Supporting Information

A new Zn(II)-based 3D metal–organic framework with uncommon *sev* topology and its photocatalytic property for the degradation of organic dyes

Materials and Methods

General Considerations

All the chemicals were purchased from commercial sources and used without further purification. The powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer that was equipped 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°. The simulated powder X-ray diffraction patterns for **1** were obtained using Mercury 2.0 software. The FT-IR spectra as KBr pellet were recorded using a Nicolet Impact 750 FTIR in the range of 400-4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere from room temperature to 650°C at a heating rate of 10°C min^{-1}, using a SDT Q600 thermogravimetricanalyzer.

X-ray Crystallography

The single crystal X-ray diffraction data was collected using Bruker SMART APEX diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å) by using the ω-scan technique. The intensities were corrected for absorption effects by using SADABS. The structure was solved by direct method (SHLEXS-2014) and refined using full-matrix least-squares procedures based on F^2 (SHELXL-2014).[1] All the hydrogen atoms were generated geometrically and refined isotropically using a riding model. The hydrogen atom of hydroxyl group has not been added due to its disordered.All non-hydrogen atoms were refined with anisotropic displacement parameters. The solvent molecules in **1** were highly disordered and hence their reflections were removed from the diffraction data using the SQUEEZE routine of PLATON.[2]For the compound, the volume fractions of disordered solvents in the pores could not be modeled in terms of atomic sites and were treated by using the MASK routine. The contents of the removed solvent region are not represented in the unit cell contents in the crystal data.The structure was then refined again by using the data generated. The atoms from one of the NDC ligands were treated as disordered refinement with half occupies. Thermogravimetric analyses suggested the presence of 1.7 DMF molecules for **1**.The topological network with the Schläfli symbol was analyzed by TOPOS 4.0.[3]CCDC number: 1898141.

Computational Details

The geometry optimizations were performed using the B3LYP exchange-correlation functional.[4] For all the atoms 6-31G** basis set was used for geometry optimization. All the calculations were performed using Gaussian 09 programme.[5]

Photocatalytic Measurement

The photocatalytic reactions were performed as follows: The sample of **1** (80 mg) was dispersed in 50 mL of an aqueous solution of methyl violet (MV)and rhodamine B (Rh B) (10 mg/L) under stirring in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium. The photocatalytic degradation of MV/Rh Bwasconducted on an XPA-7 type photochemical reactor equipped with a 100W mercurylamp (mean wavelength 365 nm) with light intensities at quartztube positions of 12.7 mW/cm^2.Aliquots of 5.0 mL was taken out atgiven time intervals and separated through centrifugation andthen subsequently analyzed by using a UV–visible spectrophotometer. A control experiment was also performed under the same conditions but without the addition of catalyst.

Gas Sorption Measurement

The nitrogen adsorption-desorption measurements were carried out at liquid nitrogen temperature (77K) by using an automatic volumetric adsorption equipment (Micromeritics, ASAP2020). Prior to the measurements, all the samples were degassed at 80 ºC for 10 h to remove the adsorbed impurities.

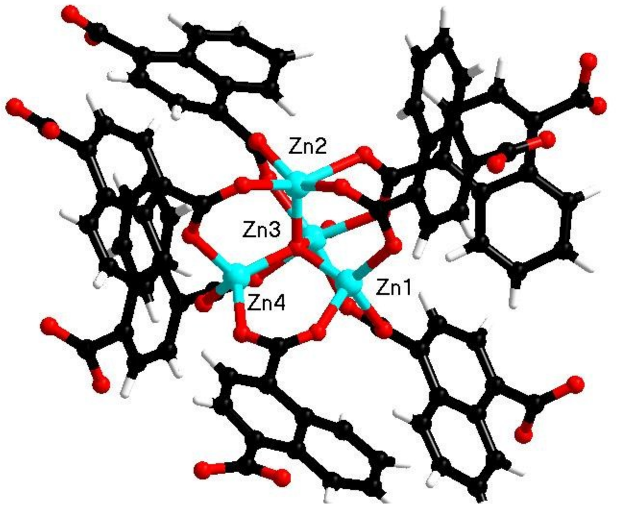
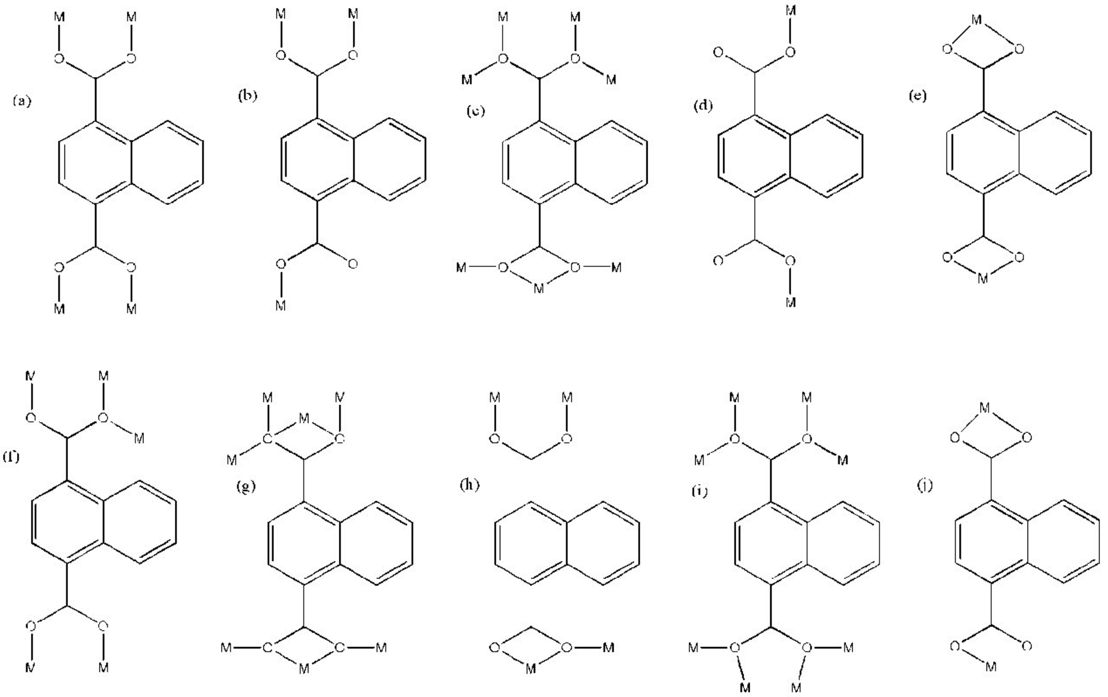


Fig. S1[Zn4(NDC)3.5(μ4-OH)(DMF)]unit showing the pentagonal antiprismaticsecondary buildingunits.



Scheme S1 Perspective view of the different potential coordination mode of NDCligandsinthe MOFs.

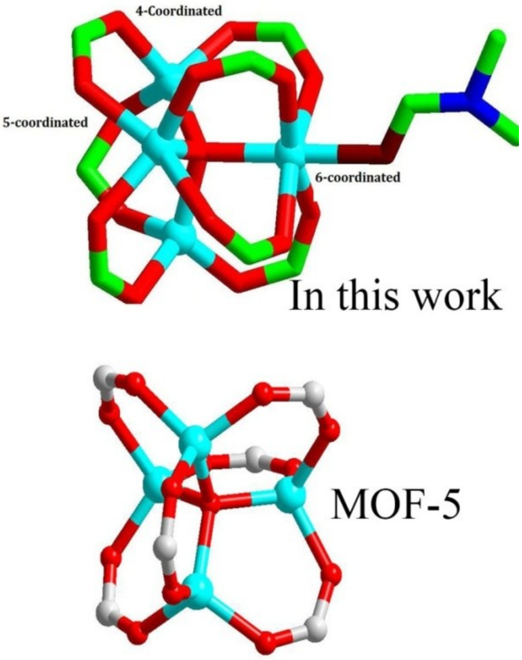


Fig. S2 View of the different cores between **1** and MOF-5.

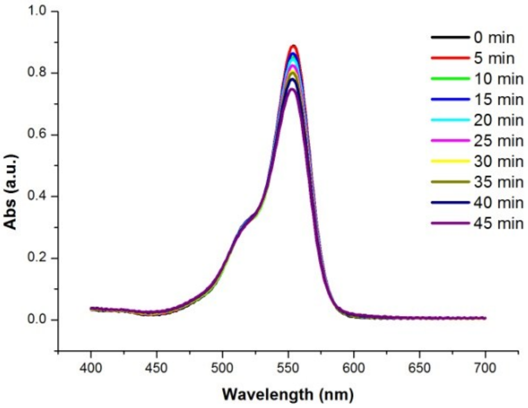


Fig.S3 The UV-vis absorption spectra of the MV solution in the presence of NDCduring the decomposition reaction.

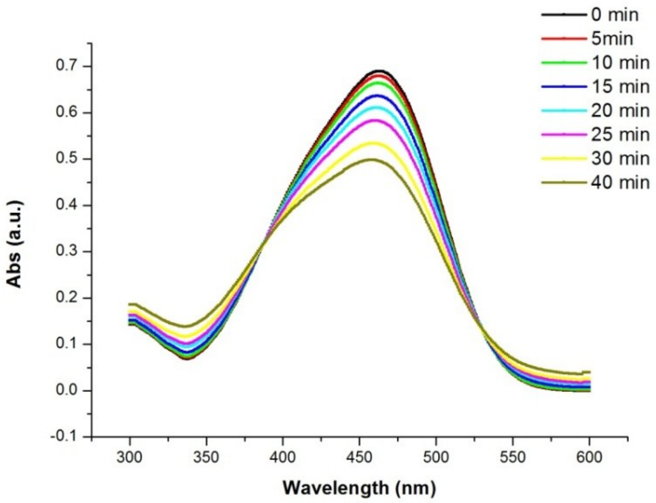
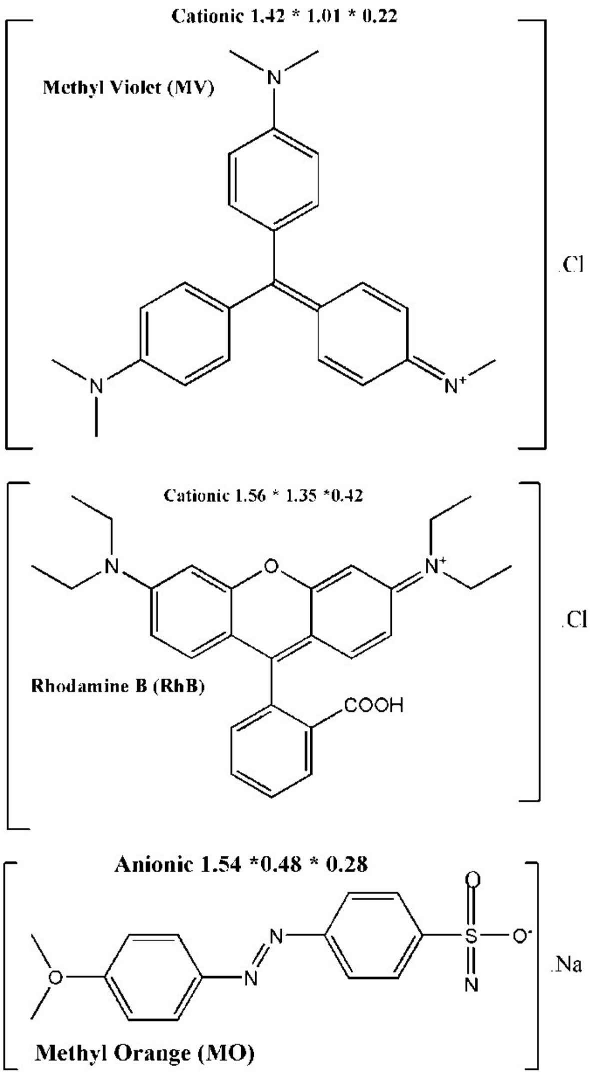


Fig.S4 The UV-vis absorption spectra of the MO solution during the decomposition reaction.



Scheme S2 The structure and nature of the organic pollutants in this study.

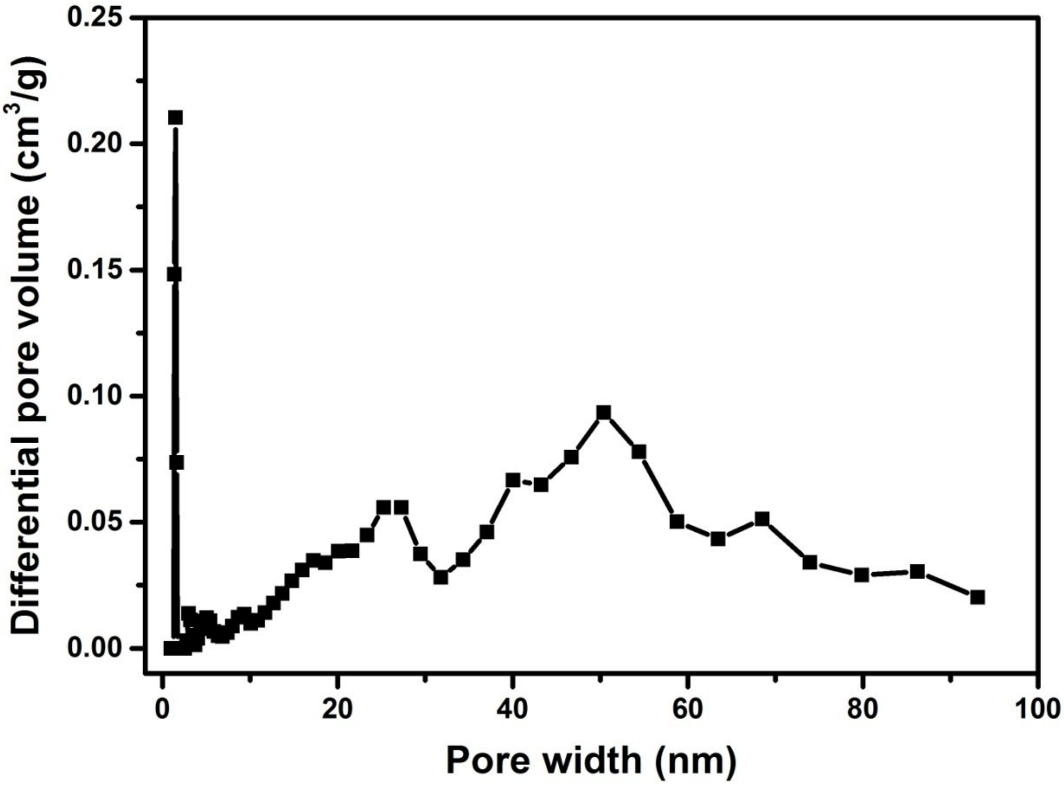


Fig. S5 The pore-size distribution of **1**.

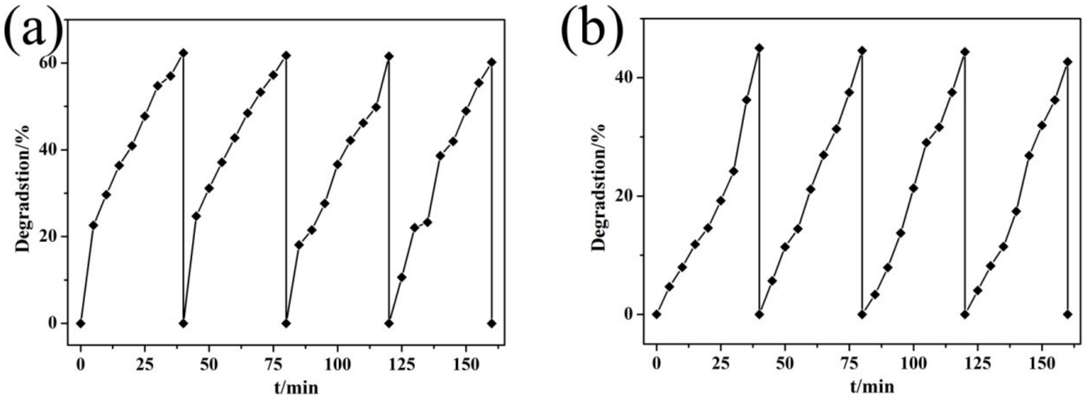


Fig.S6 Recycling experiments using **1**for the photocatalytic degradation of MV (a)and RhB (b) under UV irradiation.

IR spectra

The IR spectra of **1** are determined in the frequency range of 500–4000 cm^{-1}, as shown in Fig. S5. Thestrong peaks at 1620 and 1440 cm^{-1}may attribute to the asymmetric andsymmetric vibrations of the carboxyl group, respectively. Thepresence of the characteristic bands at*ca*. 1360 and 1073 cm^{-1}suggests the $\nu_{C–N}$ stretching vibrations of the DMF molecules.

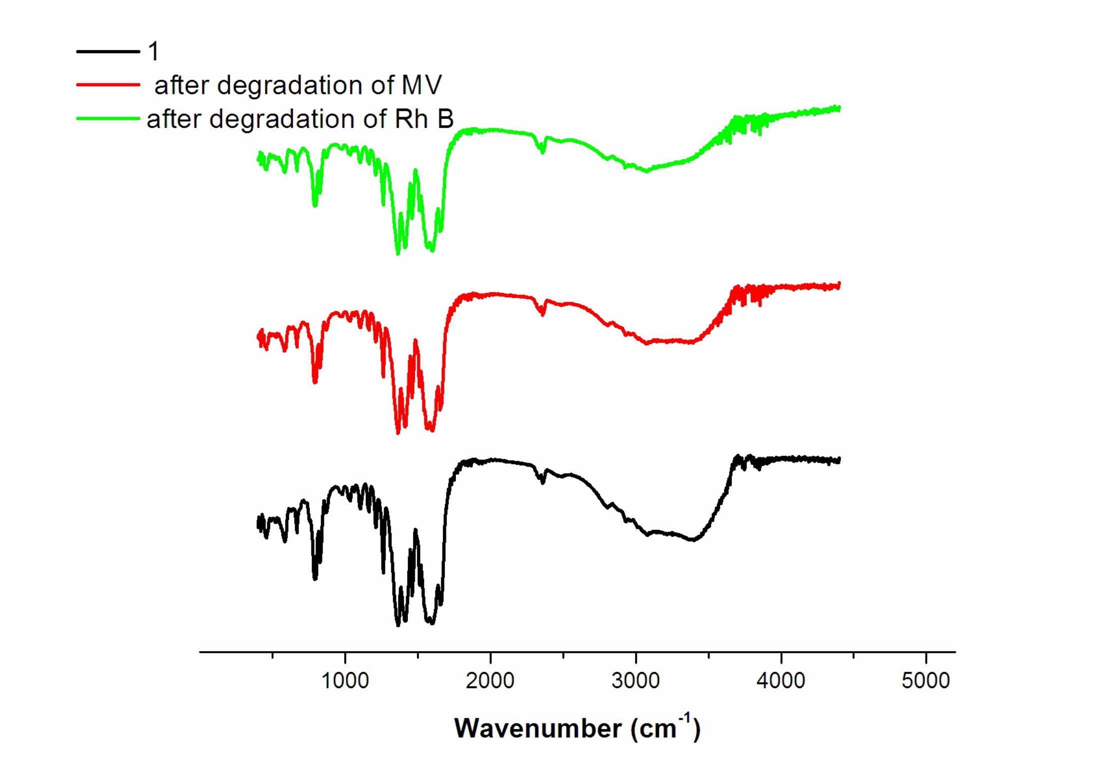
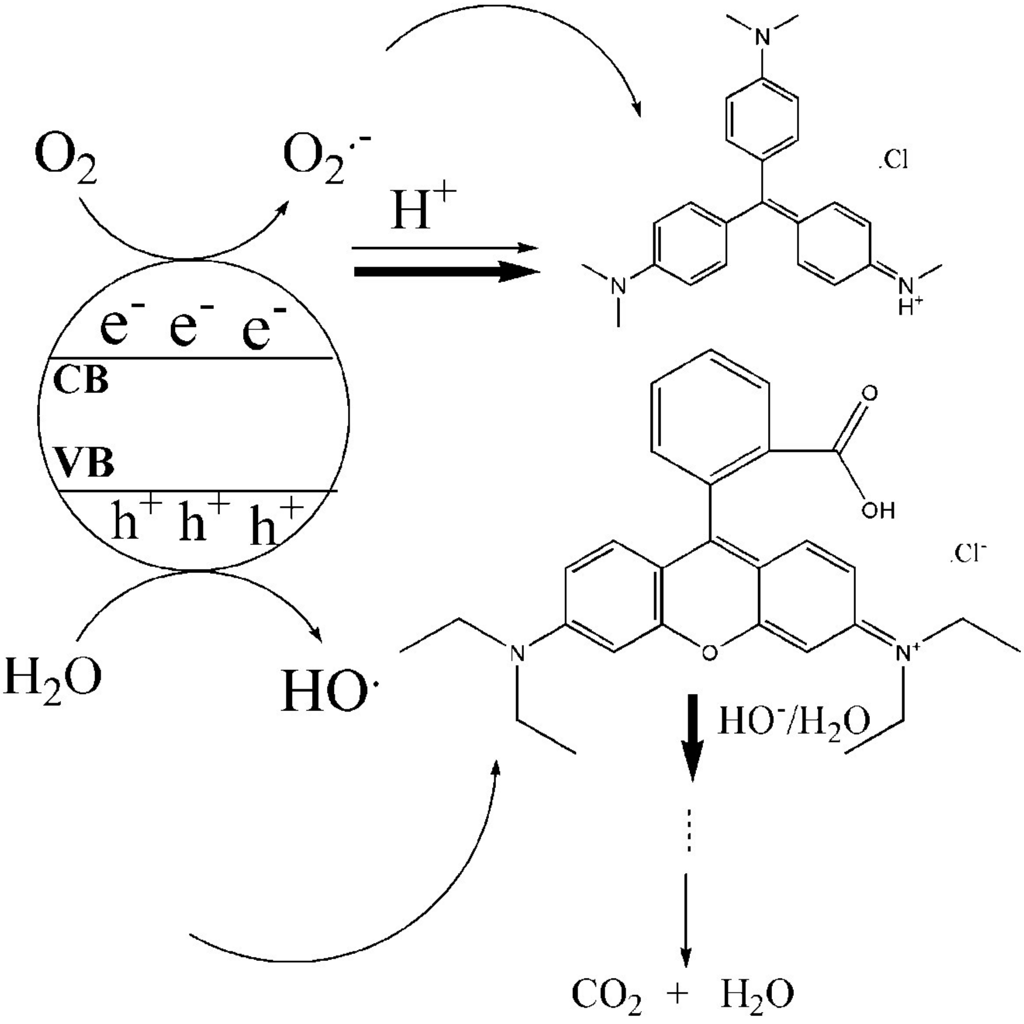


Fig.S7IR spectra of the recycling samples for the photocatalytic degradation of MV (a)and RhB (b) under UV irradiation.



Scheme S3 Possiblephotocatalytic mechanism for this work.

Thermal Analyses

Thermogravimetric analysis (TGA) performed in N_2atmosphere with a heating rate of 10 °C min^{-1} was carried out to establish the thermal stability of MOF **1** (Fig. S8). The TGA experiments reveal that the removal of molecules in **1** takes place with a weight loss of 18.2% (calcd.17.6 %) in thetemperature range of 55–305°C,which is consistent with the removal of 1.7 DMFfree molecules and one coordinatedDMF molecule. The TGA suggested that**1** remains stable up to 355 °C, thereafter the ligands starts decomposing. The remaining residue is attributed to the generation ofZnO.

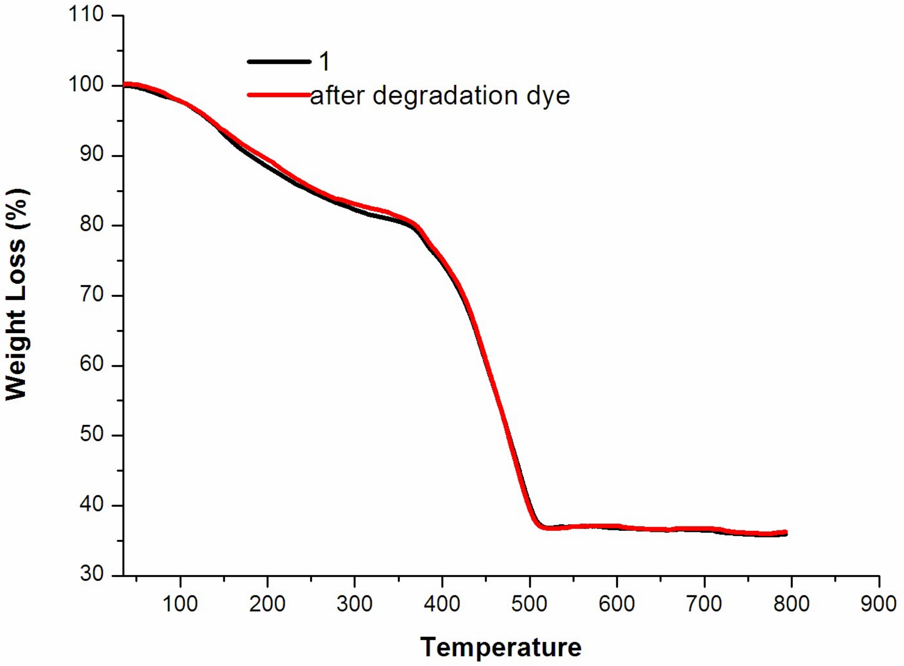


Fig. S8 TGA curvesof**1** and **1** afterphotocatalytic degradation of MV.

References

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