

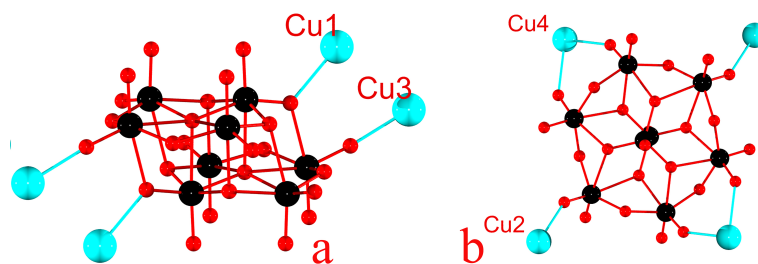
## Electronic Supplementary Information

### Three Hybrid Networks Based on Octamolybdate: Ionothermal Synthesis, Structure and Photocatalytic Properties

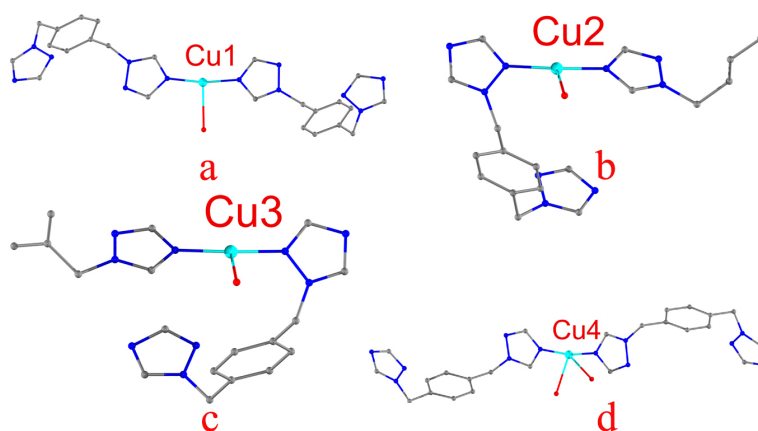
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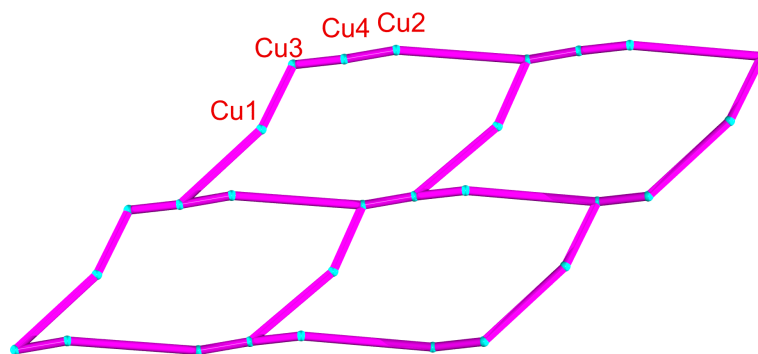
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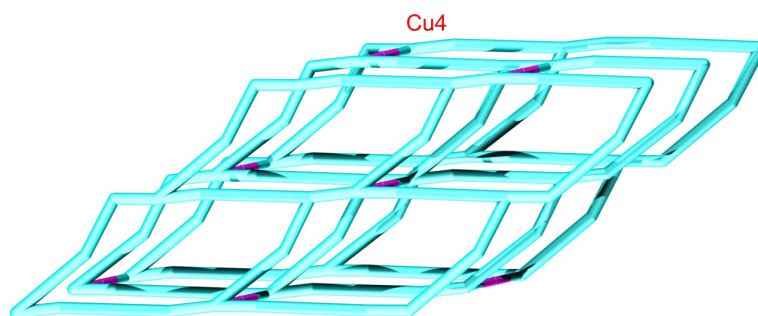
**Fig. S1.** The ball-and-stick representation of  $\alpha/\beta$ - $\text{Mo}_8\text{O}_{26}^{4-}$  anions in compound 1. (light blue ball symbolize the Cu atoms and the red polyhedron symbolize the  $\text{MoO}_6/\text{MoO}_4$  polyhedron, a:  $\beta$ - $\text{Mo}_8\text{O}_{26}^{4-}$ , b:  $\alpha$ - $\text{Mo}_8\text{O}_{26}^{4-}$ )



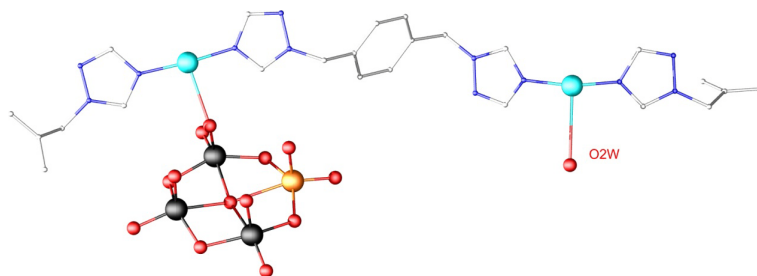
**Fig. S2.** The ball and stick representation of the Cu coordination environments in compound 1 (light blue symbolize the Cu atoms, grey balls symbolize the C atoms and dark blue balls symbolize the N atoms, red balls symbolize the O and water atoms).



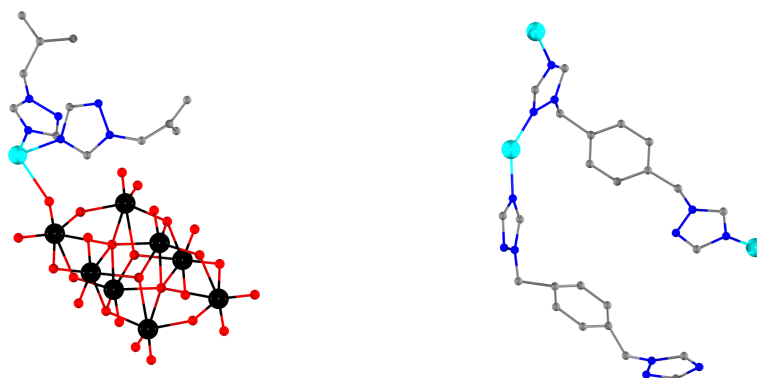
**Fig. S3.** The ball and stick representation of 2D metal-organic layer in compound 1. (light blue balls symbolize the Cu atoms, the pink stick symbolize Cu-Cu bonds connected by BBTZ organic ligands)



**Fig. S4.** The ball and stick representation of 3D nets formed by the 2D metal-organic layers and  $(\beta\text{-Mo}_8\text{O}_{26})^{4-}$  anions connected through Cu4 in compound 1 (the light blue balls symbolize Cu atoms, the light blue sticks symbolize the Cu-Cu bonds connected by BBTZ organic ligands, and the pink balls symbolize the  $(\beta\text{-Mo}_8\text{O}_{26})^{4-}$  anions).

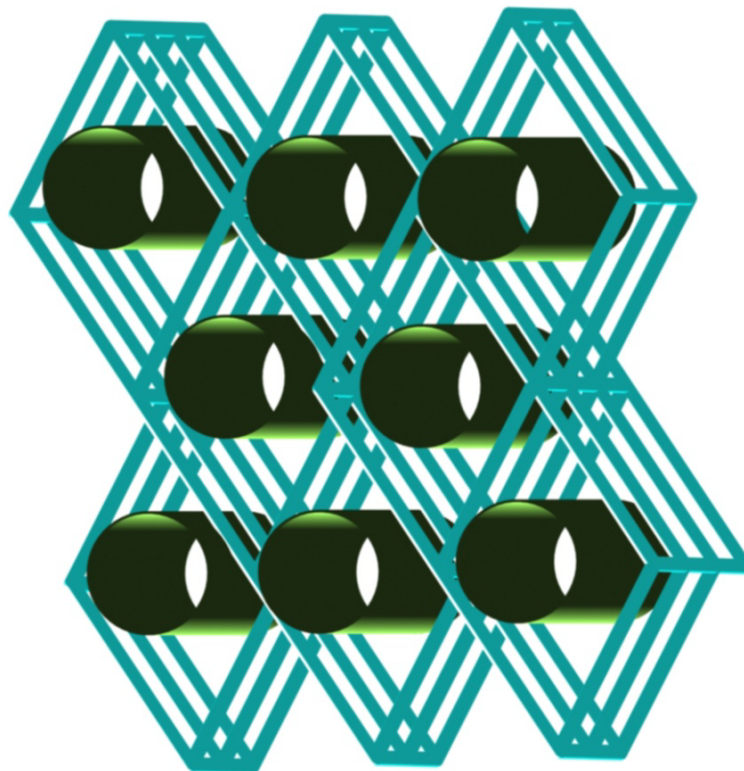


**Fig. S5.** The ball and stick representation of unit cell of compound 2 (light blue balls symbolize the Cu atoms, grey atoms symbolize the C atoms, the dark blue balls symbolize the N atoms, black balls symbolize the Mo atoms, red balls symbolize the O atoms, and the yellow ball symbolize the Mo/Cu 50% disorder)

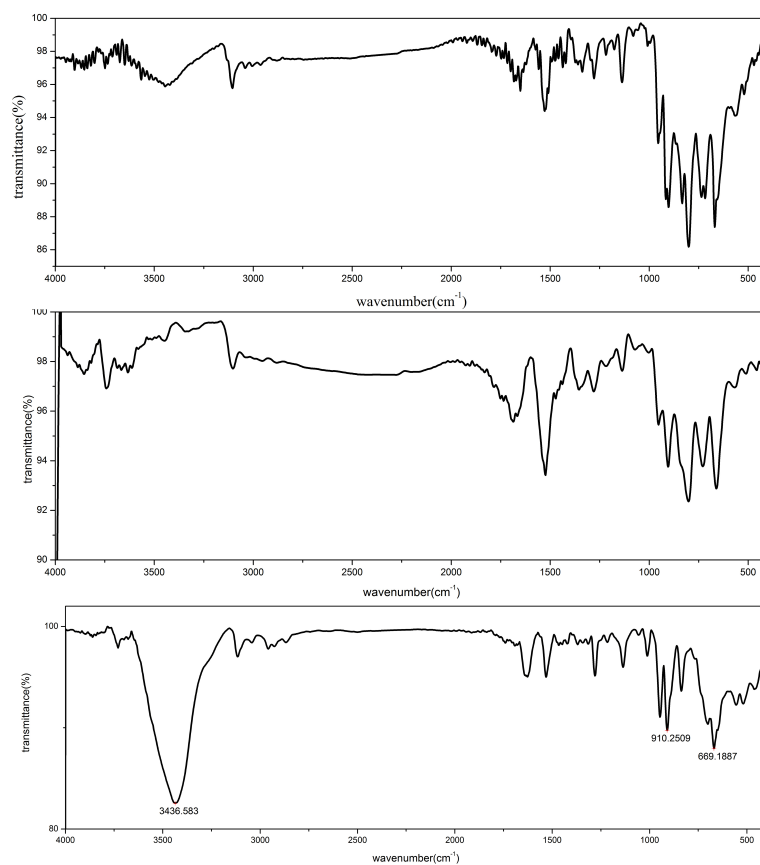


**Fig. S6.** The ball and stick representation of unit cell of compound 3 (light blue balls symbolize the Cu atoms, grey atoms symbolize the C atoms, the dark blue balls symbolize the N atoms, black

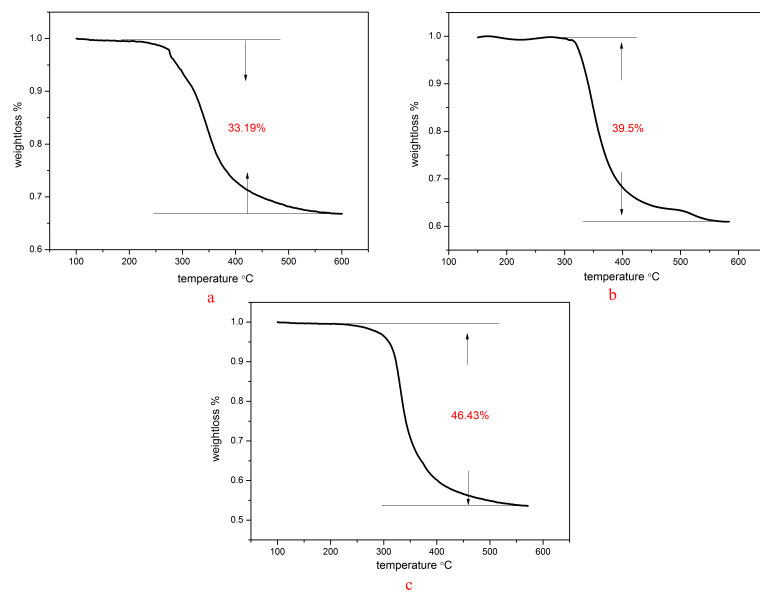
balls symbolize the Mo atoms, and the red balls symbolize the O atoms)



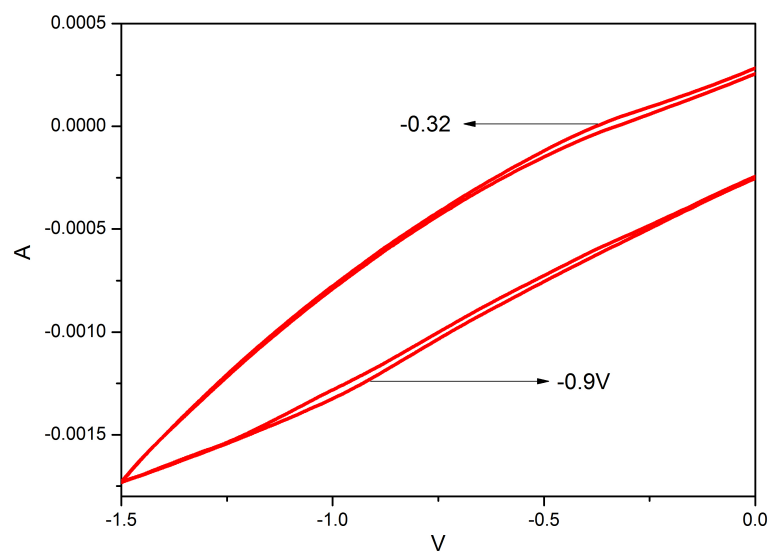
**Fig. S7.** The ball and stick representation of the 3D  $\alpha$ -Po nets with 1D channels in it of **3** (light blue balls symbolize the Cu atoms, the light blue bonds symbolize the Cu-Cu bonds connected by BBTZ organic ligands, dark green 1D tubes symbolize the 1D open channels in the nets of compound **3** along  $a$ -axis )



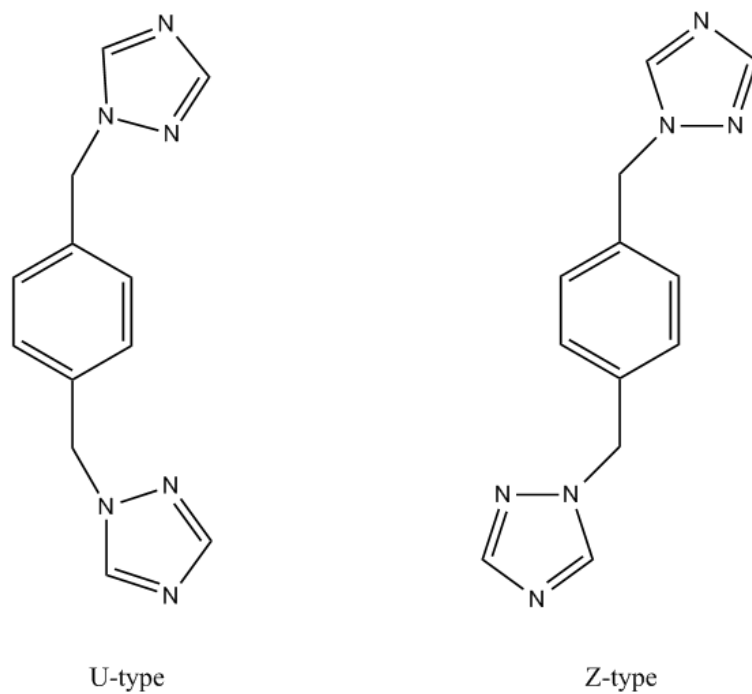
**Fig. S8.** The IR spectrum of compound 1-3



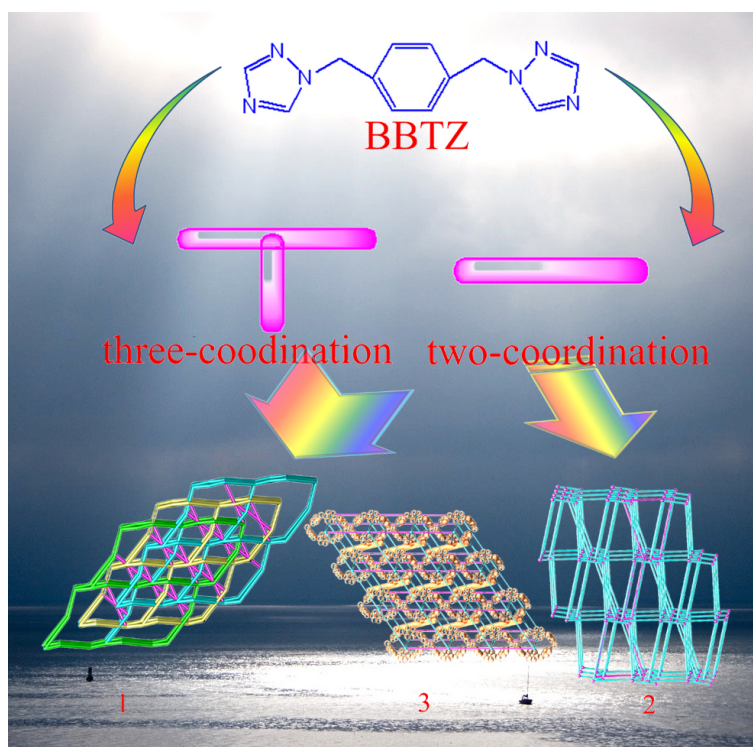
**Fig. S9.** The TG spectrum of compound 1-3



**Fig. S10.** The CV action of compound 1



**Scheme S1.** The two type of steric configuration of the organic ligand BBTZ, U type and Z type



**Scheme S2.** There are three kinds of coordination modes for organic ligand BBTZ, two-coordinated, three-coordinated and four-coordinated. In this article, there are only two kinds two/three-coordinated. When the BBTZ adopt only two-coordinated, it play the role of line-bridge, and results compound 2 with the simple 3D topology. However, when BBTZ adopts two and three-coordinated type, there are two coordination types: T-type and line-bridge type, and results more complicated structures such as SPN, and poly-rings or even more beautiful structures.