Supporting Information

Correlation between the Photoactive Character and the Structures of Two Novel Metal Organic Frameworks

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Experimental Section

All the reagents were purchased from commercial channels and used without further purification; tpt was synthesized as reported.[12]

1: tpt (0.06g, 0.19mmol) was added to a mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.15g, 0.5 mmol) and m-bdc (0.05g, 0.3mmol) in H_2O/Ethylene glycol monoethyl ether (2:3, 10ml). The mixture was sealed in a 25ml Teflon-lined steel bomb and heated at 120ºC for 24h. Yellow needle-like crystals were collected by filtration, washed by water and ethanol, and dried at room temperature (0.029 g, 27% yield based on tpt).

2: It was synthesized in the same approach as **1** except the use of p-bdc. Yellow crystals were collected by filtration, washed by water and ethanol, and dried at room temperature (0.024 g, 16% yield based on tpt).

Crystal data for **1**: $C_{26}H_{17}N_6O_{4.50}Zn$, *fw*= 550.83g·mol^{-1}, monoclinic, space group *C 2/c*, *a*=15.264(3) Å, *b*=12.908(3) Å, *c*=24.867(5) Å, β=99.40(3)º, *V*= 4833.7(17) Å^3, *Z*=8, ρ_{calcd}=1.514 g·cm^{-3}, final R_1= 0.0331 and wR_2= 0.975 for 4218 independent reflections [$I>2\sigma(I)$]. **2**: $C_{34}H_{22}N_6O_9Zn_2$, *fw*= 789.32 g·mol^{-1}, monoclinic, space group *P21/c*, *a*=10.106(2) Å, *b*=20.726(4) Å, *c*=16.394(3) Å, β=93.71(3)º, *V*= 3426.8(12) Å^3, *Z*=4, ρ_{calcd}=1.530 g·cm^{-3}, final R_1= 0.0530 and wR_2= 0.1380 for 5920 independent reflections [$I>2\sigma(I)$]. The data were measured on a Rigaku R-AXIS SPIDER CCD diffractormeter with MoKα radiation (λ=0.71073 Å) at 298K. The structures were solved by direct methods and refined by full-matrix least-squares methods with SHELXL. CCDC 752722 and 752723 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ukf/data_request/cif. More information is available in the Supporting Information.

Gerneral Methods

IR spectra were characterized by a BRUKE Tensor 27 FTIR spectrometer in the range of 4000-400 cm^{-1} using a KBr disk. A TA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the TGA curve in N_2 at a rate of 20 ºC min^{-1}. The emission/excitation spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer excited at 360nm. The ESR spectra were recorded at room temperature with a JES-FA200 Electron Spin Resonance Spectrometer.

IR Spectra

The incorporation of bdc ligand in the products is supported by the C=O vibrations at 1616 cm^{-1} and 1394 cm^{-1}. And the large band at 3421cm^{-1} corresponds to the guest H_2O molecules.

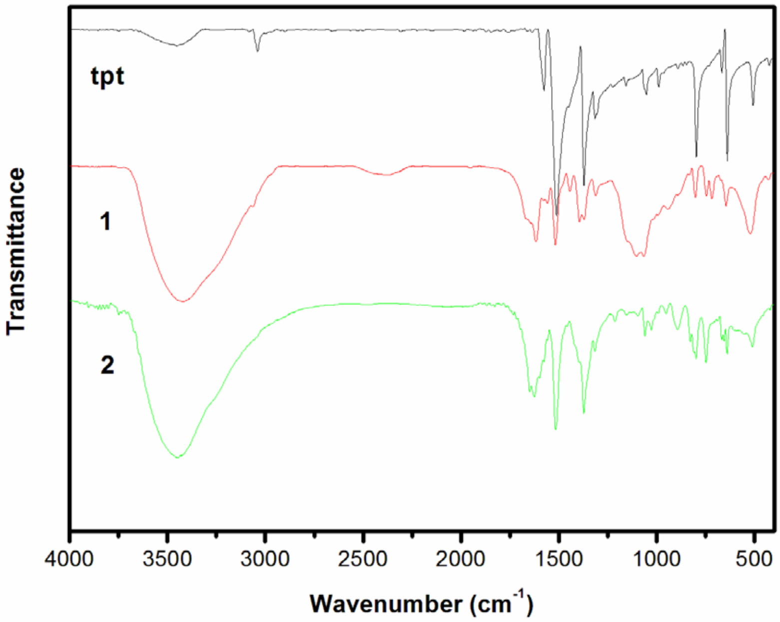


Figure S1. IR spectra of tpt, compound **1** and **2**.

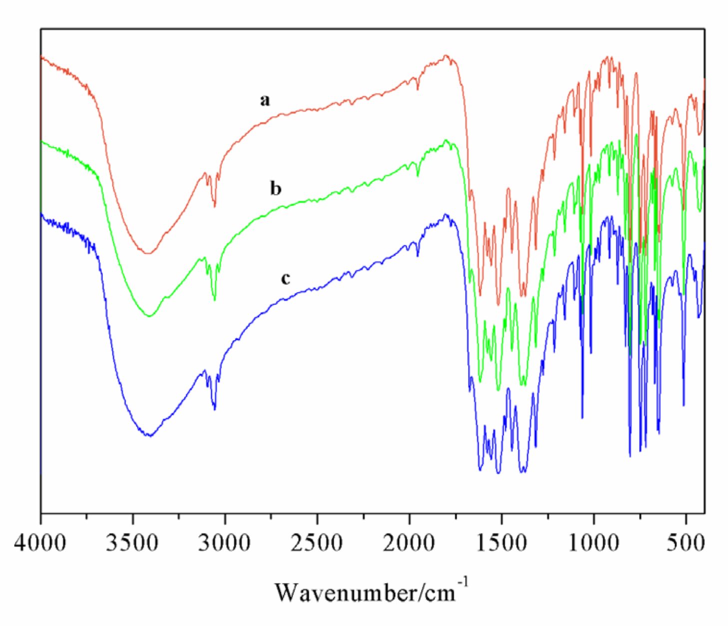


Figure S2. IR spectra of **1** recorded during UV irradiation: (a) 0min; (b) 20min (c) 120min.

Thermal gravimetric analysis

The TGA curve of **1** exhibits an initial weight loss before 400°C which correspond to the removal of the guest H_2O molecules and then the leaving of m-bdc and tpt ligand induce the second weight loss at 400°C to produce ZnO. The TGA curve of **2** shows three characteristic weight losses: the first one occurs at 35°C corresponding to the departure of one guest H_2O molecule per formula unit. The weight loss occurs at 200°C and 290°C corresponding to the decomposition of the mixed ligands.

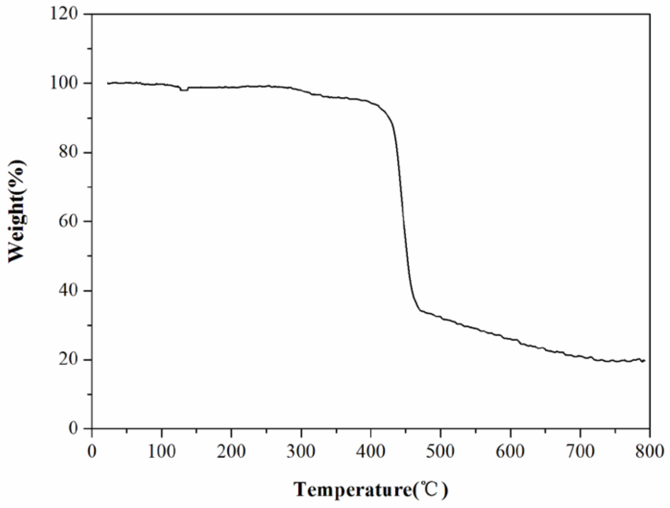


Figure S3. Thermal gravimetric curve of **1.**

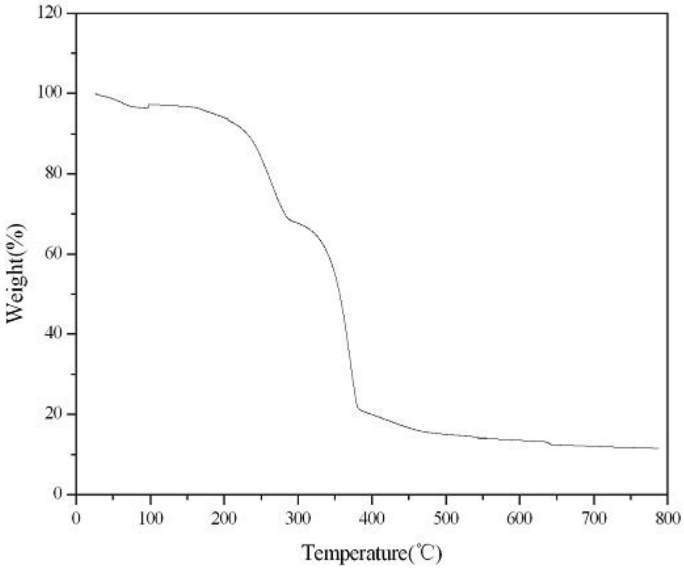


Figure S4. Thermal gravimetric curve of **2**.

Solid-state luminescence data

When excited at room temperature, **tpt** emits significant blue luminescence with a broad emission maximum peak centered at 456 nm. Compound **1** has a strong luminescence with a broad emission maximum peak at 492 nm. And compound **2** emits a broad emission maximum peak at 522 nm.

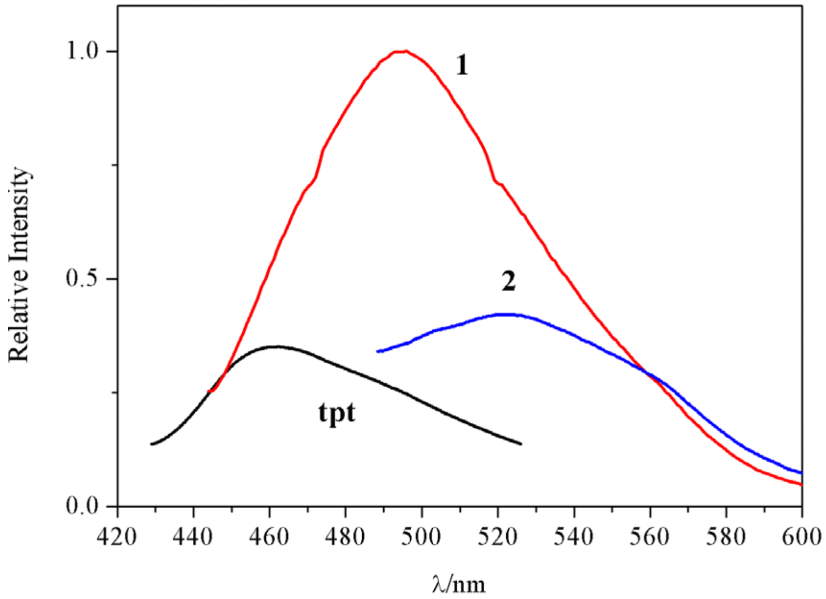


Figure S5. Relative fluorescence intensity for the above complexes: (a) compound **1**, λ_{EX} = 433nm; (b) compound **2,** λ_{EX} = 474nm**;** (c) TPT, λ_{EX} = 416nm.

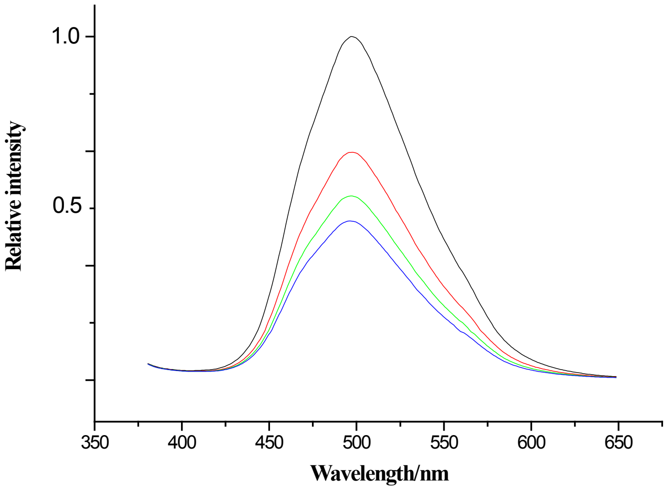
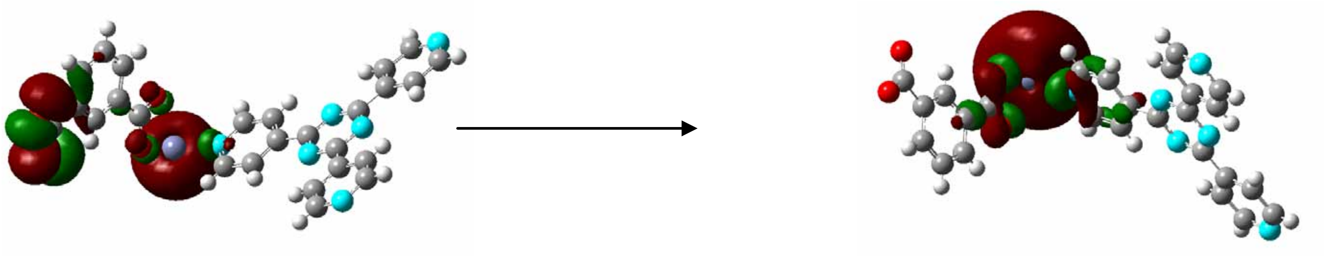


Figure S6 Relative fluorescence intensity at 492 nm for compound **1** during 4 measurements excitation at 360 nm. The irradiation time in each measurement is 50s.



(A) (B)

Figure S7 The HOMO plots of compound **1** before and after irradiation.

The theoretical calculations was performed at the B3LYP level with Gaussian 03 software package. The basis sets used for C, N, H, and O atoms was 6-31G*. And a Lanl2dz basis set was employed for the zinc center. During the calculations, singlet and triplet states were set for compound **1** before and after irradiation, respectively.

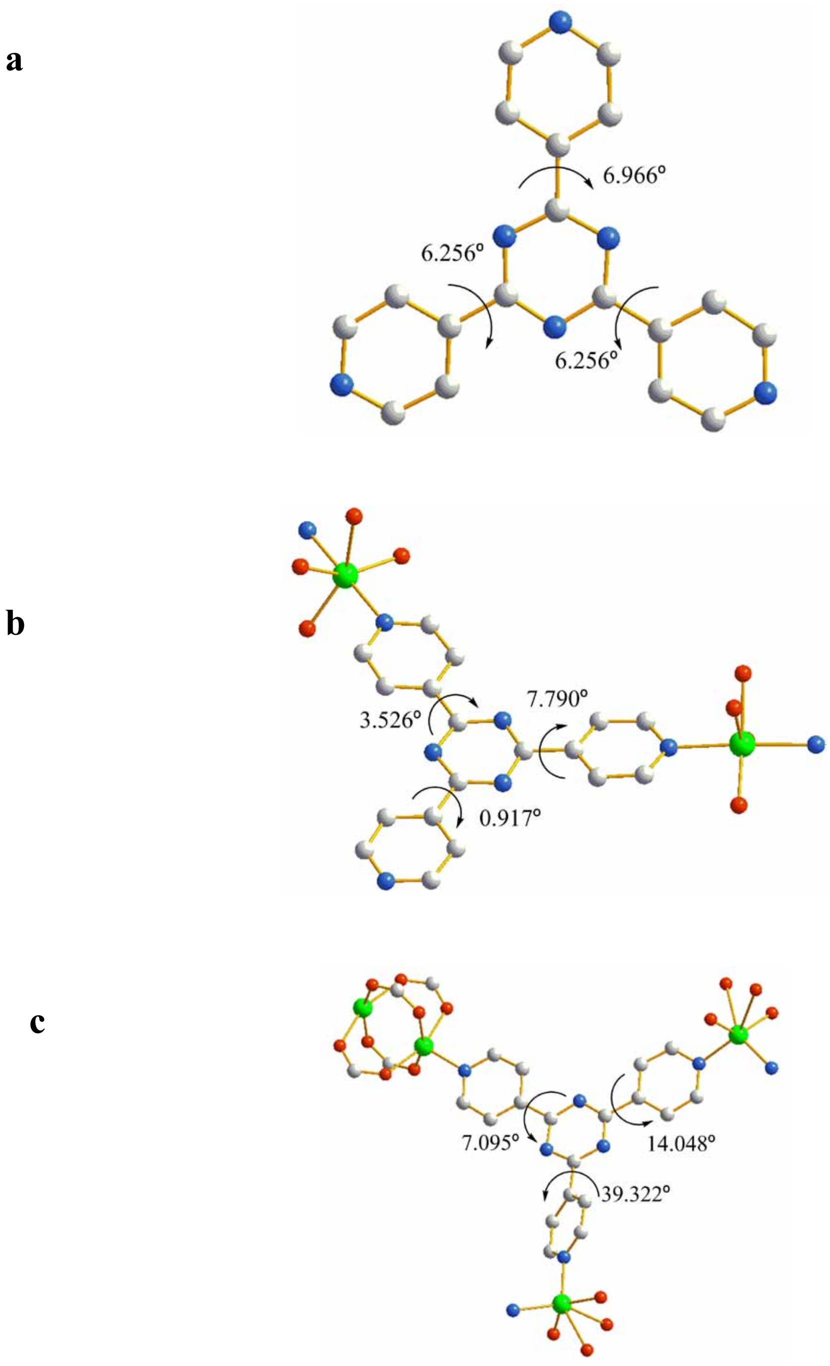


Figure S8 The dihedral angles of the planes in: (a) tpt; (b) compound **1**; (c) compound **2**.