Electronic Supplementary Information

A New POM-MOF hybrid Microporous Material with Ultrahigh Thermal Stability And Selective Adsorption of Organic Dyes

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Dye adsorption selective kinetic experiments

Crystalline sample of compound **1** (50mg) was added into the aqueous solution (10 mg L^{-1},100 mL) of methylene blue(MB^+), methyl orange (MO^-) and rhodamine 6G ($R6G^+$), respectively, at room temperature under stirring. At given time intervals, the change of the concentration of dye solutions were monitored using UV-Vis spectra at the characteristic absorption peak of each dye (664nm, 464nm, 527nm, for MB^+, MO^-, $R6G^+$, respectively). The results are shown in Fig.4 in text. Similarly, crystalline sample (100 mg) of **1** was added into 100 mL a binary mixture of MB^+/MO^-, $MB^+/R6G^+$ or MB^+/RhB^+ at room temperature under stirring. The staring concentration of each dye component in the binary mixture is 10 mg L^{-1}. At given time intervals, the change of the concentration of each dye component was monitored by UV-Vis spectra. The results are shown in Fig. 5 in text.

Photodegradation experiments of MO^-

Crystalline sample (50 mg) of **1** was dispensed into a solution (10.0 mg L^{-1}, 100 mL) of MO^- under stirring. After adding 2.0 mL hydrogen peroxide (30%), the reaction mixture was irradiated with 300W Xe lamp as the visible light source. At given time intervals, the concentration of dyes was measured with UV-Vis spectra at the maximum absorbance of the MO^- dye. In comparison, blank experiments were also carried out: (1) without catalyst **1** but in the presence of peroxide (2.0 mL); (2) without light irradiation but in the presence of catalyst **1** and peroxide (2.0 mL). The results are shown in Fig. 6 in text.

Table S1. Selected Bond Lengths (Å) for Compound **1**.

W(1)-O(5)	1.695(6)	W(2)-O(2)	1.919(6)	P(1)-O(7)	1.556(5)
W(1)-O(3)#1	1.897(6)	W(2)-O(4)	1.936(6)	P(1)-O(7)#1	1.556(5)
W(1)-O(6)	1.898(6)	W(2)-O(7)	1.427(5)	P(1)-O(7)#3	1.556(5)
W(1)-O(4)	1.916(6)	W(3)-O(9)	1.694(6)	P(1)-O(7)#2	1.557(5)
W(1)-O(10)#2	1.931(6)	W(3)-O(6)#2	1.894(6)	Cu(1)-N(1)#4	1.999(7)
W(1)-O(7)	2.437(5)	W(3)-O(8)	1.901(6)	Cu(1)-N(1)#2	1.999(7)
W(2)-O(1)	1.689(6)	W(3)-O(2)#1	1.919(6)	Cu(1)-N(2)#5	2.033(7)
W(2)-O(8)	1.896(6)	W(3)-O(10)	1.916(6)	Cu(1)-N(2)	2.033(7)
W(2)-O(3)	1.895(6)	W(3)-O(7)#1	2.429(5)		

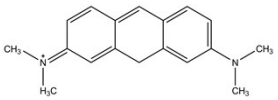
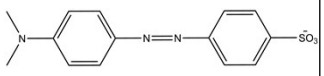
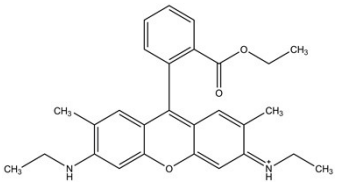
Symmetry codes: #1 -y+3/4,x-1/4,-z+5/4; #2 y+1/4,-x+3/4,-z+5/4; #3 -x+1,-y+1/2,z; #4 -y+5/4,-x+3/4,z-1/4; #5 -x+3/2,y,-z+1 #6 -x+1,-y+1,-z+1

Table S2. Selected Bond Angles (º) for Compound **1**.

O(5)-W(1)-O(3)#1	104.0(3)	O(8)-W(2)-O(2)	155.5(3)	O(8)-W(3)-O(10)	155.6(3)
O(5)-W(1)-O(6)	103.2(3)	O(3)-W(2)-O(2)	89.0(3)	O(2)#1-W(3)-O(10)	86.4(3)
O(3)#1-W(1)-O(6)	85.5(3)	O(1)-W(2)-O(4)	100.9(3)	O(9)-W(3)-O(7)#1	169.2(3)
O(5)-W(1)-O(4)	101.3(3)	O(8)-W(2)-O(4)	88.5(3)	O(6)#2-W(3)-O(7)#1	84.2(2)
O(3)#1-W(1)-O(4)	88.6(3)	O(3)-W(2)-O(4)	155.8(3)	O(8)-W(3)-O(7)#1	84.2(2)
O(6)-W(1)-O(4)	155.5(3)	O(2)-W(2)-O(4)	86.2(3)	O(2)#1-W(3)-O(7)#1	70.8(2)
O(5)-W(1)-O(10)#2	100.8(3)	O(1)-W(2)-O(7)	168.5(3)	O(10)-W(3)-O(7)#1	71.5(2)
O(3)#1-W(1)-O(10)#2	155.2(3)	O(8)-W(2)-O(7)	84.8(2)	O(7)-P(1)-O(7)#1	109.5(2)
O(6)-W(1)-O(10)#2	88.5(3)	O(3)-W(2)-O(7)	84.6(2)	O(7)-P(1)-O(7)#3	109.3(4)
O(4)-W(1)-O(10)#2	87.0(3)	O(2)-W(2)-O(7)	70.9(2)	O(7)#1-P(1)-O(7)#3	109.5(2)
O(5)-W(1)-O(7)	169.1(3)	O(4)-W(2)-O(7)	71.5(2)	O(7)-P(1)-O(7)#2	109.5(2)
O(3)#1-W(1)-O(7)	84.4(2)	O(9)-W(3)-O(6)#2	103.3(3)	O(7)#1-P(1)-O(7)#2	109.3(4)
O(6)-W(1)-O(7)	84.2(2)	O(9)-W(3)-O(8)	103.6(3)	O(7)#3-P(1)-O(7)#2	109.5(2)
O(4)-W(1)-O(7)	71.8(2)	O(6)#2-W(3)-O(8)	85.7(2)	N(1)#4-Cu(1)-N(1)#2	115.9(4)
O(10)#2-W(1)-O(7)	71.5(2)	O(9)-W(3)-O(2)#1	101.6(3)	N(1)#4-Cu(1)-N(2)#5	110.8(2)
O(1)-W(2)-O(8)	103.3(3)	O(6)#2-W(3)-O(2)#1	155.0(3)	N(1)#2-Cu(1)-N(2)#5	106.7(2)
O(1)-W(2)-O(3)	103.9(3)	O(8)-W(3)-O(2)#1	88.6(3)	N(1)#4-Cu(1)-N(2)	106.7(2)
O(8)-W(2)-O(3)	86.0(3)	O(9)-W(3)-O(10)	100.8(3)	N(1)#2-Cu(1)-N(2)	111.0(2)
O(1)-W(2)-O(2)	100.6(3)	O(6)#2-W(3)-O(10)	88.7(3)	N(2)#5-Cu(1)-N(2)	105.3(4)

Symmetry codes: #1 -y+3/4,x-1/4,-z+5/4; #2 y+1/4,-x+3/4,-z+5/4; #3 -x+1,-y+1/2,z; #4 -y+5/4,-x+3/4,z-1/4; #5 -x+3/2,y,-z+1 #6 -x+1,-y+1,-z+1

Table S3. Molecular Dimensions of Dye Molecules with Different Charges used here.

	MB^+	MO^-	$R6G^+$
			
x (Å)	4.59	5.31	10.89
y (Å)	8.01	7.25	15.72
z (Å)	16.75	17.39	15.79

References:

Y.-C. He, J. Yang, W.-Q. Kan, H.-M. Zhang, Y.-Y. Liu and J.-F. Ma, *J. Mater. Chem. A*, 2015, **3**, 1675-1681.

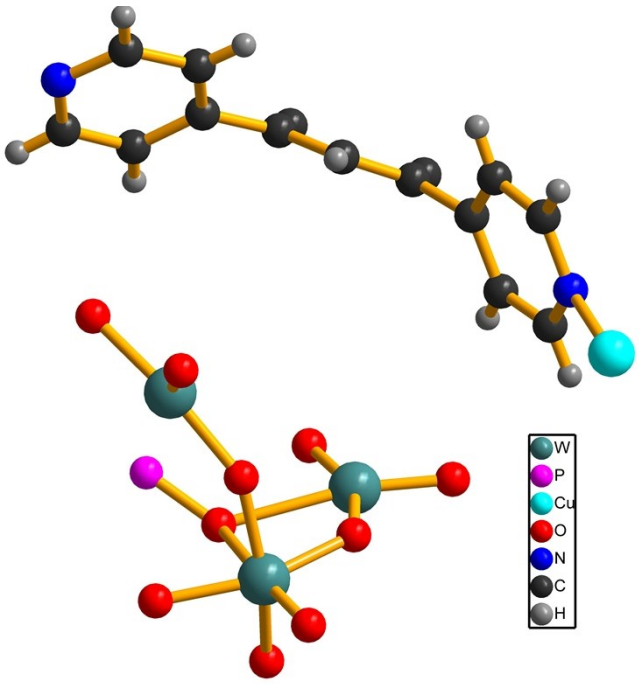


Fig. S1 The asymmetric unit of Compounds **1**.

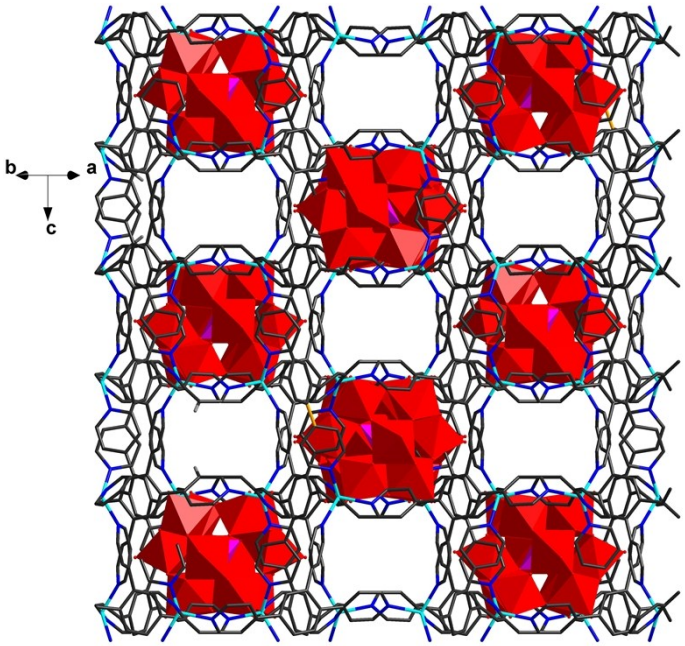


Fig. S2 A view of the 1D channels along the [110] direction, which are available for accommodate solvent molecules and dimethylamine cations. Keggin anions are highlighted in polyhedral.

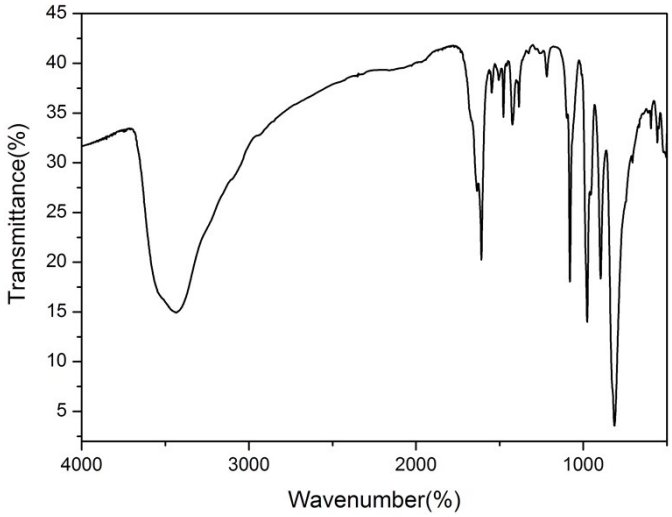


Fig. S3 The IR spectrum of Compound **1**. Main peaks (cm^{-1}): 3440(s), 1610(s), 1544(w), 1479(w), 1421(m), 1382(w), 1218(w), 1076(s), 978(s), 893 (s), 815(s), 594(w), 554(w).

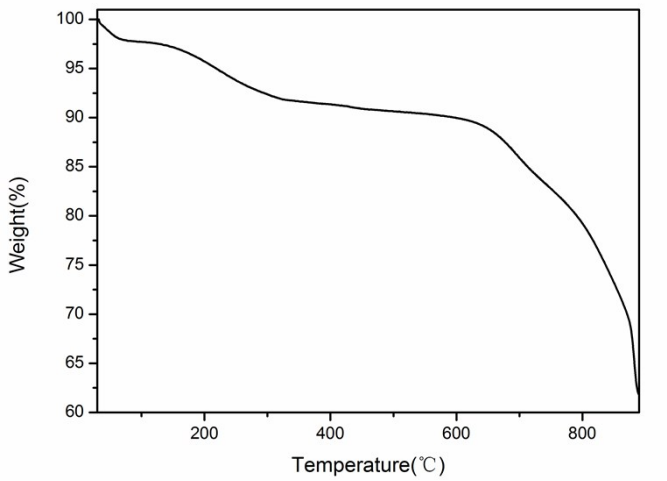


Fig. S4 The TGA curve of Compounds **1**.

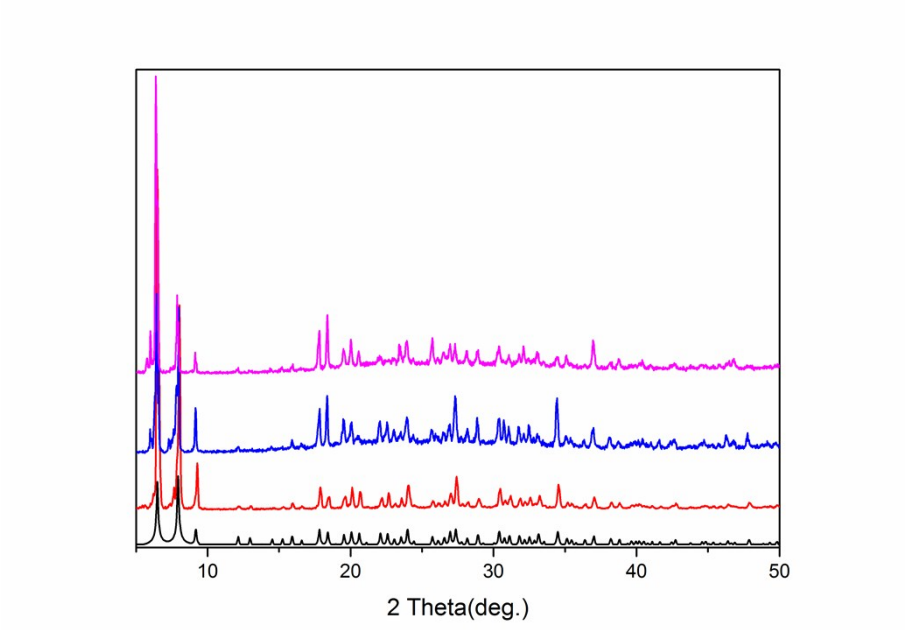


Fig.S5 PXRD Patterns of **1** (black, simulated; red, as-synthesized; blue, after N_2 absorption; magenta, after MO^- degradation).

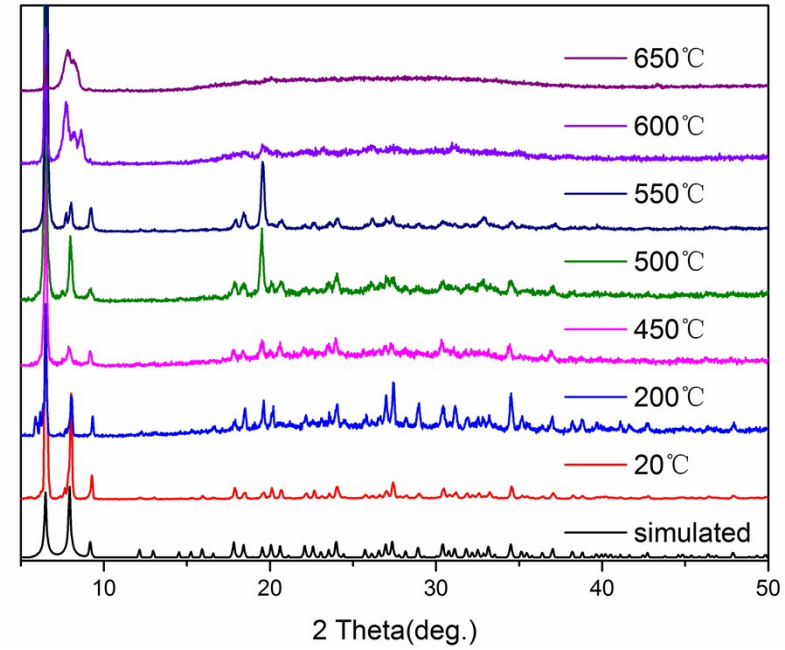


Fig.S6 PXRD patterns of **1** in different temperatures

N_2 Sorption Experiment for 1

A Micromeritics (Accelerated Surface Area and Porosimetry) 2020 System was used to measure gas adsorption. Crystalline sample of **1** (200mg) was immersed in methanol for three days at room temperature. The solvent was replaced by fresh methanol every five hours. Crystalline sample of **1** was then degassed under dynamic vacuum at 100 °C for 10 hours to obtain the completely activated samples. The N_2 gas adsorption isotherms was measured at 77 K. Upon loading of MB in **1**, the deep blue powder solid obtained by filtration and washing with water was dried in open air for several days and then degassed under dynamic vacuum at 100 °C for overnight to obtain the completely activated samples. The N_2 gas adsorption isotherms of **1** after the treatment with MB^+ was measured at 77 K.

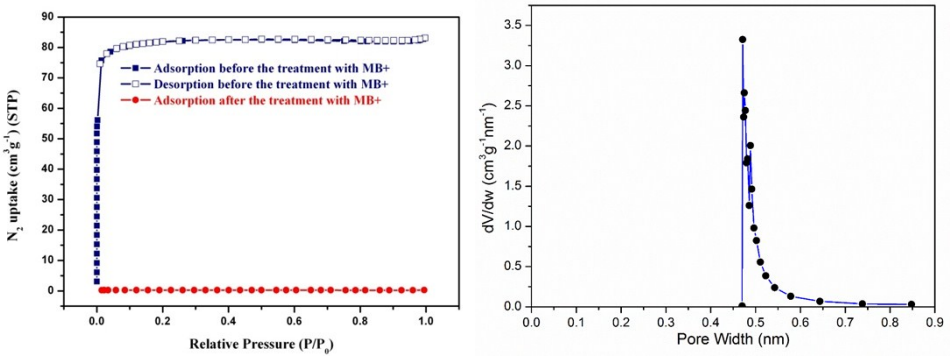


Fig. S7 a) N_2 adsorption isotherms at 77K before and after the treatment with MB^+, b) Horvath-Kawazoe Differential Pore Volume Plot for **1** before the treatment with MB^+.

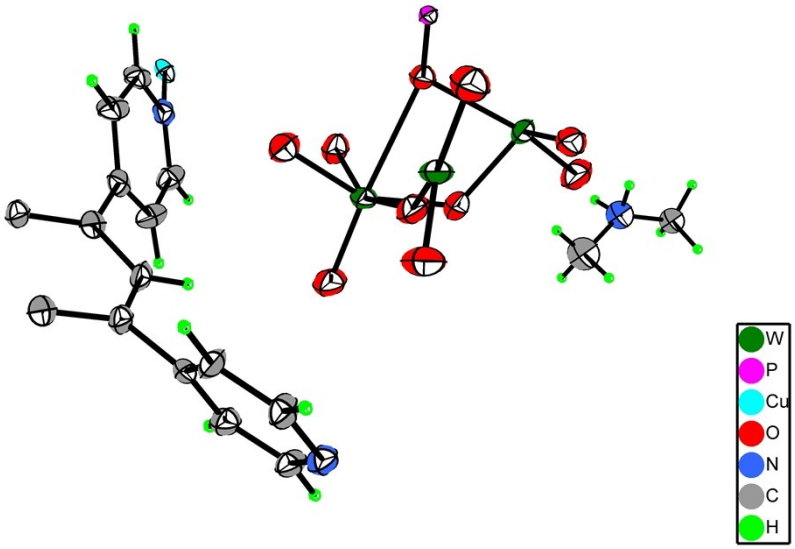


Fig. S8 Ellipsoid plot of the asymmetric unit of compound **1**

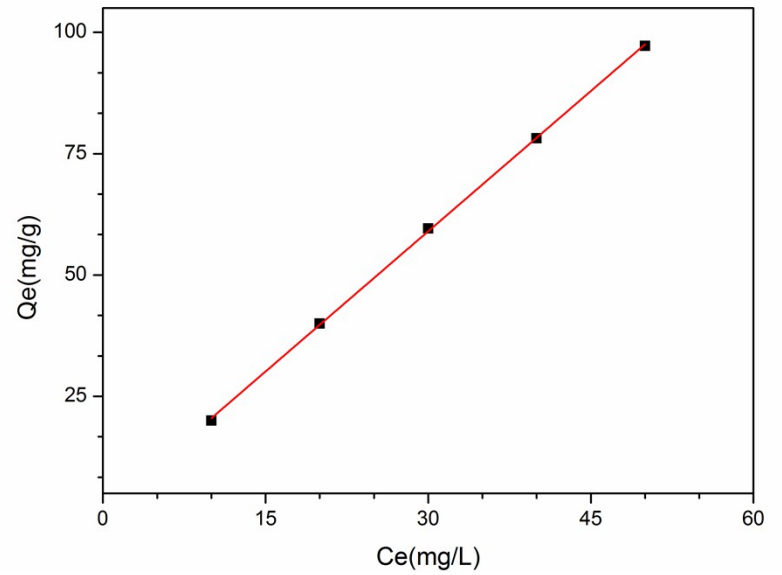
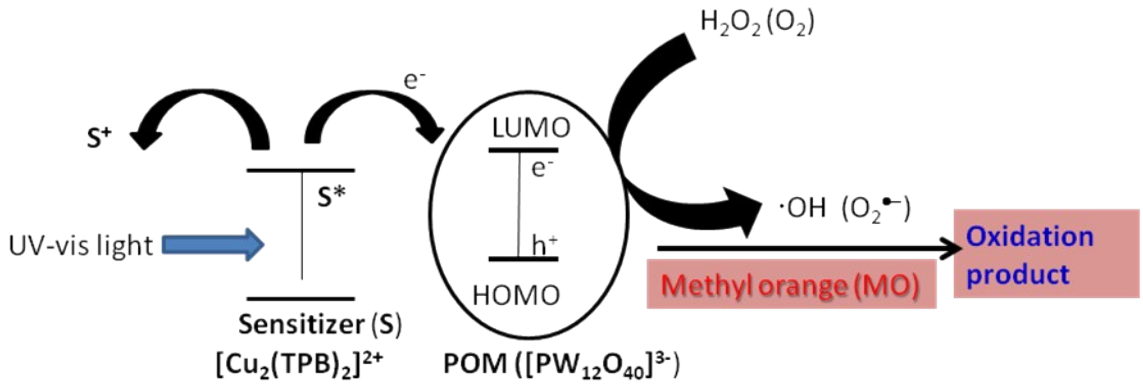


Fig. S9 MB^{+} adsorption isotherm at room temperature for **1**.



$$S \xrightarrow{h\nu} S \longrightarrow S^{+} + e^{-} \quad (1)$$

$$POM(e\text{-}) \xrightarrow{h\nu} POM^{-} \quad (2)$$

$$H_2O_2 + POM^{-} \longrightarrow POM + OH^{-} + {}^{\bullet}OH \quad (3)$$

$$O_2 + POM^{-} \longrightarrow POM + O_2^{\bullet-} \quad (4)$$

$$O_2^{\bullet-} + H_2O_2 \longrightarrow {}^{\bullet}OH + OH\text{-} + O_2 \quad (5)$$

$${}^{\bullet}OH + O2^{\bullet-} + MO \longrightarrow \text{oxidation product} \quad (6)$$

Scheme S1. Photo-catalytic degradation mechanism of MO on **1** under UV-vis light irradiation.