1W)-Cu(1)-O(2)     | 90.73(2)  | O(1W)-Cu(1)-O(2)#1   | 89.27(2)  |
| N(1)-Cu(1)-O(2)      | 88.44(2)  | N(1)-Cu(1)-O(2)#1    | 91.56(2)  |
| O(2)-Cu(1)-O(2)#1    | 180       |                      |           |

Symmetry codes for **1**: #1 -x+2, -y+2, -z+2. For **2**: #1 -x, -y+1, -z+1.

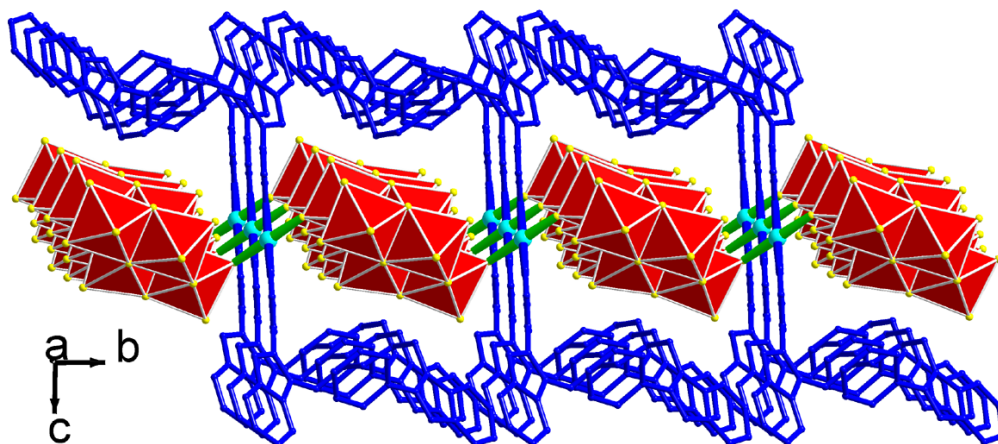
**Table S2.** Hydrogen-bond geometries for compound **1** (Å, °)

| D-H...A              | D-H [Å]   | H...A [Å] | D...A [Å] | <D-H...A [°] |
|----------------------|-----------|-----------|-----------|--------------|
| N(5)-H(5A)...O(7)#5  | 0.850(10) | 1.96(3)   | 2.776(8)  | 159(9)       |
| N(2)-H(2A)...O(23)#6 | 0.849(10) | 2.11(4)   | 2.809(8)  | 140(6)       |

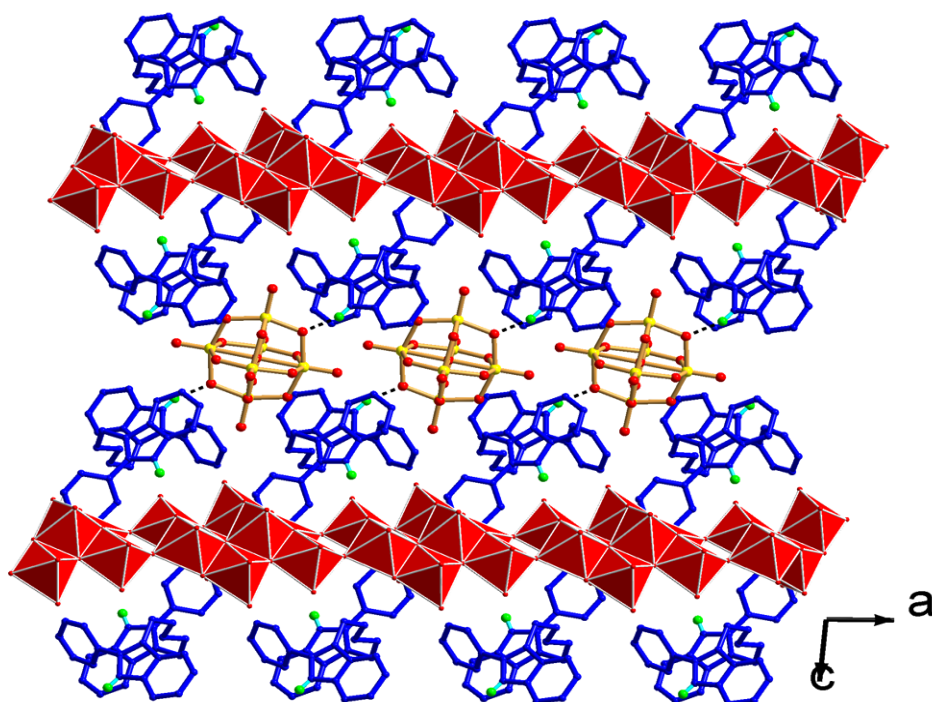
Symmetry codes for **1**: #5 -x+3, -y+1, -z+1; #6 -x+3, -y+2, -z+2.



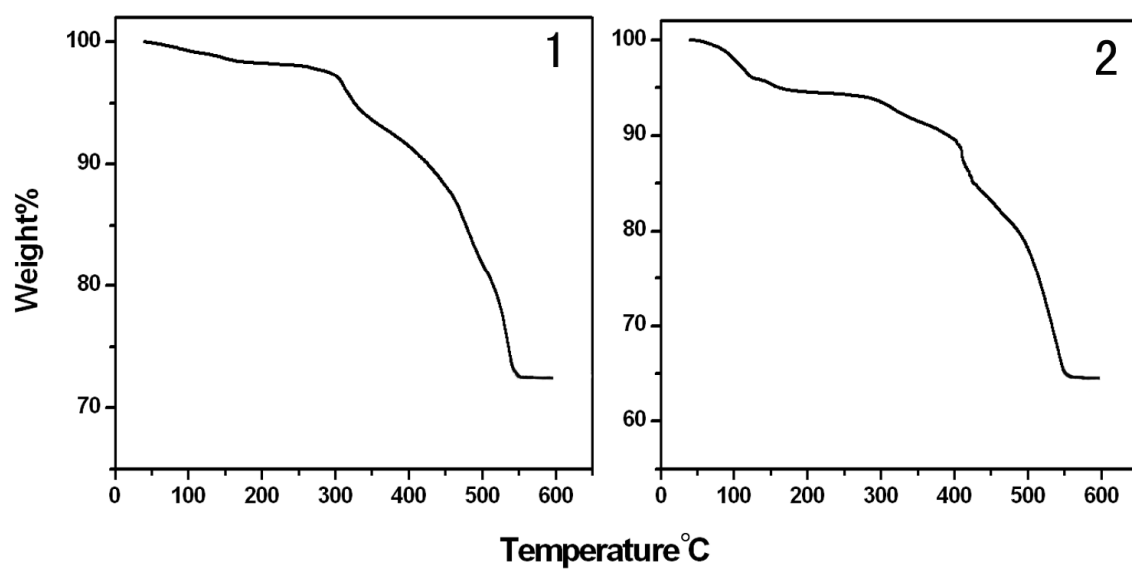
**Fig. S1** The 1D molybdenum oxide chain of **1**.



**Fig. S2** View of 2D copper(II)-organic-octamolybdate layer in **1**.



**Fig. S3** View of the 3D supramolecular architecture formed *via* hydrogen bonds between the host layers and the guest hexamolybdate anions in **1**.



**Fig. S4** TGA curves of compounds **1** and **2**.