Sunlight-driven photosalient effect of 1D coordination polymer and release of an of elusive cyclobutane derivative

Basudeb Dutta,[a] Chittaranjan Sinha,[b] and Mohammad Hedayetullah Mir*[a]

[a]Department of Chemistry, Aliah University, New Town, Kolkata 700 156, India.

[b]Department of Chemistry, Jadavpur University, Jadavpur, Kolkata 700 032, India.

Supporting 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. Thermogravimetric analysis was recorded on a Perkin–Elmer Pyris Diamond TG/DTA in the temperature range between 30°C and 600°C under a nitrogen atmosphere at a heating rate of 12°C min^{-1}. The PXRD data was collected on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2θ range of 5–50. Photodimerization reaction was carried out using Luzchem photoreactor (8 W UVA lamps) at ~350 nm for 2 hrs at room temperature. Morphology and energy-dispersive X-ray spectroscopy (EDS) analyses of compound **1** before and after UV irradiation were performed via field emission scanning electron microscopy (FESEM; JEOL, JSM-6700F). The ESI–MS spectrum was recorded on a Water HRMS model XEVO-G2QTOF#YCA351 spectrometer.

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 $Zn(NO)_3 \cdot 6H_2O$ (0.06 g, 0.2 mmol), in H_2O (2 mL) using a 2 mL 1 : 1 (

= v/v) buffer solution of MeOH and H_2O followed by layering of H_2glu (0.026 g, 0.2 mmol) neutralized with Et_3N (0.042 g, 0.4mmol) in 2 mL EtOH. The yellow color needle shaped crystals of $\{[Zn(glu)(4\text{-nvp})]\}_n$, (**1**) were obtained after three days (0.056 g, yield 65%). Elemental analysis (%) calcd for $C_{22}H_{19}NO_4Zn$: C 61.91, H 4.49, N3.28; found: C 61.60, H 4.51, N 3.33. ^{1}H NMR (400 MHz, DMSO, TMS): δ 8.58 (d, 2H, py-H), 8.45 (d, 1H, naphthalene-H), 8.36 (d, 1H, CH=CH), 7.95 (m, 3H, naphthalene-H), 7.74 (d, 2H, py-H), 7.59 (m, 3H, naphthalene-H), 7.30 (d, 1H, CH=CH).

UV Irradiation of **1:** Colourless needle-like single crystals of **1** (0.071 g, 0.1 mmol) were irradiated using a UV-lamp (LZC-UVA; Luzchem) centred at ~350 nm wavelength for 2 h to obtain photodimerized product in almost quantitative yield. ^{1}H NMR (400 MHz, DMSO, TMS): 8.27 (d, 1H, naphthalene-H), δ 8.08 (d, 2H, py-H), 7.77 (m, 2H, naphthalene-H), 7.68 (m, 1H, naphthalene-H), 7.44 (m, 3H, naphthalene-H), 7.26 (d, 2H, py-H), 5.18 (s, 2H, CH–CH).

Synthesis of **2**: The powder residue (obtained by UV irradiation of **1** for 2 h) was dissolved in ethanol and kept for slow evaporation. Colourless needle shaped crystals of $C_{71}H_{60}N_4O$, **2** were appeared after few days (yield 55%). ^{1}H NMR (400 MHz, DMSO, TMS): 8.28 (d, 1H, naphthalene-H), δ 8.07 (d, 2H, py-H), 7.78 (m, 2H, naphthalene-H), 7.68 (m, 1H, naphthalene-H), 7.47 (m, 3H, naphthalene-H), 7.26 (d, 2H, py-H), 5.18 (s, 2H, CH–CH).

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] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. CCDC 1911202-1911203 contain the supplementary crystallographic data for this paper.

Crystal data of **1**: Triclinic space group $P\bar{1}$, a = 7.8987(7), b = 11.2682(10), c = 11.2825(10) Å, α = 74.239(3), β = 70.908(3), γ = 87.139(3), V = 912.44(14) Å^3, Z = 2, ρ_{calcd} = 1.553 g.cm^{-3}, μ = 1.375 mm^{-1}, T = 296 K, $R1$ = 0.0473, $wR2$ = 0.1280 with $I > 2\sigma(I)$, GOF = 0.968.

Crystal data of **2**: Monoclinic space group $P2_1/C$, a = 13.8251(15), b = 15.8177(18), c = 13.4161(15) Å, β = 112.749(3), V = 2705.6(5) Å^3, Z = 2, ρ_{calcd} = 1.209 g.cm^{-3}, μ = 0.071 mm^{-1}, T = 296 K, $R1$ = 0.0673, $wR2$ = 0.1918 with $I > 2\sigma(I)$, GOF = 1.133.

Crystal data of **1′**: Triclinic space group $P\bar{1}$, a = 14.061(4), b = 13.654(4), c = 16.597(4) Å, α = 72.172(18), β = 79.890(18), γ = 68.482(18), V = 2814.8(14) Å^3, Z = 2.

It is to be mentioned that only cell parameters and space group of **1′** can be reported with confidence because of the poor quality of single crystal data.

Results and Discussion

Table S1. Selected bond lengths and bond angles in **1**

Zn(1) - O(1)	2.026(2)	C(22)-O(3) - Zn(1)d	125.52(18)
Zn(1) - N(1)	2.039(2)	C(22)-O(4) - Zn(1)b	128.48(19)
Zn(1) - O(4)a	2.050(2)	Zn(1) - N(1) - C(1)	118.22(19)
Zn(1) - O(2)c	2.048(2)	Zn(1) - N(1) - C(5)	123.51(18)
Zn(1) - O(3)d	2.053(2)	C(18)-O(2) - Zn(1)c	124.65(17)
O(1) - Zn(1) - N(1)	100.12(9)	Zn(1)- O(1) - C(18)	129.82(17)
O(1) - Zn(1) - O(4)a	91.55(9)	O(2)c -Zn(1) - O(3)d	85.88(9)
O(1) - Zn(1) - O(2)c	159.55(8)	O(4)a- Zn(1) - O(3)d	159.89(8)
O(1) - Zn(1) - O(3)d	87.49(9)	O(4)a- Zn(1) - O(2)c	88.13(9)
N(1) - Zn(1) - O(4)a	101.80(9)	N(1)- Zn(1) - O(3)d	98.14(9)
N(1) - Zn(1) - O(2)c	99.96(8)		

Symmetry Code: a = -1+x, y, z; b = 1+x, y, z; c = -x, 2-y, 2-z; d = 1-x, 2-y, 2-z

Table S2. Selected bond lengths and bond angles in **2**

N(1) - C(1)	1.314(6)	N(1)-C(1) - C(2)	124.7(3)
N(1) - C(5)	1.325(4)	C(1)-C(2)-C(3)	119.4(3)
N(2) - C(18)	1.330(5)	N(1)-C(5)-C(4)	124.0(3)
N(2) - C(22)	1.326(5)	C(2)-C(3)-C(4)	115.9(2)
C(1) - C(2)	1.384(5)	C(2)-C(3)-C(6)	121.0(2)
C(2) - C(3)	1.384(3)	C(4)-C(3)-C(6)	123.1(2)
C(3)-C(4)	1.377(3)	C(3)-C(4)-C(5)	120.3(2)
C(3)-C(6)	1.501(3)	C(3)-C(6)-C(7)	119.1(2)
C(1)-N(1)-C(5)	115.7(3)	C(3)-C(6)-C(24)	119.06(19)
C(18)-N(2)- C(22)	115.7(3)	C(7)-C(6)-C(24)	88.79(17)

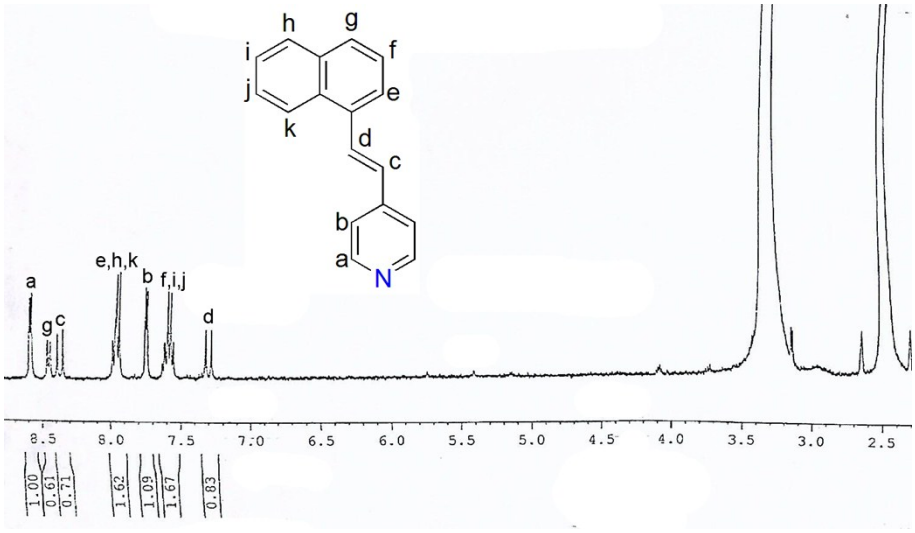

Fig. S1. ^{1}H NMR spectrum of **1** in d_6-DMSO.

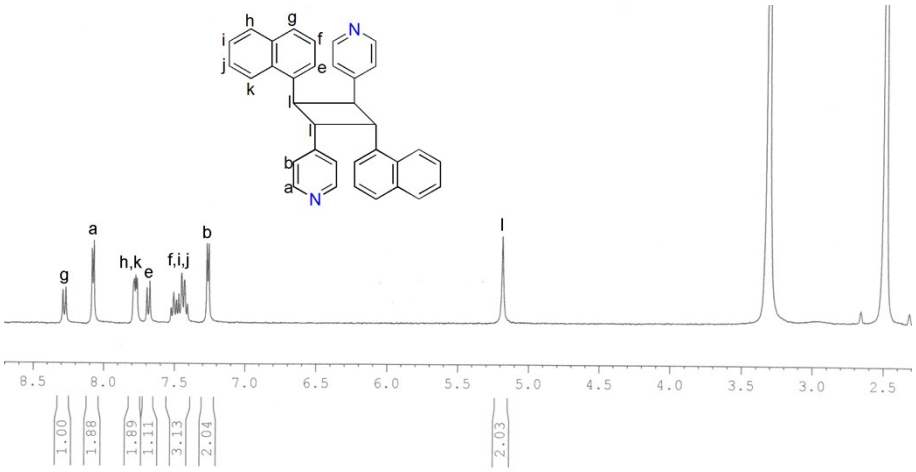

Fig. S2. ^{1}H NMR spectrum of UV irradiated **1** in d_6-DMSO.

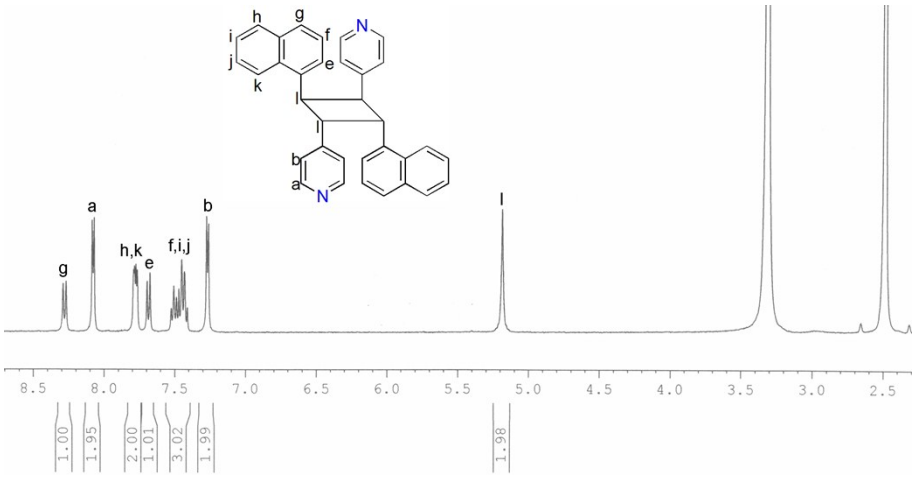

Fig. S3. ^{1}H NMR spectrum of sunlight irradiated **1** in d_6-DMSO.

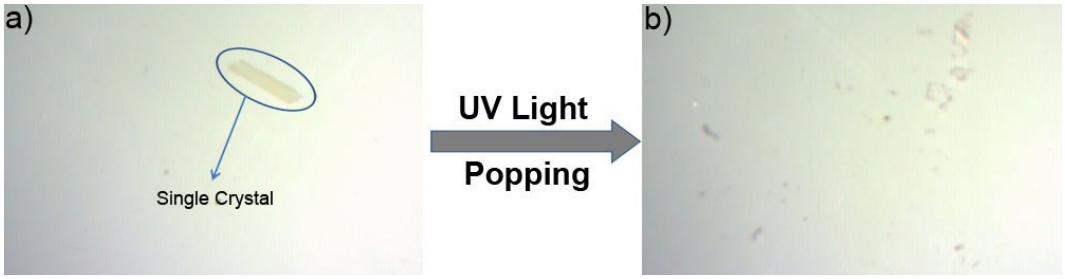

Fig. S4. Optical microscopic picture of a single crystal of compound **1** a) before and b) after UV irradiation.

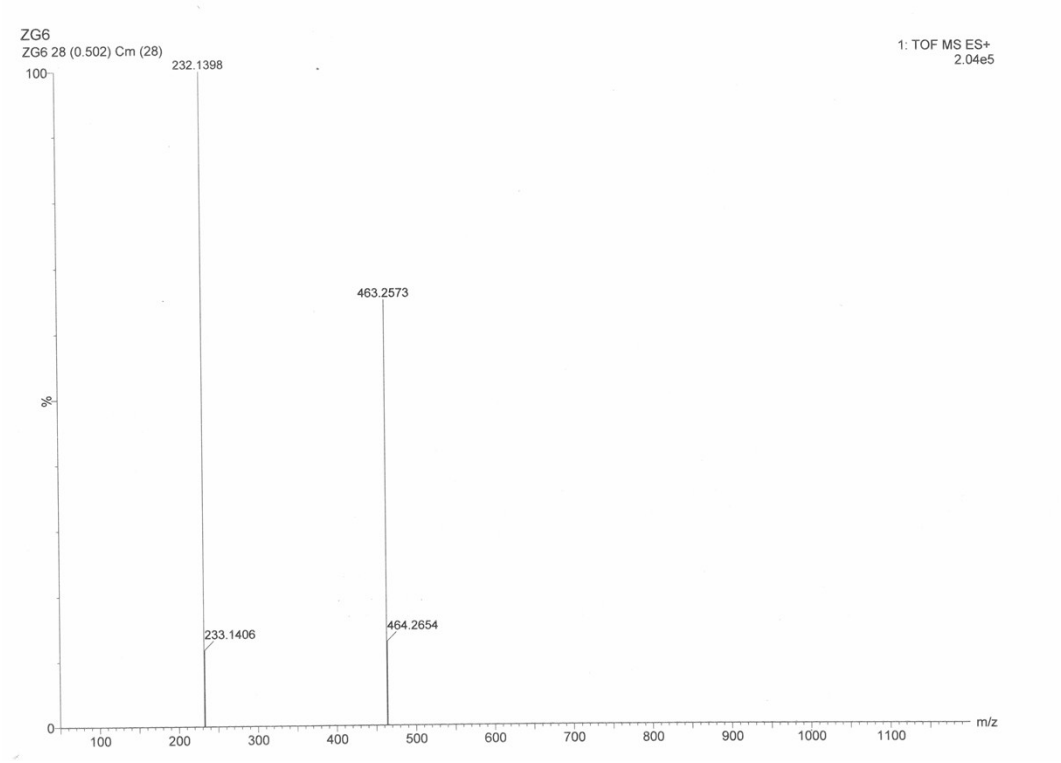

Fig. S5. ESI–MS spectrum of photoirradiated **1**.

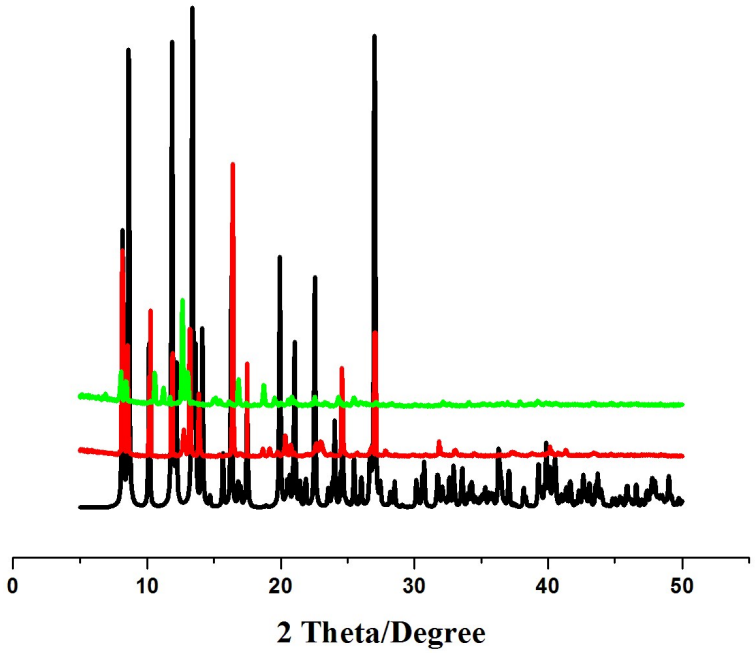

Fig. S6. PXRD patterns of simulated **1** (black), as-synthesized **1** (red) and photoirradiated **1** (green).

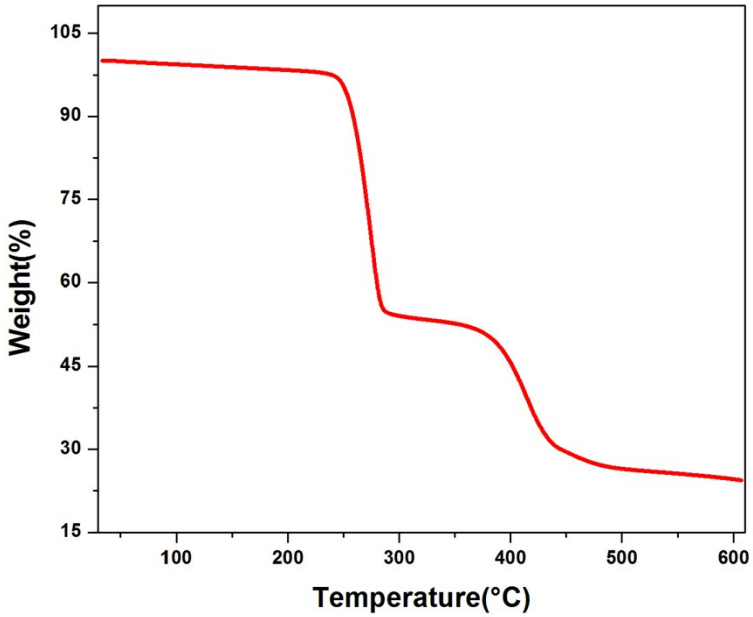

Fig. S7. TGA plot of **1** at N_2 atmosphere.

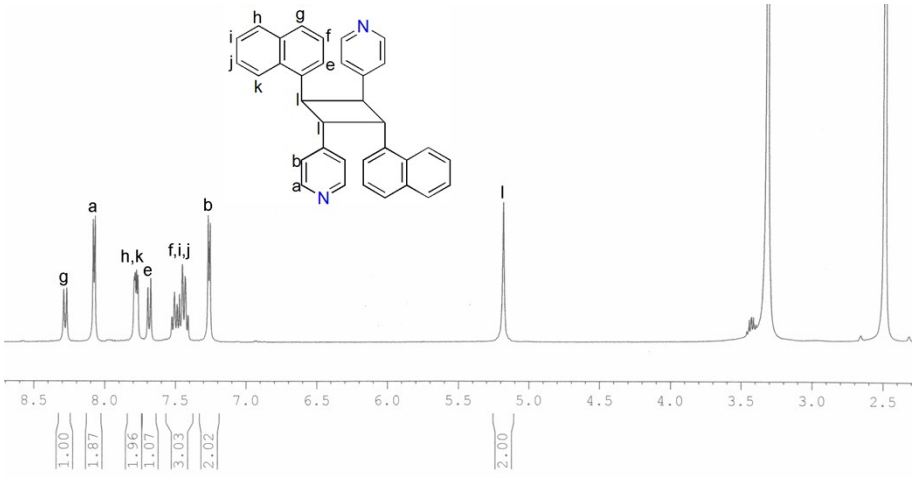

Fig. S8. ^{1}H NMR spectrum of **2** in d_6-DMSO.

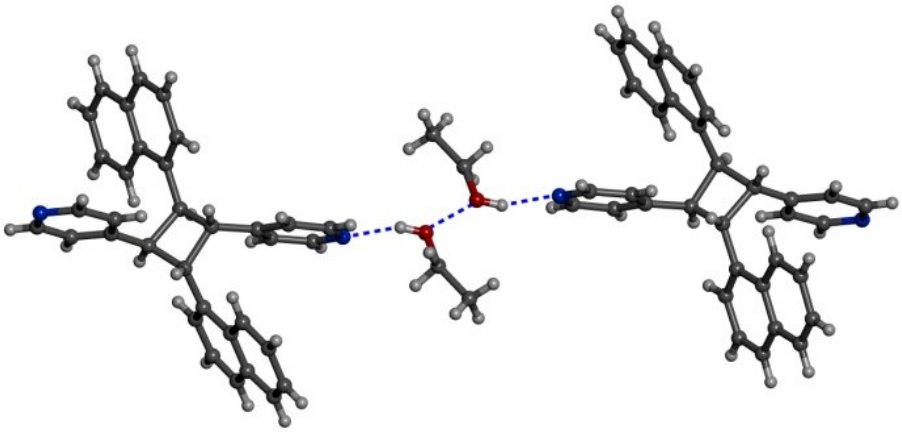

Fig. S9. Formation of ethanol dimer in **2**.

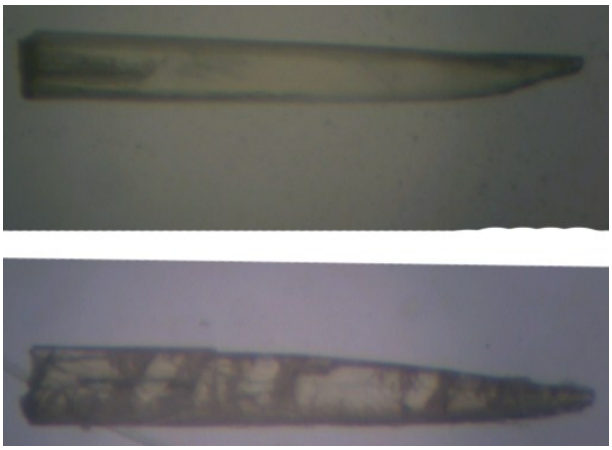

Fig. S10. Cracking of the crystal of **1** in paratone oil.

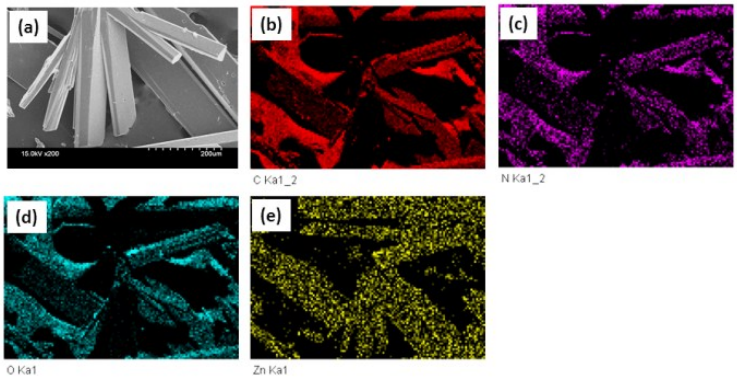

Fig. S11. (a) FESEM image of compound **1**. (b, c, d and e) EDS mapping of **1**.

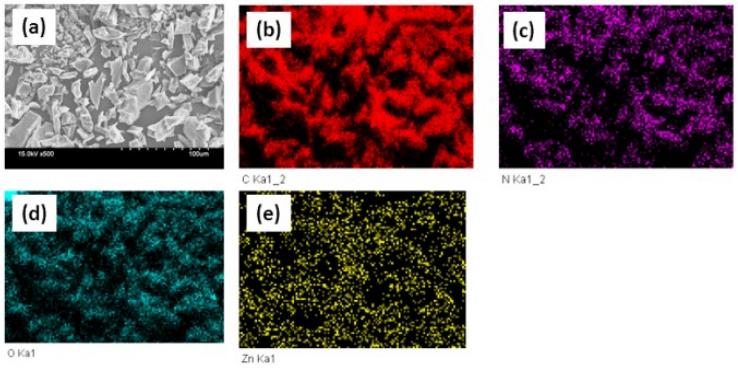

Fig. S12. FESEM image of **1** after UV irradiation. (b, c, d and e) EDS mapping of **1** after UV irradiation.

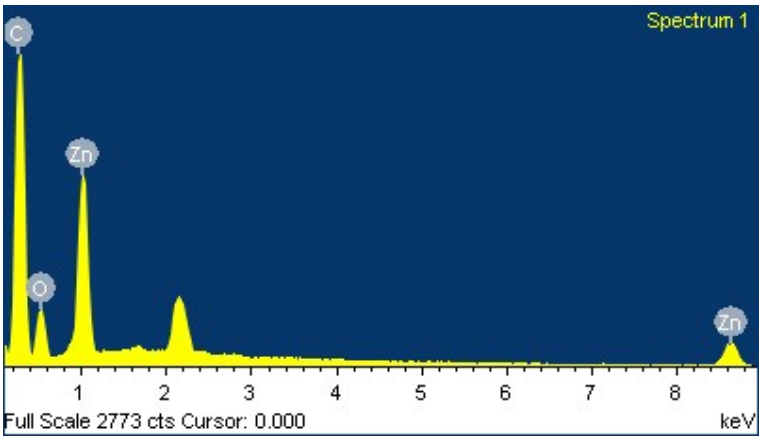

Fig. S13. EDS spectrum of compound **1**.

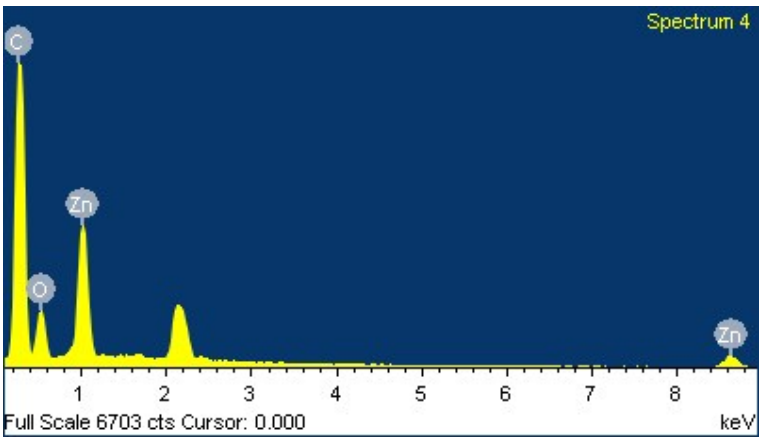

Fig. S14. EDS spectrum of compound **1** after UV irradiation.

Table S3. Elemental analysis for compound **1**

Element	Weight%	Atomic%
C K	61.60	79.27
O K	15.97	15.43
Zn L	22.43	5.30
Totals	100.00	

Table S4. Elemental analysis for compound **1** after UV irradiation

Element	Weight%	Atomic%
C K	63.24	79.17
O K	17.43	16.38
Zn L	19.33	4.45
Totals	100.00	

Table S5. Unit cell data of **1**, **2** and **1′**.

Unit cell parameters	**Crystal 1**	**Crystal 2**	**Crystal 1′**
a (Å)	7.8987(7)	13.8251(15)	14.061(4)
b (Å)	11.2682(10)	15.8177(18)	13.654(4)
c (Å)	11.2825(10)	13.4161(15)	16.597(4)
α (°)	74.239(3)	90	72.172(18)
β (°)	70.908(3)	112.749(3)	79.890(18)
γ (°)	87.139(3)	90	68.482(18)
V (Å^3)	912.44(14)	2705.6(5)	2814.8(14)

References

(1) G. M. Sheldrick, *Acta Cryst. A*, **2015**, *71*, 3-8.