

Supplementary Material (ESI) for Dalton Transactions
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**Assembly and photocatalysis of two novel 3D Anderson-type
polyoxometalate-based metal-organic frameworks constructed from
isomeric bis(pyridylformyl)piperazine ligands**

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Table. S1. Selected bond distances (\AA) and angles ($^{\circ}$) for complexes **1** and **2**.

Complex 1			
Cu(1)–N(1)	2.010(10)	Cu(1)–O(2)#1	2.021(7)
Cu(1)–O(1)	1.937(6)	Cu(1)–O(3)	2.278(7)
Cu(1)–O(2)	1.973(6)	Cu(1)–O(4)	2.441(6)
O(1)–Cu(1)–O(2)	171.7(3)	O(1)–Cu(1)–O(2)	89.2(3)
O(1)–Cu(1)–N(1)	91.8(3)	O(2)–Cu(1)–O(2)	83.1(3)
O(2)–Cu(1)–N(1)	96.0(3)	N(1)–Cu(1)–O(2)	178.9(3)
O(1)–Cu(1)–O(3)	92.9(3)	O(2)–Cu(1)–O(3)	89.8(3)
N(1)–Cu(1)–O(3)	92.6(3)	O(2)#2–Cu(1)–O(3)	86.8(3)
Complex 2			
Cu(1)–N(1)	1.989(3)	Cu(1)–O(3)	2.384(3)
Cu(1)–O(1)	1.976(3)	Cu(1)–O(1W)	1.981(3)
Cu(1)–O(3)	2.384(3)	Cu(1)–O(2W)	1.950(3)
O(1W)–Cu(1)–N(1)	91.71(12)	N(1)–Cu(1)–O(3)	90.21(12)
O(2W)–Cu(1)–O(1)	85.84(13)	O(1)–Cu(1)–N(1)	91.56(12)
O(1W)–Cu(1)–O(3)	85.83(11)	O(2W)–Cu(1)–N(1)	161.76(14)
O(1)–Cu(1)–O(3)	87.43(11)	O(1)–Cu(1)–O(1W)	172.52(12)
O(2W)–Cu(1)–O(3)	107.67(12)	O(2W)–Cu(1)–O(1W)	93.11(13)

Symmetry codes for **1**: #1 $-x, -y+3, -z+1$;

Figures

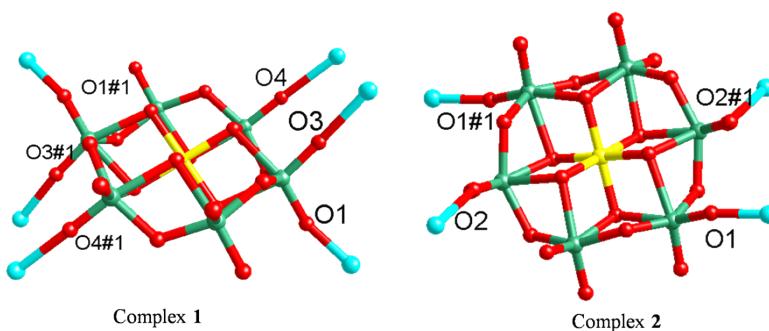


Fig. S1. The coordination modes in the title complexes. Symmetry codes for **1**: #1 $1-x, -y+3, -z$, for **2**: #1 $1-x, -y, -z$

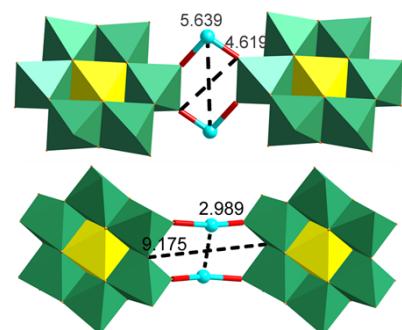


Fig. S2. Two kinds of the Cu₂(POM)₂ loops in complex **1**.

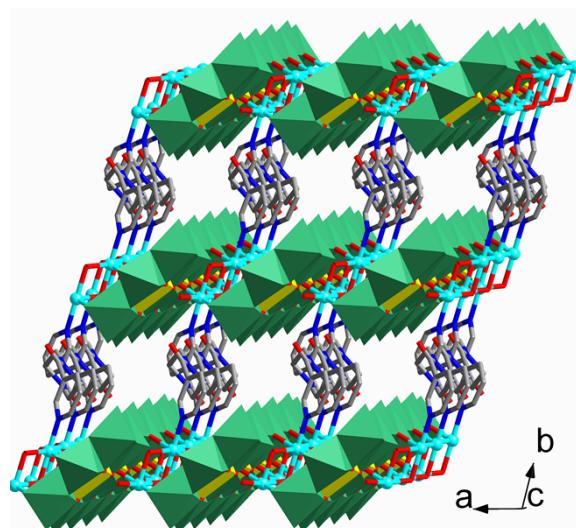


Fig. S3. The 3D framework of **1**.

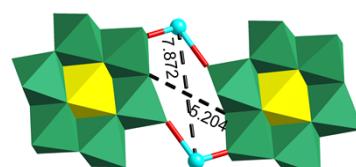


Fig. S4. The Cu₂(POM)₂ loop in **2**.

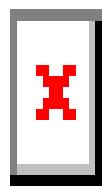


Fig. S5. The $[\text{Cu}_2\text{L}^2_2]$ metal-organic loop in **2**.

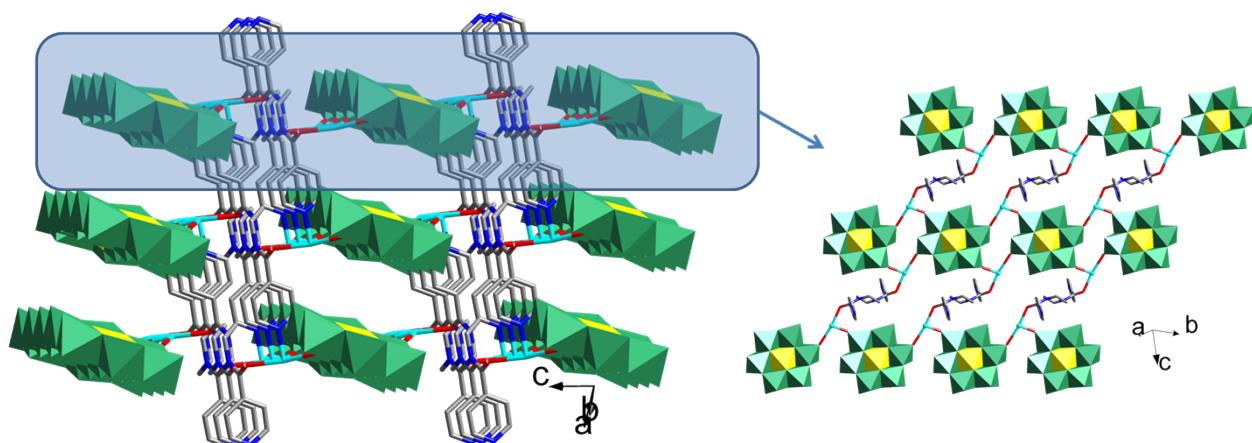


Fig. S6. The 3D framework of **2**.

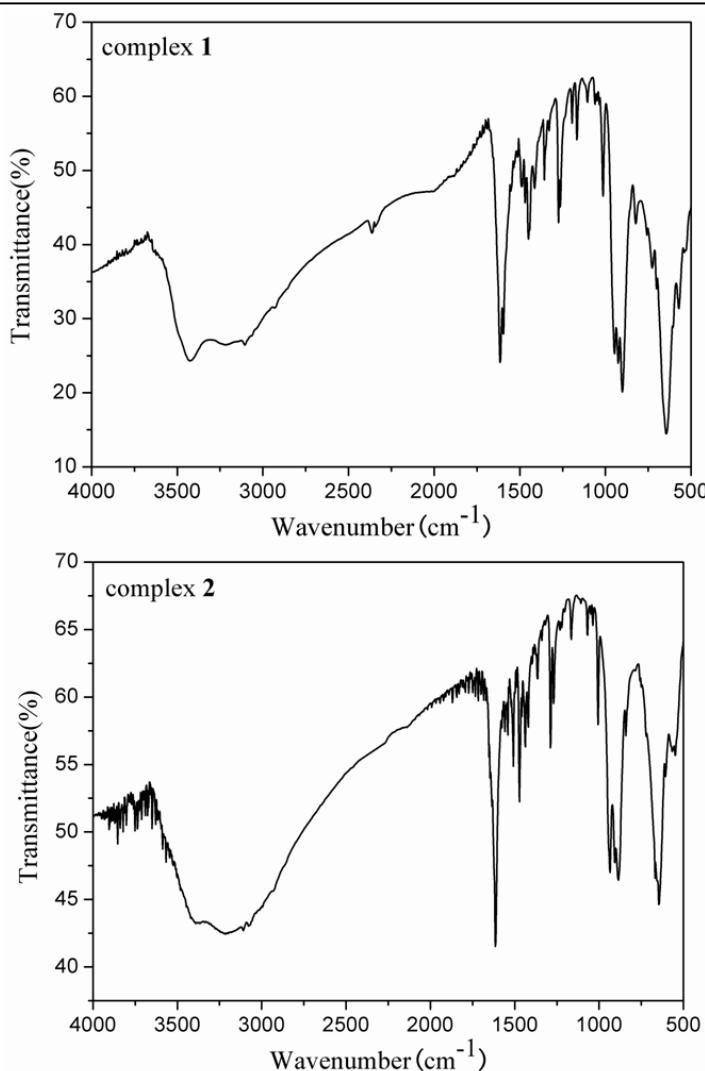


Fig. S7. The IR spectra of complexes **1** and **2**.

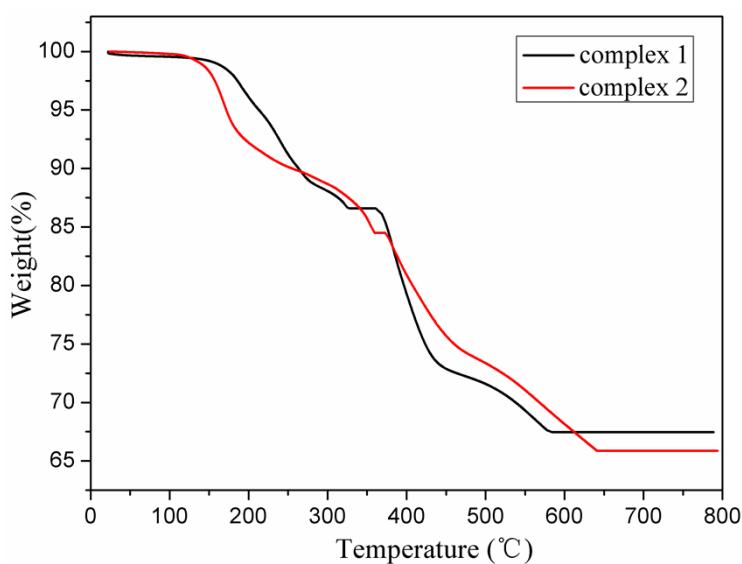


Fig. S8. The TGA curves of complexes **1** and **2**.

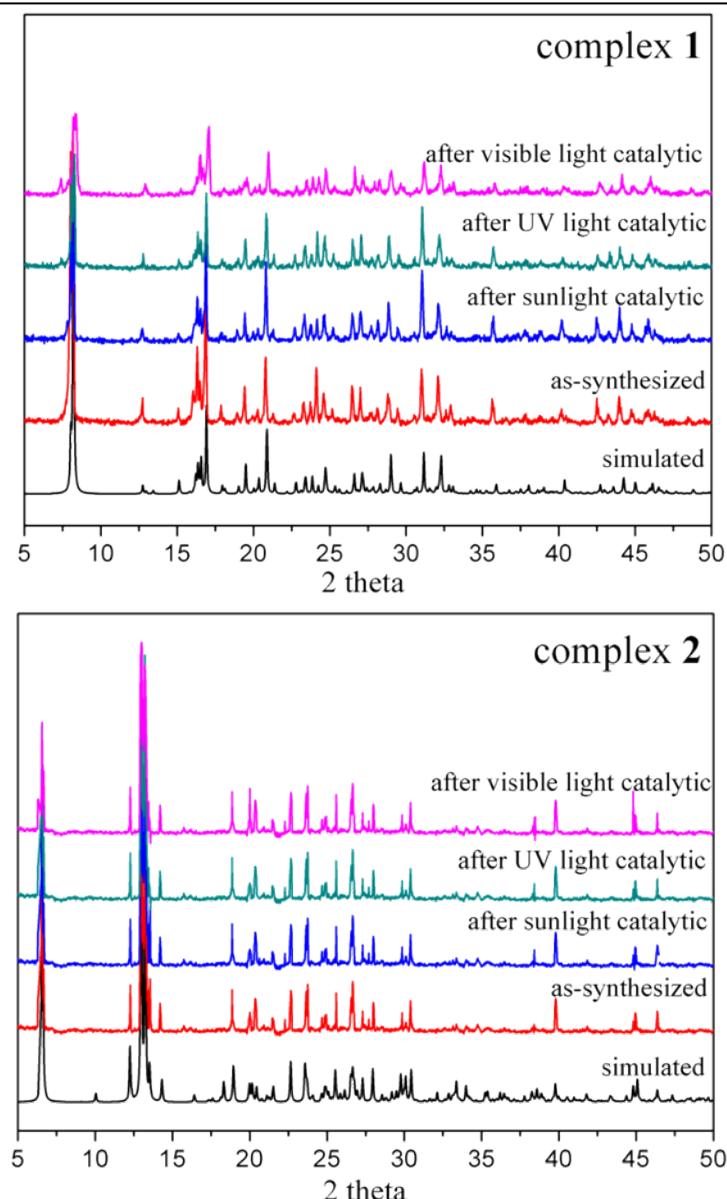


Fig. S9. Powder X-ray diffraction patterns of complexes **1** and **2**.