Supporting Information

Engineering the heterogeneous photocatalytic activity of crystalline decatungstate-based coordination polymers

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EXPERIMENTAL SECTION

Synthesis of tetrabutylammonium decapolytungstate (TBADT)

TBADT was synthesized according to a literature[1]. Sodium tungstate dihydrate (16 g, 48.5 mmol) was dissolved in 100 mL of deionized water and heated to boil under stirring. Another 8.4 mL of concentrated hydrochloric acid (12 $mol \cdot L^{-1}$, 100 mmol) was poured slowly into 25 mL of deionized water, heated and stirred until nearly boiling. The diluted hot hydrochloric acid solution was poured quickly into the sodium tungstate solution under vigorous stirring, and finally a bright yellow solution was obtained. After stirring for 3 min under near-boiling condition, a solution of tetrabutylammonium bromide (6.4 g, 19.8 mmol) dissolved in 10 mL of hot water was rapidly added, resulting in a large amount of light-yellow precipitate. After stirring for 5 min, the hot suspension was filtered immediately. The filter cake was washed with hot deionized water and ethanol in turn and then dried. Light yellow powder-like TBADT with a yield of about 89% (based on sodium tungstate dihydrate) was thus obtained.

Synthesis of 2,5-bis(3-pyridyl)-1,3,4-oxadiazole (3-bpo) and 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (4-bpo)

Hydrazine hydrochloride (4.90 g, 46.7 mmol), nicotinic acid (9.96 g, 80.9 mmol), and polyphosphoric acid (169 g, containing 85% P_2O_5) were added into a 250 mL flask. The mixture was then heated to 120 ^oC under stirring, and then slowly raised to 160^oC and held for 5 hours. After the reaction, the mixture was cooled slightly and then neutralized with 20% NaOH aqueous solution in an ice-water bath until the pH reached 7. After restoring to room temperature and filtering, a pink crude product was obtained. The crude product was recrystallized with 95% ethanol to obtain light yellow needle-like crystals of 2,5-bis(3-pyridyl)-1,3,4-oxadiazole (3-bpo) with a yield of 44% (based on nicotinic acid).

Hydrazine hydrochloride (5.05 g, 48.1 mmol), isonicotinic acid (9.93 g, 80.7 mmol), and polyphosphoric acid (165 g, containing 80% P_2O_5) were added to a 250 mL flask. The mixture was then heated to 120 ^oC under stirring and then slowly raised to 160^oC and held for 4 hours. After the reaction, the mixture was cooled slightly and then

neutralized with 20% NaOH aqueous solution in an ice-water bath until the pH reached 7. After restoring to room temperature and filtering, a white crude product was obtained. The crude product was recrystallized with 95% ethanol. to obtain white needle-like crystals of 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (4-bpo) with a yield of 50% (based on nicotinic acid).

Crystallographic data

Table S1 Crystallographic data and structure refinement for compounds.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{28}H_{60}Cu_2N_8O_{52}S_2W_{10}$	$C_{32}H_{40}Cu_2N_8O_{38}S_4W_{10}$	$C_{40}H_{34}Cu_2N_8O_{32}W_{10}$	$C_{48}H_{71}CuN_7O_{35}SW_{10}$
Formula weight	3370.4	3238.4	3104.2	3240.1
Wavelength (Å)	1.34138	1.34138	1.34138	1.34138
Crystal System	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$Pbca$	$P2_1/c$
a (Å)	10.3627(6)	10.8085(4)	16.7303(8)	15.4754(4)
b (Å)	18.5962(11)	16.8447(6)	17.5503(8)	20.7480(6)
c (Å)	16.5939(10)	18.0408(7)	18.9281(9)	22.0378(5)
α (°)	90	90	90	90
β (°)	106.222(2)	106.909(2)	90	90.7830(10)
γ (°)	90	90	90	90
V (Å^3)	3070.4(3)	3142.6(2)	5557.7(5)	7075.32(3)
Z	2	2	4	4
Reflns collected	29098	48744	76802	127260
GOF on F^2	1.115	1.032	1.080	1.143
R_1 ($I>2\sigma$ (I))[a]	0.0413	0.0396	0.0297	0.0485
wR_2 (all data)[b]	0.1159	0.1164	0.0706	0.1124

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$

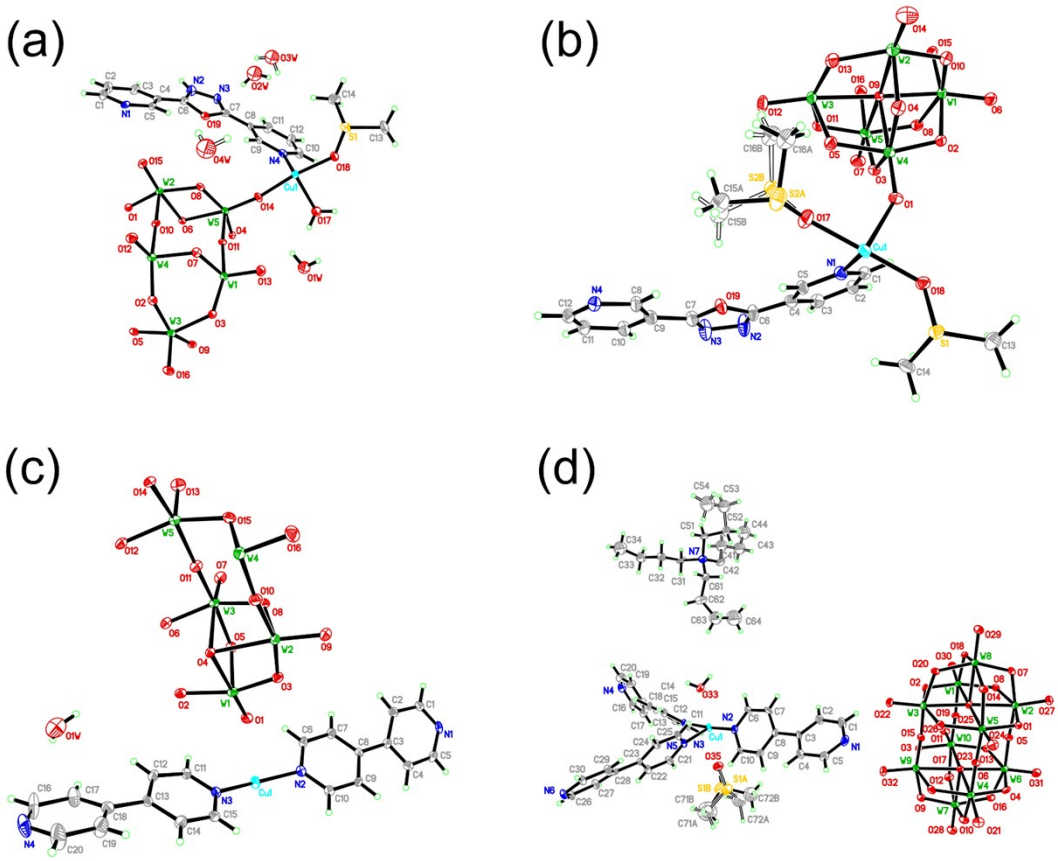


Fig. S1. Structural drawings of compounds **1**-**4** showing ADPs.

Selected W-O_t bond lengthes and W-O_b-W bond angles

Table S2. Bond lengths of W-O_t and bond angles of W-O_b-W in compounds **1**-**4**.

	W1-O_t (Å)	W2-O_t (Å)	W3-O_t (Å)	W4-O_t (Å)	W5-O_t (Å)	W2-O_b-W4 (°)	W3-O_b-W5 (°)
1	1.723	1.694	1.726	1.692	1.708	176.7	173.8
2	1.753	1.768	1.676	1.708	1.730	176.1	171.8
3	1.710	1.686	1.689	1.695	1.698	175.5	175.1
4	1.719	1.684	1.704	1.720	1.730	177.0	174.5

Bond valence sum analysis

To determine the oxidation state of Cu atoms, bond valence sum (BVS) analysis was conducted based on the bond lengths derived from SC-XRD. Sum of bond valence (N) was calculated based on the equations below[2].

$$N = \Sigma s_i \quad (1)$$

$$s_i = \exp\left[\frac{r_0 - r_i}{B}\right] \quad (2)$$

where s_i and r_i represent bond valence and bond length of each bond, respectively, r_0 is an empirical data determined by experiments, and B is generally chosen as 0.37. For Cu^{2+}-O and Cu^{2+}-N bonds in compounds **1**, **2** and **4**, the reported r_0 values are 1.679 Å and1.719 Å[3]. For Cu^{+}-O and Cu^{+}-N bonds in compound **3**, the reported r_0 values for Cu^{2+}-O and Cu^{2+}-N bonds are 1.593 Å[4] and 1.595 Å[2], respectively. Calculated bond valence sums of compounds **1-4** are shown in **Table S3**.

Table S3. Bond valence sum of compounds **1-4**.

Compound	Bond	Bond length (Å)	Bond valence	BVS
1	Cu(1)-O(18)	1.980	0.443	
	Cu(1)-O(14)	2.004	0.415	
	Cu(1)-N(1)#1	2.008	0.458	2.109
	Cu(1)-N(4)	2.019	0.444	
	Cu(1)-O(17)	2.245	0.217	
	Cu(1)-O(15)#1	2.427	0.132	
2	Cu(1)-N(4)#2	2.007	0.459	
	Cu(1)-O(17)	2.009	0.410	
	Cu(1)-N(1)	2.014	0.451	2.097
	Cu(1)-O(18)	2.029	0.388	
	Cu(1)-O(6)#3	2.262	0.207	
	Cu(1)-O(1)	2.309	0.182	

3	Cu(1)-N(3)	1.963	0.370	0.973
	Cu(1)-N(2)	1.969	0.364	
	Cu(1)-N(4)#4	2.250	0.170	
	Cu(1)-O(1)	2.580	0.069	
4	Cu(1)-N(4)	1.9938	0.47557	2.035
	Cu(1)-N(3)#5	2.0153	0.43972	
	Cu(1)-N(2)	2.0228	0.41997	
	Cu(1)-N(5)	2.0405	0.44933	
	Cu(1)-O(35)	2.4479	0.12513	
	Cu(1)- O(36)	2.4488	0.1248	

Powder X-ray diffraction results

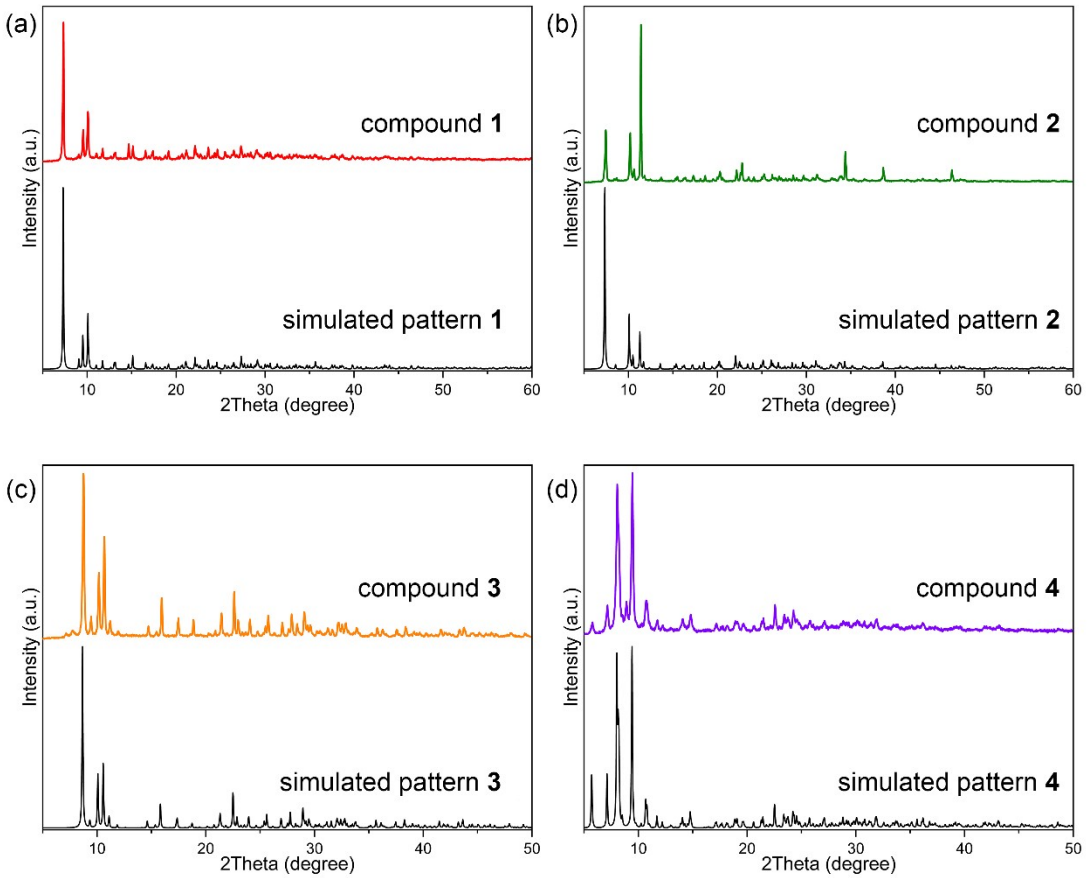


Fig. S2. PXRD patterns of compounds **1**-**4**, compared with simulated results.

N_2 adsorption results

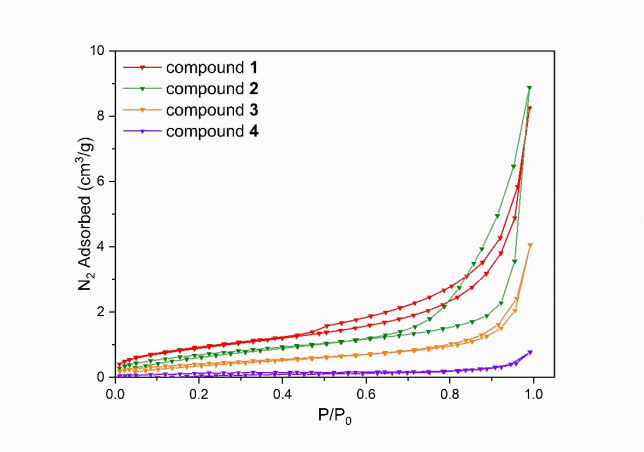


Fig. S3. N_2 Adsorption curves of compounds **1-4**.

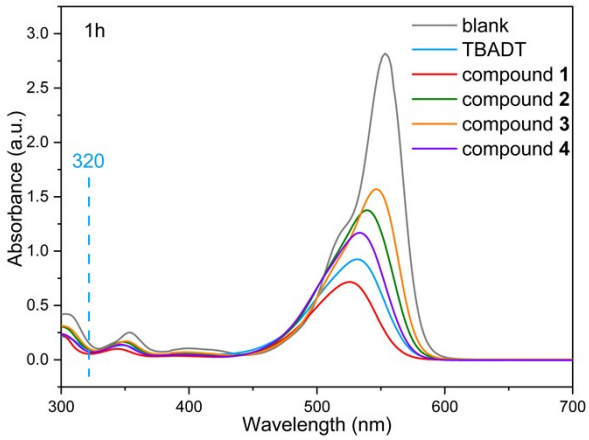
Table S4. Specific surface area and pore volume data of compounds **1-4**.

Compound	**1**	**2**	**3**	**4**
BET Surface Area (m^2/g)	3.4063	2.6924	1.5862	0.5125
Langmuir Surface Area (m^2/g)	5.4302	4.3498	2.5410	0.8687
BJH Adsorption cumulative volume[c] (cm^3/g)	0.012331	0.013319	0.006049	0.001072
BJH Desorption cumulative volume[c] (cm^3/g)	0.012524	0.013515	0.006077	0.001125
BJH Adsorption average pore width (Å)	145.641	217.110	165.795	156.198
BJH Desorption average pore width (Å)	125.969	154.702	148.981	149.056

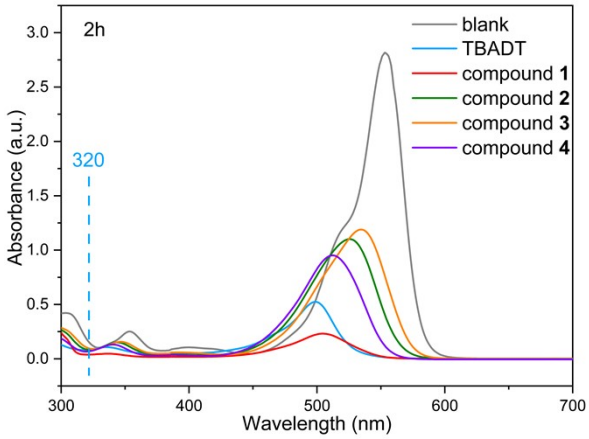
[c]Cumulative volume of pores between 17.000 Å and 3,000.000 Å width.

Photodegradation Results

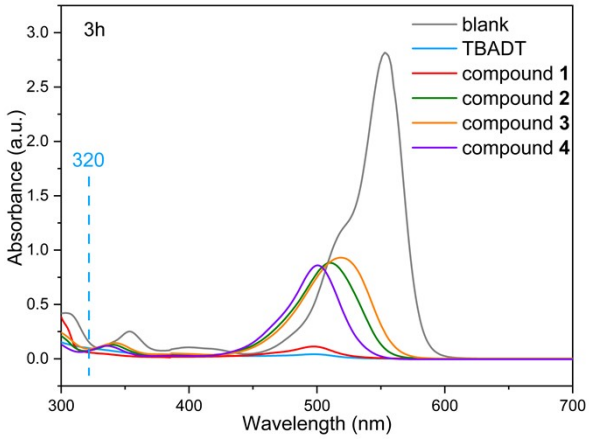
(a)



(b)



(c)



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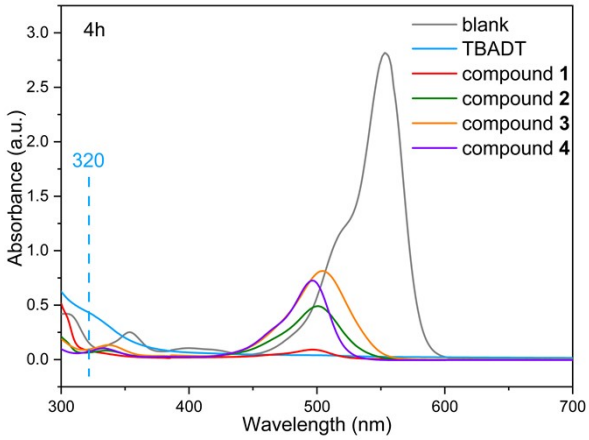

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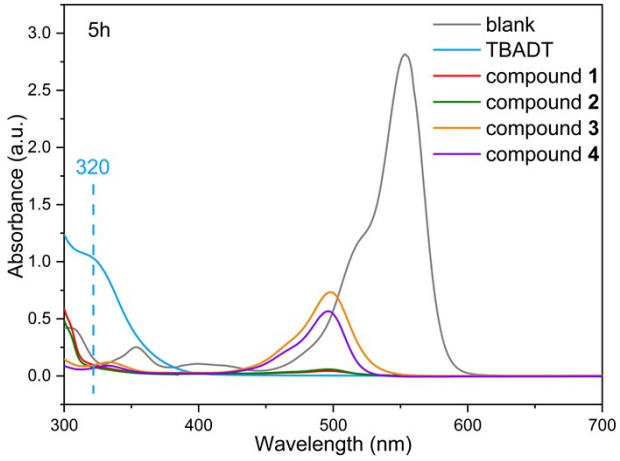

Fig. S4. UV-Vis DRS results of the solution after the photocatalytic degradation of RhB for 1-5 h.

References

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