Supporting Information

A robust polyoxometalate-templated four-fold interpenetrating metal-organic framework showing efficient organic dyes photodegradation in various pH aqueous solution

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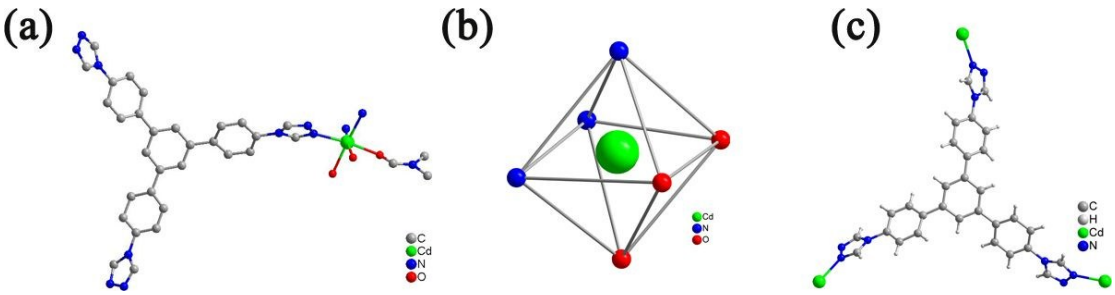

Fig. S1 (a) Coordination environment of Cd atom in **1**. (b) Coordination geometry of Cd nodes. (c) Coordination mode of **TTPB-4** ligand.

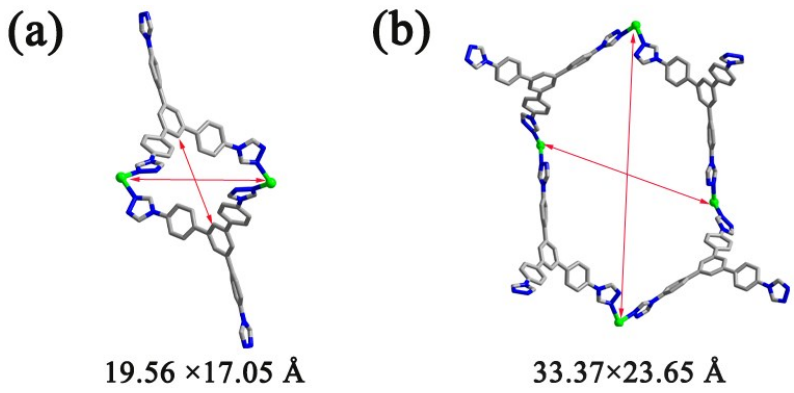

Fig. S2 (a) Quadrilateral channel **A** (19.56 × 17.05 Å) in **1**. (b) Hexagon channel **B** (33.37 × 23.65 Å, Cd-to-Cd distance at opposite position) in **1**.

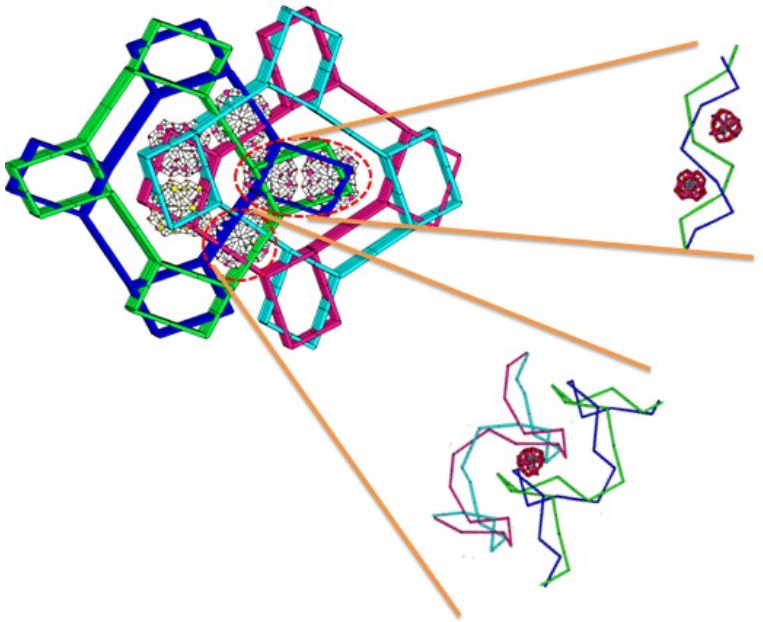

Fig. S3 View of the position of POMs in the four-fold interpenetrating structure of **1**.

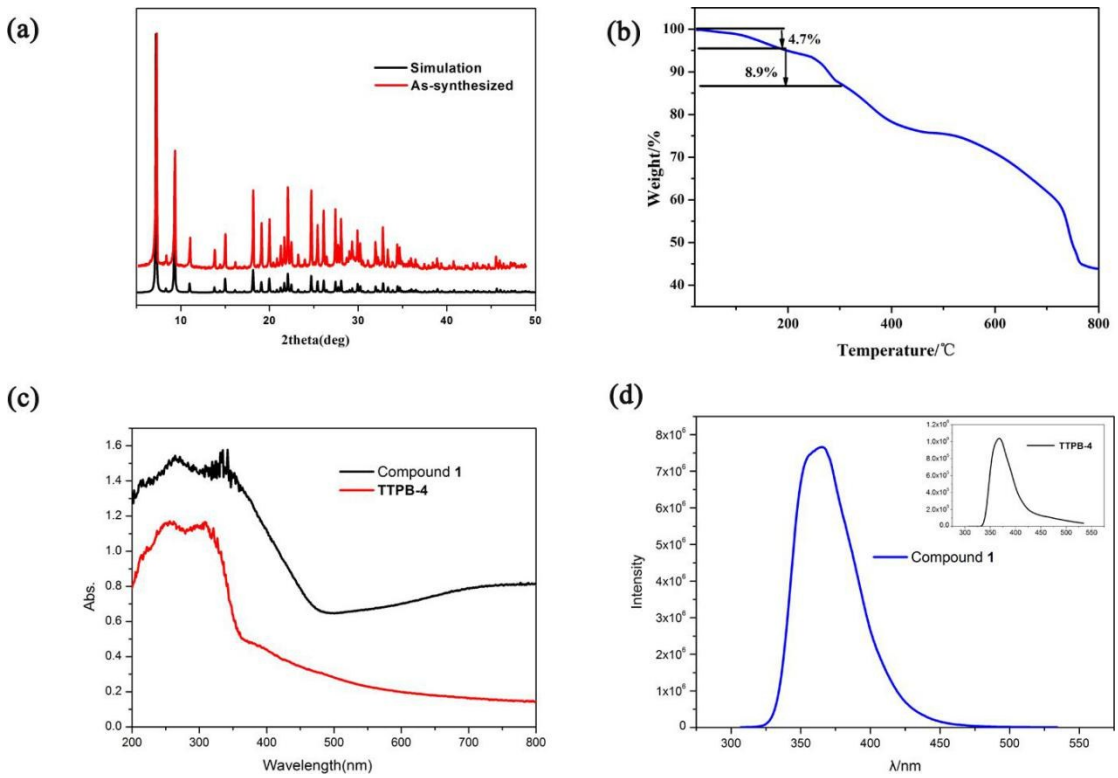

Fig. S4 (a) Powder X-ray diffraction (PXRD) patterns of compound **1**. (b) TGA curves of compound **1**. (c) Solid-state UV-Vis absorption spectra of ligand **TTPB-4** (red line) and crystal **1** (black line). (d) Photoluminescent spectra of **TTPB-4** and crystal **1** in DMF solution at room temperature.

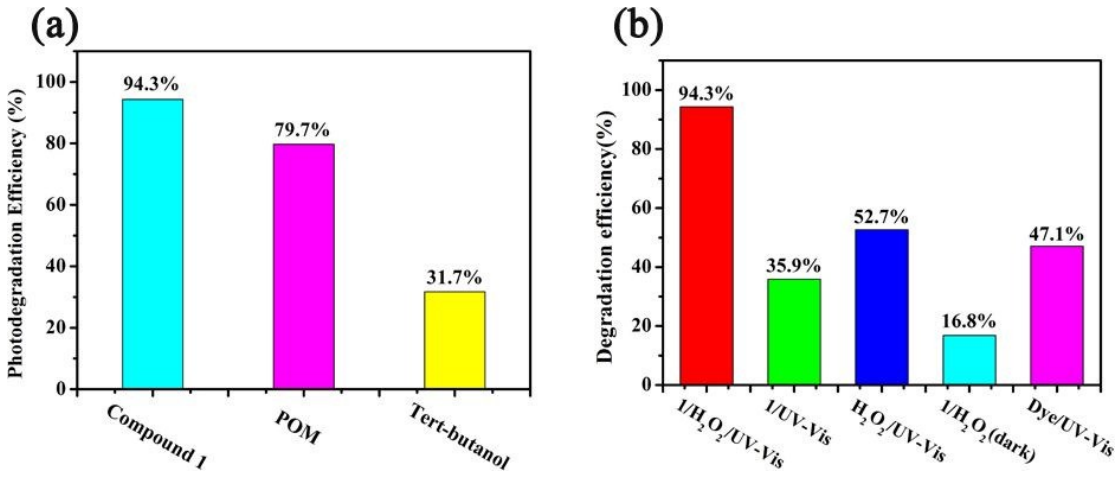

Fig. S5 (a) Photodegradation efficiency of CV with 1，POM as well as 1/tert-butanol. (b) Degradation efficiency of CV under different conditions.

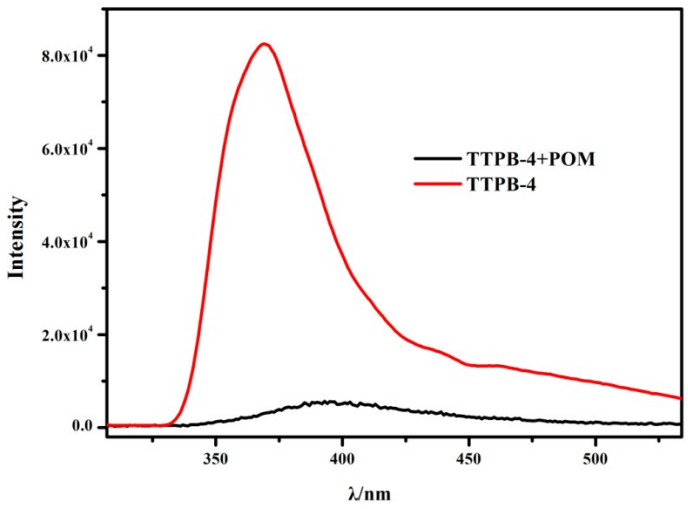

Fig. S6 Fluorescence spectra of **TTPB-4** in DMF solution with (black line) or without POM (red line).

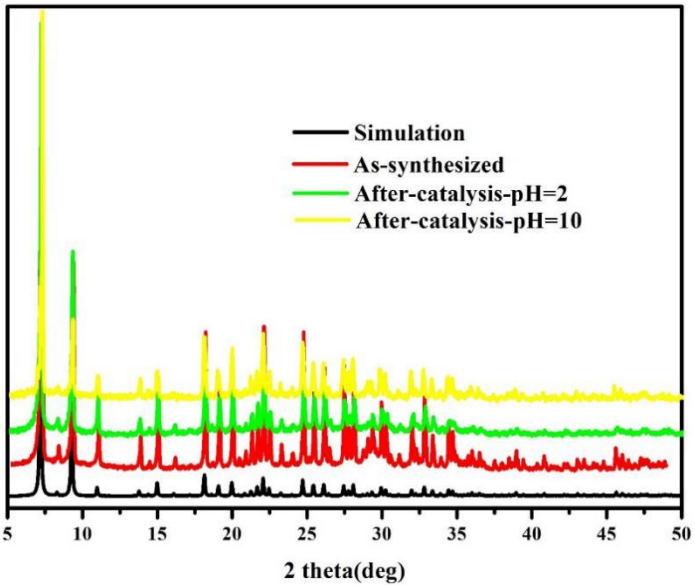

Fig. S7 PXRD patterns of **1** during photocatalysis process in different initial pH.

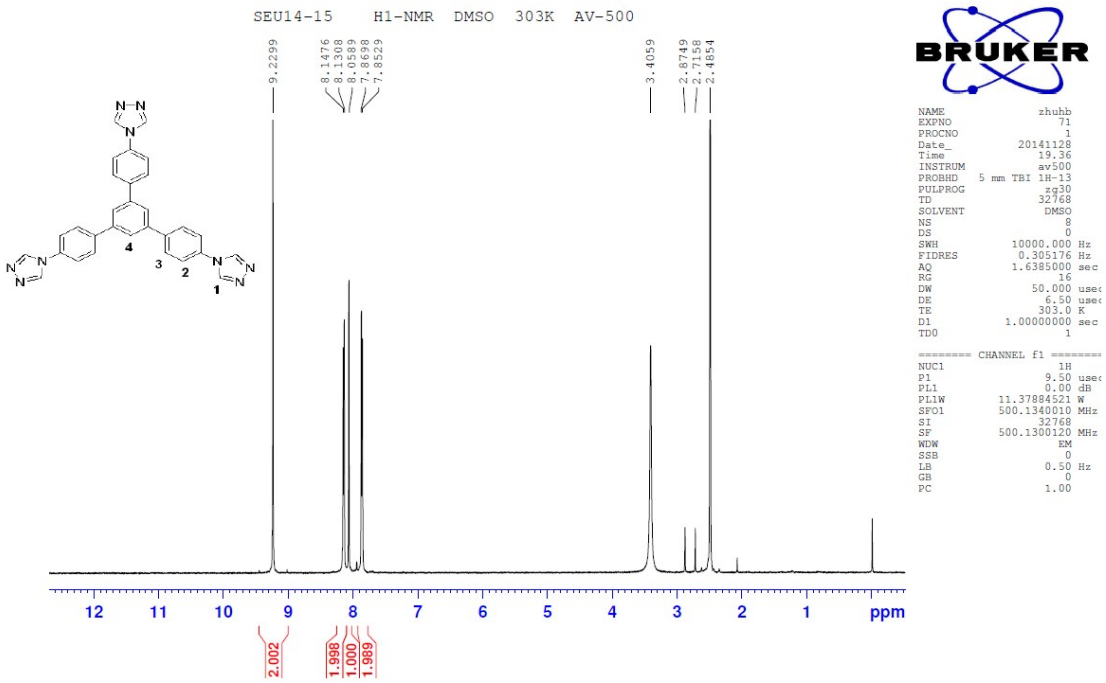

Fig. S8 ^{1}H NMR of **TTPB-4.**

Table S1 Reported POM-MOFs for dyes photodegradation.

Formula	Dyes	Photodegradation efficiency	Irradiation time	Light	Ref.
$[Cu(H_2tda)(H_2O)_2]_4[SiW_{12}O_{40}]\cdot 12H_2O$	RhB	90%	360min	UV	1
$\{[Ag_5(INA)_5(HINA)][H_3PM_{12}O_{40}](H_2O)\}\cdot H_2O$	GV	91.2%	70min	UV	2
$\{[Ag_5(INA)_5(HINA)][H_3PM_{12}O_{40}](H_2O)\}\cdot H_2O$	MB	95.6%	90min	UV	2
$H_2[Cu_{11}(btb)_{19}(H_2O)_6(P_2W_{16}{}^{VI}W_2{}^{V}O_{62})_3]\cdot 12H_2O$	MB	81.5%	150min	UV	3
$[\{Cu^{II}_6Cu^{I}_{10}(H_2O)_5(pzc)_{10}(pz)_6\}\{P_2W_{18}O_{62}\}_2]\cdot 4H_2O$	RhB	92.18%	120min	UV	4

$[\{Cu^{II}_6Cu^{I}_{10}(H_2O)_5(pzc)_{10}(pz)_6\}\{P_2W_{18}O_{62}\}_2]\cdot 4H_2O$	MB	97.41%	120min	UV	4
$[H_2L][CuL][SiW_{12}O_{40}]\cdot 2H_2O$	MB	89.5%	90min	UV	5
$[CuL]_4[GeW_{12}O_{40}]\cdot H_2O$	MB	84.7%	90min	UV	5
$[Cu_2(btx)_2(C_2O_4)][H_2SiW_{12}O_{40}]\cdot 12H_2O$	MB	78.1%	60min	Visible	6
$[Cu_2(btx)_2(C_2O_4)][H_2SiW_{12}O_{40}]\cdot 12H_2O$	MB	91.35%	60min	UV	6
[Cd(TTPB-4)$(DMF)_3]_4[PMo_{12}O_{40}]_2[HPMo_{12}O_{40}]$❿11DMF	CV	94.3%	36min	UV-Vis	This work
[Cd(TTPB-4)$(DMF)_3]_4[PMo_{12}O_{40}]_2[HPMo_{12}O_{40}]$❿11DMF	BR 2	95.0%	18min	UV-Vis	This work

Table S2 Selected distance (Å) and angles(°) of complex **1**

Cd1—$N1^{iii}$	2.258 (8)	Cd1—$N1^{iv}$	2.258 (8)
Cd1—O1	2.292 (11)	Cd1—$O1^{iii}$	2.292 (11)
Cd1—$O1^{iv}$	2.292 (11)	Cd1—N1	2.258 (8)
N1—Cd1—$N1^{iii}$	95.9 (3)	N1—Cd1—$N1^{iv}$	95.9 (3)
$N1^{iii}$—Cd1—$N1^{iv}$	95.9 (3)	N1—Cd1—O1	172.5 (4)
$N1^{iii}$—Cd1—O1	91.6 (4)	$N1^{iv}$—Cd1—O1	84.2 (4)
N1—Cd1—$O1^{iii}$	84.2 (4)	$N1^{iii}$—Cd1—$O1^{iii}$	172.5 (4)

N1^{iv}—Cd1—O1^{iii}	91.6 (4)	O1—Cd1—O1^{iii}	88.3 (6)
N1—Cd1—O1^{iv}	91.6 (4)	N1^{iii}—Cd1—O1^{iv}	84.2 (4)
N1^{iv}—Cd1—O1^{iv}	172.5 (4)	O1—Cd1—O1^{iv}	88.3 (6)
O1^{iii}—Cd1—O1^{iv}	88.3 (6)		

Symmetry codes: Symmetry codes: (i) $y-1/2, -z+1/2, -x$; (ii) $-z, x+1/2, -y+1/2$; (iii) z, x, y;(iv) y, z, x; (v) $z-1/4, -y+1/4, -x+7/4$; (vi) $-z+7/4, -y+1/4, x+1/4$; (vii) $-x+3/2, y, -z+2$.

Table S3 The bond valence sum (BVS) calculations of **1**

BVP	**R**	**s**	**BVP**	**R**	**s**	**BVP**	**R**	**s**
Mo1—O2	1.671	1.8923	Mo2—O5	1.681	1.8419	Mo3—O7	1.7	1.7497
Mo1—O8	1.892	1.0413	Mo2—O4	1.88	1.0757	Mo3—O9	1.867	1.1141
Mo1—O3	1.9	1.0190	Mo2—O11	1.904	1.0081	Mo3—O11	1.892	1.0413
Mo1—O4	1.9	1.0190	Mo2—O3	1.923	0.9576	Mo3—O6	1.928	0.9448
Mo1—O9	1.95	0.8902	Mo2—O6	1.939	0.9171	Mo3—O8	1.939	0.9171
Mo1—O10	2.398	0.2652	Mo2—O10	2.429	0.2439	Mo3—O10	2.415	0.2533
Calculated value		6.1275	**Calculated value**		6.0445	**Calculated value**		6.0205

References.

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