Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information

High photodegradation efficiency of phenol by mixed-metal–organic frameworks

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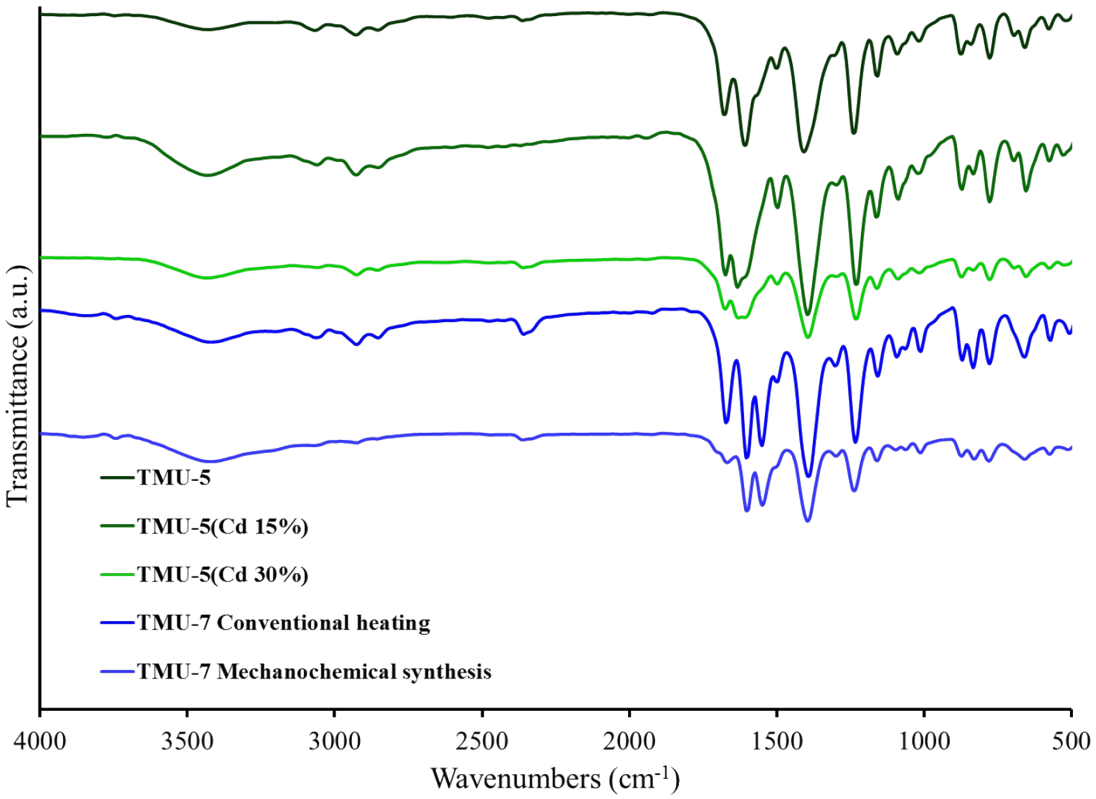

Fig. S1 IR spectra of TMU-5, TMU-5(Cd 15%), TMU-5(Cd 30%), TMU-7 crystals produced by conventional heating and TMU-7 powder produced by mechanosynthesis.

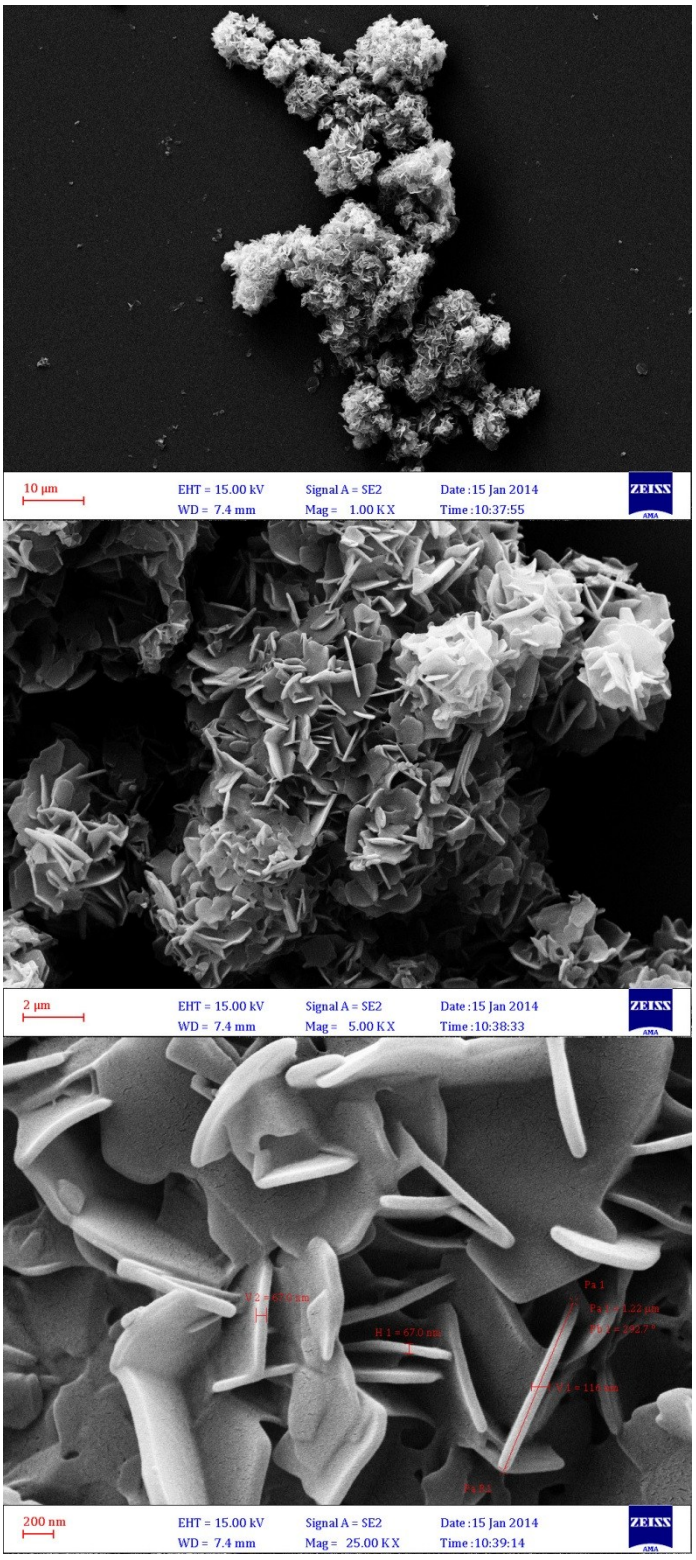

Fig. S2. FE-SEM images TMU-7 synthesized by mechanochemical reaction.

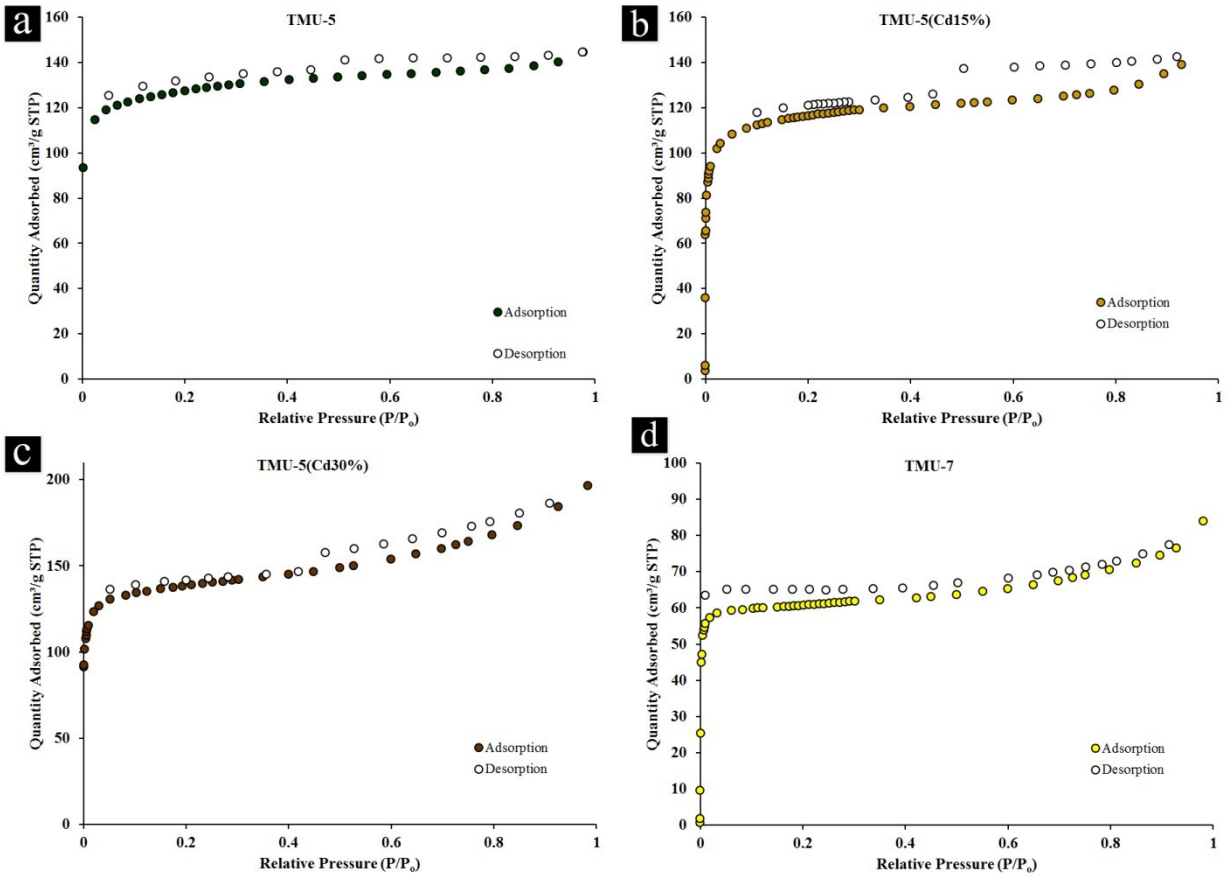

Fig. S3. N_2 adsorption isotherms collected at 77 K of (a) TMU-5, (b) TMU-5(Cd15%), (c) TMU-5(Cd30%) and (d) mechanosynthesized TMU-7.

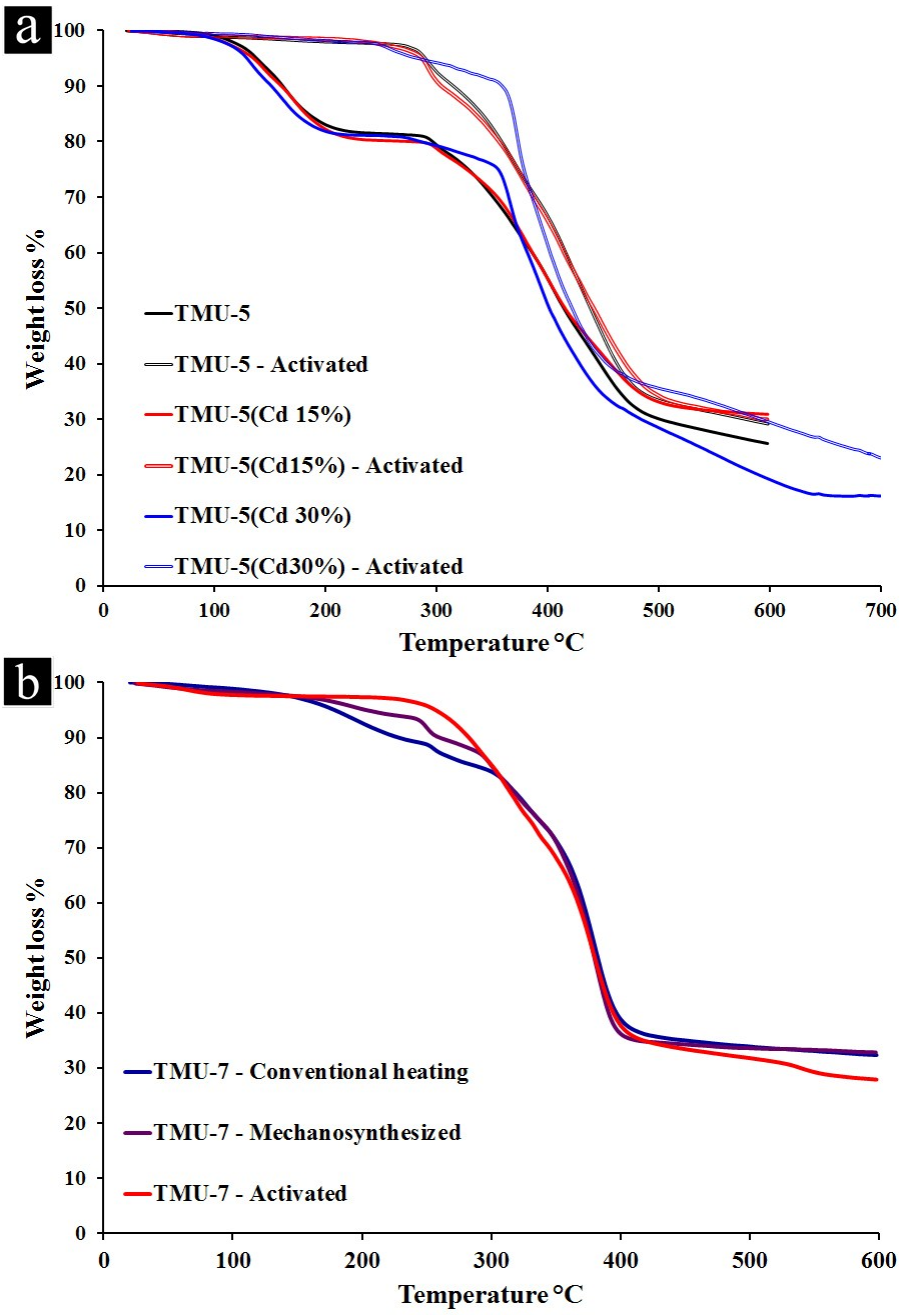

Fig. S4. Thermogravimetric profiles of (a) TMU-5, TMU-5(Cd 15%), TMU-5(Cd 30%) crystals produced by conventional heating and activated samples. (b) TMU-7 crystals produced by conventional heating and TMU-7 powder produced by mechanosynthesis and activated TMU-7.

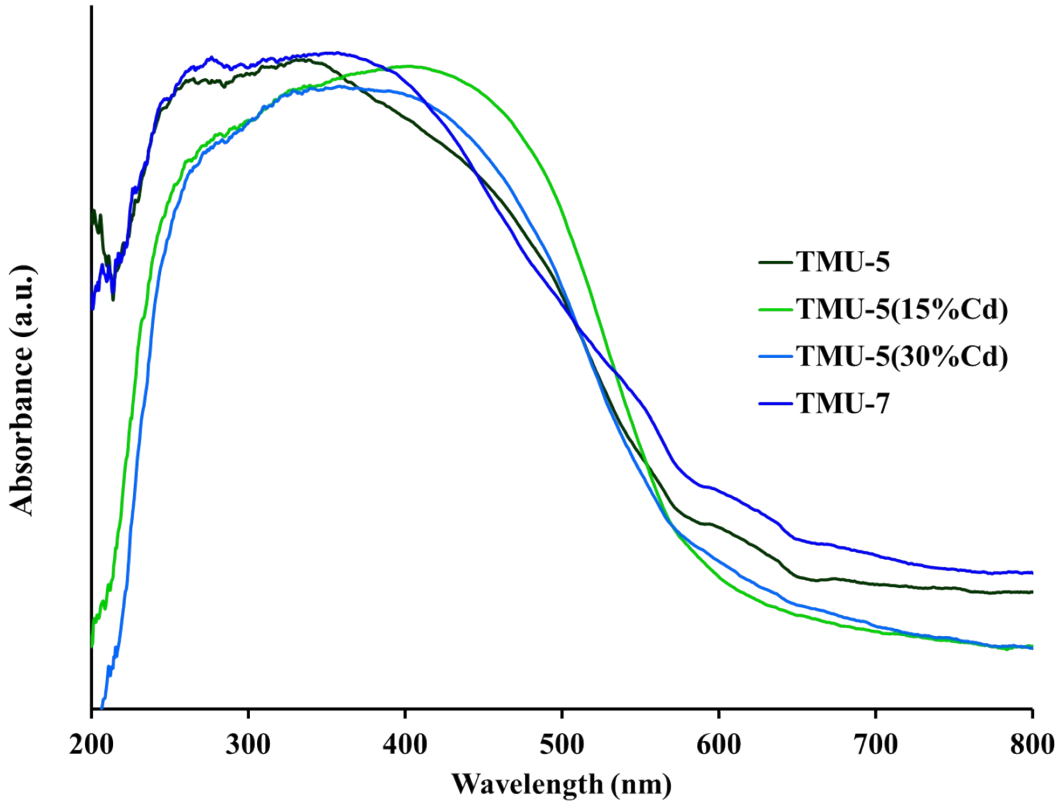

Fig. S5. UV-Vis diffuse reflectance spectra of the MOFs.

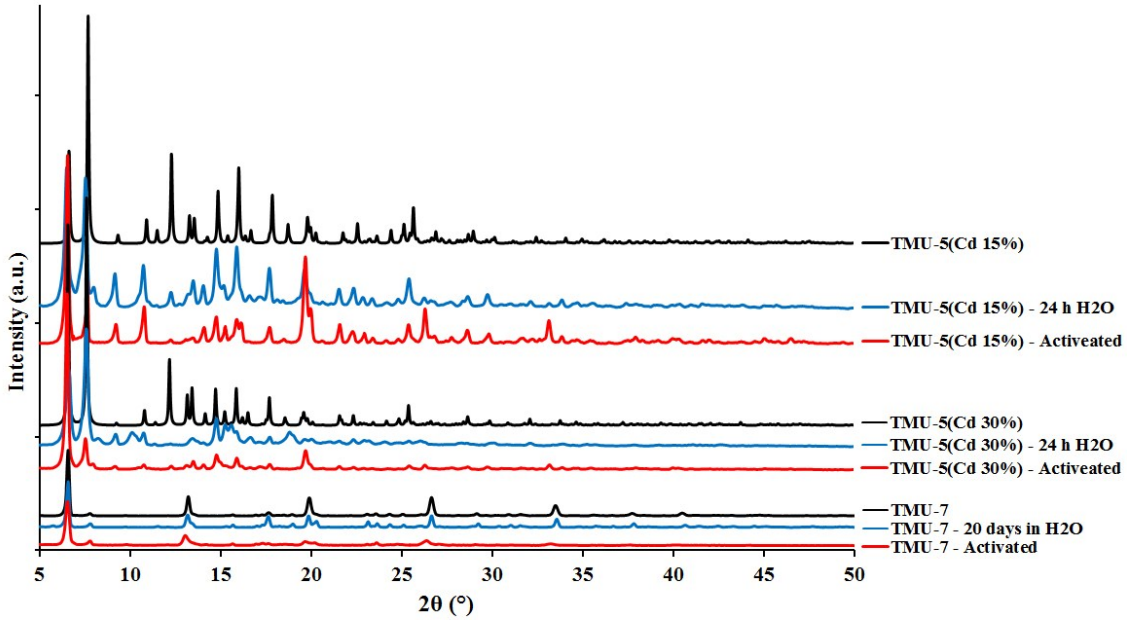

Fig. S6. Comparison of XRPD patterns for TMU-5(Cd 15%), TMU-5(Cd 30%) and TMU-7 after activate or immersing in H_2O.

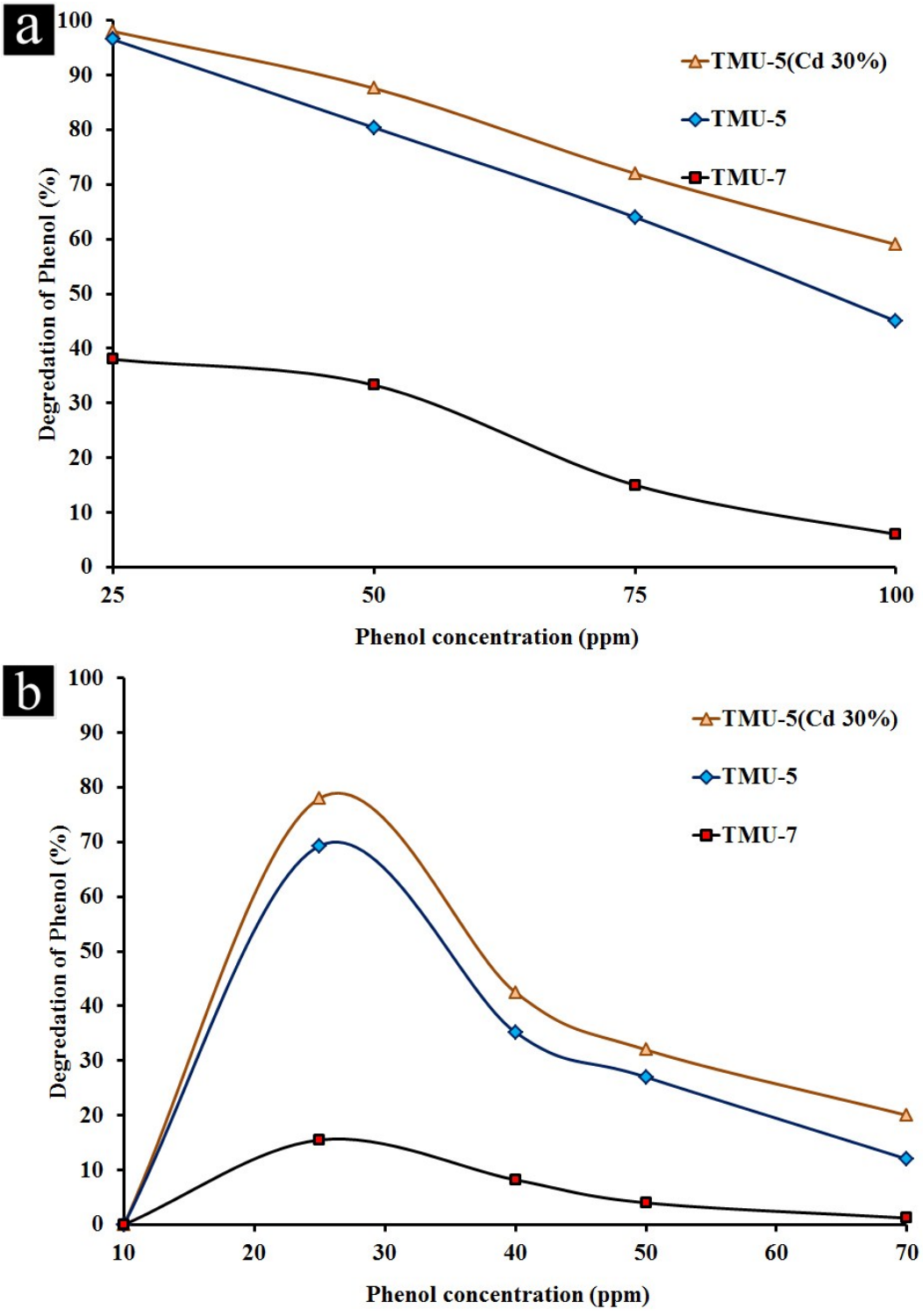

Fig. S7. Effect of phenol initial concentrations in presence of TMU-5, TMU-5(Cd 30%) and TMU-7 under a) UV and b) visible light for 2 h.

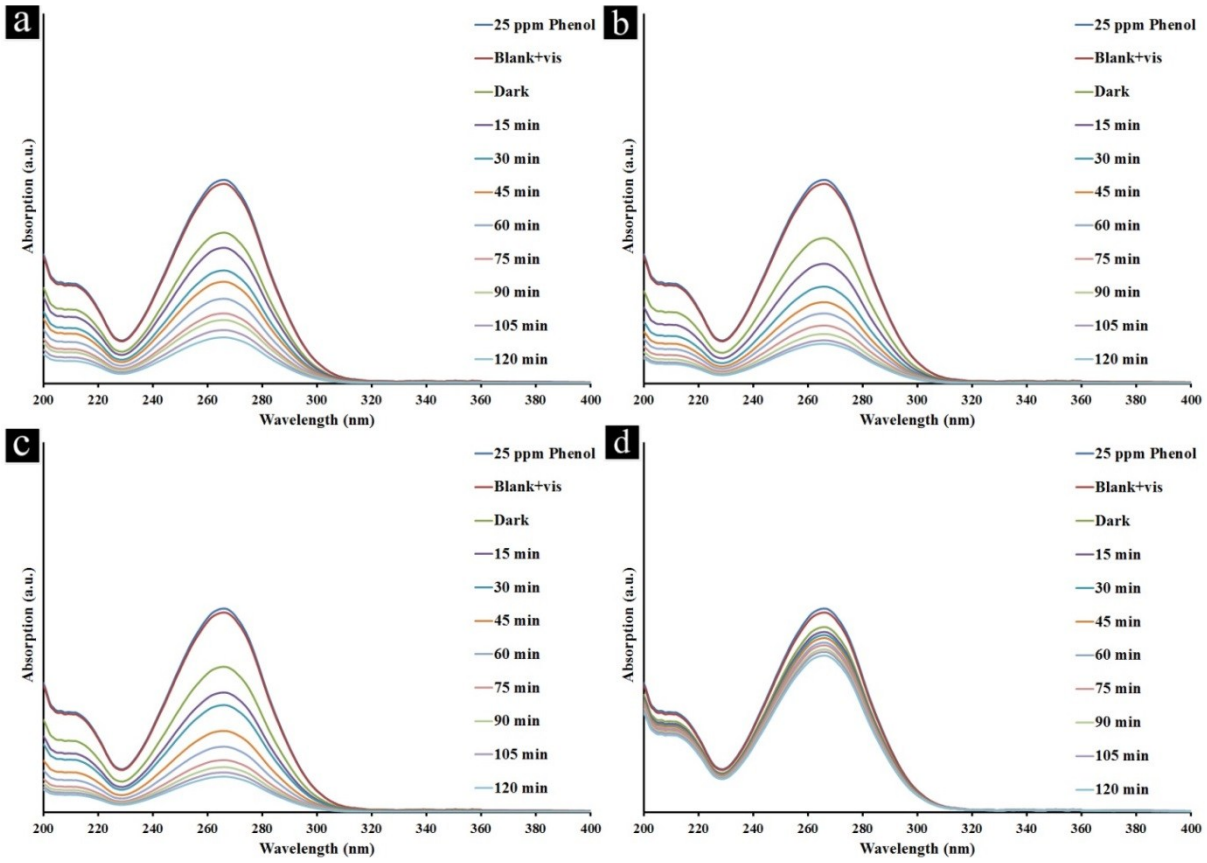

Fig. S8. Absorption spectra of a solution of 25 ppm phenol in the presence of a) TMU-5, b) TMU-5(Cd 15%) c) TMU-5(Cd 30%) and d) TMU-7 under visible light irradiation for 120 min.

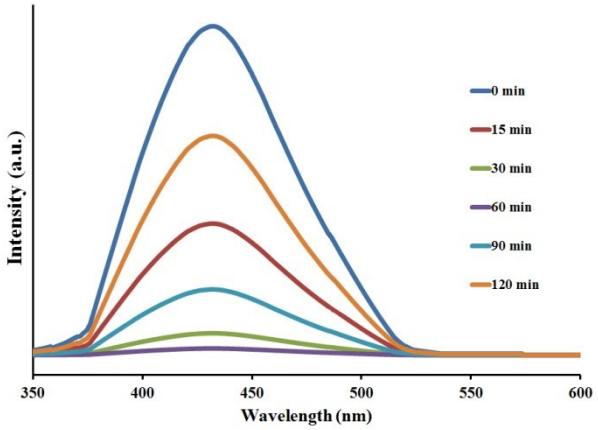

Fig. S9. Fuorescence spectra changes observed during UV illumination of 25 mg TMU-5(Cd 30%) in aqueous solution of terephthalic acid (4×10^{-4} M). (excitation at 320 nm).

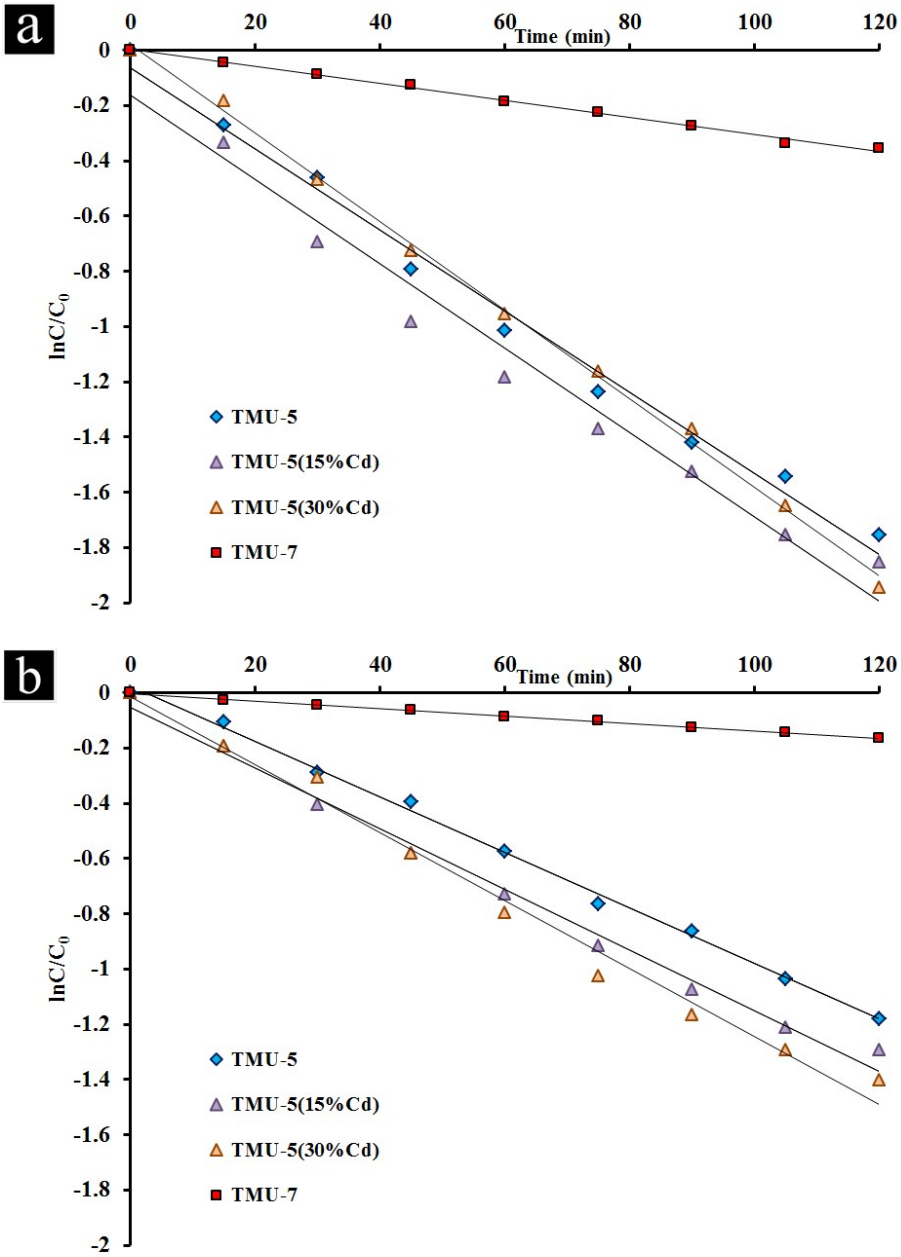

Fig. S10. Reaction kinetics of photodegradation of phenol.

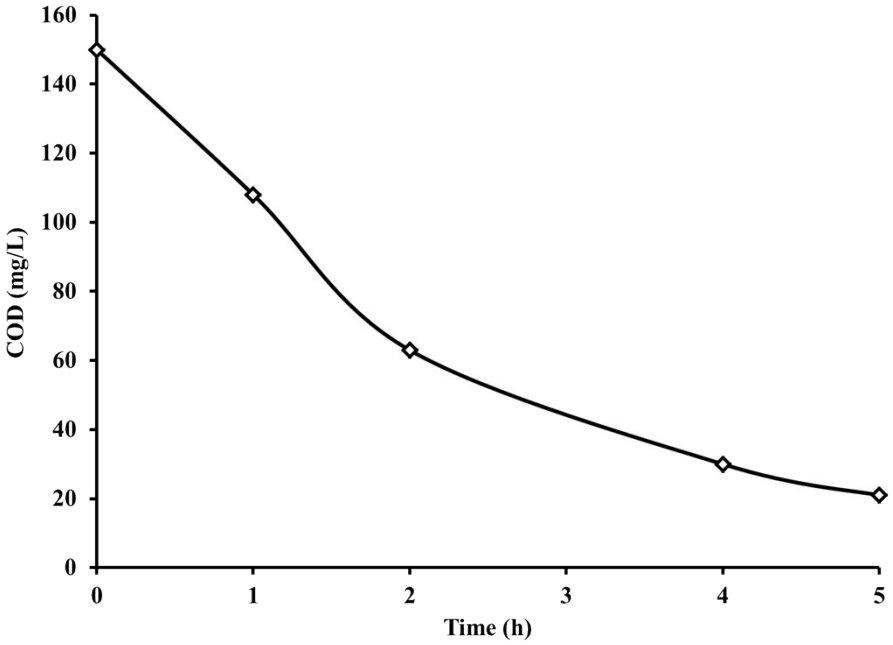

Fig. S11. Change of COD removal efficiency of TMU-5(Cd 30%) photpcatalyst in presence of phenol.

Table S1. Crystal data and structure refinement of $[Cd_{0.15}Zn_{0.85}(oba)(4\text{-}bpdh)_{0.5}]_n.1.5DMF$ (**TMU-5(Cd 15%)**), $[Cd_{0.3}Zn_{0.7}(oba)(4\text{-}bpdh)_{0.5}]_n$ (**TMU-5(Cd 30%)**) and $[Cd(oba)(4\text{-}bpdh)]_n.1DMF$ (**TMU-7**).

Identification code	**TMU-5(Cd 15%)**	**TMU-5(Cd 30%)**	**TMU-7**
Empirical formula	$C_{22.50}H_{18.50}Cd_{0.15}N_{2.50}O_{5.50}Zn_{0.85}$	$C_{21}H_{15}Cd_{0.30}N_2O_5Zn_{0.70}$	$C_{31}H_{29}CdN_5O_6$
Formula weight	484.32	454.83	679.99
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	P2(1)/n
Unit cell dimensions	a = 26.982(13) Å	a = 27.221(7) Å	a = 9.5711(8) Å
	b = 8.033(4) Å	b = 8.1040(19) Å	b = 12.438(1) Å
	c = 23.293(12) Å	c = 23.537(6) Å	c = 26.565(2) Å
	β = 98.992(9)°	β = 98.906(4)°	β = 90.493(4)°
Cell volume, $Å^3$	4987(4)	5130(2)	3162.4(5)
Z value	8	8	4
Density (calc.) ($g.cm^{-3}$)	1.290	1.178	1.428
Absorption coefficient	1.004 mm^{-1}	0.953 mm^{-1}	0.740 mm^{-1}
F(000)	1982	1843	1384
θ range for data collection	2.15 to 28.59°	2.73 to 27.50°	1.81 to 26.00°
Reflections collected/unique	15225/5969 [R_{int} = 0.0621]	15462/5813 [R_{int} = 0.0526]	6510/6209 [R(int) = 0.0000]
Max. and min. transmission	0.9063 and 0.8640	0.9277 and 0.6473	0.9297 and 0.8367
Data/restraints/parameters	5969/54/308	5813/0/272	6209/26/311
Goodness-of-fit on F^2	1.079	0.952	1.241
Final R indices (I>2.00σ(I))	R_1 = 0.0821, wR_2 = 0.2028	R_1 = 0.0503, wR_2 = 0.1357	R1 = 0.0673, wR2 = 0.1545
R indices (all data)	R_1 = 0.1215, wR_2 = 0.2243	R_1 = 0.0718, wR_2 = 0.1432	R1 = 0.0700, wR2 = 0.1558
Largest diff. Peak, hole	0.988 and -0.746 $e.A^{-3}$	0.414 and -0.411 $e.A^{-3}$	1.170 and -1.660 $e.Å^{-3}$

Table S2. Selected Bond Lengths (Å) and Angles (deg) for **TMU-5(Cd 15%)**, **TMU-5(Cd 30%)** and **TMU-7**

TMU-5(Cd 15%)			
Cd(1)-N(1)	2.026(4)	O(2)#1-Cd(1)-O(1)	159.62(14)
Cd(1)-O(2)#1	2.028(4)	N(1)-Cd(1)-O(5)#2	103.22(16)
Cd(1)-O(1)	2.037(3)	O(2)#1-Cd(1)-O(5)#2	87.94(17)
Cd(1)-O(5)#2	2.038(4)	O(1)-Cd(1)-O(5)#2	87.85(16)
Cd(1)-O(4)#3	2.038(4)	N(1)-Cd(1)-O(4)#3	97.44(16)
Cd(1)-Zn(1)#1	2.9305(13)	O(2)#1-Cd(1)-O(4)#3	89.57(17)
N(1)-Zn(1)#1	2.026(4)	O(1)-Cd(1)-O(4)#3	87.37(16)
O(1)-Zn(1)#1	2.037(3)	O(5)#2-Cd(1)-O(4)#3	159.31(15)
O(2)-Zn(1)#1	2.028(4)	N(1)-Cd(1)-Zn(1)#1	172.58(11)
O(4)-Zn(1)#4	2.038(4)	O(2)#1-Cd(1)-Zn(1)#1	85.12(10)
O(5)-Zn(1)#5	2.038(4)	O(1)-Cd(1)-Zn(1)#1	74.55(10)
N(1)-Cd(1)-O(2)#1	100.19(15)	O(5)#2-Cd(1)-Zn(1)#1	82.03(10)
N(1)-Cd(1)-O(1)	100.19(15)	O(4)#3-Cd(1)-Zn(1)#1	77.30(11)
		C(8)-O(3)-C(5)	118.6(5)
TMU-5(Cd 30%)			
Cd(1)-O(2)#1	2.048(4)	N(1)-Cd(1)-O(4)#2	97.30(14)
Cd(1)-N(1)	2.058(3)	O(2)#1-Cd(1)-O(5)#3	88.48(14)
Cd(1)-O(4)#2	2.067(3)	N(1)-Cd(1)-O(5)#3	103.14(15)
Cd(1)-O(5)#3	2.068(3)	O(4)#2-Cd(1)-O(5)#3	159.48(16)
Cd(1)-O(1)	2.077(3)	O(2)#1-Cd(1)-O(1)	159.04(16)
Cd(1)-Zn(1)#1	2.969(4)	N(1)-Cd(1)-O(1)	100.03(15)
O(1)-Zn(1)	2.054(3)	O(4)#2-Cd(1)-O(1)	87.12(14)

N(1)-Zn(1)	2.061(4)	O(5)#3-Cd(1)-O(1)	87.69(15)
O(2)-Zn(1)#1	2.071(4)	O(2)#1-Cd(1)-Cd(1)#1	85.18(14)
O(4)-Zn(1)#5	2.059(4)	N(1)-Cd(1)-Zn(1)#1	171.77(16)
O(5)-Zn(1)#6	2.074(4)	O(4)#2-Zn(1)-Cd(1)#1	77.10(13)
O(2)#1-Cd(1)-N(1)	100.91(14)	O(5)#3-Zn(1)-Cd(1)#1	82.39(13)
O(2)#1-Cd(1)-O(4)#2	89.31(16)	O(1)-Cd(1)-Zn(1)#1	73.88(11)
		C(5)-O(3)-C(8)	117.9(3)
TMU-7			
Cd(1)-O(3)#1	2.239(7)	O(4)#2-Cd(1)-N(1)	95.2(2)
Cd(1)-O(4)#2	2.249(6)	O(2)-Cd(1)-N(1)	89.5(2)
Cd(1)-O(2)	2.283(6)	O(3)#1-Cd(1)-N(4)#3	86.3(2)
Cd(1)-N(1)	2.307(6)	O(4)#2-Cd(1)-N(4)#3	89.4(2)
Cd(1)-N(4)#3	2.314(6)	O(2)-Cd(1)-N(4)#3	92.3(2)
Cd(1)-O(1)	2.531(7)	N(1)-Cd(1)-N(4)#3	175.0(3)
O(3)#1-Cd(1)-O(4)#2	114.5(3)	O(3)#1-Cd(1)-O(1)	98.1(3)
O(3)#1-Cd(1)-O(2)	152.1(3)	O(4)#2-Cd(1)-O(1)	145.6(2)
O(4)#2-Cd(1)-O(2)	93.3(2)	O(2)-Cd(1)-O(1)	54.3(2)
O(3)#1-Cd(1)-N(1)	89.9(2)	N(1)-Cd(1)-O(1)	95.7(3)
		C(19A)-O(5A)-C(26A)	116.6(15)

Symmetry transformations used to generate equivalent atoms for **TMU-5(Cd 15%)**: #1 -x,-y,-z #2 x,-y+1,z-1/2 #3 -x,y-1,-z+1/2 #4 -x,y+1,-z+1/2 #5 x,-y+1,z+1/2 #6 -x+1/2,-y+3/2,-z; for **TMU-5(Cd 30%):**#1 -x,-y+1,-z+1 #2 -x,y-1,-z+3/2 #3 x,-y+2,z-1/2 #4 -x+1/2,-y+5/2,-z+1 #5 -x,y+1,-z+3/2 #6 x,-y+2,z+1/2; for **TMU-7:** #1 -x+1/2,y-1/2,-z+1/2; #2 x+1/2,-y+3/2,z-1/2; #3 x-1,y-1,z; #4 x+1,y+1,z; #5 -x+1/2,y+1/2,-z+1/2; #6 x-1/2,-y+3/2,z+1/2.

Table S3. Kinetics equation of photocatalytic degradation of 50 ppm of phenol solution under UV light.

Photocatalysts	Order(s)	$K_1(min^{-1})$	R_0	R_1	R_2	$t_{1/2}$ (min)
TMU-5	$\ln (C_t/C_0)= -0.0147t - 0.0634$	0.0147	0.8917	0.9896	0.9878	47.1
TMU-5(Cd 15%)	$\ln (C_t/C_0)= -0.0152t - 0.1632$	0.0152	0.8054	0.9928	0.9728	45.6
TMU-5(Cd 30%)	$\ln (C_t/C_0)= -0.016t + 0.0211$	0.016	0.9345	0.9977	0.9126	43.3
TMU-7	$\ln (C_t/C_0)= -0.0031t + 0.0028$	0.0031	0.995	0.9961	0.9697	223.5

Table S4. Kinetics equation of photocatalytic degradation of 25 ppm of phenol solution under visible light.

Photocatalysts	Order(s)	$K_1(min^{-1})$	R_0	R_1	R_2	$t_{1/2}$ (min)
TMU-5	$\ln (C_t/C_0)= -0.01t + 0.0241$	0.01	0.9754	0.9971	0.9689	69.3
TMU-5(Cd 15%)	$\ln (C_t/C_0)= -0.011t - 0.0516$	0.011	0.9329	0.9915	0.9896	63
TMU-5(Cd 30%)	$\ln (C_t/C_0)= -0.0123t - 0.0127$	0.0123	0.9064	0.9876	0.9825	56.3
TMU-7	$\ln (C_t/C_0)= -0.0014t + 0.0029$	0.0014	0.995	0.9981	0.9697	495