Supporting Information

Efficient photocatalytic degradation of methyl violet by two new 3D

MOFs directed by different carboxylate spacers

Materials and Method

All the reagents to perform synthesis were obtained from commercial sources and were used without further purification. Powder X-ray diffraction (PXRD) data were collected using Bruker ADVANCE X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) at 50 kV, 20 mA with a scanning rate of 6°/min and a step size of 0.02°. Fourier transform infrared (FT-IR) spectra for both the MOFs as KBr discs were recorded on Nicolet Impact 750 FTIR in the range of 400-4000 cm^{-1}. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere from room temperature to 900 °C at a heating rate of 10 °C min^{-1}. The photocatalytic investigations were carried out using Shimadzu UV-Vis 2501PC recording spectrophotometer.

X-ray Crystallography

The single crystal X-ray diffraction data for both the MOFs were collected on a Bruker SMART APEX diffractometer which was equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å) by using an ω-scan technique. The structures were solved by direct method (SHLEXS-2014) and refined using the full-matrix least-square procedure based on F^2 (Shelxl-2014). All the hydrogen atoms were generated geometrically and refined isotropically using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details and selected bond dimensions for **1** and **2** are listed in Tables S1 and S2, respectively. CCDC numbers: 2021620 and 2021621.

Photocatalytic Method

The finely grounded sample of **1** or **2** (50 mg) was dispersed in 50 mL aqueous solution of methyl violet (MV) (10 mg/L) and the mixture was stirred in dark for 30 min for confirming the establishment of adsorption-desorption equilibrium. The photocatalytic degradation of MV was conducted on UV-400 type photochemical

reactor having 100 W mercury lamp (mean wavelength 365 nm). Aliquots of 5.0 mL were taken out at specified time intervals and separated through centrifugation and then subsequentlythe intensity of electronic absorption band of MV was recorded using UV−visible spectrophotometer. Additionally, a control experiment was also conducted under the identical conditions without the incorporation of MOF based catalysts **1** or **2** in the aqueous solution of MV.

Synthesis of [Zn(BDC-OH$_2$)(bib)] (1)

A mixture of H$_2$BDC-OH$_2$ (0.10 mmol, 0.020 g), bib (0.10 mmol, 0.022 g), Zn(NO$_3$)$_2$·6H$_2$O (0.15 mmol, 0.047 g) and 10 mL of DMF/H$_2$O (v/v=1:1) was stirred for 30 min and then transferred and sealed in a 25-mL Teflon-lined reactor and heated to 120 °C for 72 h, and then cooled to room temperature at a rate of 5 °C/h. Colorless block crystals of **1** were obtained in 66 % yield based on bib. Calcd (%) for **1**, C, 51.79; H, 4.78; N, 12.08; Found C, 51.65; H, 4.82; N, 12.13. IR: 3588(m); 2593(m); 1634 (v); 1580(m); 1499(v); 1431(m); 1371(v); 1295(m); 1228(m); 1160(v); 842(m); 782(v).

Synthesis of [Cd$_3$(BTC)$_2$(bib)(DMF)$_3$] (2)

A mixture of H$_3$BTC (0.10 mmol, 0.021 g), bib (0.10 mmol, 0.020 g), Cd(NO$_3$)$_2$·4H$_2$O (0.15 mmol, 0.027 g) and 10 mL of DMF/H$_2$O (v/v=1:1) was stirred for 30 min and then transferred and sealed in a 25-mL Teflon-lined reactor and heated to 120 °C for 72 h, and then cooled to room temperature at a rate of 5 °C/h. Colorless block crystals of **2** were obtained in 53 % yield based on bib. Calcd (%) for **2**, C, 54.79; H, 4.23; N, 5.96; Found C, 54.05; H, 4.12; N, 5.33. IR: 3405(v); 2925(m); 1647(v); 1580(m); 1530(v); 1390(vs); 1093(m); 1019(m); 884(m); 775(v).
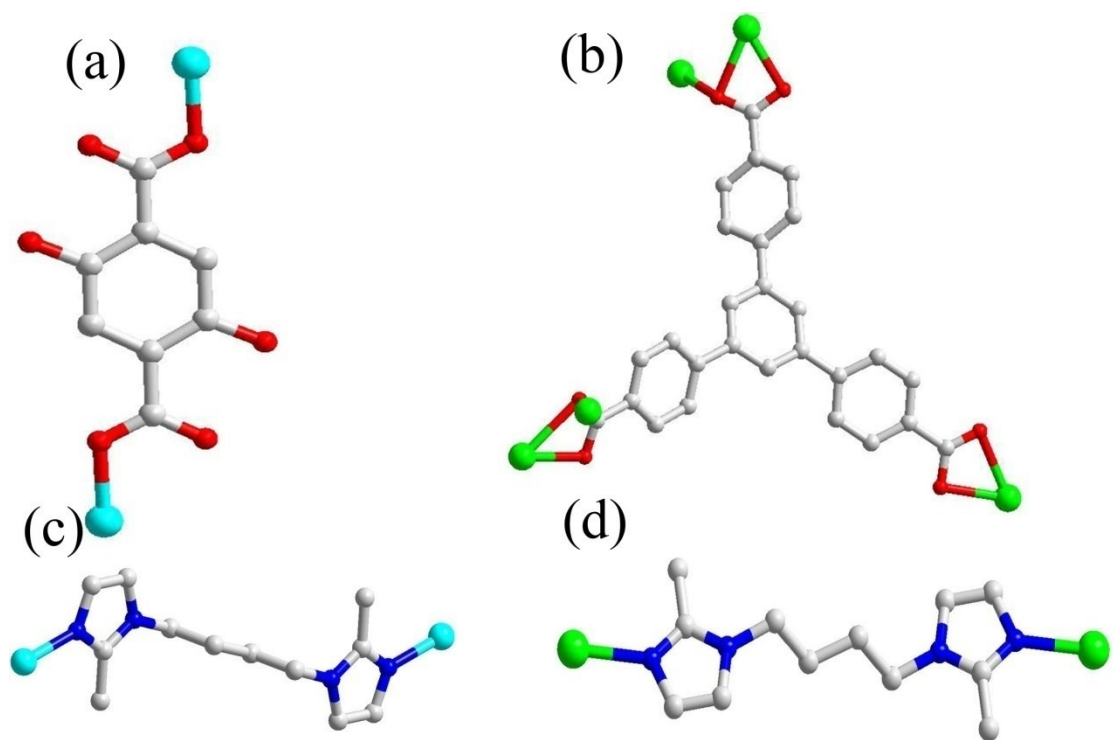
Scheme S1 the different coordination modes of carboxylate ligands and conformations of bib linker in this work.
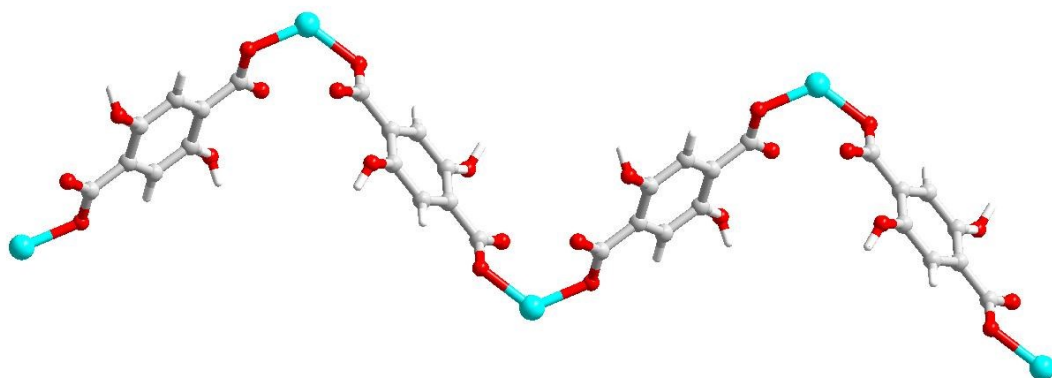

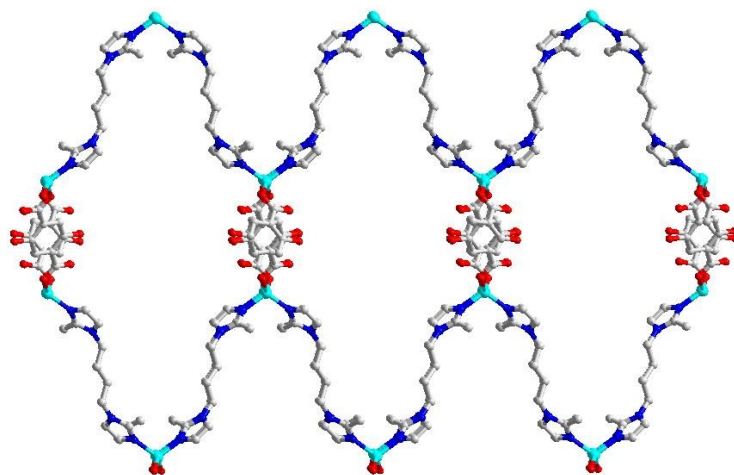Figure S1 view of the 1D chain constructed by BDC and Zn centers.

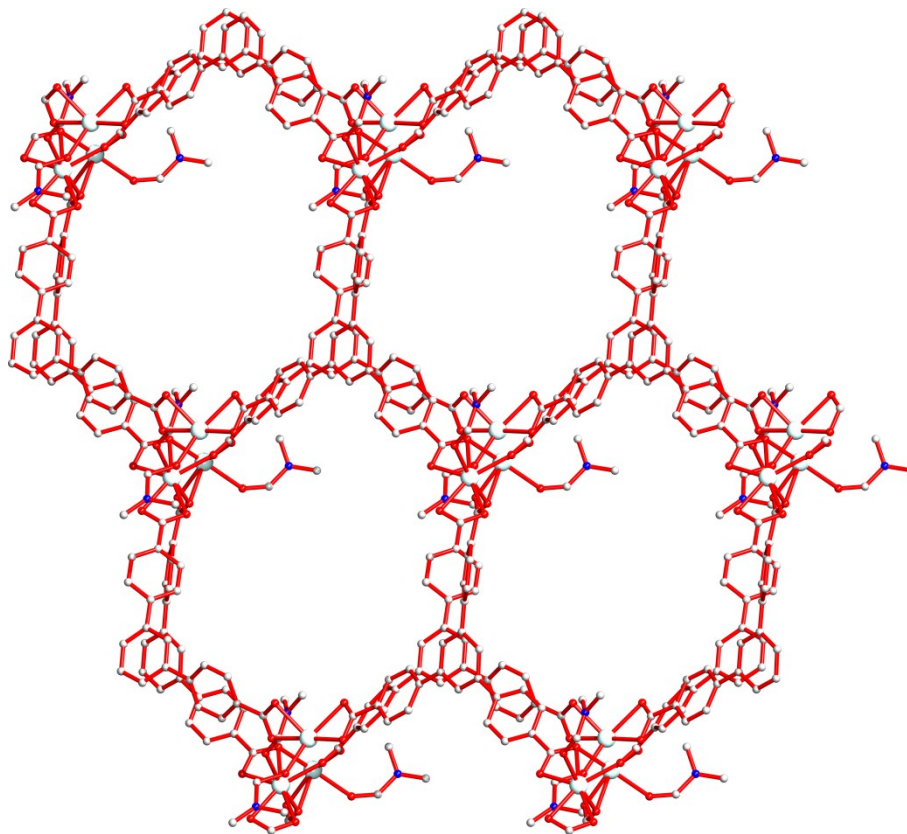Figure S2 view of the 3D network along the *bc*-plane in **1**.

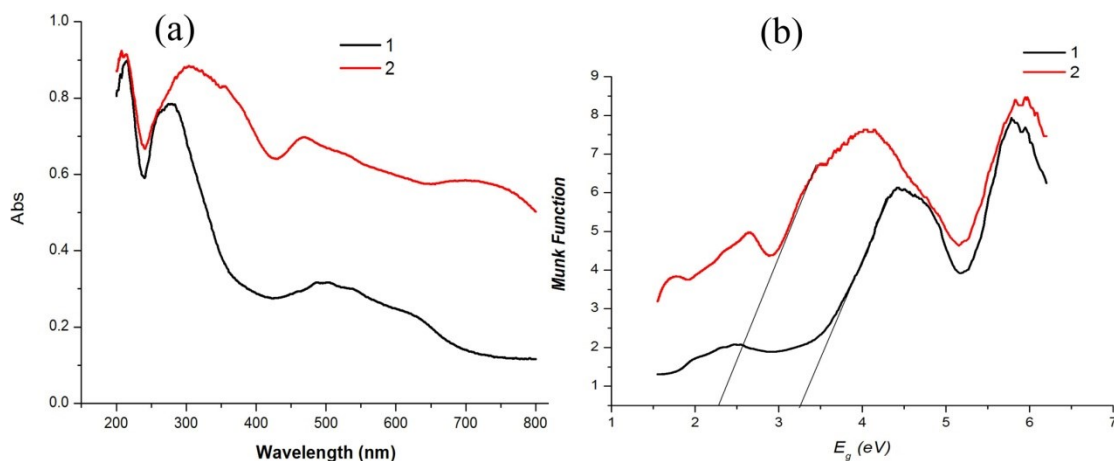Figure S3 the porous 3D network constructed by BTC and Cd center in **2**.

Figure S4 Solid-state optical diffuse-reflection spectra of **1–2** derived from diffuse reflectance data at ambient temperature.

IR, TGA and PXRD analysis

The IR spectra of **1** and **2** exhibited asymmetric and symmetric stretching vibrations of the coordinated carboxylate groups from the ligands at 1431–1634 and 1530–1647 cm^{-1}, respectively [20] (Figure S5). The [v_{as}(COO)–(COO)] values of them were calculated to be in the range of 201 and 117 cm^{-1}, indicating that the carboxyl groups of BDC and BTC ligands adopt various coordination modes (Scheme S1). There is no strong absorption band around 1700 cm^{-1} in **1** and **2**, suggesting that the –COOH groups in the carboxylate ligands are completely deprotonated [2]. The PXRD patterns of **1** and **2** measured at room temperature diffraction are consistent with the simulated ones, indicating that these compounds have pure phase (Figure S6).

 TGA was conducted to investigate the thermal stability of **1** and **2** (Fig. S). For 1, it can be stabilized up to 350°C, and then start to collapse because of decomposition of the organic ligands (calcd 80.66%). For 2, the first weight losses of 12.98% (100–270°C) correspond to the loss of 3 coordinated DMF molecules (calcd 13.31%). The last significant weight loss phenomenon occurred in the temperature range of 360–710°C, in which the product lost 73.66% (calcd 71.82 %), total quality due to the decomposition of the bib and BTC ligands. All the above results suggest **1** and **2** have thermal stability (Figure S7).
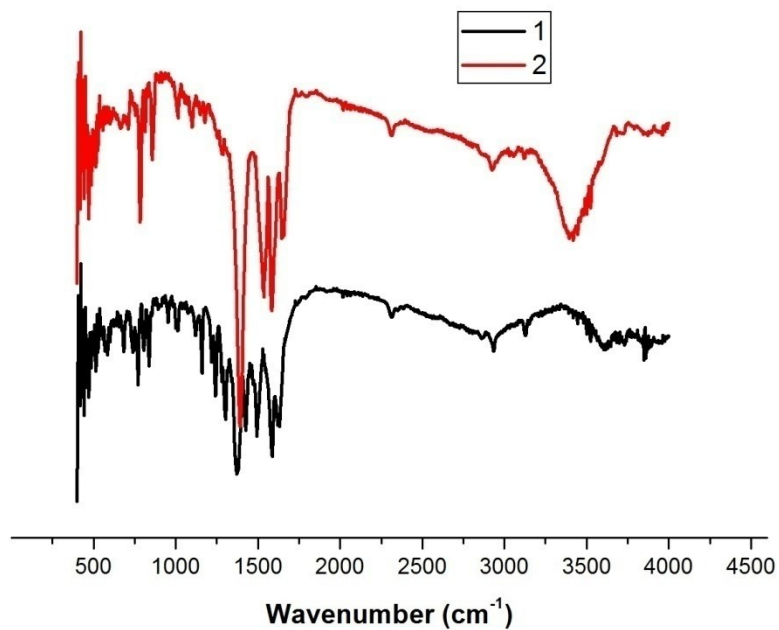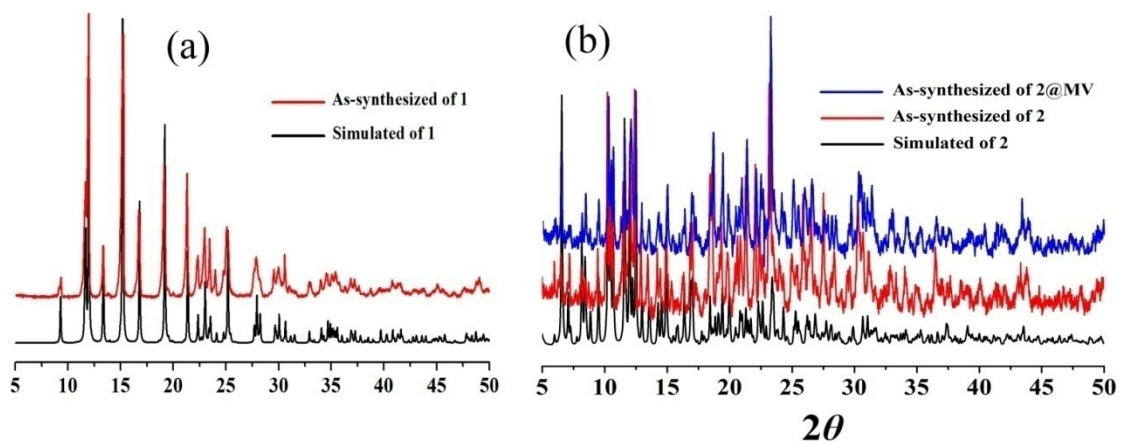
Figure S5 view of the TGA in 1 and 2.

Figure S6 (a) Powder XRD patterns of the simulated diagram from single crystal data of (black), synthesized samples (red), after a photocatalysis process for **1** and **2**, respectively.
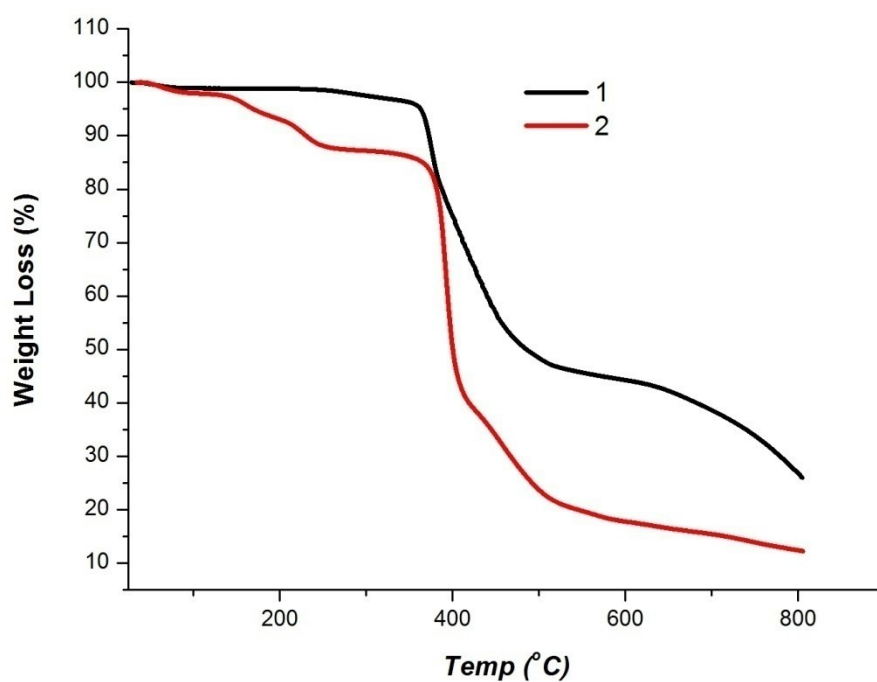
Figure S7 view of the TAG.
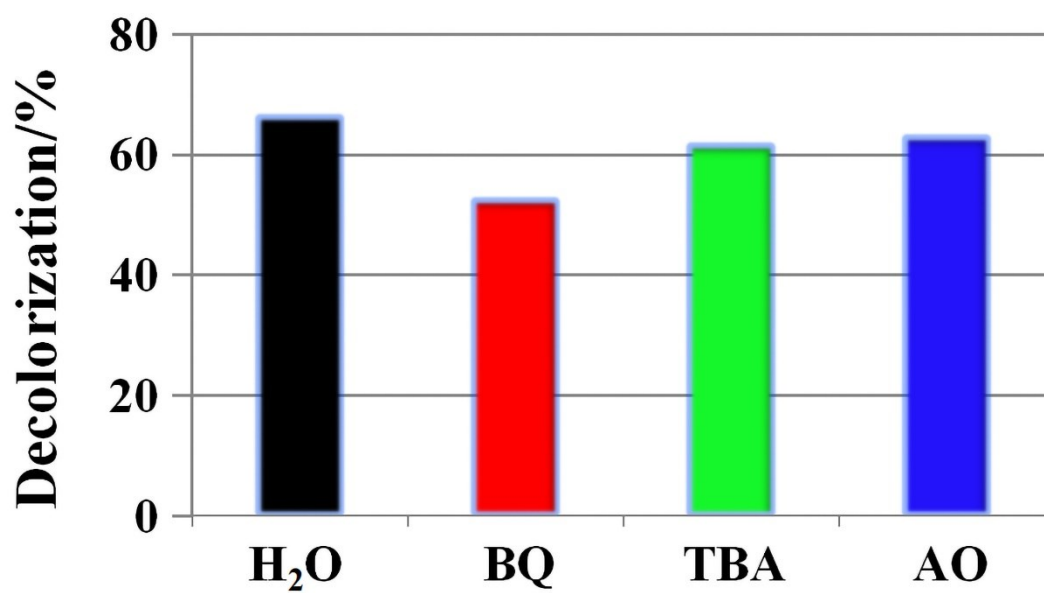

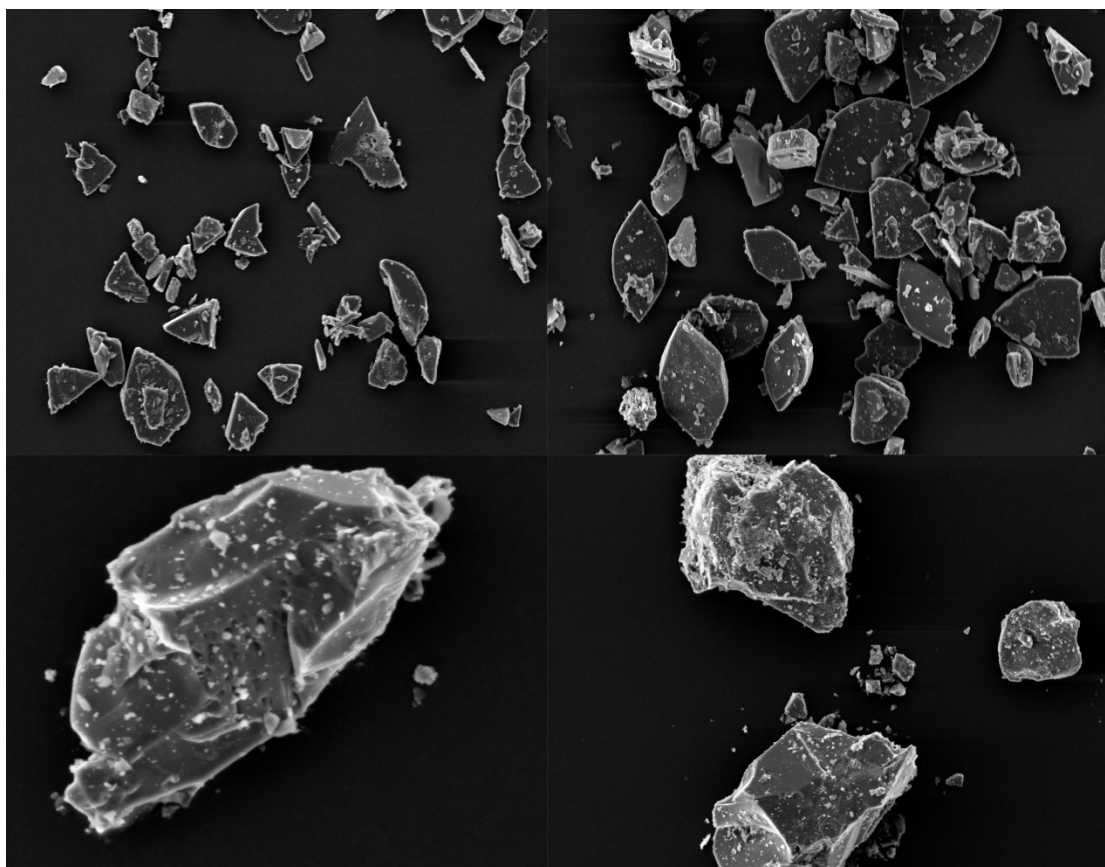Figure S8 the plot as a function of deduced mechanism of the degradation of MV by **1.**

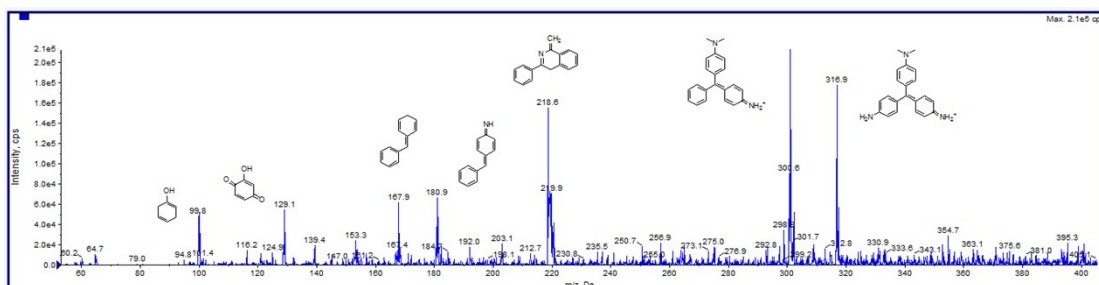Figure S9 SEM for **1** and **2** before and after photocatalysis process.

Fig. S10 MS fragmentation pattern of MV dye degraded under irradiation.

Table S1. Crystallographic data and structure refinement details for Complexes 1-2

Parameter	1	2
Formula weight	463.78	1645.57
Crystal system	Monoclinic	Triclinic
Space group	*P2/n*	$P\bar{1}$
Crystal Color	Colorless	Colorless
a, Å	9.2408(12)	14.2908(5)
b, Å	9.5080(13)	15.7878(5)
c, Å	12.6724(18)	18.8266(7)
α, °	90	97.294(3)
β, °	91.446(2)	92.079(3)
γ, °	90	109.017(3)
V, Å^3	1113.1(3)	3969.7(3)
Z	2	2
ρ_{calcd}, g/cm^3	1.384	1.377
μ, mm^{-1}	1.140	6.905
F(000)	480	1664
θ Range, deg	2.7-27.6	3.5-66.6
Reflection Collected	6549	22447
Independent reflections (R_{int})	0.037	0.079
Reflections with $I > 2\sigma(I)$	2536	13866
Number of parameters	143	946
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0475, 0.1183	0.0793, 0.2047
R_1, wR_2 (all data)**	0.0764, 0.1324	0.1034, 0.2320

* $R = \sum(F_o - F_c)/\sum(F_o)$, ** $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$.

Table S2. Selected bond distances (Å) and angles (deg) for **1-2**

1			
Zn(1)-O(3)	1.953(3)	Zn(1)-N(1)	2.017(3)
Zn(1)-O(3)#1	1.953(3)	Zn(1)-N(1)#1	2.017(3)

2			

Cd(1)-O(1)	2.378(7)	Cd(1)-O(2)	2.318(5)
Cd(1)-O(13)	2.288(8)	Cd(1)-O(5)#1	2.299(6)
Cd(1)-O(7)#1	2.378(6)	Cd(1)-O(9)#2	2.607(6)
Cd(1)-O(10)#2	2.339(7)	Cd(2)-O(6)	2.169(6)
Cd(1)-O(2)	2.434(5)	Cd(1)-O(8)	2.299(7)
Cd(2)-O(14)	2.357(10)	Cd(2)-N(1)	2.214(9)
Cd(2)-O(9)#3	2.309(8)	Cd(3)-O(11)	2.437(8)
Cd(3)-O(12)	2.322(8)	Cd(3)-O(15)	2.327(19)
Cd(3)-O(15A)	2.08(3)	Cd(3)-N(3)	2.243(9)
Cd(3)-O(3)#4	2.341(7)	Cd(3)-O(4)#4	2.355(8)

1

O(3)-Zn(1)-N(1)	101.90(11)	O(3)-Zn(1)-O(3)#1	119.68(12)
O(3)-Zn(1)-N(1)#1	112.64(11)	O(3)#1-Zn(1)-N(1)	112.64(11)
N(1)-Zn(1)-N(1)#1	107.94(11)	O(3)#1-Zn(1)-N(1)#1	101.90(11)

2

O(1)-Cd(1)-O(2)	55.1(2)	O(1)-Cd(1)-O(13)	88.5(3)
O(1)-Cd(1)-O(5)#1	140.5(2)	O(1)-Cd(1)-O(7)#1	100.4(2)
O(1)-Cd(1)-O(9)#2	138.3(3)	O(1)-Cd(1)-O(10)#2	85.4(3)
O(2)-Cd(1)-O(13)	102.6(2)	O(2)-Cd(1)-O(5)#1	89.87(19)
O(2)-Cd(1)-O(7)#1	85.99(18)	O(2)-Cd(1)-O(9)#2	162.6(2)
O(5)#1-Cd(1)-O(7)#1	93.8(2)	O(7)#1-Cd(1)-O(10)#2	87.8(2)
O(6)-Cd(2)-O(7)	100.9(2)	O(6)-Cd(2)-O(8)	155.0(2)
O(6)-Cd(2)-O(14)	87.4(3)	O(6)-Cd(2)-N(1)	108.2(3)
O(7)-Cd(2)-O(8)	54.9(2)	O(7)-Cd(2)-O(14)	86.3(3)
O(7)-Cd(2)-N(1)	150.8(3)	O(8)-Cd(2)-N(1)	95.9(3)
O(14)-Cd(2)-N(1)	92.6(4)	O(9)#3-Cd(2)-N(1)	99.7(3)
O(11)-Cd(3)-O(12)	55.1(3)	O(11)-Cd(3)-O(15)	141.1(5)
O(11)-Cd(3)-N(3)	90.9(3)	O(3)#4-Cd(3)-O(11)	89.5(3)
O(4)#4-Cd(3)-O(11)	128.3(3)	O(12)-Cd(3)-O(15)	88.4(6)
O(12)-Cd(3)-N(3)	89.8(3)	O(15)-Cd(3)-N(3)	103.3(5)
O(3)#4-Cd(3)-O(15)	103.5(5)	O(4)#4-Cd(3)-O(15)	87.6(5)

Symmetry Codes: **For 1**: #1= 1/2-x, y, 3/2-z. **For 2**: #1= 1+x, 1+y, z; #2 = 1+x, 2+y, z; #3 = x, 1+y, z; #4 = -2+x, -1+y, -1+z.

Table S3 The pseudo first-order rate constants and the corresponding square of the correlation coefficients for the photocatalytic degradation reactions

Material	MV

	k (min^{-1})	R^2
blank	0.00607(2)	0.99588
1	0.0272(10)	0.99182
2	0.0431(2)	0.98329
2+BQ	0.0173(6)	0.98862
2+TBA	0.0474(8)	0.98733
2+AO	0.0494(6)	0.99478