

ESI

A series of organic-inorganic hybrids based on lanthanide-substituted Dawson-type phosphotungstate dimers and copper-en linkers

Hai-Yan Zhao,^a Jun-Wei Zhao,^{*b} Bai-Feng Yang,^a Huan He^a and Guo-Yu Yang^{*ac}

^a DOE Key Laboratory of Cluster Science, School of Chemistry, Beijing Institute of Technology, Beijing 100081, China. E-mail: ygy@bit.edu.cn

^b Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, China. E-mail: zhaojunwei@henu.edu.cn

^c State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China. Fax: (+86) 591-8371-0051; E-mail: ygy@fjirsm.ac.cn

The details during the course of the refinements of structures of 1-4

Fig. S1. Comparison of the simulated and experimental PXRD patterns of 1-4.

Fig. S2. IR spectra of 1-4 and {P₂W₁₂} precursor.

Fig. S3. TG curves of 1-4.

Table S1. Bond valence sum calculations of 4.

The details during the course of the refinements of structures of 1-4:

Because structures of 1-4 are larger than those simple coordination complexes and there are a large amount of weight atoms in the structures, it is very difficult to refine these large structures. Moreover, the quality of crystals is not very good and the absorption coefficient is large, which usually leads to the case that the quality of intensity data is not perfect, as a result, some atoms have the ADP max/min ratios. Therefore, some unit-occupancy atoms have been isotropically refined and restrainedly refined.

1: The ISOR instruction is used for O2, O4, O5, O24, O27, O34 and O60. The DFIX instruction is used for C3 and C4. The SIMU instruction is used for C5. Now, 43 restraints are used in the refinement.

2: The ISOR instruction is used for O38, O58 and O8W. The DFIX instruction is used for C5 and C6. Now, 19 restraints are used in the refinement.

3: The ISOR instruction is used for O3, O17, O9, O41, O8, O12, O14, O11, O49, O10, O18, O7, N5 and O12W. The DFIX instruction is used for C5 and C6, C3 and C4, N5 and C5. The SIMU instruction is used for N5. Now, 89 restraints are used in the refinement.

4: The ISOR instruction is used for C6, N4, C4, C5, C1, O7, O1, O10, O6, O35, O17, O26, O18 and O29. The SIMU instruction is used for C1, C4, C6 and N4. Now, 90 restraints are used in the refinement. For compound 4, SQUEEZE method was used to show the structure contains voids located at $x = 0, y = 0, z = 0$, $x = 0, y = 0, z = 0.5000$, $x = 0.249, y = 0.153, z = 0.950$, $x = 0.751, y = 0.153, z = 0.500$, $x = 0.500, y = 0.500, z = 0$, $x = 0.500, y = 0.500, z = 0.500$, $x = 0.251, y = 0.347, z = 0.050$, $x = 0.749, y = 0.347, z = 0.450$, $x = 0.251, y = 0.653, z = 0.550$, $x = 0.749, y = 0.653, z = 0.950$, $x = 0.249, y = 0.847, z = 0.450$, and $x = 0.751, y = 0.847, z = 0.050$ ($\sim 179 \text{ \AA}^3$). These voids might be suitable to take up solvent (crystals from en/H₂O), but none was seen in difference Fourier syntheses and squeezing with program PLATON did not give significant improvement or change. Based on the count of void electrons obtained from SQUEEZE result, these voids in a unit cell can accommodate about four disordered en molecules or four disordered water molecules. This information has been added into cif file and Supporting Information. In addition, the OMIT instruction are used to resolve the issue of large minimum residual electron density, which has been added to the CIF file.

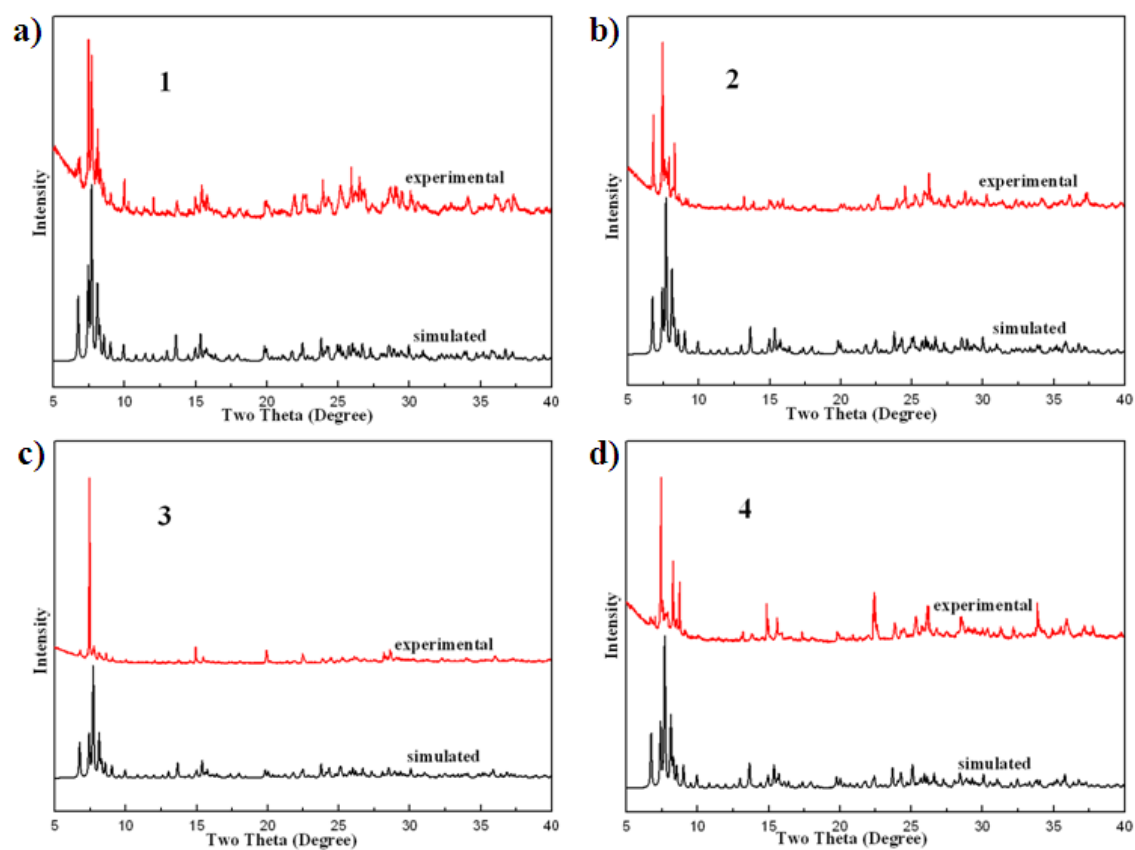


Fig. S1. Comparison of the simulated and experimental PXRD patterns of 1-4.

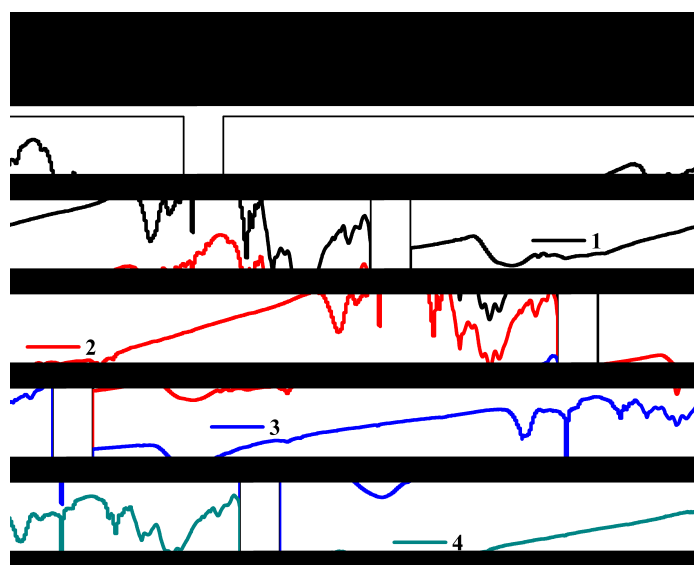


Fig. S2. IR spectra of 1-4 and $\{P_2W_{12}\}$ precursor.

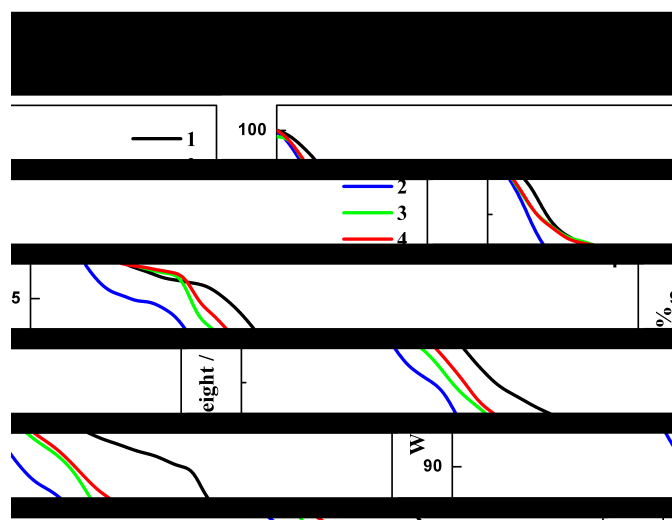


Fig. S3. TG curves of 1–4.

Table S1. Bond valence sum calculations of 4^{*11-2}

Bonds	Bond length (Å)	BVS	Bonds	Bond length (Å)	BVS
Ce(1)-O(11)	2.456(17)	0.438531	Cu(1)-N(1)	2.02(2)	0.499276
Ce(1)-O(13)	2.484(16)	0.406569	Cu(1)-N(2)	2.02(2)	0.499276
Ce(1)-O(14)	2.460(17)	0.433815	Cu(1)-N(1B)	2.02(2)	0.499276
Ce(1)-O(16)	2.484(16)	0.406569	Cu(1)-N(2B)	2.02(2)	0.499276
Ce(1)-O(11A)	2.456(17)	0.438531	Cu(1)-O(45C)	2.74(7)	0.056837
Ce(1)-O(13A)	2.484(16)	0.406569	Cu(1)-O(45D)	2.74(7)	0.056837
Ce(1)-O(14A)	2.460(17)	0.433815			
Ce(1)-O(16A)	2.484(16)	0.406569			
$\sum V_{Ce(1)} = 3.37$			$\sum V_{Cu(1)} = 2.11$		

*Symmetry transformations used to generate equivalent atoms: A = $-x+1, y, -z+1/2$; B = $-x+2, -y+1, -z$; C = $3/2-x, -1/2+y, 1/2-z$; D = $1/2+x, 3/2-y, -1/2+z$.

1. I. D. Brown and D. Altermatt (1985) *Acta Crystallogr. Sect. B: Struct. Sci.* **41**, 244.

2. H. H. Thorp (1992) *Inorg. Chem.* **31**, 1585.