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Photoreactivity of Polymorphs of a Ladder Polymer with Crisscross and Parallel Orientations of C=C Bonds

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Supporting Information

Experimental Section:

Synthesis of $[Zn_2(\mu\text{-}O_2C\text{-}p\text{-}Tol)_2(O_2C\text{-}p\text{-}Tol)_2(\mu\text{-}bpe)_2]$ (1). An aqueous solution (10.0 ml) of $Zn(NO_3)_2{\cdot}6H_2O$ (29.8 mg, 0.1 mmol) was mixed with *para*-toluic acid (27.2 mg, 0.2 mmol) and bpe (18.2 mg, 0.1 mmol) in 10 ml of acetone and then with NaOH (0.4 ml). Slow evaporation of the clear solution resulted in colourless rhombus blocks in 2 days. ^{1}H-NMR δ_H (300 MHz, D_6-DMSO, ppm), 8.60 (4H, d, J = 6.1 Hz pyridyl protons), 7.83 (4H, d, J = 8.2 Hz phenyl protons), 7.62 (4H, d, J = 6.2 Hz pyridyl protons), 7.55 (2H, s, -CH=CH-), 7.21 (4H, d, J = 8.2 Hz phenyl protons), 2.34 (6H, s, methyl-H). Elemental analysis, (%) Found: C, 64.92; H, 4.88; N, 5.35 Calcd for $ZnC_{28}N_2H_{24}O_4$: C, 64.93; H, 4.67; N, 5.41. Thermogravimetric analysis shows the stability of the polymer until 190°C without any weight loss.

Synthesis of $[Zn_2(\mu\text{-}O_2C\text{-}p\text{-}Tol)_2(O_2C\text{-}p\text{-}Tol)_2(\mu\text{-}bpe)_2]$ (2) and $[Zn_2(O_2C\text{-}p\text{-}Tol)_4(\mu\text{-}bpe)]$ (3). An aqueous solution (5.0 ml) of $Zn(CH_3COO)_2{\cdot}6H_2O$ (22 mg, 0.1 mmol) was mixed with a solution of *p*-toluic acid (27.2 mg, 0.2 mmol) and bpe (18.2 mg, 0.1 mmol) along with NaOH (8 drops) in 5.0 ml of acetone. Slow evaporation of the clear solution resulted in colourless monoclinic thin crystals of **2** in a day and the colourless needle crystals of **3** overnight. The mixture of crystals was separated by handpicking for further characterization.

Characterization of $[Zn_2(\mu\text{-}O_2C\text{-}p\text{-}Tol)_2(O_2C\text{-}p\text{-}Tol)_2(\mu\text{-}bpe)_2]$ (2). ^{1}H-NMR δ_H (300 MHz, D_6-DMSO, ppm), 8.60 (4H, d, J = 6.1 Hz pyridyl protons), 7.83 (4H, d, J = 8.2 Hz phenyl protons), 7.61 (4H, d, J = 6.2 Hz pyridyl protons), 7.54 (2H, s, -CH=CH-), 7.21 (4H, d, J = 8.2 Hz phenyl protons), 2.34 (6H, s, methyl-H). Elemental analysis, (%) Found: C, 63.67; H, 4.31; N, 5.20 Calcd for $ZnC_{28}N_2H_{24}O_4$: C, 64.93; H, 4.67; N, 5.41. Thermogravimetric analysis shows the stability of the polymer until 200°C without any weight loss.

Characterization of [Zn_2 (O_2C-*p*-Tol)$_4$ (μ-bpe)] (3) ^{1}H-NMR δ_H (300 MHz, D_6-DMSO, ppm), 8.60 (4H, d, *J* = 6.1 Hz pyridyl protons), 7.83 (8H, d, *J* = 8.2 Hz phenyl protons), 7.61 (4H, d, *J* = 6.2 Hz pyridyl protons), 7.54 (2H, s, -CH=CH-), 7.21 (8H, d, *J* = 8.2 Hz phenyl protons), 2.34 (12H, s, methyl-H). Elemental analysis, (%) Found: C, 61.61; H, 3.88; N, 3.16 Calcd for $Zn_2C_{44}N_2H_{38}O_8$: C, 61.91; H, 4.49; N, 3.28. Thermogravimetric analysis shows no weight loss until 180°C.

UV irradiation. The UV irradiation experiments were conducted by using Luzchem Photoreactor (Intensity ~ 1.75 mW-cm^{-2}) and a radiation of wavelength 350 nm.

Synthesis of [Zn_2(μ-O_2C-*p*-Tol)$_2$(O_2C-*p*-Tol)$_2$(*rctt*-tpcb)] (4) Compound **4** was obtained as single crystals when the single crystals of **1** were subjected to UV irradiation for 2 h using Luzchem photoreactor (wavelength = 350 nm). ^{1}H-NMR δ_H (300 MHz, D_6-DMSO, ppm), δ_H (ppm): 8.34 (8H, d, *J* = 4.6 Hz pyridyl protons), 7.83 (8H, d, *J* = 8.0 Hz phenyl protons), 7.24 – 7.20 (16H, m, phenyl protons and pyridyl protons), 4.67 (4H, s, cyclobutane protons), 2.34 (12H, s, methyl-H). Elemental analysis, (%) Found: C, 63.67; H, 4.31; N, 5.20 Calcd for $ZnC_{28}N_2H_{24}O_4$: C, 64.93; H, 4.67; N, 5.41. Thermogravimetric analysis shows no weight loss until 170°C.

Synthesis of [Zn_2(μ-O_2C-*p*-Tol)$_2$(O_2C-*p*-Tol)$_2$ (*rctt*-tpcb)] (5)

Compound **5** was obtained by UV irradiation of **2** for 1.5 h using Luzchem photoreactor (wavelength = 350nm). The single crystals were not retained under these conditions. ^{1}H-NMR δ_H (300 MHz, D_6-DMSO, ppm), 8.34 (d, 8H, *J* = 4.6 Hz, pyridyl protons), 7.83 (d, 8H, *J* = 8.0 Hz phenyl protons), 7.24 – 7.20 (m, 16H, phenyl protons and pyridyl protons), 4.66 (s, 4H, cyclobutane protons), 2.34 (s, 12H, methyl-H). Elemental analysis, (%) Found: C, 63.67; H, 4.31; N, 5.20 Calcd for $ZnC_{28}N_2H_{24}O_4$: C, 64.93; H, 4.67; N, 5.41. Thermogravimetric analysis shows no weight loss until 170°C.

Materials and General Methods. All chemicals purchased were of reagent grade and were used without further purification. The elemental analyses were carried out at the Elemental Analysis Laboratory, CMMAC, Department of Chemistry, National University of Singapore. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 5^{o}C min^{-1} using a SDT 2960 Thermal Analyser. The NMR spectra were

recorded with a 300 MHz FT-NMR spectrometer with TMS as internal reference. Powder X-ray diffraction patterns (PXRD) were recorded on a Siemens D500 diffractometer with graphite monochromatized Cu-Kα radiation (λ = 1.54056 Å) at room temperature (23°C).

X-ray Crystallography. Intensity data for **1, 2, 3 and 4** were collected at 100(2) K on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated MoKα (λ = 0.71073 Å) radiation using a sealed tube (2.4 kW). An empirical absorption correction was applied to the data using the SADABS program.[1] All the structures were solved by using direct methods and refined on F^2 by full- matrix least squares procedures with SHELXTL.[2,3] Crystal data as well as details of data collection and refinement are summarized in Table 1.

Compound	**1**	**2**	**3**	**4**
CCDC deposition No.	**957292**	**957293**	**957294**	**957295**
Empirical Formula	$C_{56}H_{48}N_4O_8Zn_2$	$C_{56}H_{48}N_4O_8Zn_2$	$C_{44}H_{38}N_2O_8Zn_2$	$C_{56}H_{48}N_4O_8Zn_2$
Formula Weight	1035.72	1035.72	853.50	1035.72
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength λ, (Å)	0.71073	0.71073	0.71073	0.71073
Crystal System	Triclinic	Monoclinic	Triclinic	Triclinic
Space Group	Pī	C2/c	Pī	Pī
a(Å)	10.2881(15)	15.6758(14)	8.2441(10)	10.208(7)
b(Å)	11.0671(16)	13.6884(12)	11.3889(13)	10.368(7)
c(Å)	11.2031(16)	22.957(2)	11.8203(15)	11.703(8)
α, (deg)	88.609(3)	90.00	67.142(5)°	87.864(12)
β, (deg)	70.855(3)	102.617(2)	72.808(5)°	74.045(12)
γ, (deg)	79.324(3)	90.00	77.218(5)°	81.843(12)
V, (Å^3)	1183.3(3)	4807.1(7)	969.8(2) Å^3	1178.8(13)
Z	1	4	1	1
D_{calcd}, Mg cm^{-3}	1.453	1.431	1.461	1.459
Absorption Coefficient μ,mm^{-1}	1.076	1.059	1.294	1.080
F(000)	536	2144	440	536
Crystal Size, mm^3	0.44 x 0.28 x 0.06	0.43 x 0.19 x 0.08	0.100 x 0.060 x 0.040	0.50 x 0.28 x 0.10
Theta range for data	1.87 to 27.49°.	1.82 to 27.50°.	1.955 to 27.499°.	1.81 to 27.50°.

collection(°)				
Index Ranges	-13<=h<=13, -14<=k<=14, -14<=l<=14	-17<=h<=20, -17<=k<=17, -29<=l<=27	-10<=h<=10, -14<=k<=14, -15<=l<=15	-13<=h<=12, -13<=k<=13, -15<=l<=15
Reflections Collected	15217	16581	39075	13686
Independent reflections	5435 [R(int) = 0.0596]	5518 [R(int) = 0.0632]	4458 [R(int) = 0.0636]	5400 [R(int) = 0.0587]
Completeness to theta = 27.50°	99.8 %	99.7 %	99.9 %	99.7 %
Data[I> 2σ(I)]/ restraints/ parameters	5435 / 0 / 318	5519 / 0 / 318	4458 / 0 / 255	5400 / 0 / 318
GOF on F^2	1.045	1.071	1.011	1.003
Final R indies[I> 2σ(I)][a,b]	R1 = 0.0522, wR2 = 0.1220	R1 = 0.0506, wR2 = 0.1200	R1 = 0.0296, wR2 = 0.0596	R1 = 0.0498, wR2 = 0.1166
Final R indies (all data) [a,b]	R1 = 0.0672, wR2 = 0.1278	R1 = 0.0680, wR2 = 0.1348	R1 = 0.0406, wR2 = 0.0626	R1 = 0.0775, wR2 = 0.1267
Largest diff. peak and hole	0.879 and -0.697 e.Å^{-3}	0.668 and -0.535 e.Å-3	0.410 and -0.354 e.Å^{-3}	1.268 and -0.863 e.Å^{-3}

References

1. Bruker, Bruker AXS Inc., Madison, Wisconsin, USA., Editon edn., 2001.
2. G. M. Sheldrick, *Acta Crystallographica Section A*, 2008, **A64**, 112-122.
3. P. Müller, *Crystal structure refinement: a crystallographers guide to SHELXL*, Oxford University Press, 2006.

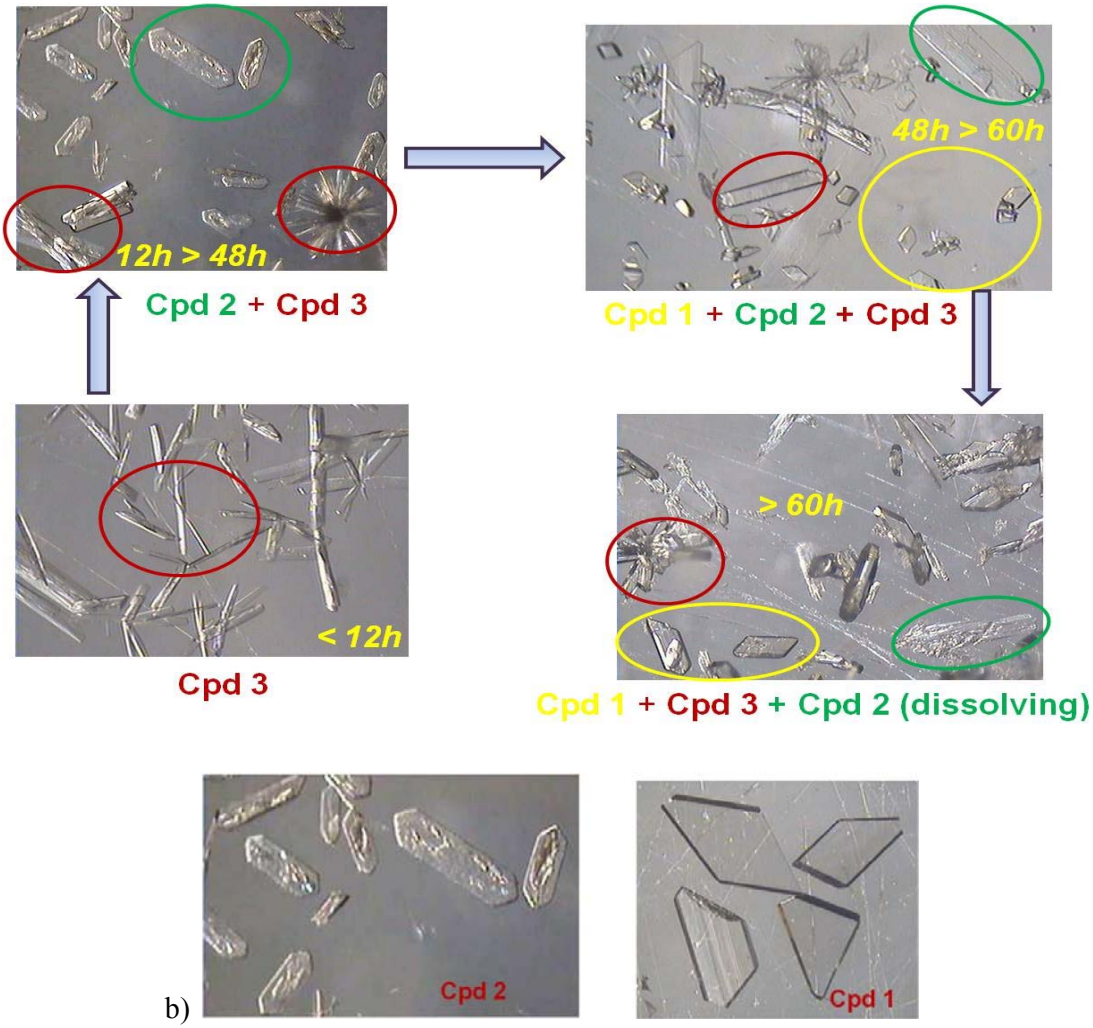

Figure S1: (a) Photographs of **1-3** during crystallization over the period of time, (b) the crystal morphology of the polymorphs **1** and **2**.

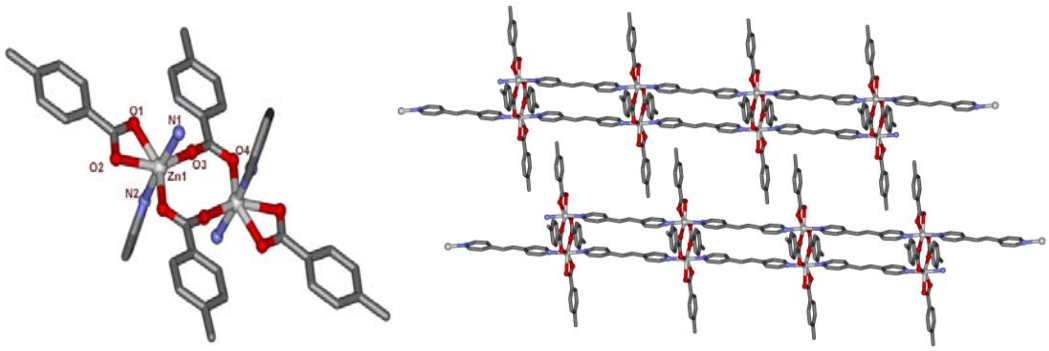

Figure S2: (a) A perspective view showing the coordination environment around Zn(II) in **1,** (b) the relative orientation of the ladder chains in **1**. The hydrogen atoms are omitted for clarity.

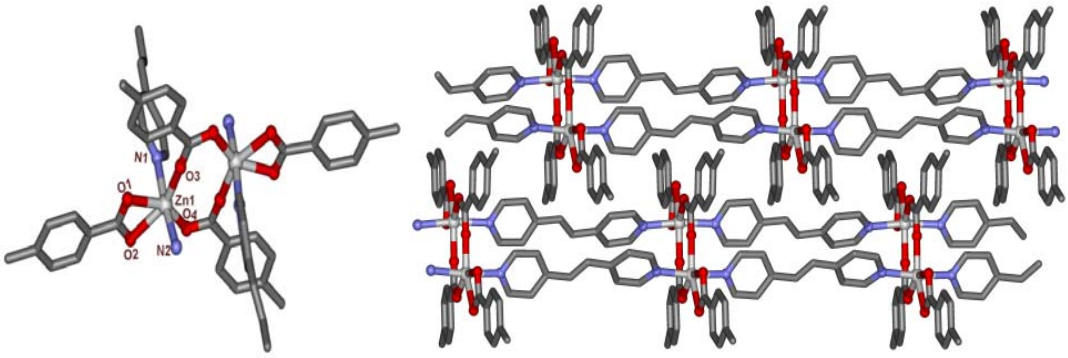

Figure S3: (a) A perspective view showing the coordination environment around Zn(II) in **2,** (b) the relative orientation of the ladder chains in **2**. The hydrogen atoms are omitted for clarity.

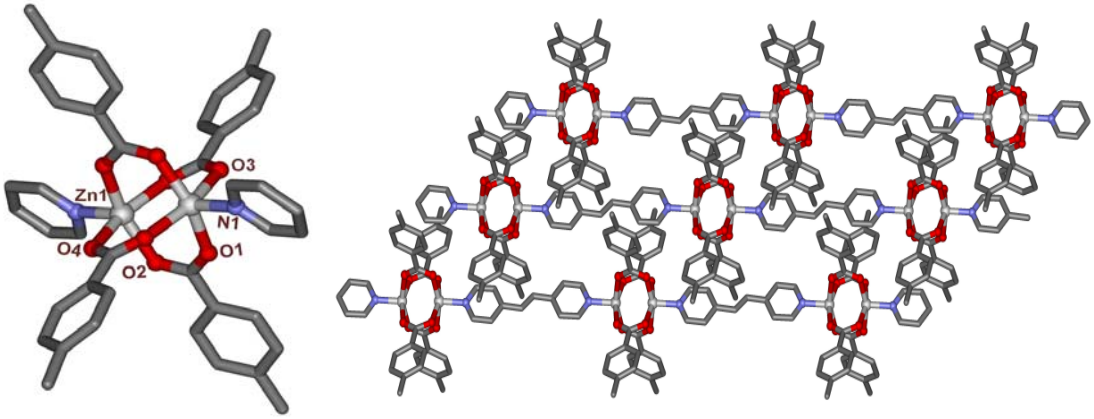

Figure S4: (a) A perspective view showing the coordination environment around Zn(II) in **3,** (b) the relative orientations of the ladder chains in **3**. The hydrogen atoms are omitted for clarity.

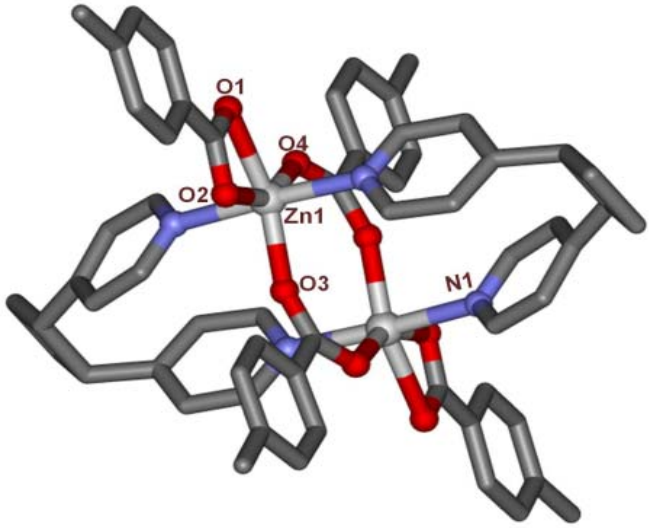

Figure S5: (a) A perspective view showing the coordination environment around Zn(II) in **4.** The hydrogen atoms are omitted for clarity.

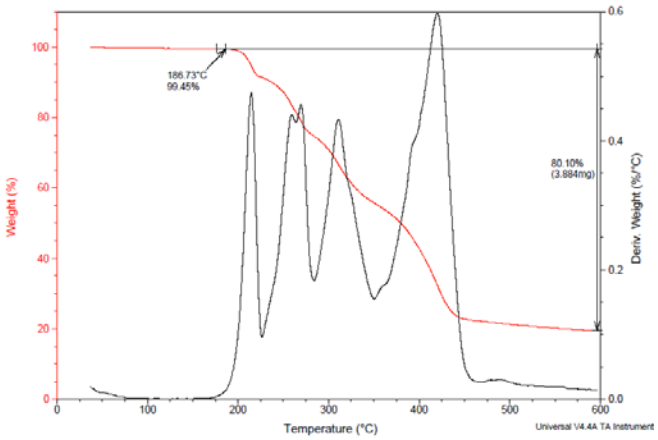

Figure S6: TGA curve of **1**, showing the stability of structure up to 190ºC.

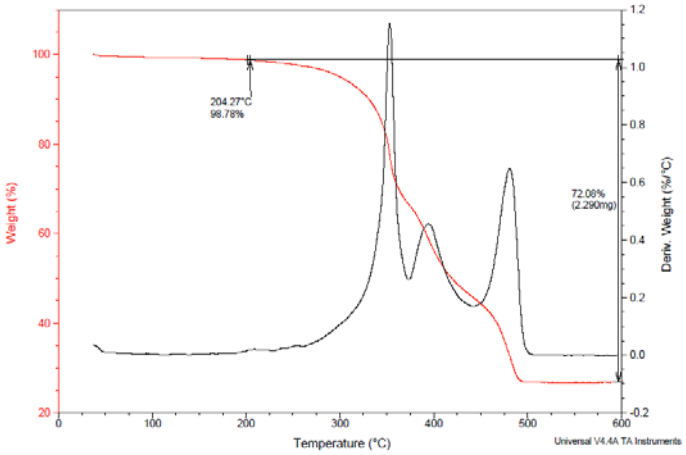

Figure S7: TGA curve of **2**, showing the stability of structure up to 190ºC.

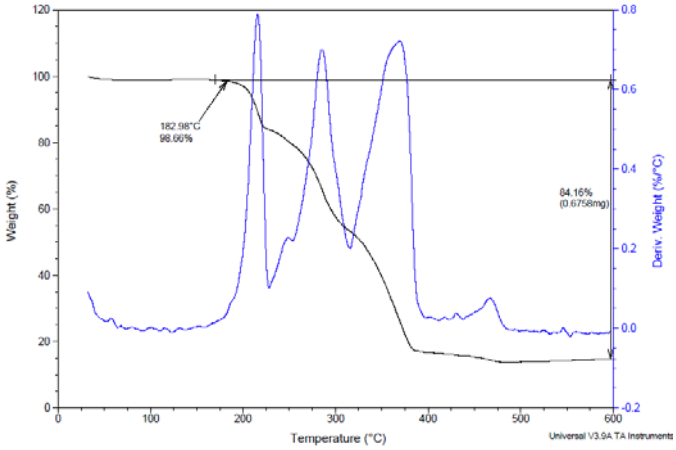

Figure S8: TGA curve of **3**, showing the stability of structure up to 180ºC.

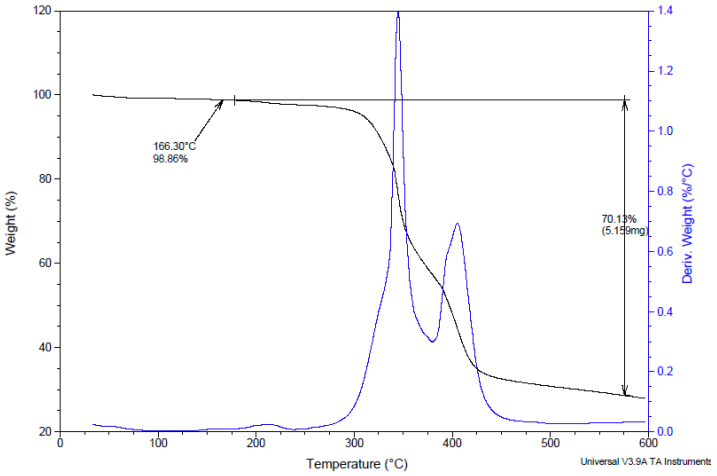

Figure S9: TGA curve of **4**, showing the stability of structure up to 170ºC.

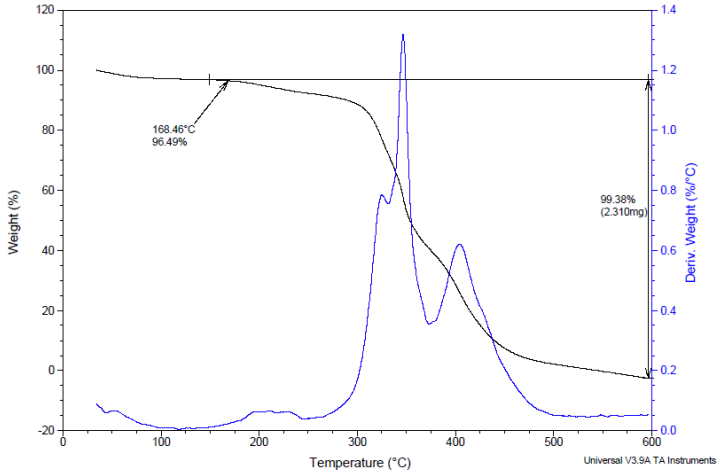

Figure S10: TGA curve of **5**, showing the stability of structure up to 170ºC.

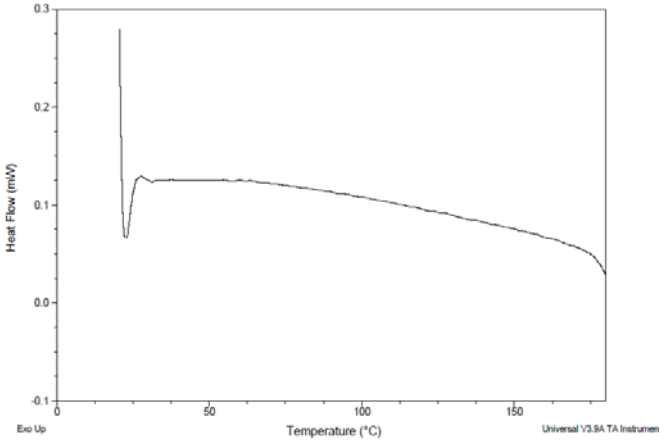

Figure S11: DSC curve of **1.**

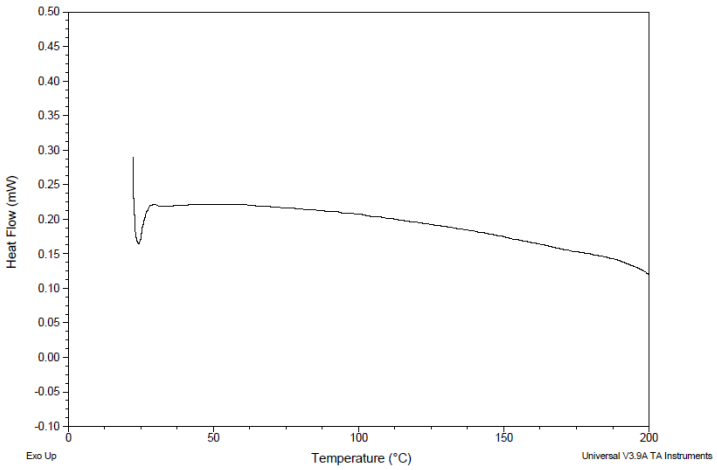

Figure S12: DSC curve of **2.**

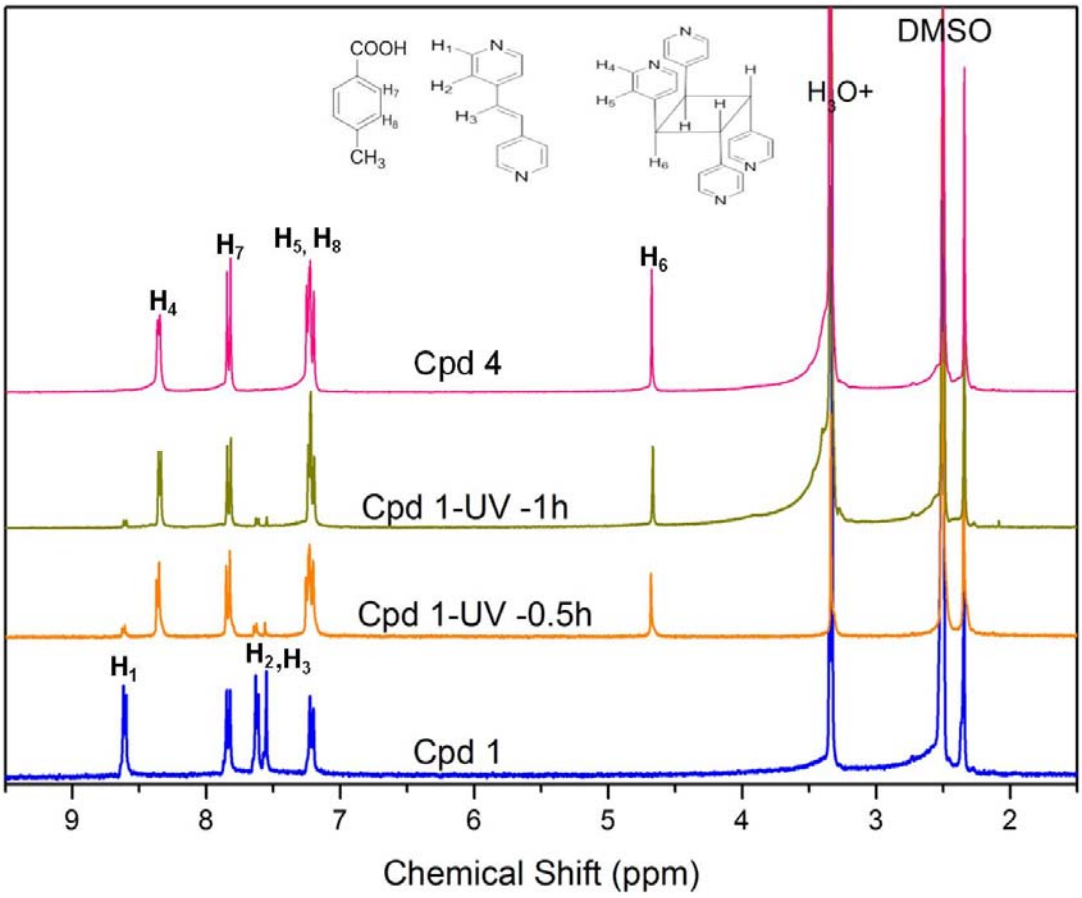

Figure S13: ^{1}H-NMR spectra of single crystals of **1**, and the irradiated product **4** after dissolved in D_6-DMSO.

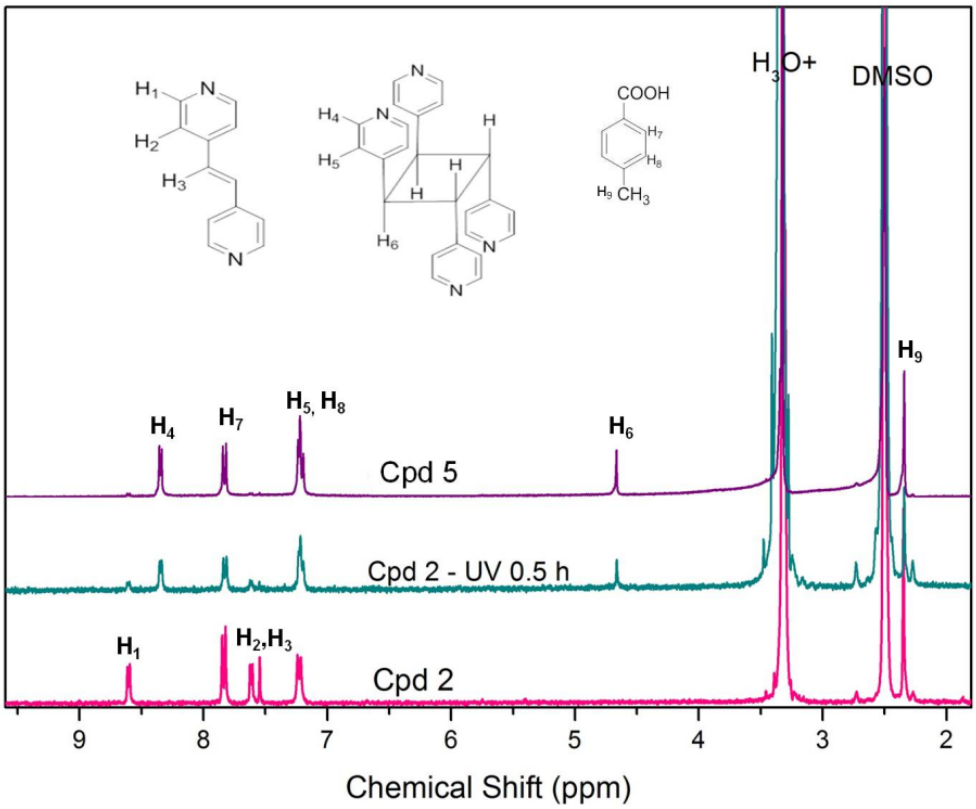

Figure S14: ^{1}H-NMR spectra of the single crystals of **2**, and the photo product **5** after dissolved in D_6-DMSO.

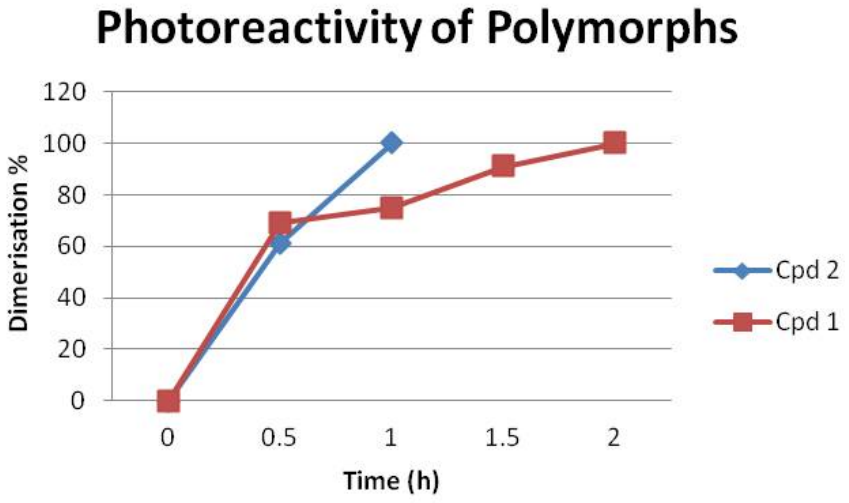

Figure S15: Percentage conversion versus time plots for the single crystals of **1** and **2** under UV light derived from ^{1}H-NMR spectral analysis

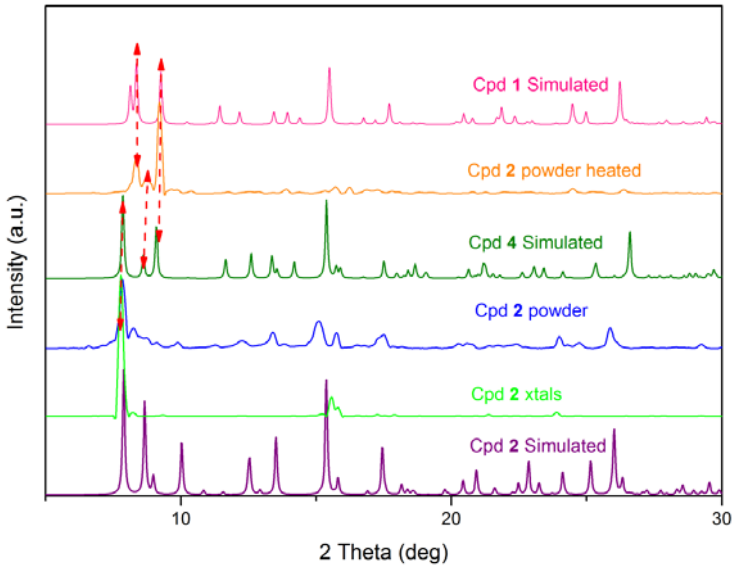

Figure S16: PXRD patterns of **1**, **2** and **4** crystals and the phase change on grinding and heating.

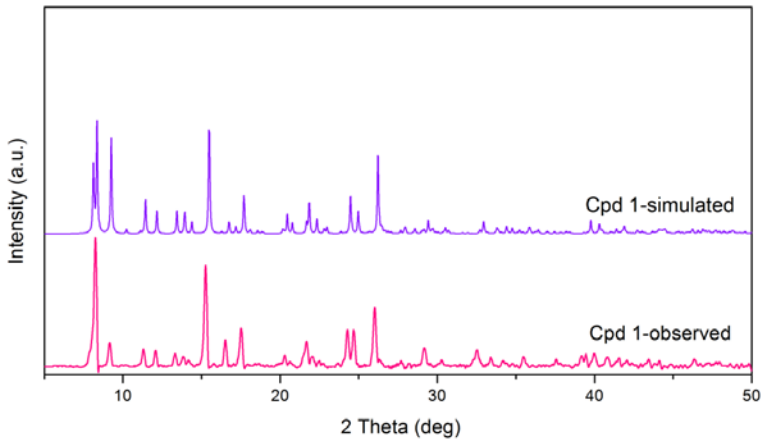

Figure S17: PXRD pattern of **1** with the simulated pattern obtained from single crystal data.

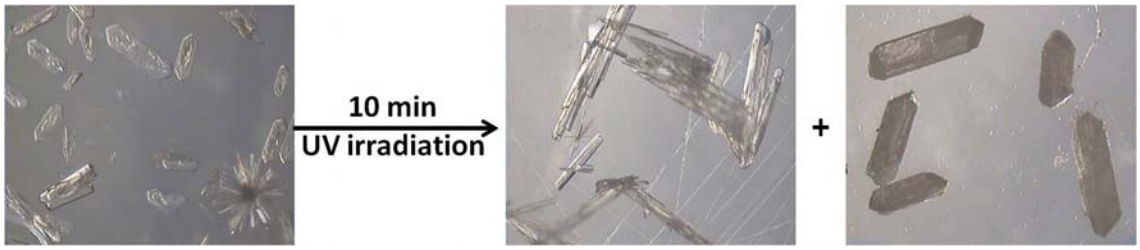

Figure S18: Photographs of Cpd **2** and Cpd **3** after 10 min of UV irradiation.

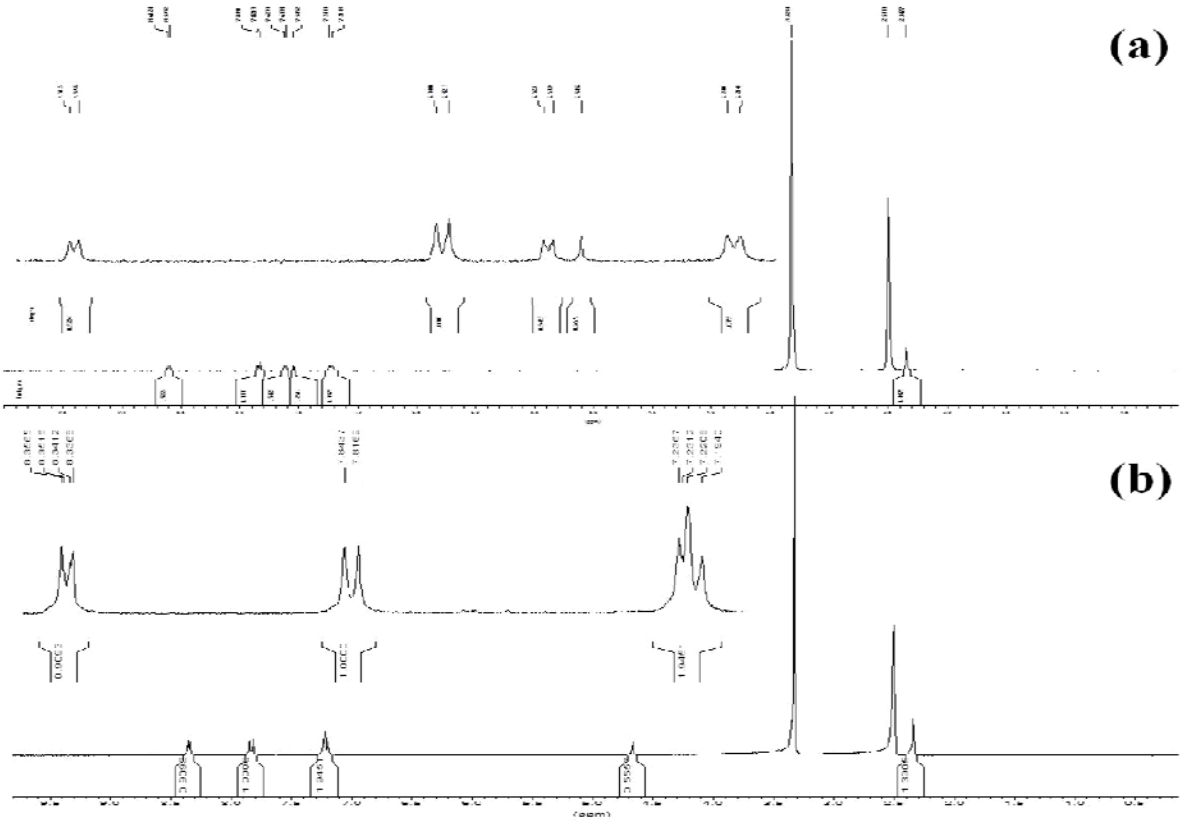

Figure S19: NMR spectra of (a) Cpd **2** (b) Cpd **4**.

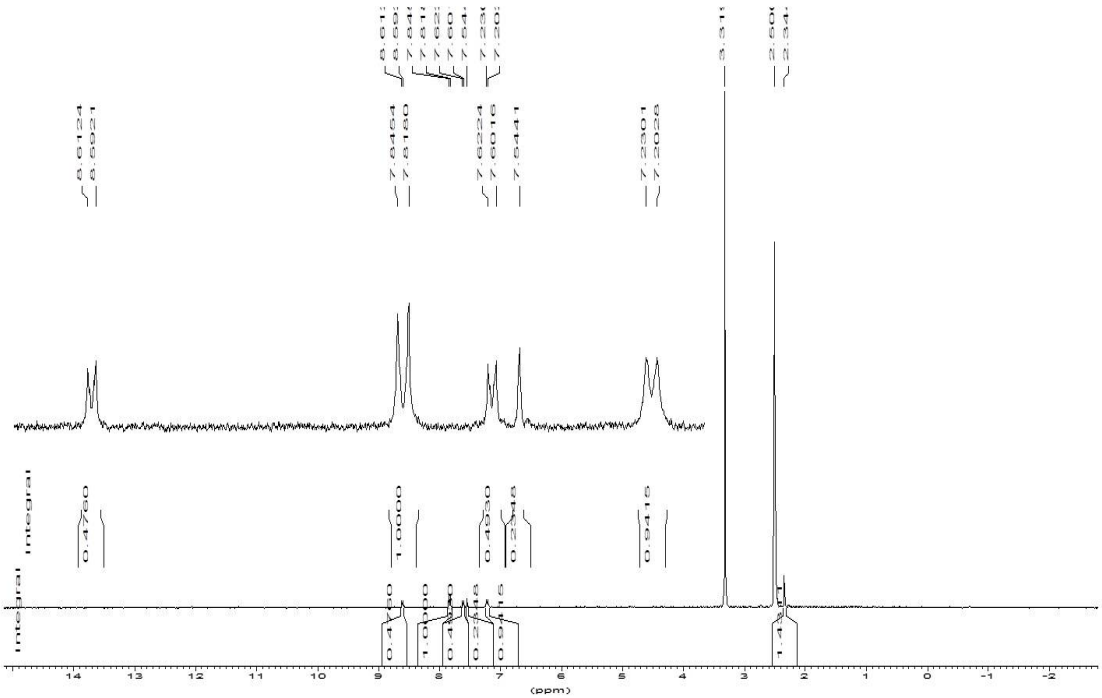

Figure S20: NMR spectrum of Cpd **3** after UV irradiation.