Supplementary information

Two new molecular zinc phosphonates with bright luminescence for sensing UV radiation

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Materials and instrumentation

Chemicals were obtained from commercial sources without further purification. Elemental analyses were carried out with a Vario EL III element analyzer. Infrared spectra were obtained on a Nicolet Magna 750 FT-IR spectrometer. The emission and excitation spectra were performed in solid state at room temperature with a F-7000 FL spectrophotometer. While the lifetime, as well as the emission and excitation spectra at 10 K were investigated in solid state with an Edinburgh FLS920 fluorescence spectrometer. The diffuse reflectance spectrum of solid **2** was recorded on a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer. Thermogravimetric analysis (TGA) was performed on a Netzsch STA449C at a heating rate of 10 °C $\cdot$min^{-1} from room temperature to 1000 °C under an air gas flow. Powder XRD patterns were acquired on a DMAX-2500 diffractometer using CuKα radiation under ambient environment.

Synthesis of 1-$C_{10}H_7$-$CH_2N(CH_2COOH)(CH_2PO_3H_2)$ **(H_3L)**. A solution of glyphosate (40.56 g, 240 mmol), 1-(chloromethyl)naphthalene (35.3 g, 200 mmol) and triethylamine (135 mL) in ethanol (400 mL) was refluxed under a nitrogen atmosphere for 15 h. The solvent was removed in vacuo, and the residue was dissolved in water. The solution was acidified to pH 1.9 with concentrated hydrochloric acid. Unreacted glyphosate precipitated immediately and removed by filtration. Then the water of the filtration was removed in vacuo, and the residue was suspended in ethanol for two days. The desired white H_3L precipitated, which was collected by filtration, washed with ethanol. Yield: 61% (38 g) based on 1-(chloromethyl)naphthalene. MS *m*/*e* 308.7 (H_2L^-). IR (KBr pellet, cm^{-1}): 3043w, 3006w, 2976w(υ_{C-H}), 2942w(υ_{C-H}), 1742s, 1638s, 1513w, 1450w, 1421w, 1385m, 1353m, 1242m, 1192s($\upsilon_{P=O}$), 1157s(υ_{P-O}), 1077s(υ_{P-O}), 914m, 835w, 803m, 777m, 712w. 677w, 566m, 475m. Anal. Calc. for $C_{14}H_{16}NO_5P$: C 54.37, H 5.21, N 4.53 %. Found: C 54.61, H 5.15, N 4.42 %.

Synthesis of $(HN(C_2H_5)_3)_4[Zn_7(L)_6]\cdot 2H_2O$ (1). A mixture of H_3L (0.0788 g, 0.255

mmol), $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.0636 g, 0.290 mmol), 0.5 mL triethylamine and 8.0 mL distilled water, was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at 140 °C for 120 h. After slow cooling to room temperature with a rate of 0.045 °C·min^{-1}, colorless crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0393 g (35 %). Anal. Calc. for $C_{108}H_{146}N_{10}O_{32}P_6Zn_7$: C 47.34, H 5.37, N 5.11 %. Found: C 46.87, H 5.37, N 5.03 %. IR (KBr pellet, cm^{-1}): 3436s(υ_{O-H}), 3046w, 3010w, 2977w(υ_{C-H}), 2920w(υ_{C-H}), 2851w(υ_{C-H}), 1653s(υas_{CO}), 1618s(υas_{CO}), 1512w, 1457w, 1393m, 1362m, 1324m, 1272w, 1128s($\upsilon_{P=O}$), 1073m(υ_{P-O}), 986m(υ_{P-O}), 919w, 803w, 782w, 608w, 549w. Anal. Calc. for irradiated **1** ($C_{108}H_{146}N_{10}O_{32}P_6Zn_7$): C 47.34, H 5.37, N 5.11 %. Found: C 46.92, H 5.21, N 5.10 %.

Synthesis of $[Zn_9(L)_6(H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2)_2]{\cdot}18H_2O$ (2). A mixture of H_3L (0.1579 g, 0.5110 mmol), $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.1356, 0.6183 mmol), 0.2 mL triethylenetetramine and 8.0 mL distilled water, was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at 140 °C for 120 h. After slow cooling to room temperature with a rate of 0.045 °C·min^{-1}, colorless crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.1313 g (63 %). Anal. Calc. for $C_{96}H_{150}N_{14}O_{48}P_6Zn_9$: C 37.90, H 4.97, N 6.44 %. Found: C 37.37, H 5.16, N 6.56 %. IR (KBr pellet, cm^{-1}): 3422s(υ_{O-H}), 2926w(υ_{C-H}), 1601s(υas_{CO}), 1510w, 1454w, 1396m, 1332m, 1265w, 1119s($\upsilon_{P=O}$), 1073m(υ_{P-O}), 986m(υ_{P-O}), 927w, 804m, 784m, 729w, 610w, 549w. Anal. Calc. for irradiated **2** ($C_{96}H_{150}N_{14}O_{48}P_6Zn_9$): C 37.90, H 4.97, N 6.44 %. Found: C 37.56, H 4.91, N 6.66 %.

Heating treatment: Solids **1-200** and **2-250** were obtained after polycrystalline of **1** and **2** were heated at 200 and 250 °C for two hours under an air atmosphere, respectively, and then naturally cooled to room temperature. Anal. Calc. for solid **1-200** ($C_{108}H_{142}N_{10}O_{30}P_6Zn_7$): C 47.97, H 5.29, N 5.18 %. Found: C 47.04, H 5.43, N 5.43 %. Anal. Calc. for **2-250** ($C_{96}H_{114}N_{14}O_{30}P_6Zn_9$): C 42.42, H 4.23, N 7.21 %. Found: C 40.66, H 4.44, N 7.08 %.

Thermogravimetric analysis: Thermogravimetric analysis (TGA) curve of solid **1** indicates that under an air atmosphere an initial step occurs from 38 to 120 °C with 0.77% weight loss, which is attributed to the loss of two free water molecules per formula (calculated 1.31%). TGA curve of solid **2** indicates that under an air atmosphere an initial step occurs from 38 to 120 °C with 9.27% weight loss, which is attributed to the loss of eighteen free water molecules per formula (calculated 10.65%).

X-Ray crystallography

X-ray data were collected on a Rigaku Mercury CCD/AFC diffractometer at 293(2) K (for **1**), a Rigaku Saturn724 CCD diffractometer at 293 K (for irradiated **1**), as well

as a Rigaku Saturn70 CCD diffractometer at 113 K (for **2**) and 293(2) K (for irradiated **2**), using graphite-monochromated Mo Kα radiation (λ(Mo-Kα) = 0.71073 Å). Data of **1-2** and irradiated **1-2** were reduced with CrystalClear v1.3.6.[1] These structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELX.[2] All non-hydrogen atoms were treated anisotropically. C32-C42, C45-C48 and N5-N7 atoms in **2** and irradiated **2** are disordered over two sites. Hydrogen atoms in **1** and irradiated **1,** as well as hydrogen atoms of carbon and nitrogen atoms in **2** and irradiated **2**, were generated geometrically. While no attempts were performed to locate hydrogen atoms of free water molecules in **2** and irradiated **2**. Crystallographic data for compounds **1-2** and irradiated **1-2** are summarized in Table S1 and S2, respectively. Selected bond lengths and angles for compounds **1** and **2** are listed in Table S3 and S4, respectively. CCDC 925302 (**1**), 925303 (**2**), 958269 (irradiated **1**) and 954975 (irradiated **2**).

Table S1. Crystallographic data for compounds **1** and **2**

Compounds	**1**	**2**
Formula	$C_{108}H_{146}N_{10}O_{32}P_6Zn_7$	$C_{96}H_{150}N_{14}O_{48}P_6Zn_9$
FW	2739.76	3042.45
Crystal system	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/n
a (Å)	15.8046(10)	15.836(6)
b (Å)	18.7688(10)	22.682(8)
c (Å)	20.6949(12)	18.490(7)
β (deg)	102.839(3)	105.990(6)
V (Å^3)	5985.3(6)	6384(4)
Z	2	2
T(K)	293(2)	113(2)
Measured/unique/ observed reflections	46114 /13700 / 10251	49552/14387/13184
D_{calcd} (g cm^3)	1.520	1.583
μ (mm^{-1})	1.539	1.824
GOF on F^2	1.097	1.121
R_{int}	0.0478	0.0310
R1[a] [I>2σ(I)]	0.0632	0.0609
wR2[b] [all data]	0.1593	0.1730

[a] $R1 = \sum(||F_o| - |F_c||) / \sum |F_o|$. [b] $wR2 = \{\sum w [(F^2_o - F^2_c)] / \sum w [(F^2_o)^2]\}^{0.5}$.

Table S2. Crystallographic data for irradiated **1-2**

Compounds	irradiated **1**	irradiated **2**
Formula	$C_{108}H_{146}N_{10}O_{32}P_6Zn_7$	$C_{96}H_{150}N_{14}O_{48}P_6Zn_9$
FW	2739.76	3042.45
Crystal system	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/n
a (Å)	15.789(6)	15.827(6)
b (Å)	18.802(7)	22.632(8)
c (Å)	20.840(8)	18.636(6)
β (deg)	103.286(7)	106.024(6)
V (Å^3)	5985.3(6)	6416(4)
Z	2	2
T(K)	293(2)	293(2)
Measured/unique/ observed reflections	50745 /13638 / 10860	50612/14651/12053
D_{calcd} (g cm^3)	1.511	1.575
μ (mm^{-1})	1.530	1.815
GOF on F^2	1.039	1.211
R_{int}	0.0364	0.0641
R1[a] [I>2σ(I)]	0.0451	0.0859
wR2[b] [all data]	0.1338	0.2085

[a] $R1 = \sum(||F_o| - |F_c||) / \sum |F_o|$. [b] $wR2 = \{\sum w [(F^2_o - F^2_c)] / \sum w [(F^2_o)^2]\}^{0.5}$.

Table S3. Selected bond lengths (Å) and angles (°) for **1**

Zn(1)-O(1)	2.127(3)	Zn(3)-N(1)	2.177(4)
Zn(1)-O(1)^{a}	2.127(3)	Zn(3)-O(1)	2.184(3)
Zn(1)-O(6)	2.109(3)	Zn(3)-O(4)	2.040(4)
Zn(1)-O(6)^{a}	2.109(3)	Zn(3)-O(7)	1.962(3)
Zn(1)-O(11)	2.106(3)	Zn(3)-O(12)	1.957(3)
Zn(1)-O(11)^{a}	2.106(3)	Zn(4)-N(2)	2.159(3)
Zn(2)-N(3)	2.163(4)	Zn(4)-O(3)^{a}	1.942(3)
Zn(2)-O(2)^{a}	1.951(3)	Zn(4)-O(6)	2.176(3)
Zn(2)-O(8)^{a}	1.952(3)	Zn(4)-O(9)	2.079(3)
Zn(2)-O(11)	2.162(3)	Zn(4)-O(13)	1.951(3)
Zn(2)-O(14)	2.099(3)		
O(1)-Zn(1)-O(1)^{a}	180.0	O(8)^{a}-Zn(2)-O(14)	90.27(13)
O(1)-Zn(1)-O(6)	88.31(11)	O(11)-Zn(2)-O(14)	159.37(12)
O(1)-Zn(1)-O(6)^{a}	91.69(11)	N(1)-Zn(3)-O(1)	83.88(12)
O(1)-Zn(1)-O(11)	91.91(11)	N(1)-Zn(3)-O(4)	78.47(15)
O(1)-Zn(1)-O(11)^{a}	88.09(11)	N(1)-Zn(3)-O(7)	112.11(13)
O(1)^{a}-Zn(1)-O(6)	91.69(11)	N(1)-Zn(3)-O(12)	128.50(14)
O(1)^{a}-Zn(1)-O(6)^{a}	88.31(11)	O(1)-Zn(3)-O(4)	159.81(15)
O(1)^{a}-Zn(1)-O(11)	88.09(11)	O(1)-Zn(3)-O(7)	94.56(12)
O(1)^{a}-Zn(1)-O(11)^{a}	91.91(11)	O(1)-Zn(3)-O(12)	90.50(12)
O(6)-Zn(1)-O(6)^{a}	180.00(13)	O(4)-Zn(3)-O(7)	101.09(15)
O(6)-Zn(1)-O(11)	86.25(11)	O(4)-Zn(3)-O(12)	92.83(14)
O(6)-Zn(1)-O(11)^{a}	93.75(11)	O(7)-Zn(3)-O(12)	119.37(14)
O(6)^{a}-Zn(1)-O(11)	93.75(11)	N(2)-Zn(4)-O(3)^{a}	128.97(14)
O(6)^{a}-Zn(1)-O(11)^{a}	86.31(10)	N(2)-Zn(4)-O(6)	84.35(12)
O(11)-Zn(1)-O(11)^{a}	180.0	N(2)-Zn(4)-O(9)	78.20(13)
N(3)-Zn(2)-O(2)^{a}	113.72(14)	N(2)-Zn(4)-O(13)	112.12(14)
N(3)-Zn(2)-O(8)^{a}	125.32(14)	O(3)^{a}-Zn(4)-O(6)	92.28(12)
N(3)-Zn(2)-O(11)	84.52(12)	O(3)^{a}-Zn(4)-O(9)	92.25(14)
N(3)-Zn(2)-O(14)	77.86(13)	O(3)^{a}-Zn(4)-O(13)	118.90(14)
O(2)^{a}-Zn(2)-O(8)^{a}	120.95(14)	O(6)-Zn(4)-O(9)	160.67(13)
O(2)^{a}-Zn(2)-O(11)	94.73(12)	O(6)-Zn(4)-O(13)	94.64(12)
O(2)^{a}-Zn(2)-O(14)	102.08(13)	O(9)-Zn(4)-O(13)	99.57(15)
O(8)^{a}-Zn(2)-O(11)	91.27(12)		

Symmetry codes: a - x + 1, - y, - z + 1.

Table S4. Selected bond lengths (Å) and angles (°) for **2**

Zn(1)-O(1)	2.107(3)	Zn(3)-O(11)	2.128(3)
Zn(1)-O(1)^{a}	2.107(3)	Zn(3)-O(14)	2.089(3)
Zn(1)-O(6)	2.115(3)	Zn(4)-N(1)	2.164(3)
Zn(1)-O(6)^{a}	2.115(3)	Zn(4)-O(1)	2.207(3)
Zn(1)-O(11)	2.148(3)	Zn(4)-O(4)	2.080(4)
Zn(1)-O(11)^{a}	2.148(3)	Zn(4)-O(8)	1.957(3)
Zn(2)-N(2)	2.138(4)	Zn(4)-O(13)	1.990(3)
Zn(2)-O(2)^{a}	1.974(3)	Zn(5)-N(4)	2.085(6)
Zn(2)-O(6)	2.146(3)	Zn(5)-N(5)	2.246(5)
Zn(2)-O(9)	2.119(3)	Zn(5)-N(6)	1.986(12)
Zn(2)-O(12)	1.942(3)	Zn(5)-N(6A)	2.295(15)
Zn(3)-N(3)	2.171(4)	Zn(5)-N(7)	2.185(13)
Zn(3)-O(3)^{a}	1.977(3)	Zn(5)-N(7A)	2.23(2)
Zn(3)-O(7)^{a}	1.979(3)	Zn(5)-O(10)	1.988(4)
O(1)-Zn(1)-O(1)^{a}	180.000(1)	O(7)^{a}-Zn(3)-O(14)	89.17(13)
O(1)-Zn(1)-O(6)	88.30(10)	O(11)-Zn(3)-O(14)	160.07(12)
O(1)-Zn(1)-O(6)^{a}	91.70(10)	N(1)-Zn(4)-O(1)	84.76(11)
O(1)-Zn(1)-O(11)	90.72(10)	N(1)-Zn(4)-O(4)	78.24(13)
O(1)-Zn(1)-O(11)^{a}	89.28(10)	N(1)-Zn(4)-O(8)	115.13(12)
O(1)^{a}-Zn(1)-O(6)	91.70(10)	N(1)-Zn(4)-O(13)	123.36(12)
O(1)^{a}-Zn(1)-O(6)^{a}	88.30(10)	O(1)-Zn(4)-O(4)	161.92(12)
O(1)^{a}-Zn(1)-O(11)	89.28(10)	O(1)-Zn(4)-O(8)	94.63(11)
O(1)^{a}-Zn(1)-O(11)^{a}	90.72(10)	O(1)-Zn(4)-O(13)	89.53(11)
O(6)-Zn(1)-O(6)^{a}	180.0	O(4)-Zn(4)-O(8)	98.11(14)
O(6)-Zn(1)-O(11)	88.49(10)	O(4)-Zn(4)-O(13)	94.66(13)
O(6)-Zn(1)-O(11)^{a}	91.51(10)	O(8)-Zn(4)-O(13)	121.50(12)
O(6)^{a}-Zn(1)-O(11)	91.51(10)	N(4)-Zn(5)-N(5)	80.40(19)
O(6)^{a}-Zn(1)-O(11)^{a}	88.49(10)	N(4)-Zn(5)-N(6)	120.0(4)
O(11)-Zn(1)-O(11)^{a}	180.000(1)	N(4)-Zn(5)-N(6A)	131.1(3)
N(2)-Zn(2)-O(2)^{a}	128.48(13)	N(4)-Zn(5)-N(7)	104.5(4)
N(2)-Zn(2)-O(6)	86.43(12)	N(4)-Zn(5)-N(7A)	113.8(5)
N(2)-Zn(2)-O(9)	78.95(12)	N(4)-Zn(5)-O(10)	111.4(2)
N(2)-Zn(2)-O(12)	110.11(14)	N(5)-Zn(5)-N(6)	86.6(4)
O(2)^{a}-Zn(2)-O(6)	92.91(11)	N(5)-Zn(5)-N(6A)	75.4(3)
O(2)^{a}-Zn(2)-O(9)	88.86(12)	N(5)-Zn(5)-N(7)	169.9(4)
O(2)^{a}-Zn(2)-O(12)	121.14(13)	N(5)-Zn(5)-N(7A)	149.3(5)
O(6)-Zn(2)-O(9)	162.56(11)	N(5)-Zn(5)-O(10)	101.52(17)
O(6)-Zn(2)-O(12)	96.09(11)	N(6)-Zn(5)-N(6A)	19.4(4)
O(9)-Zn(2)-O(12)	97.82(12)	N(6)-Zn(5)-N(7)	83.3(5)
N(3)-Zn(3)-O(3)^{a}	112.56(12)	N(6)-Zn(5)-N(7A)	62.6(6)
N(3)-Zn(3)-O(7)^{a}	129.74(13)	N(6)-Zn(5)-O(10)	128.6(4)
N(3)-Zn(3)-O(11)	84.83(12)	N(6A)-Zn(5)-N(7)	95.0(5)

N(3)-Zn(3)-O(14)	77.78(14)	N(6A)-Zn(5)-N(7A)	75.1(6)
O(3)[a]-Zn3)-O(7)[a]	117.27(13)	N(6A)-Zn(5)-O(10)	114.6(3)
O(3)[a]-Zn(3)-O(11)	97.64(11)	N(7)-Zn(5)-N(7A)	20.7(4)
O(3)[a]-Zn(3)-O(14)	97.98(13)	N(7)-Zn(5)-O(10)	85.1(4)
O(7)[a]-Zn(3)-O(11)	94.62(11)	N(7A)-Zn(5)-O(10)	98.2(5)
Symmetry codes: a - x, - y + 1, - z + 1.			

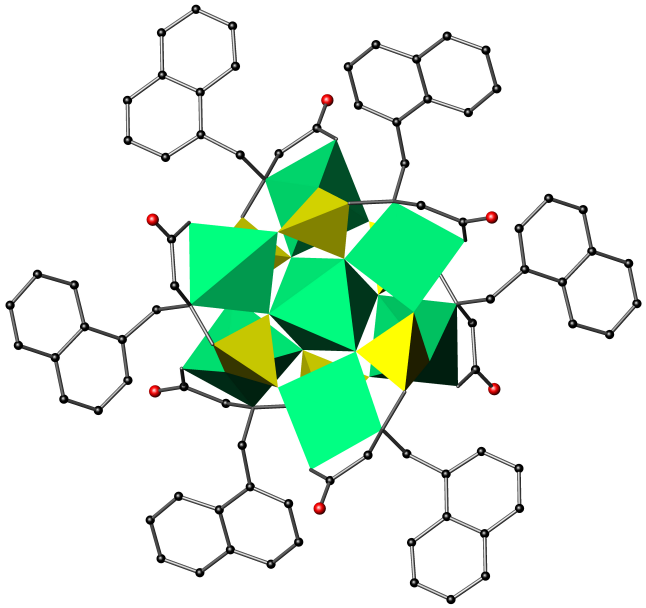

Fig. S1 Polyhedral view of the $[Zn_7(L)_6]^{4-}$ anion in **1**.

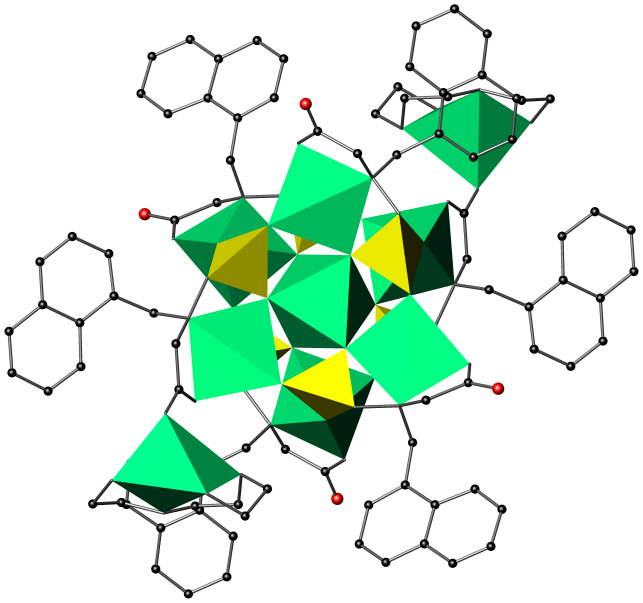

Fig. S2 Polyhedral view of the structure of **2**.

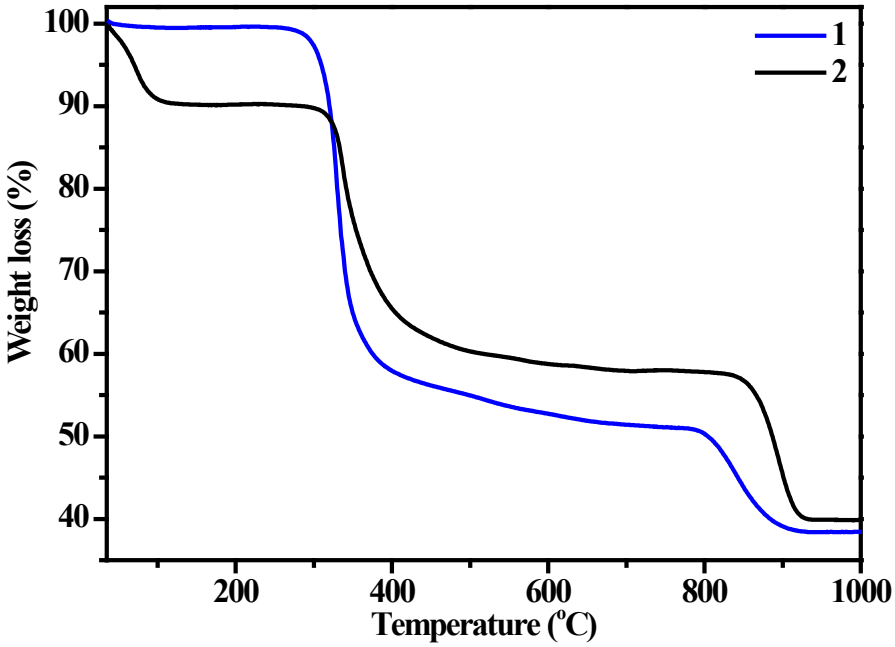

Fig. S3 TGA curves of **1**-**2**.

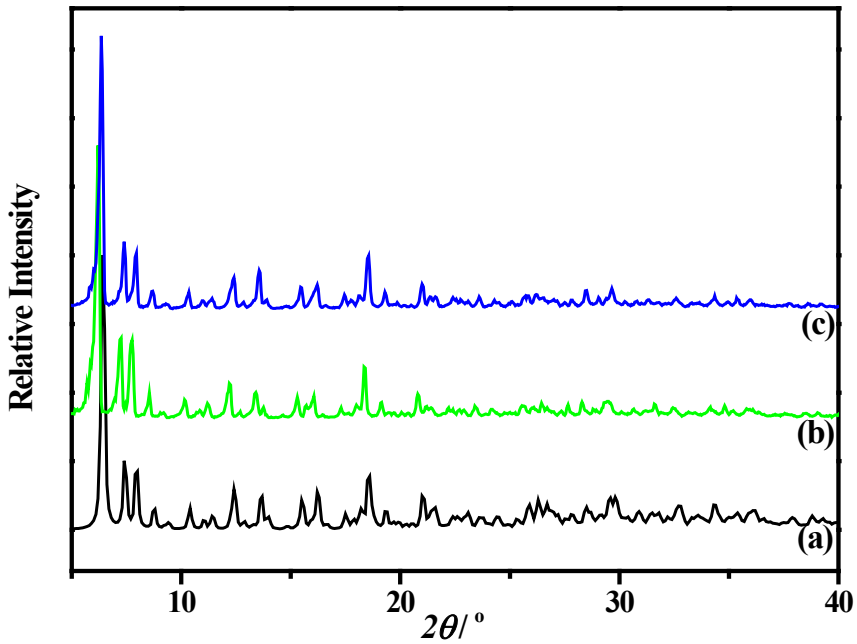

Fig. S4 XRD patterns of **1** (a) simulated from single-crystal X-ray data, and experimental data for solids **1** (b) and **1-200** (c).

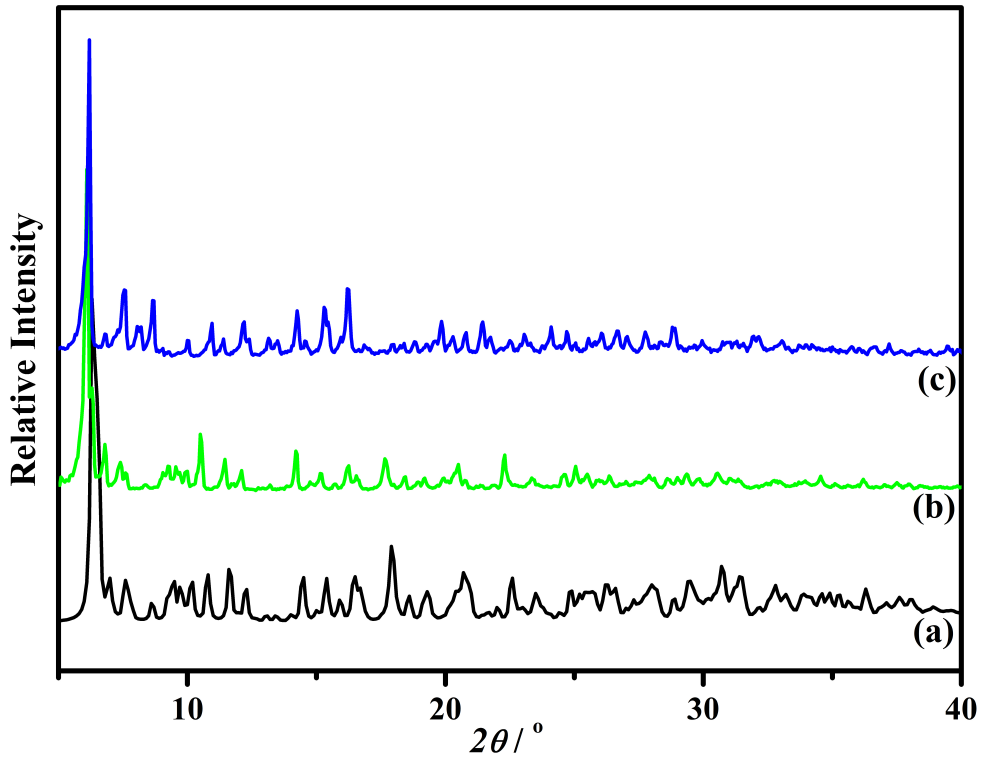

Fig. S5 XRD patterns of **2** (a) simulated from single-crystal X-ray data, and experimental data for solids **2** (b) and **2-250** (c).

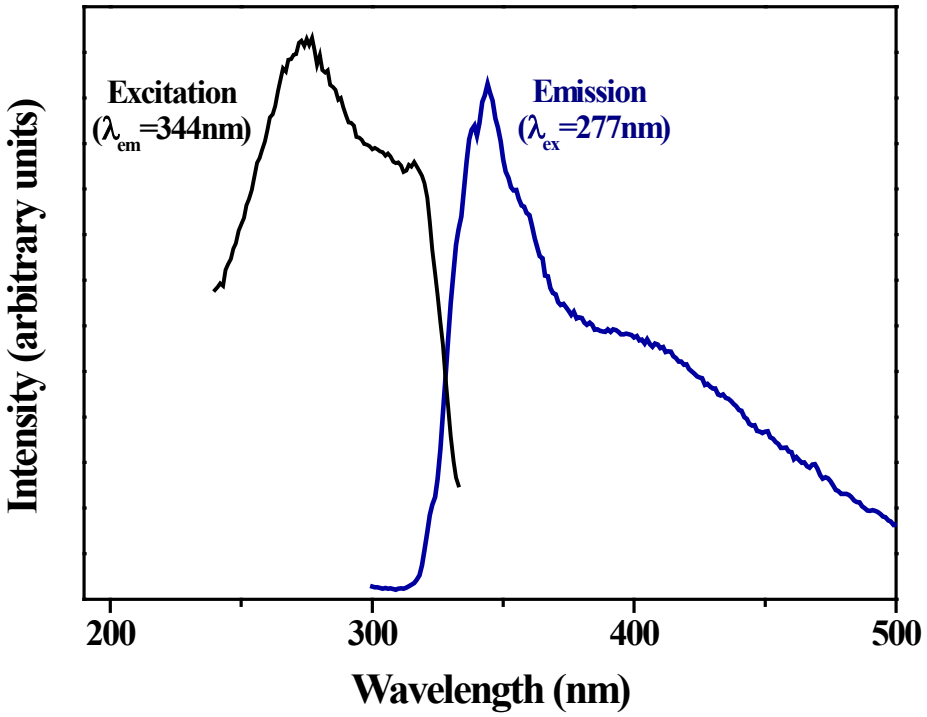

Fig. S6 Emission and excitation spectra for H_3L at room temperature.

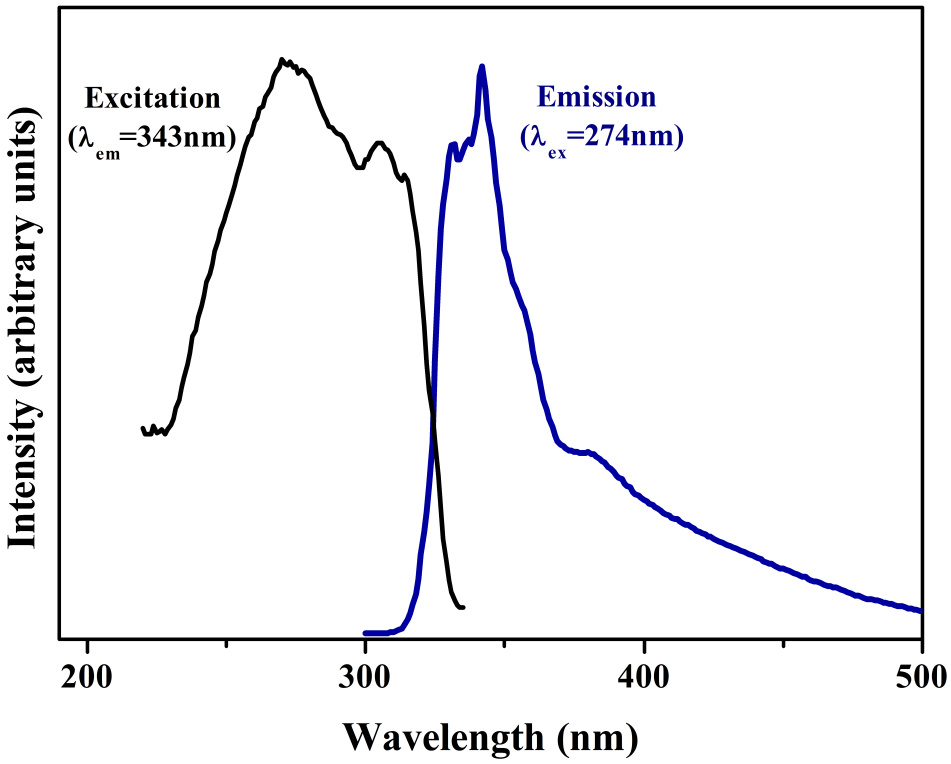

Fig. **S7** Emission and excitation spectra for solid **1** at room temperature.

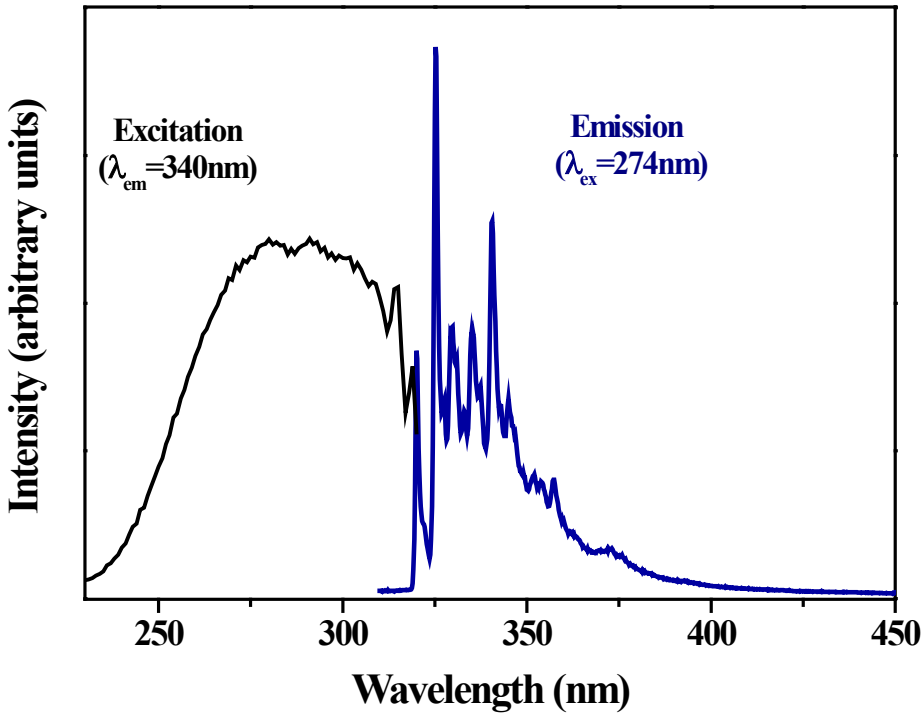

Fig. **S8** Emission and excitation spectra for solid **1** at 10 K.

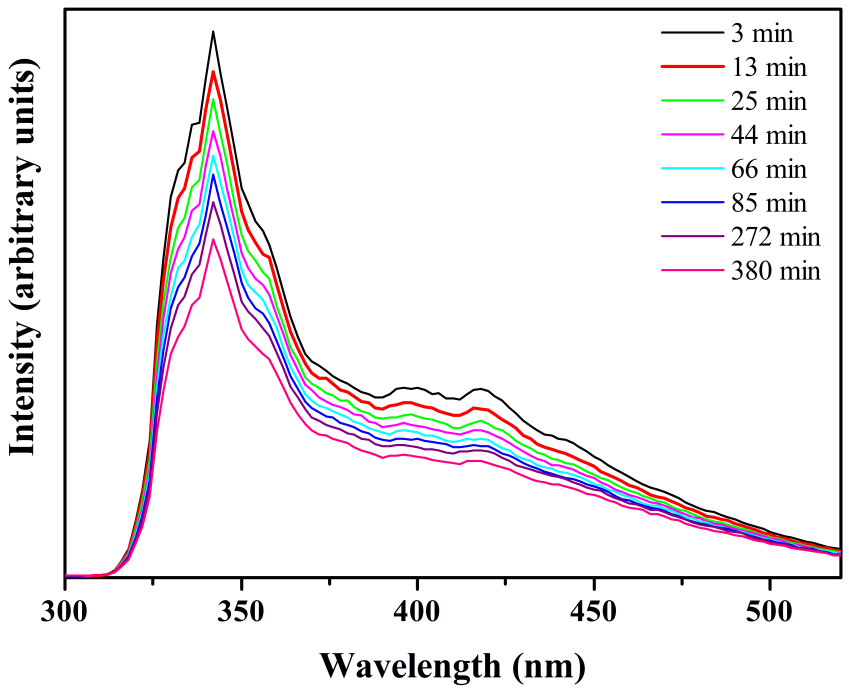

Fig. S9 Fluorescence spectra for solid **1** with different UV irradiation time at 270 nm.

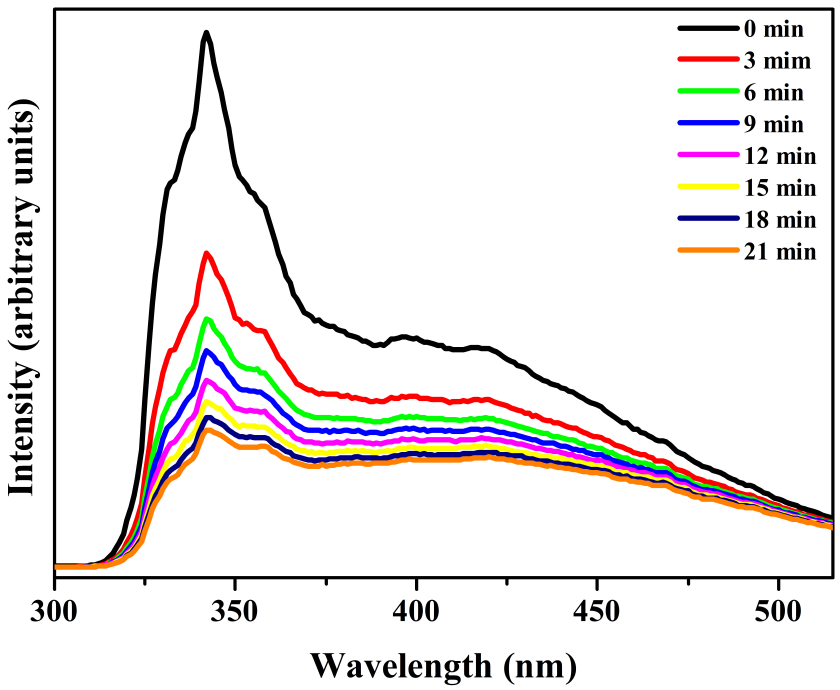

Fig. S10 Fluorescence spectra for solid **1-200** with different UV irradiation time at 270 nm.

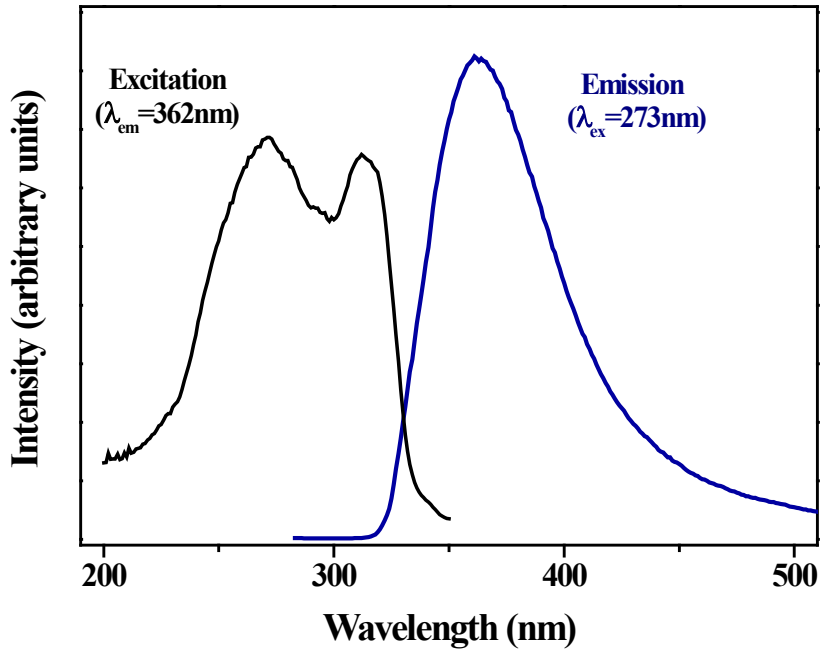

Fig. **S11** Emission and excitation spectra for solid **2** at room temperature.

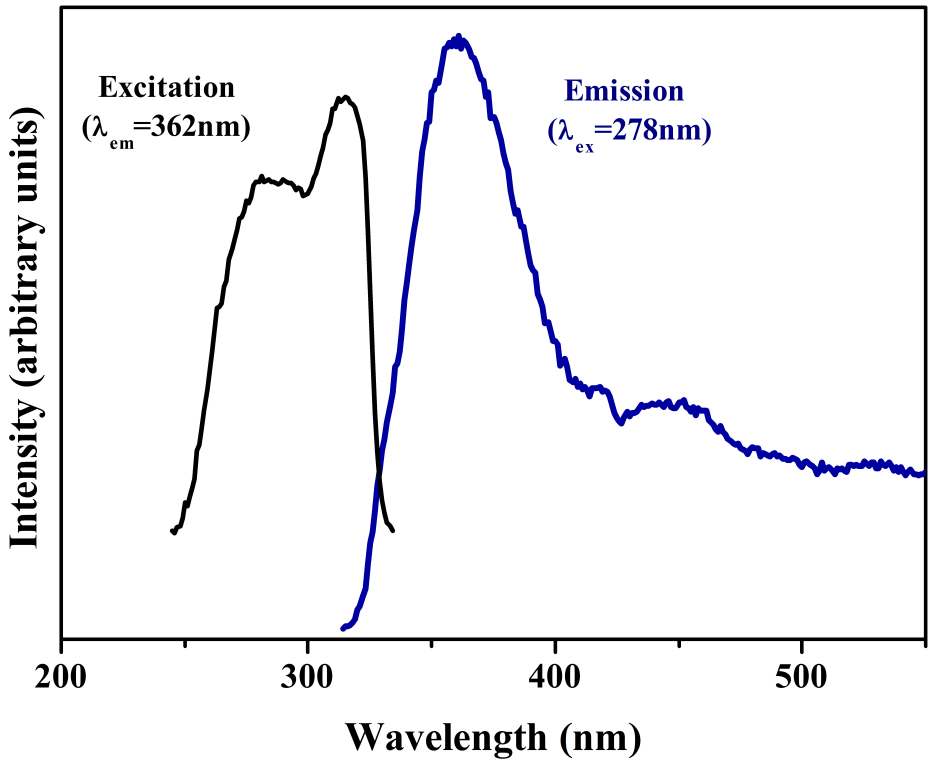

Fig. **S12** Emission and excitation spectra for solid **2** at 10 K.

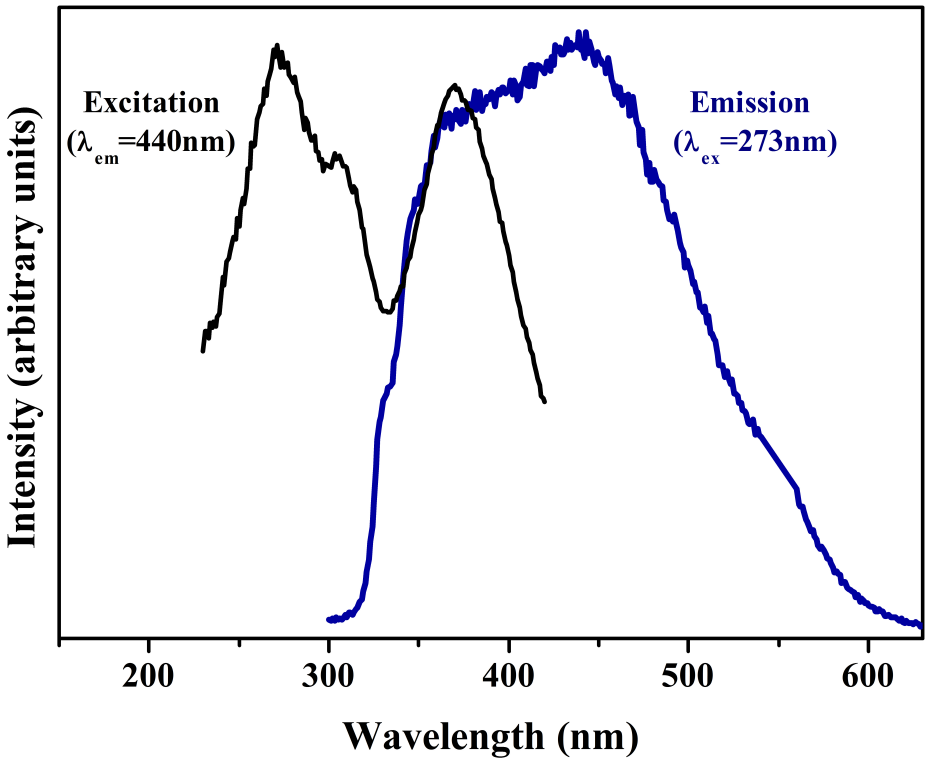

Fig. **S13** Emission and excitation spectra for solid **2-250** at room temperature.

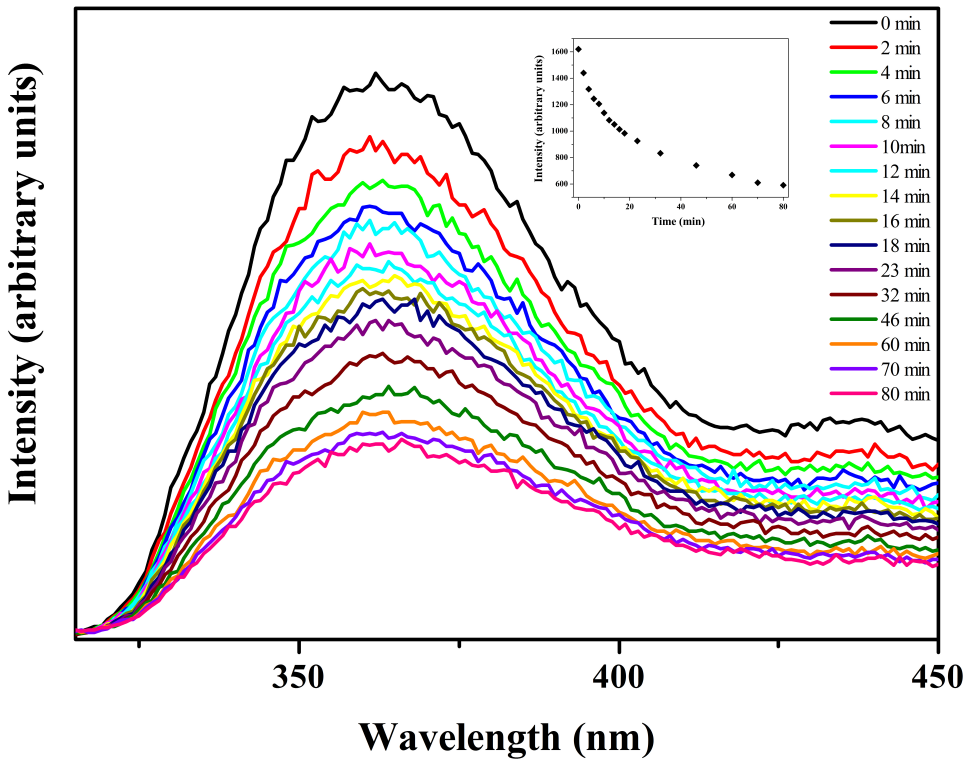

Fig. S14 Fluorescence spectra for solid **2** with different UV irradiation time at 230 nm.

Inset: fluorescence intensity at $\lambda_{max(em)}$ as a function of UV irradiation time at 230 nm.

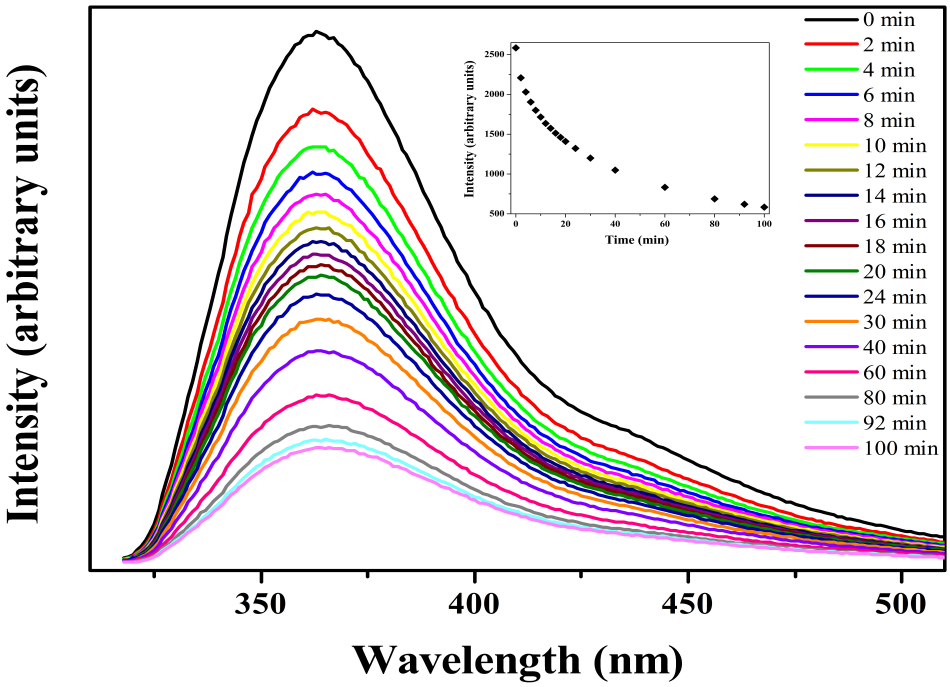

Fig. S15 Fluorescence spectra for solid **2** with different UV irradiation time at 310 nm. Inset: fluorescence intensity at $\lambda_{max(em)}$ as a function of UV irradiation time at 310 nm.

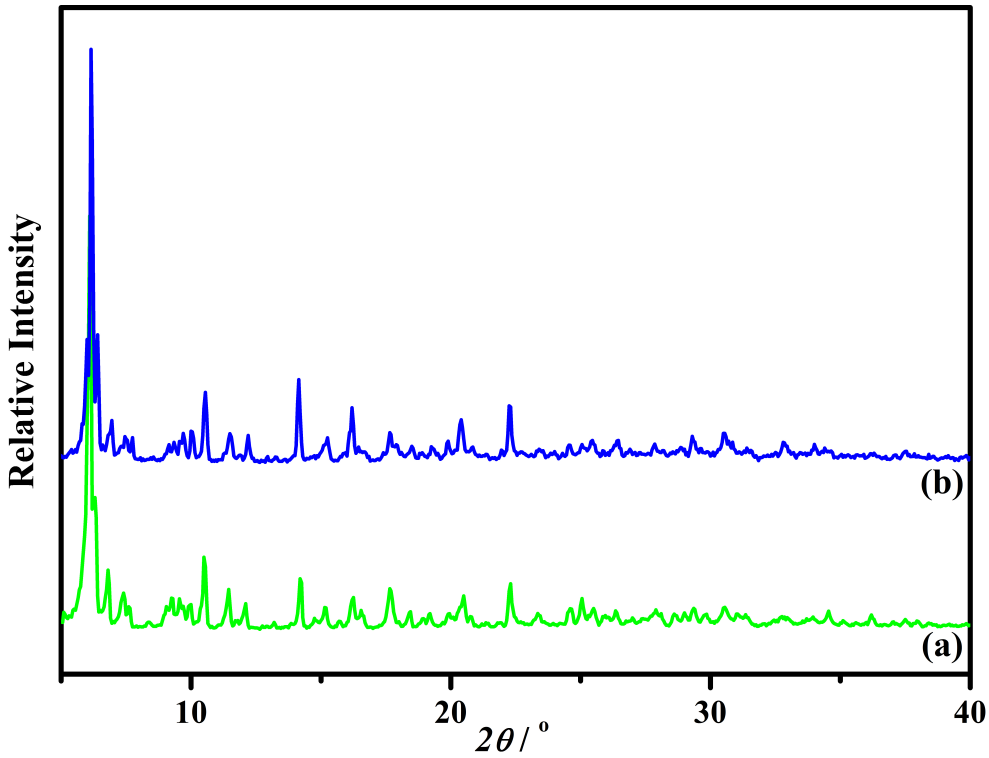

Fig. S16 XRD patterns of as-prepared **2** (a) and irradiated **2** (b).

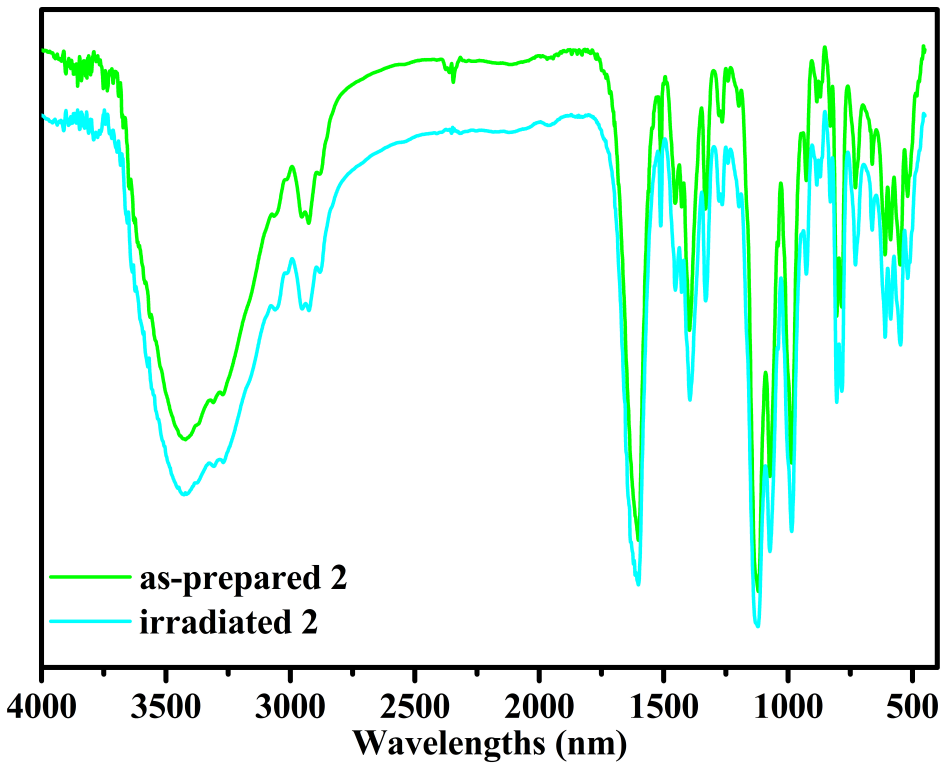

Fig. **S17** IR spectra of as-prepared **2** and irradiated **2**.

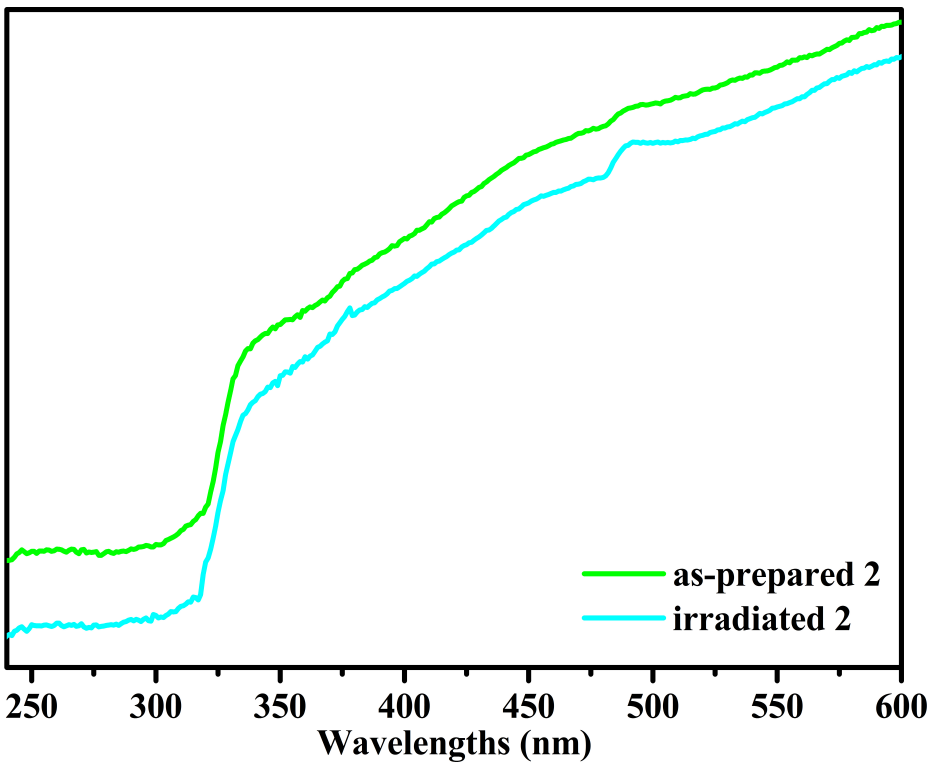

Fig. **S18** The diffuse reflectance spectra of as-prepared **2** and irradiated **2**.

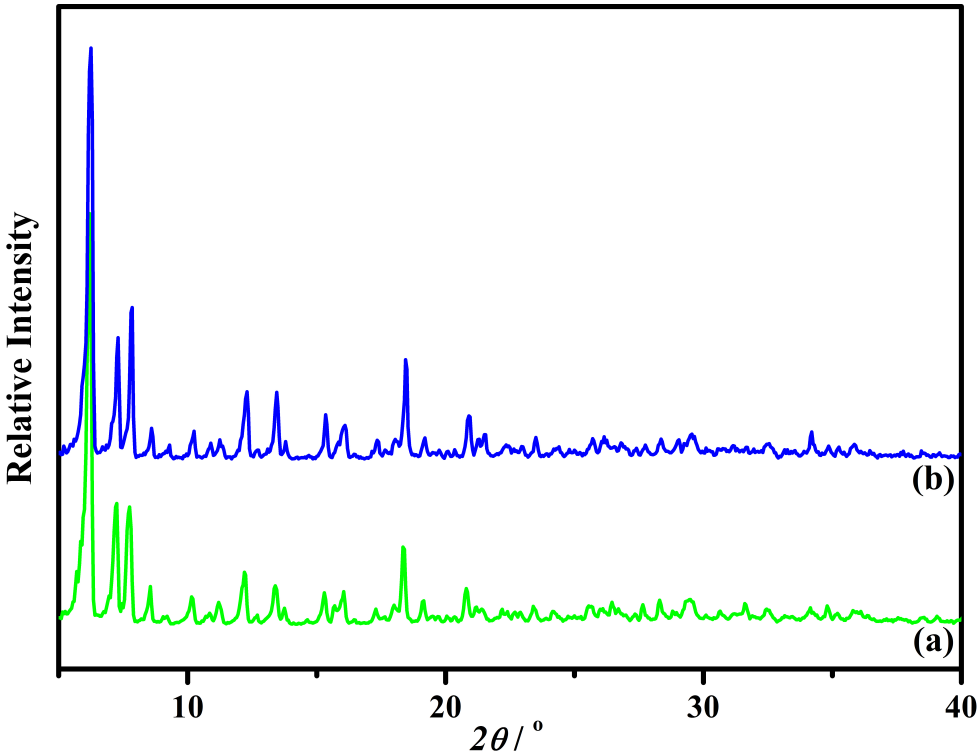

Fig. S19 XRD patterns of as-prepared **1** (a) and irradiated **1** (b).

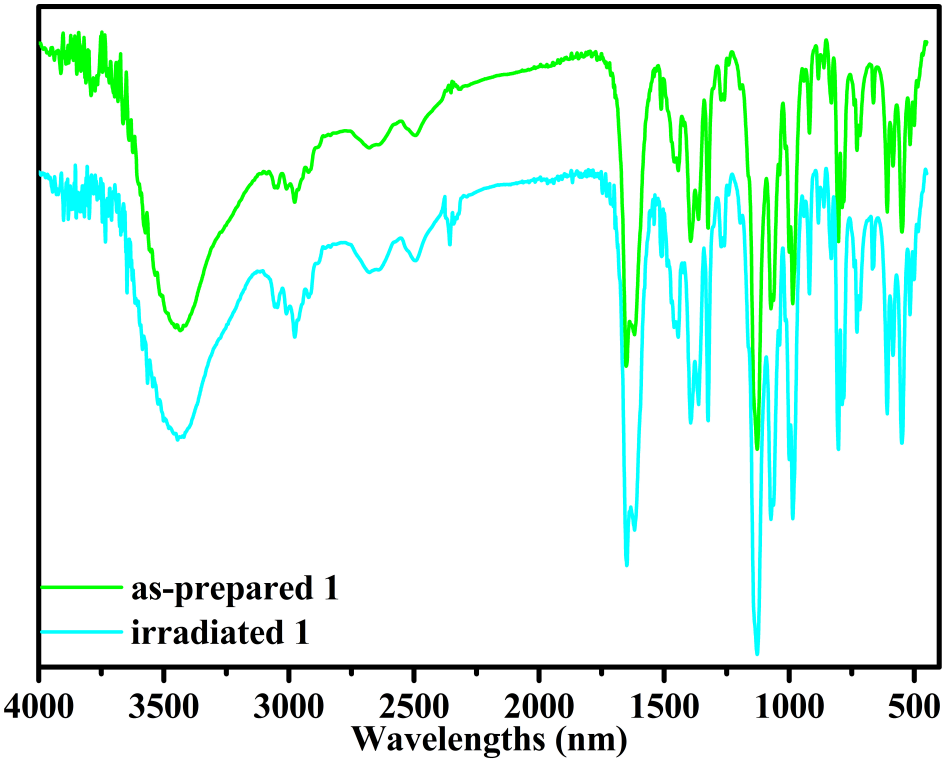

Fig. **S20** IR spectra of as-prepared **1** and irradiated **1**.

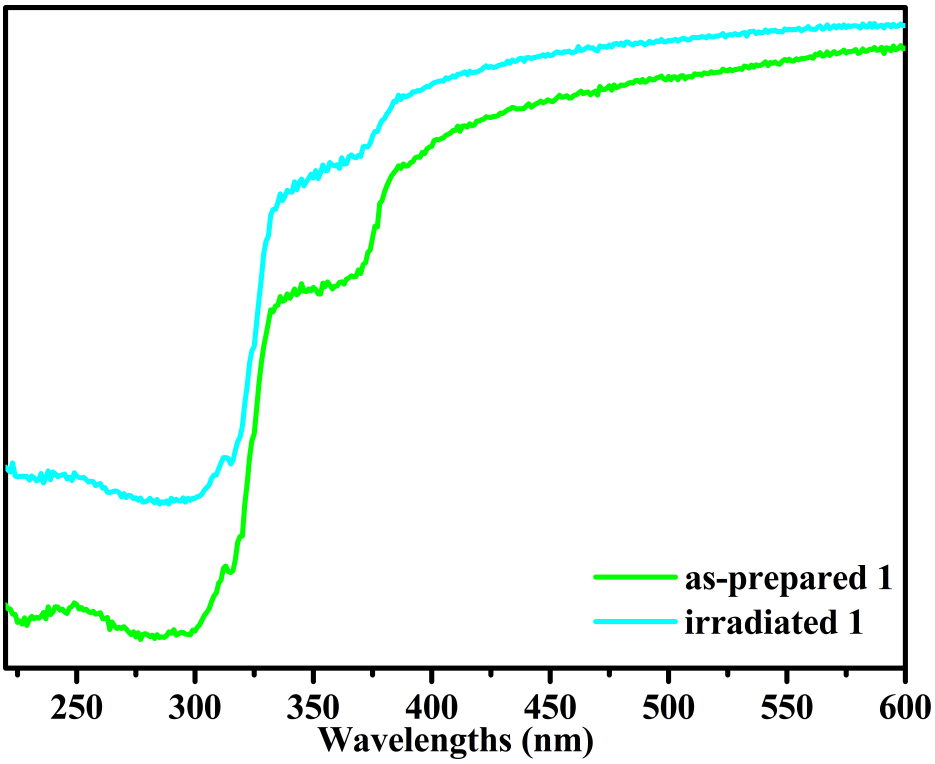

Fig. **S21** The diffuse reflectance spectra of as-prepared **1** and irradiated **1**.

Reference

(1) RIGAKU/MSC, CrystalClear Version 1.3.6, Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX77381-5209, USA, 2004.

(2) G. M. Sheldrick, SHELXTL, Acta Crystallogr., Sect. A64 (2008), 112.