

Photomechanical effect in Zn(II) and Cd(II) 1D coordination polymers: photosalient to non-salient behaviour

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Electronic Supplementary Information

Experimental Procedures

Materials and general method

All chemicals purchased were reagent grade and were used without further purification. Elemental analysis (carbon, hydrogen and nitrogen) was performed on a Perkin–Elmer 240C elemental analyzer. Infrared spectrum in KBr (4500–500 cm^{-1}) was recorded using a Perkin–Elmer FT-IR spectrum RX1 spectrometer. ^1H NMR spectra were recorded on a 400 MHz Bruker Avance 400 FT NMR spectrometer with TMS as an internal reference in $\text{DMSO-}d_6$ solution. The solid-state photoluminescence measurements were made using Horiba Fluorolog with a solid-state sample holder. The solid-state photoluminescence measurements were made using Horiba Jobin Yvon Fluoromax-4 Spectrophotometer (Excitation wavelength – 390 nm) with a solid-state sample holder. CARL ZEISS UHR Field Emission Scanning Electron Microscope (FESEM) was used for SEM images. Photodimerization reaction was carried out using Luzchem photoreactor (8 W UVA lamps) at ~ 350 nm at room temperature. Crystalline ground powder was packed between the glass slides and irradiated under UV light. Glass slides were flipped at regular intervals of time to maintain uniform exposure of UV radiation. Photosalient effects were studied by irradiating good quality single crystal with UV light using Xe-source using MAX-350 optical photoreactor under a microscope equipped with a high-quality camera for capturing videos.

Synthesis of the compounds

Synthesis of 1: A solution of 4-nvp (0.046 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered onto a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.059 g, 0.2 mmol), in H_2O (2 mL) using a 2 mL 1 : 1 (= v/v) solution of MeOH and H_2O followed by layering of 1,4- H_2chdc (0.034 g, 0.2 mmol) neutralized with Et_3N (0.042 g, 0.4 mmol) in 2 mL EtOH. The light yellow colour needle shaped crystals of $[\text{Zn}(4\text{-nvp})(\text{cis-1,4-chdc})]$ (**1**), were obtained after six days (0.060 g, yield 65%). Elemental analysis (%) calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_4\text{Zn}$: C, 64.32; H, 4.97; N, 3.00; found: C 64.5, H 4.6, N 3.2. IR (KBr pellet, cm^{-1}): 1611 $\nu_{\text{as}}(\text{COO}^-)$, 1408 $\nu_{\text{sys}}(\text{COO}^-)$.

Synthesis of 2: A solution of 4-nvp (0.046 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered onto a solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.062 g, 0.2 mmol), in H_2O (2 mL) using a 2 mL 1 : 1 (= v/v) solution of MeOH and H_2O followed by layering of 1,4- H_2chdc (0.034 g, 0.2 mmol) neutralized with Et_3N (0.042 g, 0.4mmol) in 2 mL EtOH. The light yellow colour block

shaped crystals of [Cd(4-nvp)(cis-1,4-chdc)] (**2**), were obtained after ten days (0.060 g, yield 59%). Elemental analysis (%) calcd for C₂₅H₂₃CdNO₄: C, 61.23; H, 4.73; N, 2.86; found: C, 61.5; H, 4.4; N, 2.6. IR (KBr pellet, cm⁻¹): 1542 ν_{as}(COO⁻), 1420 ν_{sys}(COO⁻).

General X-ray Crystallography

Single crystals of **1** and **2** having suitable dimensions, were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated MoK_α radiation (λ, 0.71073 Å). The crystal structure was solved using the SHELXT 2014/4 structure solution program package.¹ Least squares refinements of all reflections within the hkl range -11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16 for **1** -12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16 for **2** were used to figure out the unit cell parameters and crystal-orientation matrices. The collected data (I > 2σ(I)) was integrated by using SAINT² program, and the absorption correction was done by SADABS.³ Non-hydrogen atoms were refined by the help of anisotropic thermal parameters. All the hydrogen atoms were placed in their geometrically perfect positions and constrained to ride on their parent atoms.

Table S1 Crystal data and refinement parameters for compound **1** and **2**

Formula	C ₂₅ H ₂₃ NO ₄ Zn (1)	C ₂₅ H ₂₃ CdNO ₄ (2)
fw	466.83	513.85
cryst syst	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.6664(6)	9.4781(16)
<i>b</i> (Å)	9.5962(7)	9.8709(16)
<i>c</i> (Å)	12.8603(9)	12.141(2)
α (deg)	79.050(2)	97.577(4)
β (deg)	88.970(2)	102.802(4)
γ (deg)	84.185(2)	102.063(4)
<i>V</i> (Å ³)	1044.64(13)	1064.1(3)
<i>Z</i>	2	2
<i>D</i> _{calcd} (g/cm ³)	1.484	1.604
μ (mm ⁻¹)	1.208	1.058
T (K)	273(2)	273(2)
λ (Å)	0.71073	0.71073
GOF on <i>F</i> ²	1.069	1.056
FinalR indices [<i>I</i> > 2 σ (<i>I</i>)] ^{a,b}	<i>R</i> 1 = 0.0221 <i>wR</i> 2 = 0.0585	<i>R</i> 1 = 0.0305 <i>wR</i> 2 = 0.0803

$${}^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, {}^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table S2 Selected bond lengths and bond angles **1**

Bond length (Å)	
Zn(1)-O(1)	2.0343(11)
Zn(1)-N(1)	2.0369(12)
Zn(1)-O(3)a	2.0562(12)
Zn(1)-O(2)c	2.0327(12)
Zn(1)-O(4)d	2.0680(12)
Bond angle (°)	
O(1)-Zn(1)-N(1)	100.18(5)
O(1)-Zn(1)-O(3)a	90.63(5)
O(1)-Zn(1)-O(2)c	160.62(5)
O(1)-Zn(1)-O(4)d	87.73(5)
O(3)a-Zn(1)-N(1)	103.46(5)
O(2)c-Zn(1)-N(1)	99.07(5)
O(4)d-Zn(1)-N(1)	95.84(5)
O(2)c-Zn(1)-O(3)a	87.08(5)
O(3)a-Zn(1)-O(4)d	160.61(5)
O(2)c-Zn(1)-O(4)d	88.10(5)

Symmetry transformation a = $-1+x,y,z$; c = $-x,2-y,2-z$; d = $1-x,2-y,2-z$

Table S3 Selected bond lengths and bond angles **2**

Bond length (Å)	
Cd(1)-O(1)	2.204(3)
Cd(1)-N(1)	2.280(3)
Cd(1)-O(3)a	2.317(3)
Cd(1)-O(4)a	2.330(4)
Cd(1)-O(2)b	2.223(3)
Bond angle (°)	
O(1)-Cd(1)-N(1)	97.09(10)
O(1)-Cd(1)-O(3)a	101.43(10)
O(1)-Cd(1)-O(4)a	133.75(12)
O(1)-Cd(1)-C(25)a	120.90(10)
O(1)-Cd(1)-O(2)b	115.74(11)
O(3)a-Cd(1)-N(1)	135.65(10)
O(4)a-Cd(1)-N(1)	83.64(12)
N(1)-Cd(1)-C(25)a	110.21(10)
O(2)b-Cd(1)-N(1)	93.55(11)
O(3)a-Cd(1)-O(4)a	54.72(11)
O(3)a-Cd(1)-C(25)a	27.38(10)
O(2)b-Cd(1)-O(3)a	113.33(11)
O(4)a-Cd(1)-C(25)a	27.38(12)
O(2)b-Cd(1)-O(4)a	110.34(13)
O(2)b-Cd(1)-C(25)a	113.66(10)

Symmetry transformation a =1-x,2-y,-z; b =2-x,2-y,-z

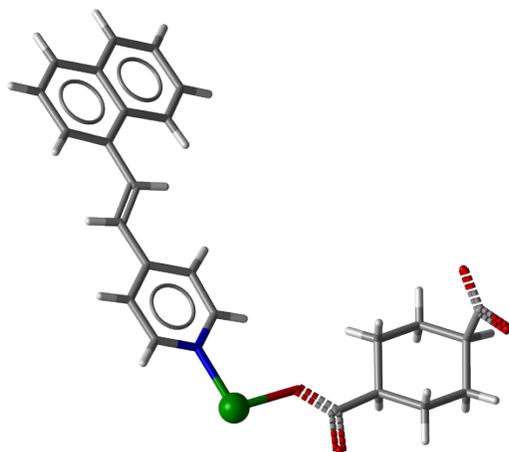


Fig. S1 Asymmetric view of compound 2.

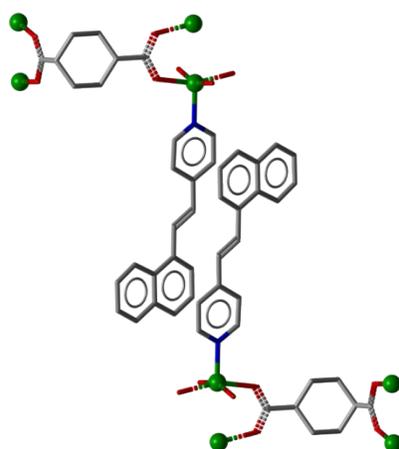


Fig. S2 Alignment of 4-nvp ligands in compound 2. Hydrogen atoms are omitted for clarity.

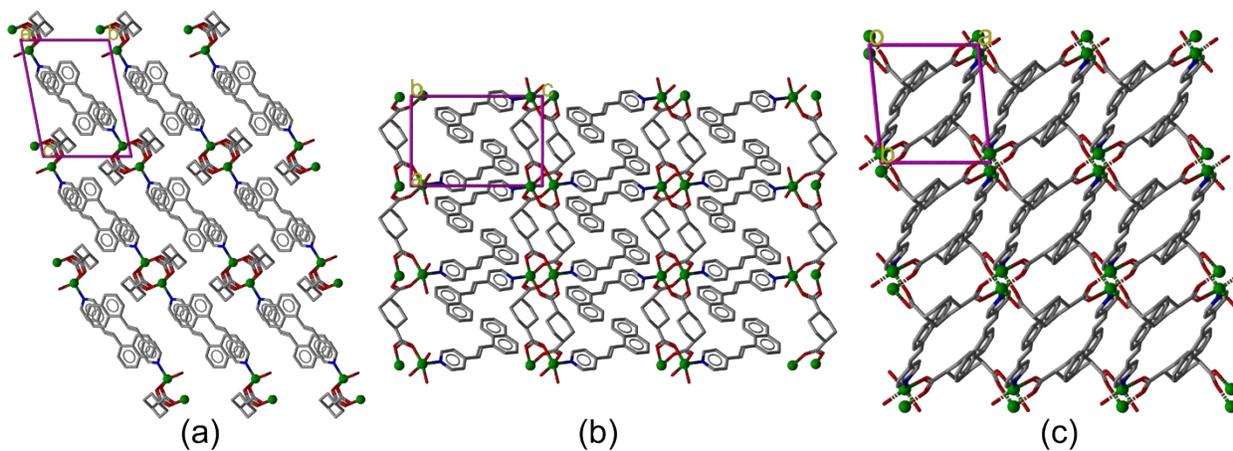


Fig. S3 Single-crystal structure of 1 viewed along different cell axes.

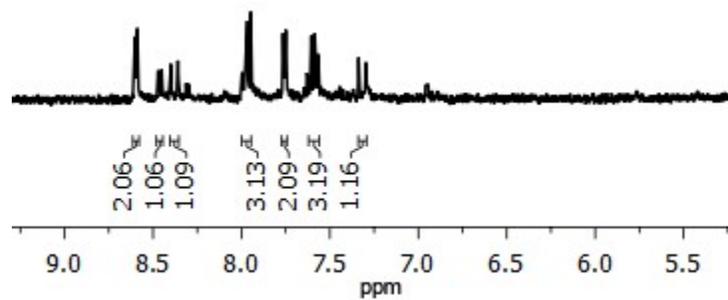


Fig. S4 ¹H NMR spectrum (400 MHz, DMSO-d₆) of compound 1.

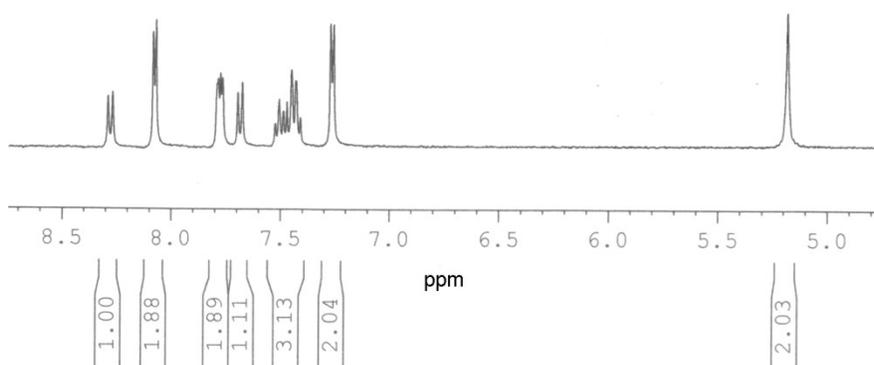


Fig. S5 ¹H NMR spectrum (400 MHz, DMSO-d₆) of dimerized *rctt*-4-pncb.

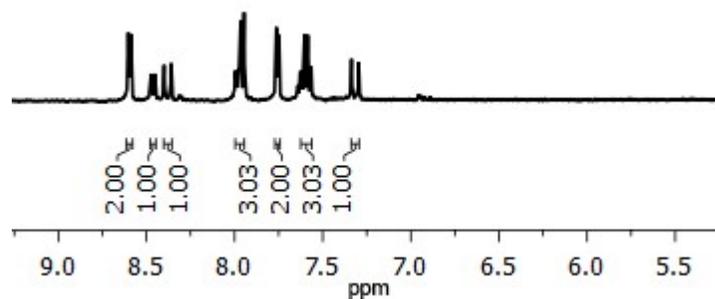


Fig. S6 ¹H NMR spectrum (400 MHz, DMSO-d₆) of compound 2.

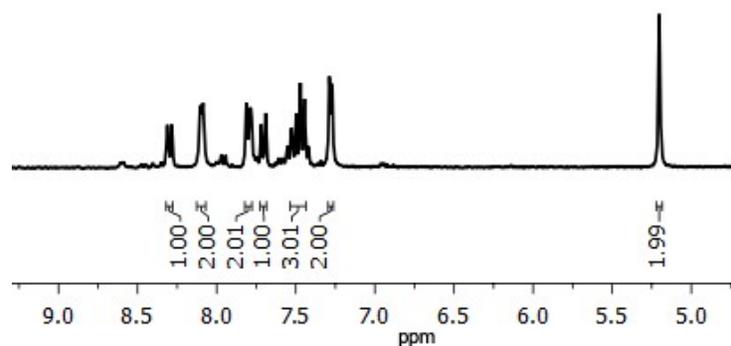


Fig. S7 ¹H NMR spectrum (DMSO-d₆) of compound 2 after UV irradiation.

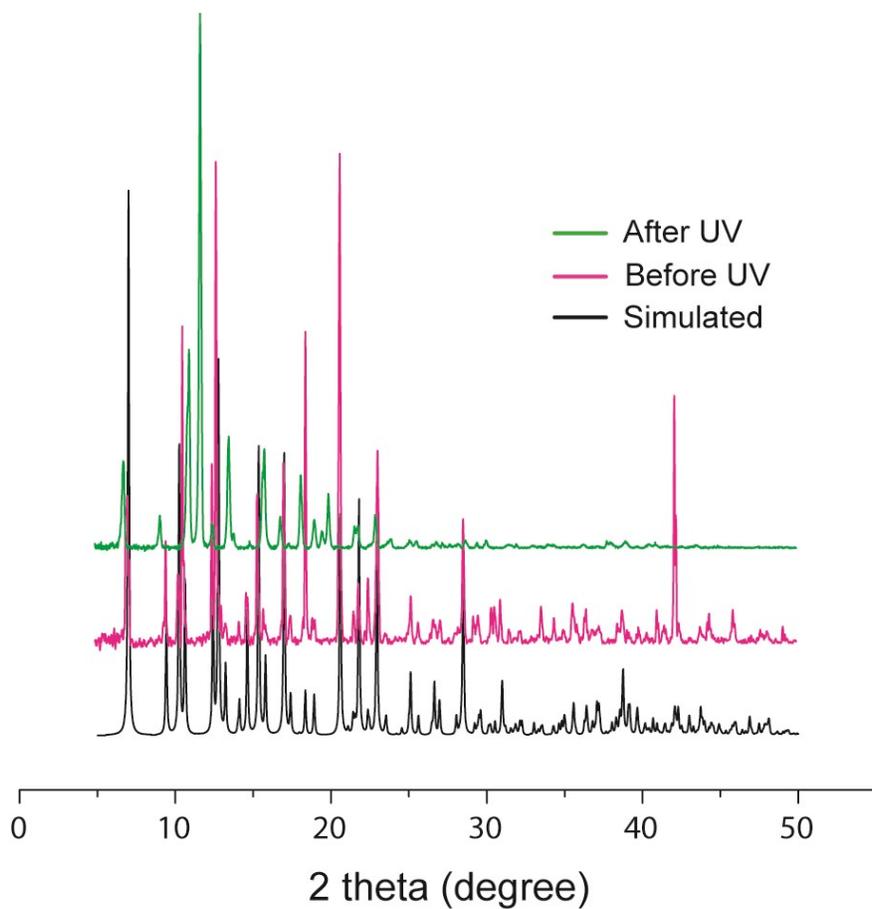


Fig. S8 PXR D patterns of simulated **1** (black), before (magenta) and after UV irradiation (olive).

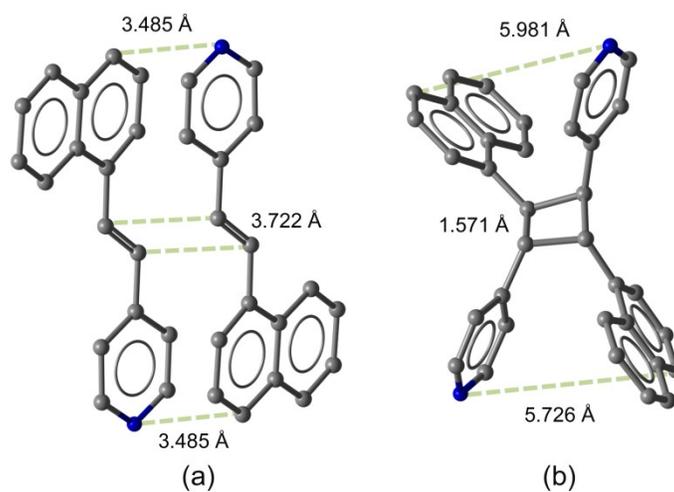


Fig. S9 Comparison between (a) aligned 4-nvp ligands in **1** and (b) isolated dimerized *rctt*-4-*pncb*.

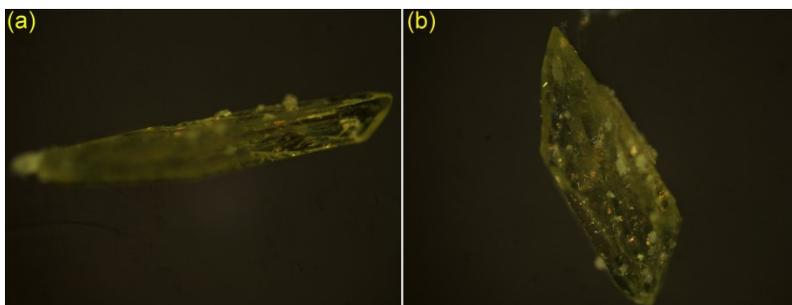


Fig. S10 Morphology dependent PS effect in **1** involving (a) needle crystal (fast photomechanical motion) and (b) thick crystal (slow motion).

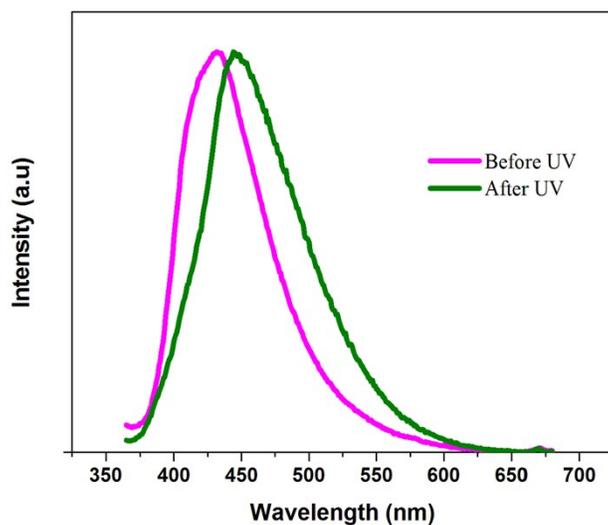


Fig. S11 Solid state photoluminescence spectra of **1** (before and after UV irradiation; excitation wavelength 350 nm with slit 3 nm).

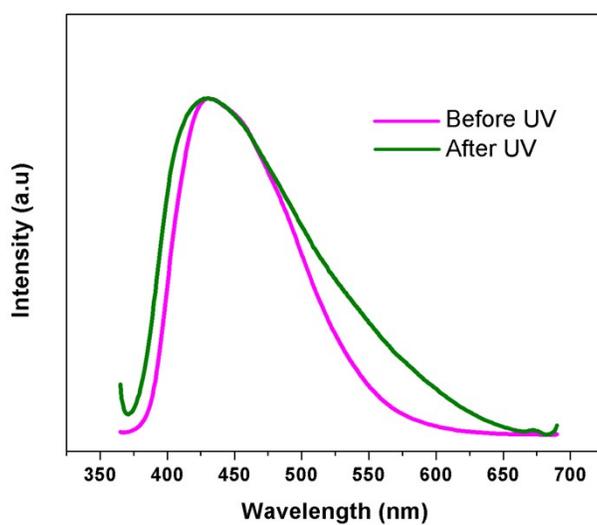


Fig. S12 Solid state photoluminescence spectra of **2** (before and after UV irradiation; excitation wavelength 350 nm with slit 3 nm).

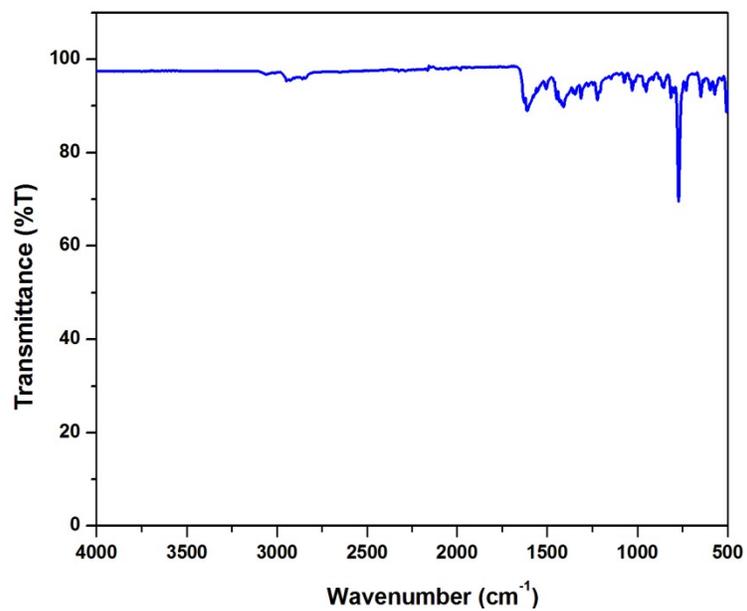


Fig. S13 IR spectrum of **1** before UV irradiation.

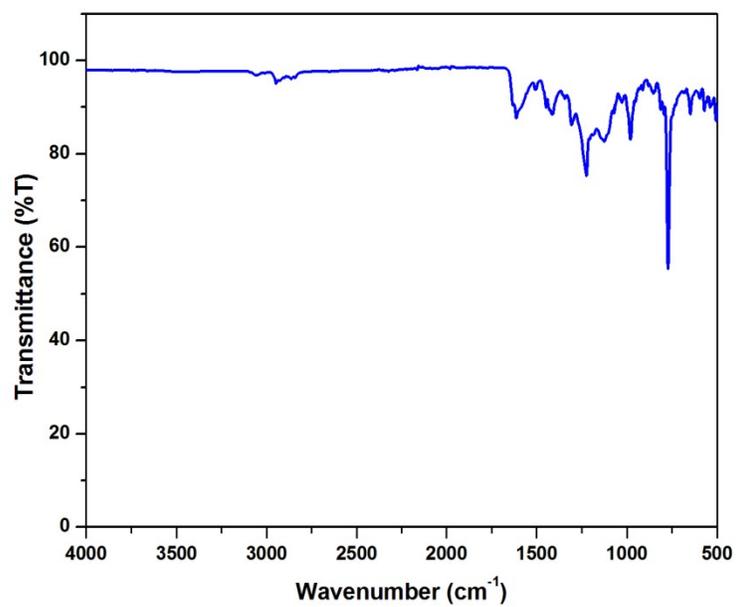


Fig. S14 IR spectrum of **1** after UV irradiation.

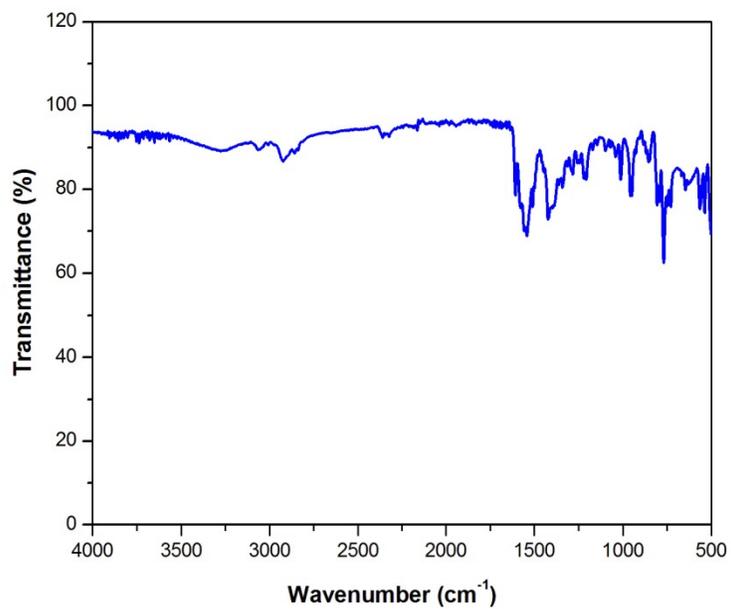


Fig. S15 IR spectrum of **2** before UV irradiation.

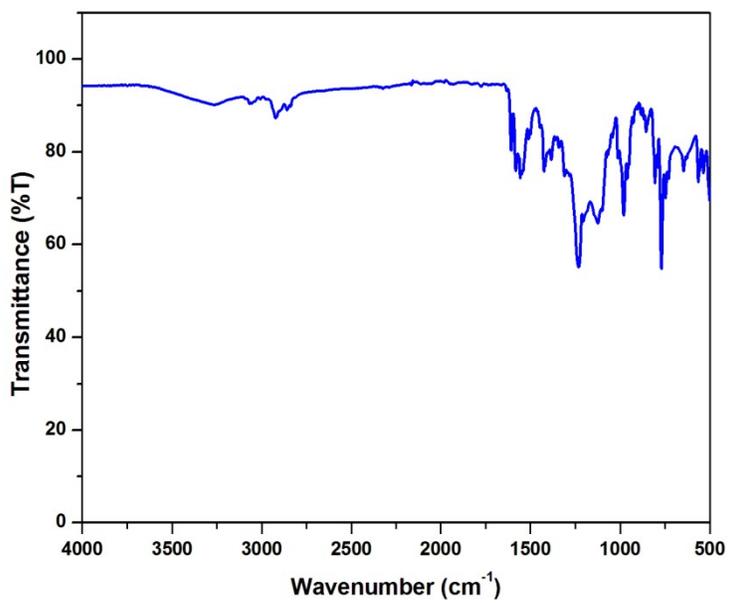


Fig. S16 IR spectrum of **2** after UV irradiation.

References

- (1) G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.
- (2) *SMART and SAINT*; Bruker AXS Inc.: Madison, WI, 1998.
- (3) *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.