Solvent- and Heat-Induced Polymorphic Transformation with Single-Crystal Integrity in Cu(II) Paddle Wheel Metal Complexes

Geetha Bolla,*[a, b] and Raghavender Medishetty*[c]

[a]Department of Chemistry, National University of Singapore, Singapore 117543.

[b]Department of Chemistry, University of Wyoming, Laramie, WY, USA, 82071.

[c]Department of Chemistry, Indian Institute of Technology Bhilai, Kutelabhata, Durg, 491001, Chhattisgarh, India.

Experiments performed and General methods

1. Materials, general methods, synthesis of the ligand, complex and photodimerization of the complexes.

All the chemicals and solvents were of reagents are better grade purchased from different commercial resources like Sigma-Aldrich, Merk and solvents from NUS lab suppliers, used without further purification. NMR spectra were recorded on a 400 MHz Bruker Avance 400 FT-NMR spectrometer by calibrating the residual solvent as the reference in D6-DMSO solution. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere with a heating rate of 10 °C min^{-1} on a TA instruments SDT-2960. Differential Scanning Calorimetry (DSC) was performed on Mettler Toledo DSC1 under nitrogen atmosphere 50 flow rate with a heating rate of 10 °C min^{-1}. The FT-IR spectra were recorded using Varian Excalibur 3100 spectrometer with KBr pellets. The C, H, N analysis was carried using Elementar Vario Micro Cube instrument at the Elemental Analysis Lab, CMMAC, Department of Chemistry, National University of Singapore. The UV irradiation experiments were conducted in a LUZCHEM UV reactor (wavelength 356 nm). Single crystals were ground and packed uniformly thin layer between the glass sides, tighten at edges with one side glue label paper tape and further exposed in the UV reactor. These twin glass slides were flipped back at regular intervals of time to maintain the uniform exposure of UV radiation. In the case of the percentage of photo-products formed versus time plots, to do time dimerization the ground single crystals were packed between the Pyrex glasses and placed in the UV reactor, then the samples were taken out at regular intervals of time, dissolved in d_6-DMSO for ^{1}H NMR experiments. Powder X-ray diffraction (PXRD) analyses were performed on a D5005 Siemens X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation (λ = 1.54056 Å), 2 theta 5 to 50 and collected samples data with low background sample holders. Bruker D8 Venture Single Crystal X-ray Diffractometer (SCXRD) diffractometer Mo $K\alpha$ radiation (λ = 0.71073 Å), was used for collecting data of single crystals at 100K. The collected diffracted data was integrated with the Bruker SAINT software using a narrow-frame integration algorithm. Analysis of the data showed negligible decay during data collection. Data was corrected for absorption effects using the multi-scan method (SADABS). The structure was solved and refined using the Bruker SHELX-TL Software.

Synthesis of the ligands:

(E)-4-(2,4-difluorostyryl)pyridine, (24F-4spy): 2,4-difluoro benzaldehyde (1g, 7.037 mmol) and 4-picoline (0.79 mL 9.1 mmol) were dissolved in acetic anhydride (4 mL), stirred and heated to 100 °C for 14 hours. Upon cooling, the reaction mixture was poured into ice water (200 mL) and basified by slow addition of 20 % NaOH solution. The solid was filtered through gravity filtration and further recrystallized from MeOH at room temperature, yielding 24F-4spy 70-80 %, from the average of three batches; ^{1}H NMR (δH; 400 MHz, DMSO-d_6, 298 K: δ = 8.55 (d, J_{HH} = 4.4 Hz 2H), 7.88-7.87 (s 1H), 7.58-7.49 (t, 3H), 7.29-7.07 (t, 3H). ^{19}F NMR: -118.28 (d 1F), -122.67 (d, 1F). Elemental analysis (%) Calculated for $C_{13}H_9F_2N$ (217.0703 $gmol^{-1}$): C, 71.88; H, 4.18; N, 6.45. Found: C, 71.57; H, 4.09; N, 6.60. m.p. 67 °C

Same procedure followed for other ligands in the present study.

(E)-4-(3,4-difluorostyryl)pyridine, (34F-4spy): Experiment was carried out as such as 24F-4spy. ^{1}H NMR (δH; 400 MHz, DMSO-d_6, 298 K: δ = 8.592 (d, 2H), 7.75-7.760 (dd, s 4H), 7.60 (d, 2H), 7.45-7.40 (m, 2H), 7.44 (d, 1H), 7.30-7.26 (m 1H).^{19}F NMR: -138.95 (d, 1F), -143.41 (d,1F). Elemental analysis (%) Calculated for $C_{13}H_9F_2N$ (217.0703 gmol^{-1}): C, 71.88; H, 4.18; N, 6.45. Found: C, 71.63; H, 3.67; N, 5.59. m.p. 85 °C

(E)-4-(2,6-difluorostyryl)pyridine, (26F-4spy): Experiment was carried out as such as 24F-4spy. ^{1}H NMR (δH; 400 MHz, DMSO-d_6, 298 K: δ = 8.60 (d, J_{HH} = 5 Hz 2H), 7.56 (t, 3H), 7.44 (t, 3H), 7.21 (t, 1H).^{19}F NMR: -109.95 (s, 2F). Elemental analysis (%) Calculated for $C_{13}H_9F_2N$ (217.0703 gmol^{-1}): C, 71.88; H, 4.18; N, 6.45. Found: C, 71.61; H, 6.64.44; N, 5.59. m.p. 77 °C

Synthesis of the complexes:

Synthesis of [Cu_2(benzoate)$_4$(24F-4spy)$_2$] form I, **1:** The complex **1** was obtained as light green plate single crystals in 3 days, at room temperature solvent evaporation crystallization. $Cu(NO_3)_2 \cdot 3H_2O$ (12.1 mg, 0.05 mmol) dissolved in 1 mL MeOH, sodium salt of benzoic acid (14.4 mg, 0.1 mmol) dissolved in 1 mL MeOH and 24F-4spy (10.8 mg, 0.05 mmol) dissolved in 1 mL MeOH, then each solution added slowly in sequence and left for crystallization at room temperature. Light green colour single crystals were obtained after 3 days are separated from the mother solvent and washed in MeOH. Yield: 75 %. Form I even synthesized by storing form II in MeOH about 3 days and also by heating of the form II (discussed below and it is labelled as complex **2** in present study) at 160 °C about 2-3 h. ^{1}H NMR (400 MHz), DMSO-d_6/TFA, 298 K: δ = 8.15-7.98 (d, 4H, Py-H of 24F-4spy), 7.20-7.13 (s, 4H, benzoate protons), 7.28-6.64 (multiple peaks, 4H, CH=CH of 24F-4spy, 6H of sodium benzoates, 10H, of 24F-4spy). Elemental analysis (%) Calculated for $C_{54}H_{38}F_4N_2O_8Cu_2$ (1045.97 gmol^{-1}): C, 62.01; H, 3.66; N, 2.68. Found: C, 61.39; H, 3.57; N, 3.08.

Synthesis of [Cu_2(benzoate)$_4$(24F-4spy)$_2$] form II, 2: The complex **2** was obtained as dark green plates/block morphology single crystals in 24h, at room temperature solvent evaporation crystallization. $Cu(NO_3)_2 \cdot 3H_2O$ (12.1 mg, 0.05 mmol) dissolved in 1 mL MeOH, sodium salt of benzoic acid (14.4 mg, 0.1 mmol) dissolved in 1 mL MeOH and 24F-4spy (10.8 mg, 0.05 mmol) dissolved in 1 mL MeOH, then each solution added slowly in sequence and left for crystallization at room temperature. Light green colour single crystals were obtained after 24h are separated from the mother liquor. Yield: 60-70 %. ^{1}H NMR (400 MHz), DMSO-d_6/TFA, 298 K: δ = 8.42 (s, 4H, Py-H of 24F-4spy), 7.94 (s, 4H, benzoate protons), 7.63-7.36 (multiple peaks, 4H, CH=CH of 24F-4spy, 6H of sodium benzoates, 10H, of 24F-4spy). Elemental analysis (%) Calculated for $C_{54}H_{38}F_4N_2O_8Cu_2$ (1045.97 gmol^{-1}): C, 62.01; H, 3.66; N, 2.68. Found: C, 61.39; H, 3.57; N, 3.08. Storing of the form II crystals in MeOH solvent for 2 days resulted in as form I.

Photodimerization of the prepared complexes: Photoproduct of 1 labeled as 3 [Cu(benzoate)$_4$(*rctt*-24F-ppcb)] (Where *rctt*-24F-ppcb = *rctt*-1,3-bis(4-pyridyl)-2,4-bis(2,4-difluoro-phenyl)cyclobutane). Fine powder of the complex **1** was packed between 3X1 inch lab glass slides and then subjected under UV 356 nm in a time spam of 24 hours and collected the sample which is **3**. ^{1}H NMR (400 MHz), DMSO-d_6/TFA, 298 K: δ = 8.41 (d, 4H, Py-H of 24F-4spy), 8.01 (s, 8H, benzoate protons), 7.32-6.81 (multiple peaks, 12H sodium benzoates, multiple peaks, 10H of 24F-4spy), 5.49-5.47 (d, 4H, cyclobutane of 24F-4spy). $C_{54}H_{38}F_4N_2O_8Cu_2$ (1045.97 gmol^{-1}): C, 62.01; H, 3.66; N, 2.68. Found: C, 61.89; H, 4.23; N, 3.01.

Synthesis of [Cu$_2$(benzoate)$_4$(26F-4spy)$_2$], 4: The complex **4** was obtained as dark green block morphology single crystals in 24h, at room temperature solvent evaporation crystallization in MeOH. $Cu(NO_3)_2 \cdot 3H_2O$ (12.1 mg, 0.05 mmol) dissolved in 1 mL MeOH, sodium salt of benzoic acid (14.4 mg, 0.1 mmol) dissolved in 1 mL MeOH and 26F-4spy (10.8 mg, 0.05 mmol) dissolved in 1 mL MeOH, then each solution added slowly in sequence and allowed for crystallization at room temperature. Single crystals were obtained are separated from the mother solution. Yield: 75 %. ^{1}H NMR (400 MHz), DMSO-d_6/TFA, 298 K: δ = 8.56 (s, 4H, Py-H of 26F-4spy), 7.92 (s, 4H, benzoate protons), 7.63-6.41 (multiple peaks, 4H, CH=CH of 26F-4spy, 6H of sodium benzoates, 10H, of 26F-4spy). Elemental analysis (%) Calculated for $C_{54}H_{38}F_4N_2O_8Cu_2$ (1045.97 gmol^{-1}): C, 62.01; H, 3.66; N, 2.68. Found: C, 61.21; H, 3.69; N, 3.18.

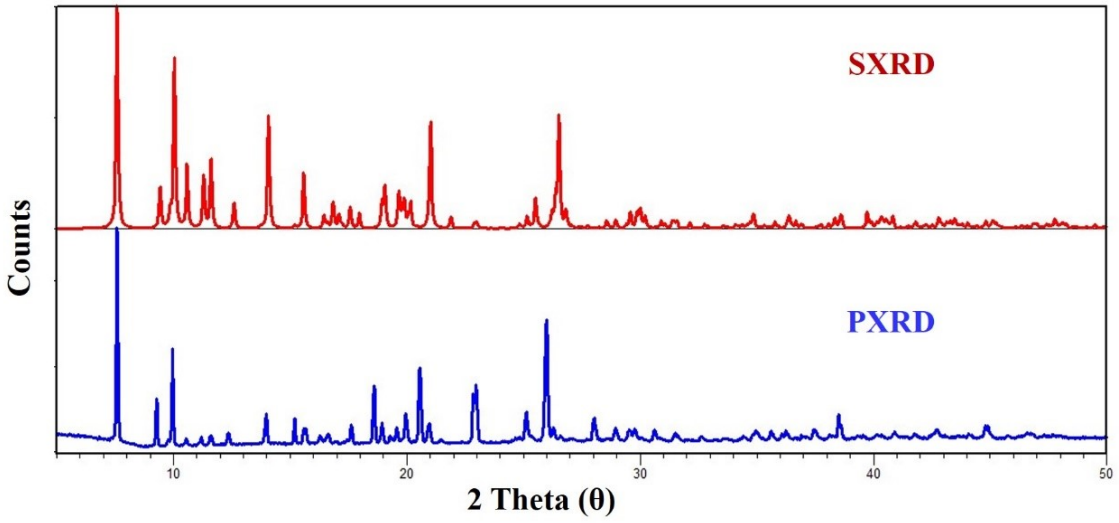
Synthesis of [Cu$_2$(benzoate)$_4$(34F-4spy)$_2$] 5: The complex **5** was obtained as light green plate single crystals in 24h, at room temperature solvent evaporation crystallization. $Cu(NO_3)_2 \cdot 3H_2O$ (12.1 mg, 0.05 mmol) dissolved in 1 mL MeOH, sodium salt of benzoic acid (14.4 mg, 0.1 mmol) dissolved in 1 mL MeOH and 34F-4spy (10.8 mg, 0.05 mmol) dissolved in 1 mL MeOH, then each solution added slowly in sequence and left for crystallization at room temperature. Green colour block morphology single crystals were obtained after 3 days are separated from the mother liquor. Yield: 75 %. ^{1}H NMR (400 MHz), DMSO-d_6/TFA, 298 K: δ = 8.47 (s, 4H, Py-H of 34F-spy), 7.36-6.72 (s, 4H, benzoate protons, multiple peaks, 4H, CH=CH of 34F-4spy, 6H of sodium benzoates, 10H, of 34F-4spy). Elemental analysis (%) Calculated for $C_{54}H_{38}F_4N_2O_8Cu_2$ (1045.97 gmol^{-1}): C, 62.01; H, 3.66; N, 2.68. Found: C, 61.98; H, 3.97; N, 2.59.

Photoproduct of 4 labeled as 6 [Cu(benzoate)$_4$(*rctt*-26F-ppcb)], (where *rctt*-26F-ppcb = *rctt*-1,3-bis(4-pyridyl)-2,6-bis(2,4-difluoro-phenyl)cyclobutane). Fine powder of the complex **4** was packed between 3X1 inch lab glass slides and then subjected under UV 356 nm in a time spam of 24 hours and collected the sample which is **6**. ^{1}H NMR (400 MHz), DMSO-d_6/TFA, 298 K: δ = 8.54-8.32 (d, 4H, Py-H of 26F-4spy), 8.54-7.05 (s, 8H, benzoate protons, multiple peaks, 12H sodium benzoates, 10H of 26F-4spy), 5.75 (d, 4H, cyclobutane of 26F-4spy). $C_{54}H_{38}F_4N_2O_8Cu_2$ (1045.97 gmol^{-1}): C, 62.01; H, 3.66; N, 2.68. Found: C, 62.45; H, 4.31; N, 3.11.

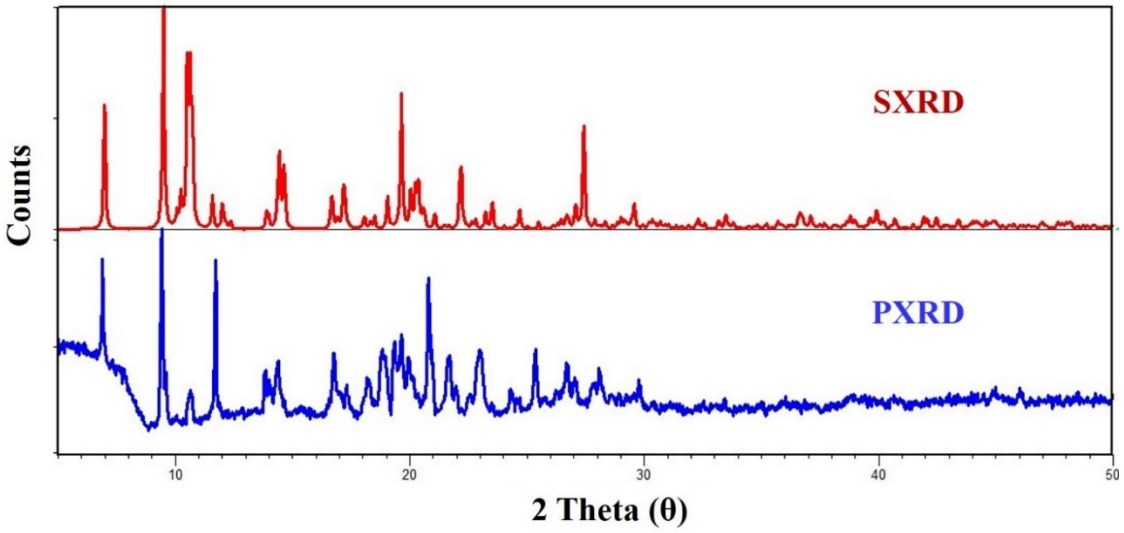
Cu(II) complexes gave broad peaks in the ^{1}H NMR spectrum due to the magnetic moment of Cu(II) usually induces very efficient nuclear magnetization relaxation in the neighbour nuclei. Hence intramolecular electronic effect of the paramagnetic Cu(II) nucleus on other atoms, giving rise to broad NMR signals.

2. Analysis: PXRD, TGA, DSC and SCXRD.

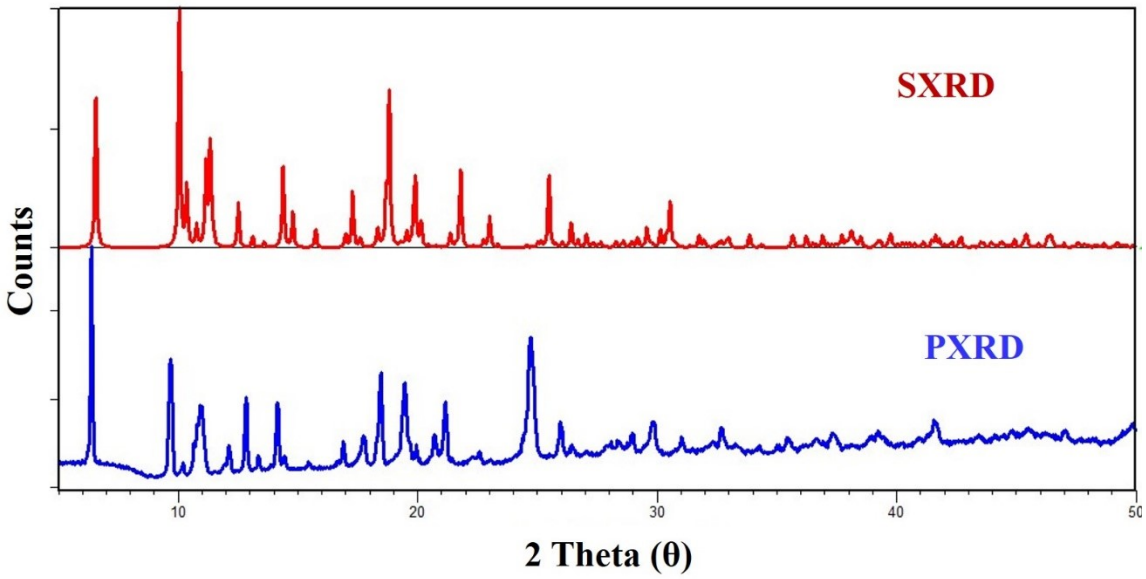
2.1. PXRD of the complexes



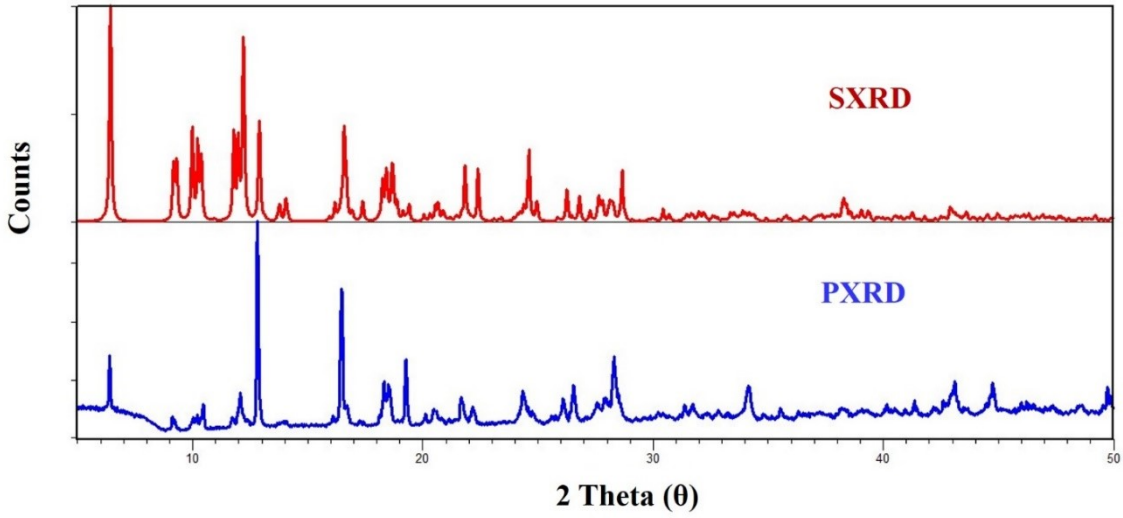
(a) Complex **1**(form I) with their simulated single crystal data powder patterns.



(b) Complex **2** (form II) with their simulated single crystal data powder patterns.



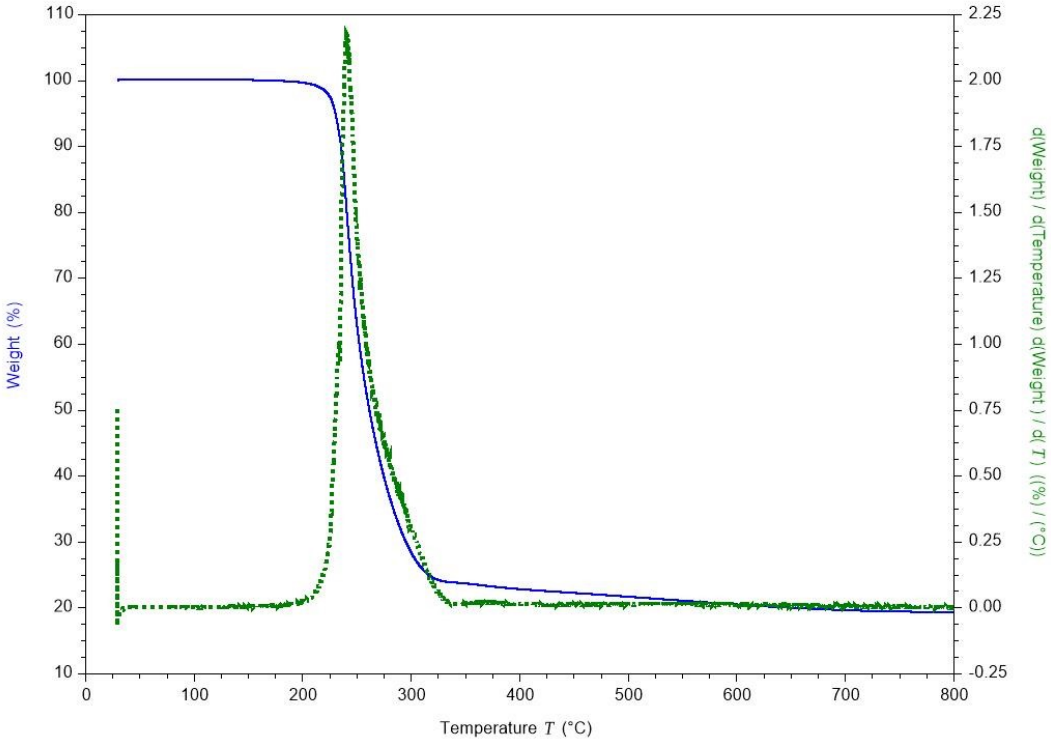
(c) Complex **4** with the simulated single crystal data powder patterns.



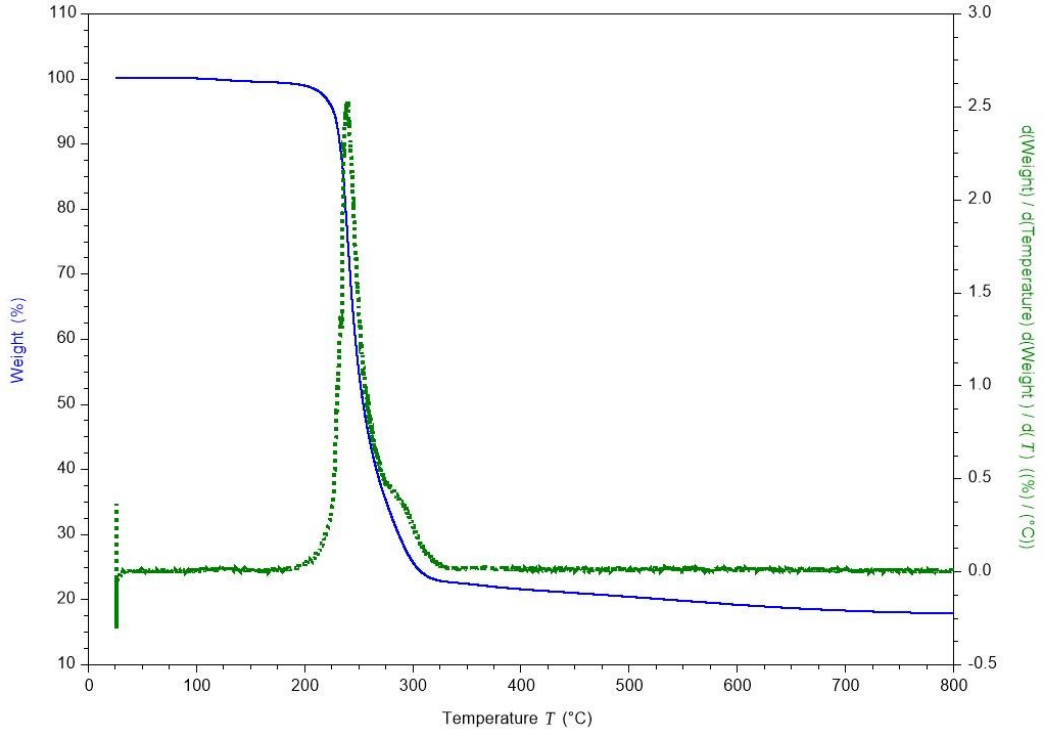
(d) Complex **5** with the simulated single crystal data powder patterns.

Figure S1. (a) Comparison and overlay powder diffraction pattern of the complex **1** (form I) and (b) complex **2** (form II) (c, d) Complex **4** and **5** with their simulated single crystal data powder patterns.

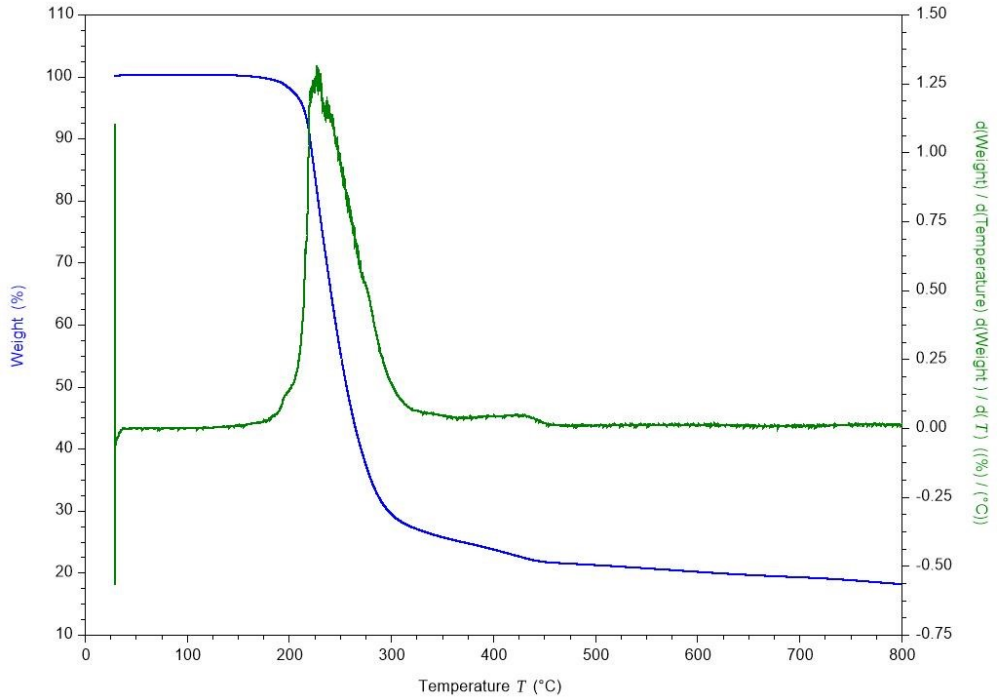
2.2. TGA of the complexes.



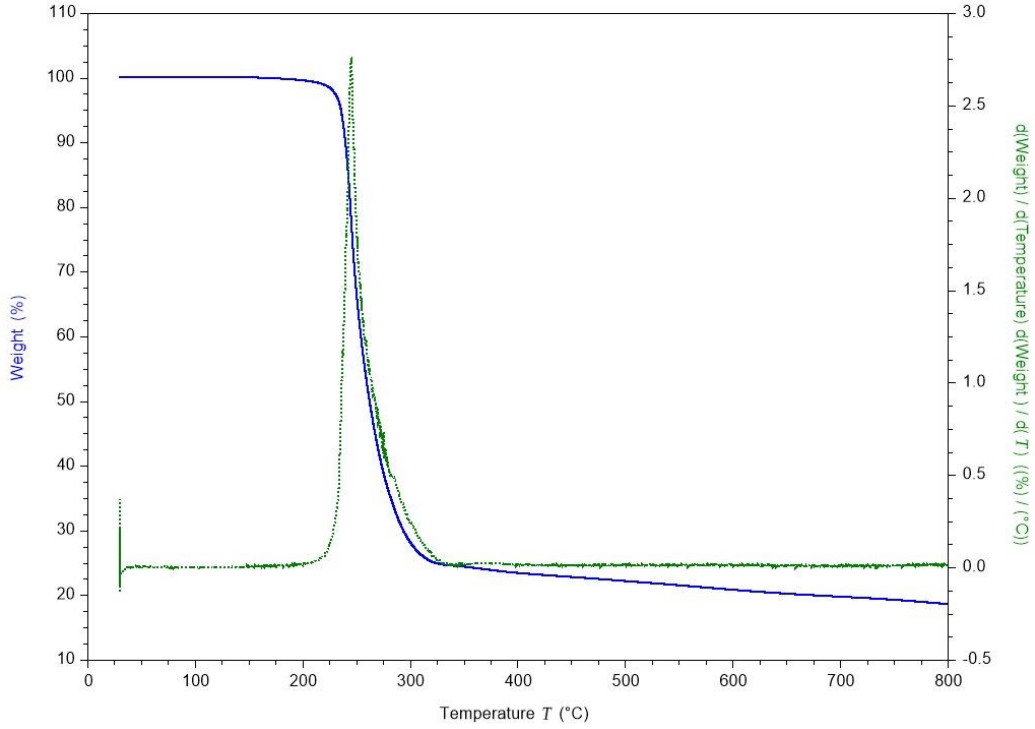
(a) TGA of the **1**



(b) TGA of the **2**



(c) TGA of the **4**



(d) TGA of the **5**

Figure S2. TGA of the complexes in present study.

2.3. DSC of the complexes

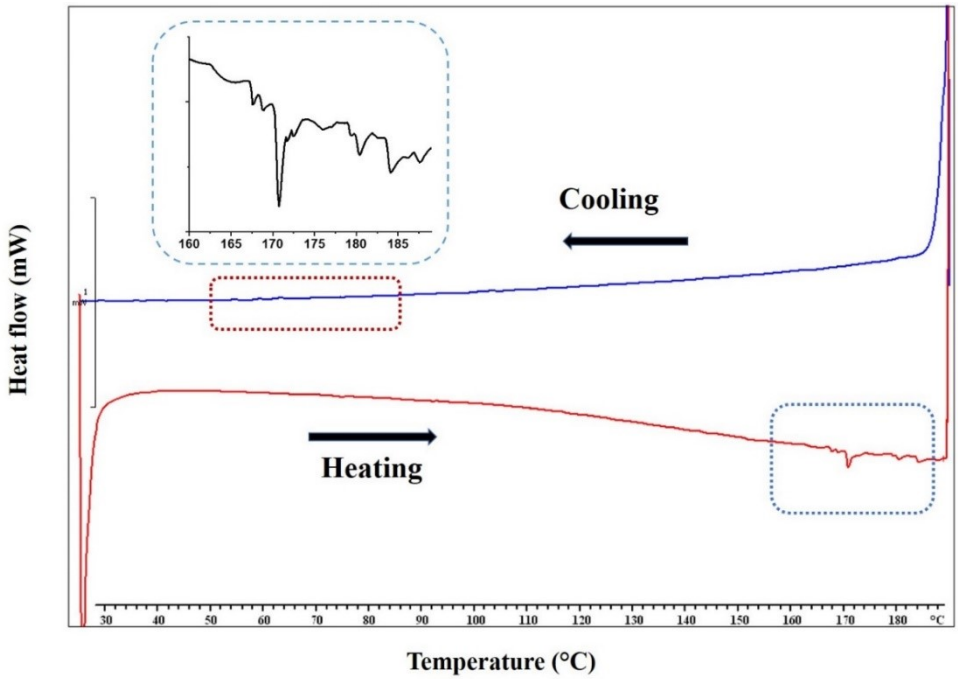


Figure S3a. DSC of the complex **2**. This confirmed reversible phase transition and the same is further confirmed by PXRD. Jumping of the crystals after 165 °C observed and during cooling cycle, we did not see any significant change.

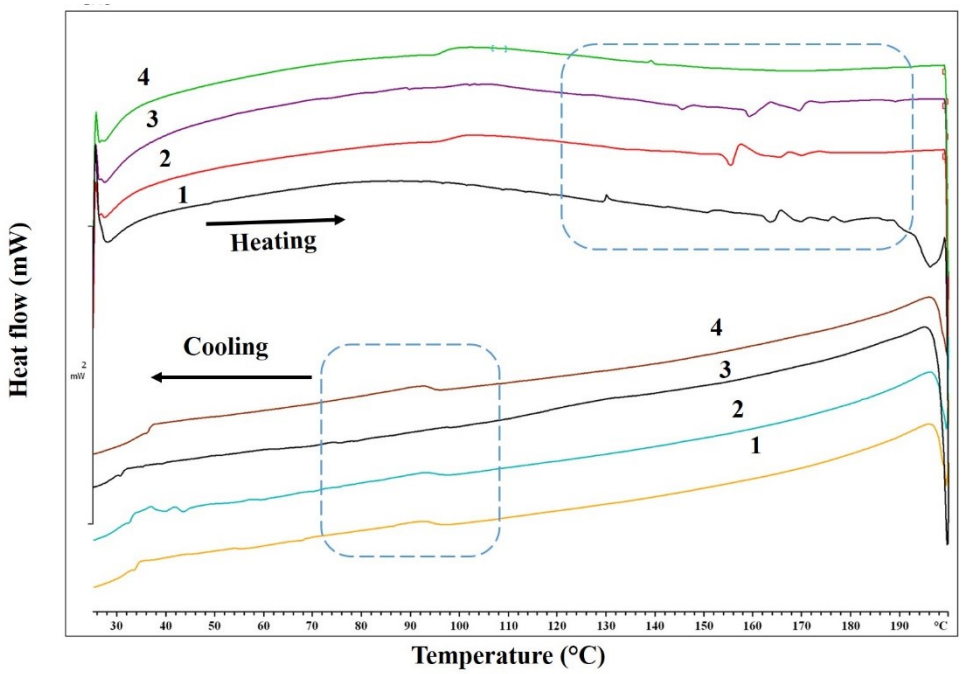


Figure S3b. DSC of the form I, single crystals, batch repeated for four cycles. This confirmed reversible phase transition and the same is further confirmed by PXRD. Jumping of the few

crystals, phase change of the form II after 160 °C was observed. During cooling cycle, we did not see any significant change. Note, **1, 2, 3** and **4** are experiment cycles.

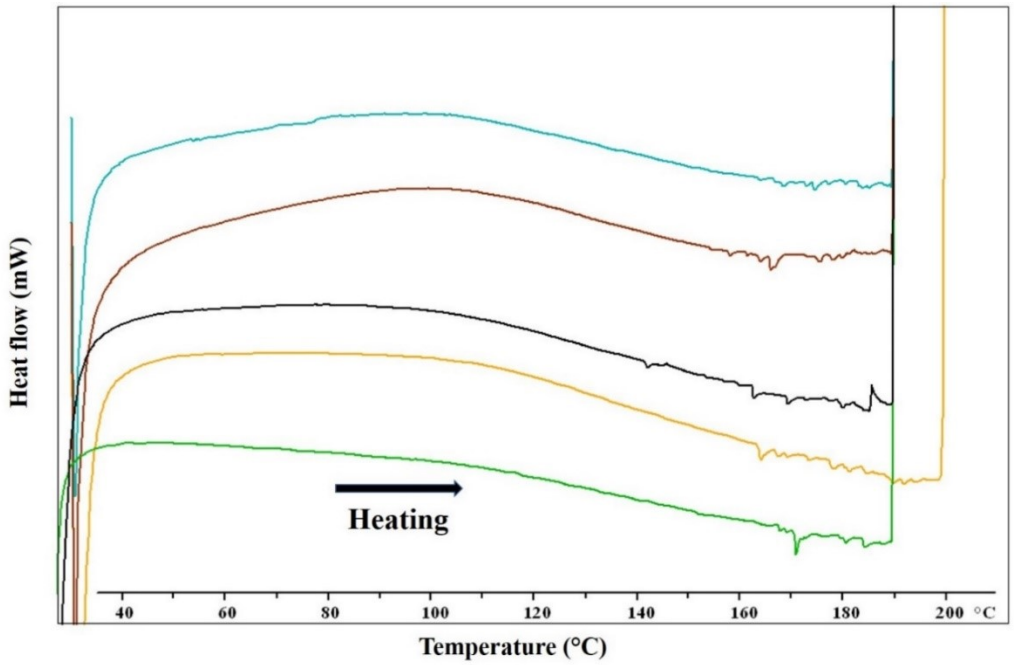


Figure S3c. DSC of the form I, **1** crystals, which are grown in five different batches, different sizes are tested to check once, how the jumping occurs in different batches. This confirmed the reproducibility in different batches. Jumping of the crystals after 160 °C observed.

2.4.1. Single crystal analysis, and single crystal face indexing study

Table S1. Crystallography information

	Complex 1, Form I	**Complex 2, Form II**	**Complex 1, Form I, after heat-cool cycle**	**Complex 4**	**Complex 5**
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1
a (Å)	10.5084(5)	10.0112(11)	10.5158(3)	10.1882(4)	9.7560(3)
b (Å)	10.5605(5)	10.5172(11)	10.5630(3)	16.7531(8)	9.7788(3)
c (Å)	12.1716(5)	25.318(3)	12.1746(3)	16.8987(8)	14.3088(4)
α (°)	86	91	86	60	77
β (°)	73	90	73	72	71
γ (°)	62	117	62	74	64
V (Å^3)	1150	2359	1151	2374	1168
D_{calc}, gcm^{-3}	1.510	1.47	1.517	1.463	1.483
Z	1	2	1	2	1
μ (mm^{-1})	1.001	0.97	1.003	0.969	0.985
No. of measured, independent, observed [$I > 2\sigma(I)$] reflections	6458, 6524, 5882	13290, 13192, 9866	6454, 6376, 5638	13306, 13240, 10053	6537, 6537, 5962,
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	2.8	4.9	3.73	4.4	6.8
Goodness-of-fit	1.039	1.040	1.061	1.129	1.050
Temperature at crystal diffracted	100K	100K	100K	100K	100K
Diffractometer, Radiation type	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture
CCDC	2484745	2484746	2487112	2486474	2486473

2.4.2 Single crystals grown in MeOH.

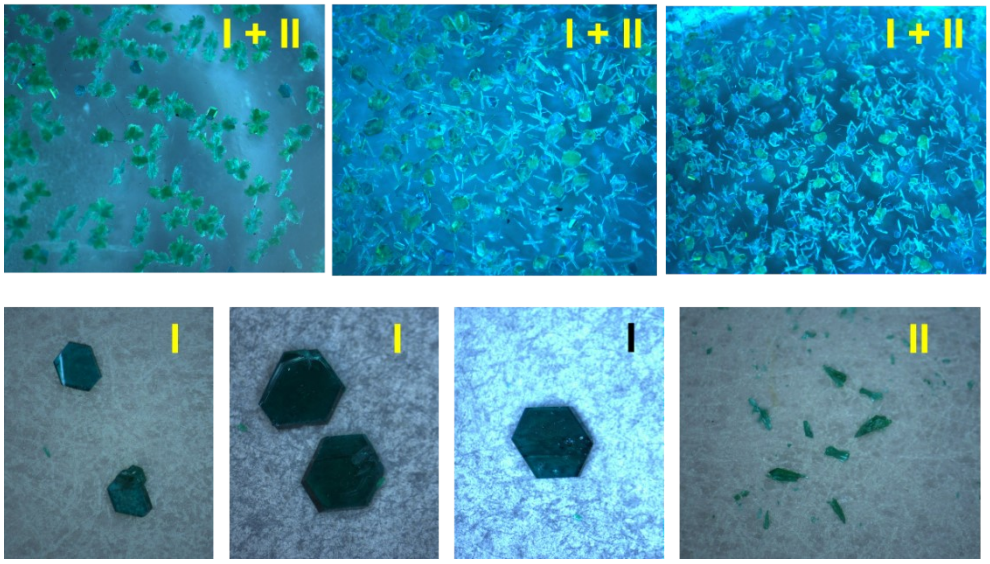
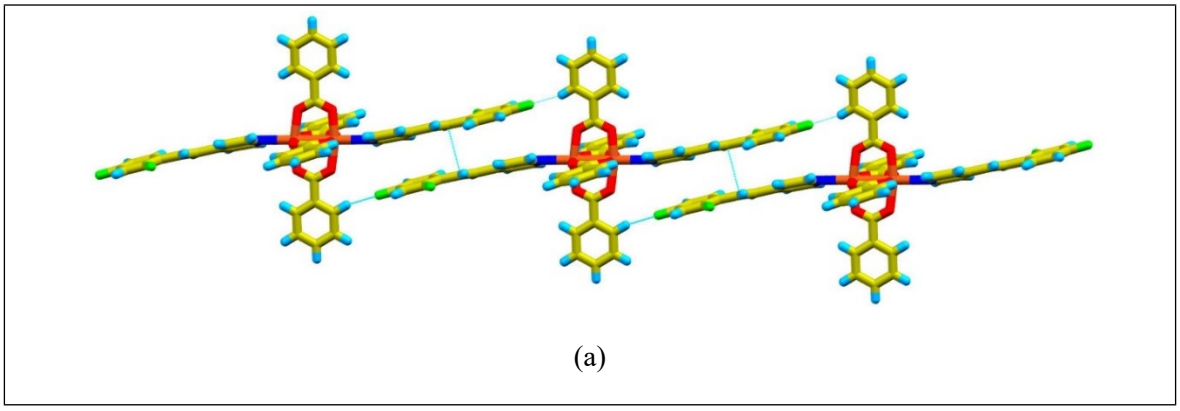
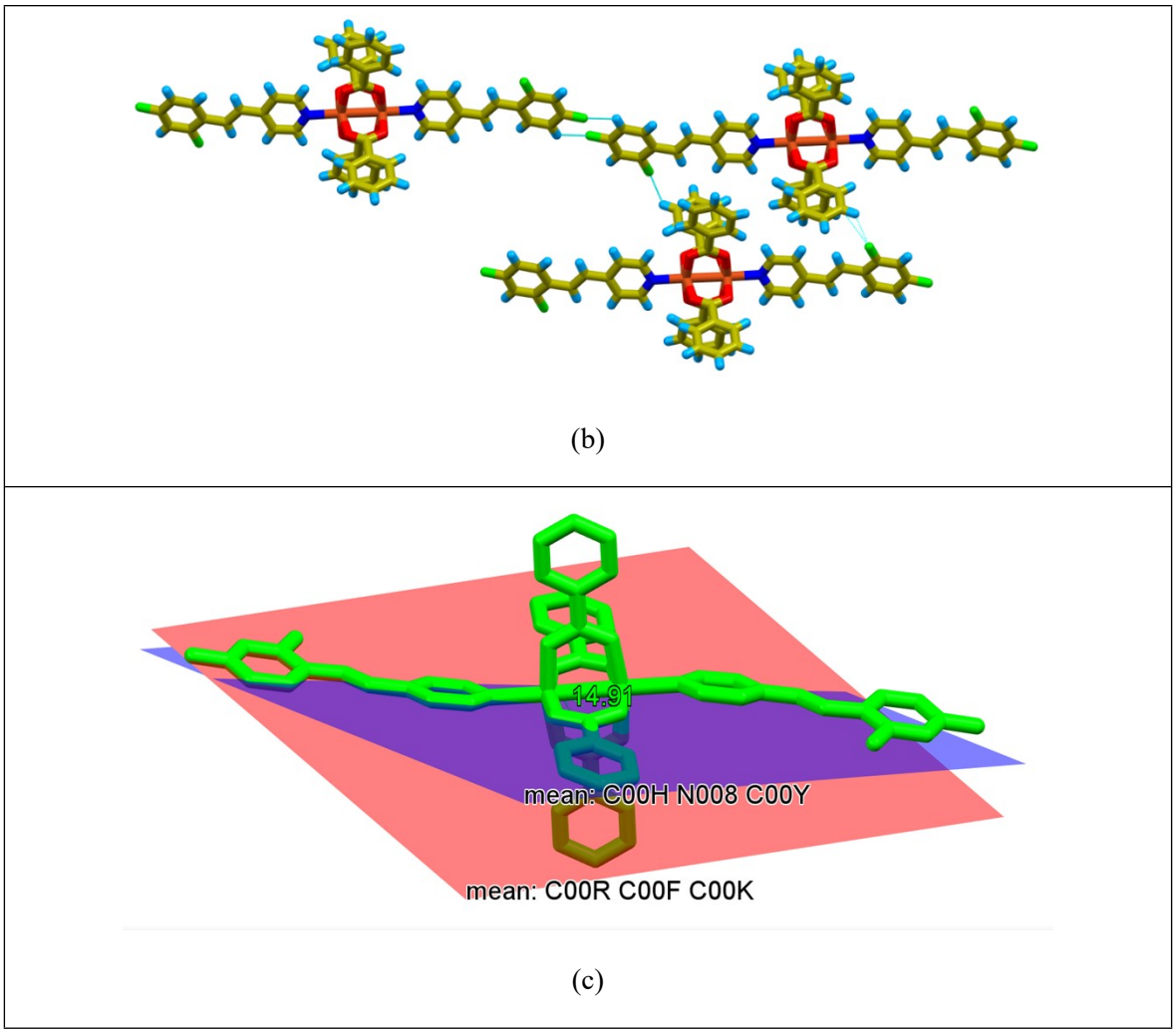


Figure S4. Single crystals grown in MeOH solution images of the complexes in present study. Form II and I crystals in crystallization batches. Form I as block morphology and form II as plates or needles.

2.4.3. Single crystal packing images of the complexes in present study.



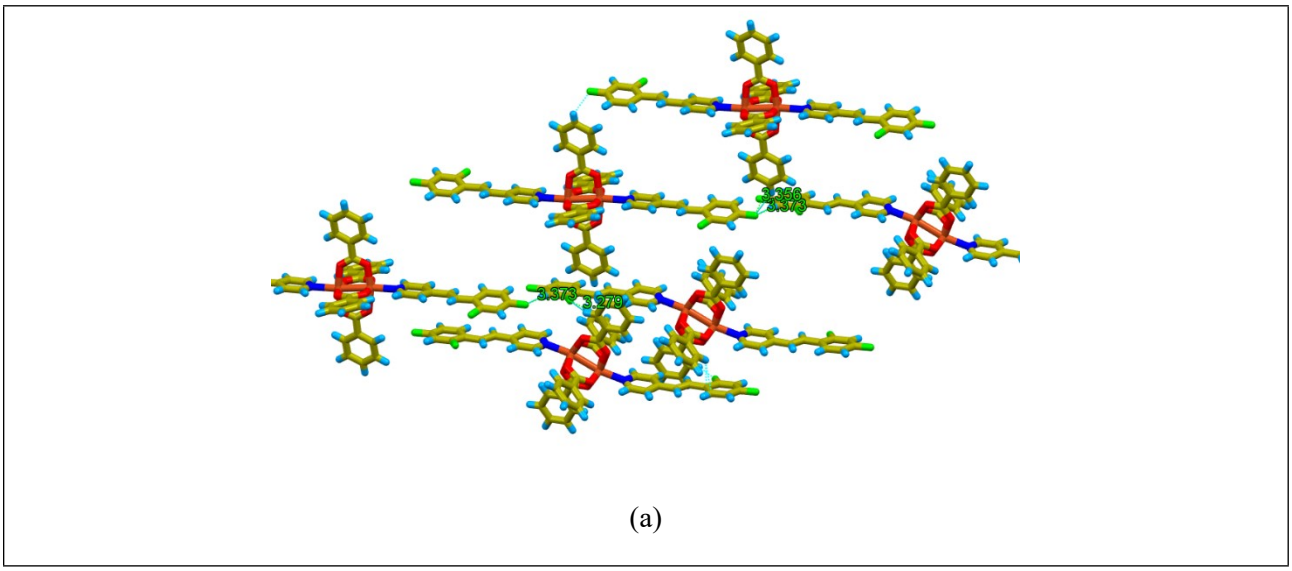
(a)



(b)

(c)

Figure S5. Crystal packing images of the **form I,** where the C–H···F interactions played key role**.**



(a)

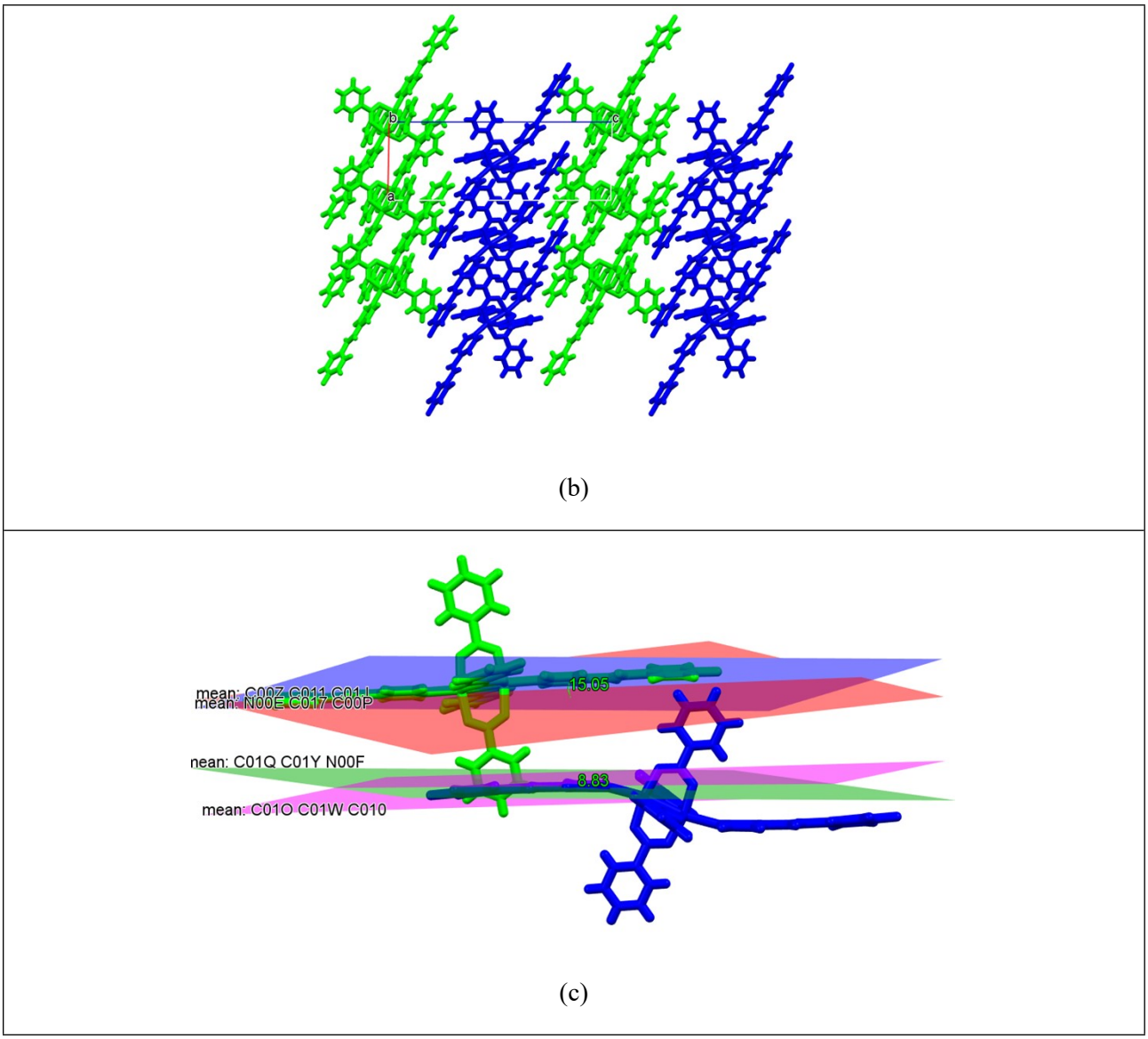


Figure S6. Crystal packing images of the **form II.**

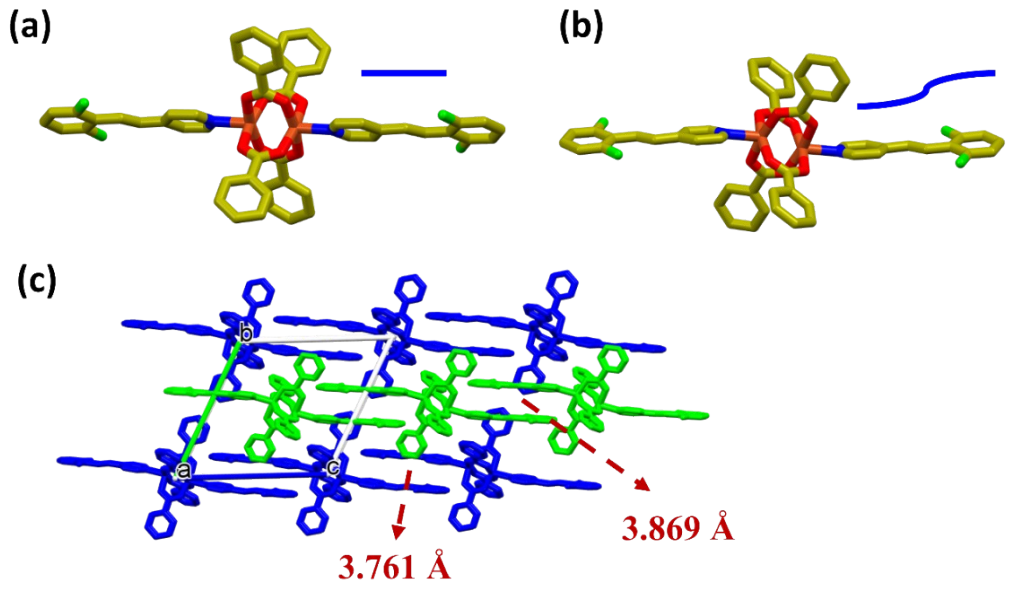


Figure S7. (a, b) The two paddle wheel units of the complex **4**, one is planar and the second one is angular. (c) 2D packing view, where in it is clearly showed that, 26F-4spy ligands are packed in head to tail manner with 3.761 and 3.869 Å distance and hence they are photoreactive. There is no photosalient effect was observed.

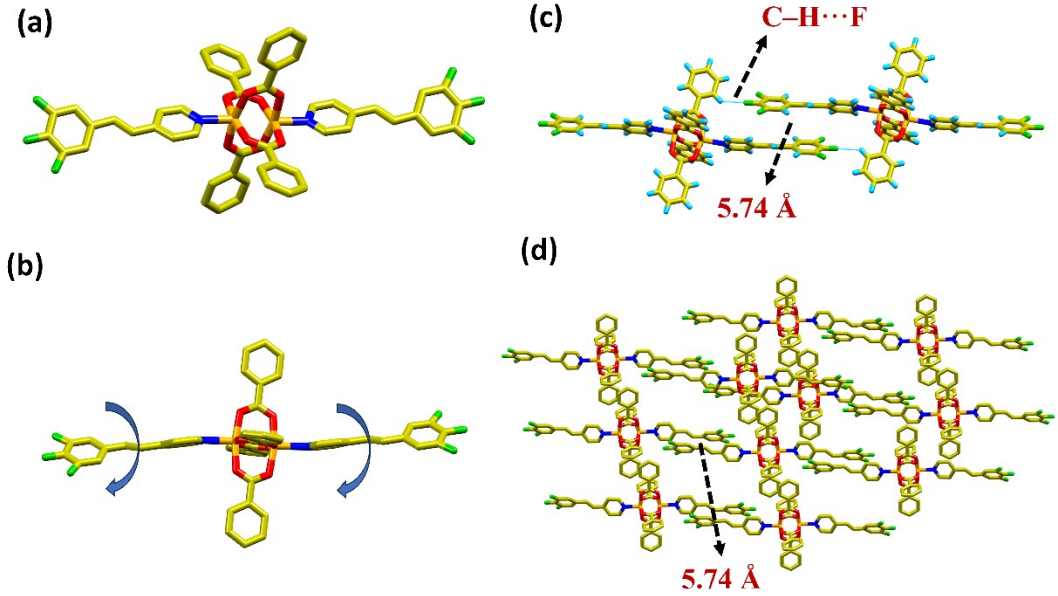


Figure S8. (a, b) The paddle wheel unit of the complex **5**, where in the paddle wheel complex is planar but the 34F-4spy ligand 34F benzene is titled, hence the whole units not planar. (c) 2D packing view, where in it is clearly showed that, 34F-4spy ligands are packed in head to tail manner with 5.74 Å distance and hence they are not photoreactive.

Note: *meta position F exists position disorder, with 50% occupancy. Hence 3 and 5 position F atom presented with 50% occupancy.*

3. Density measurements by flotation method.

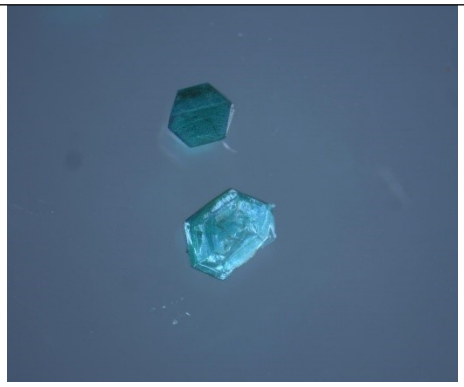
Table S2. Density measurements of before and after UV irradiated solids.

Compound	Density (experimental average)*, g cm^{-3}	Density calculated from X-ray data, g cm^{-3}	Change in volume (%)
$[Cu(benzoate)_4(24F\text{-}4spy)_2]$, Form I, **1**	1.50(2)	1.510	N/A
$[Cu(benzoate)_4(24F\text{-}4spy)_2]$, Form I (complex **1**) crystals UV irradiated, 100% converted (3**)**	1.39(1)		7.5(2)

*Density of the compounds was measured by floatation method using hexane (density = 0.6548 g cm^{-3}), 1,1,2,2-Tetrachloroethane (density= 1.594 g cm^{-3}).

4. Photosalient experiments and photo reactivity of the crystal under weak UV irradiation

Single crystals under weak UV of the $[Cu_2(benzoate)_4(24F\text{-}4spy)_2]$ form I is photoreactive but not photosalient, it is photoreactive and showed topochemical [2+2] CAR.



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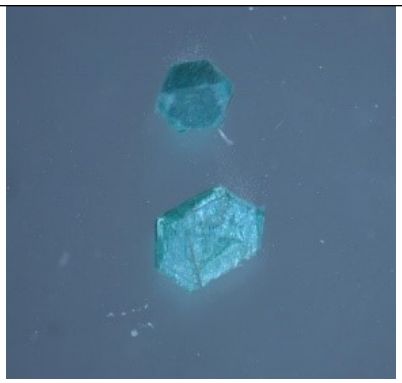
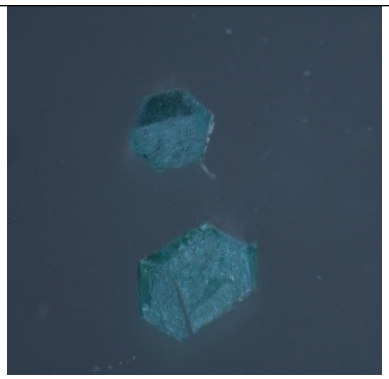
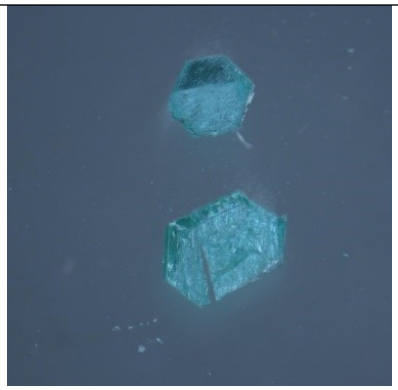


@ 06 min

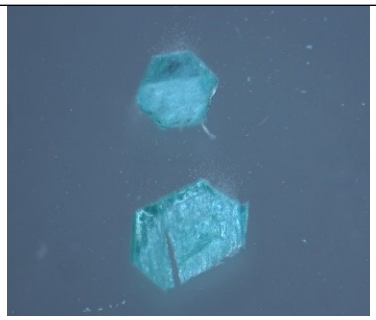


@ 10 min



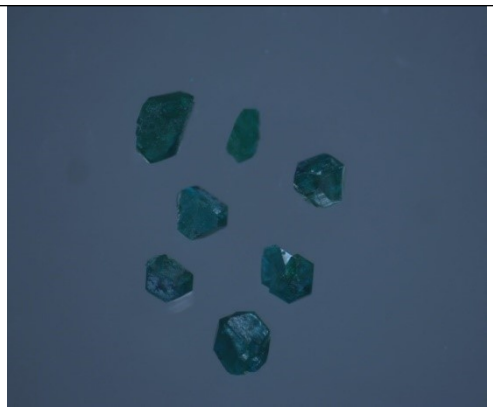
@ 15 min

@ 20 min

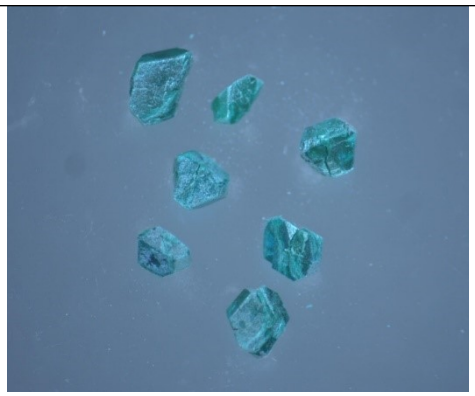


@ 25 min

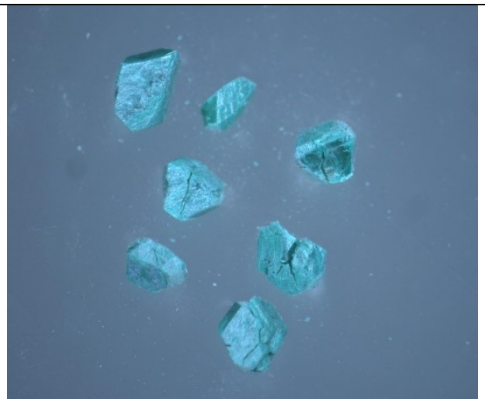
Figure S9a. Crystal cracking in time intervals, $[Cu_2(benzoate)_4(24F\text{-}4spy)_2]$ form I. Hexagonal shape crystals.



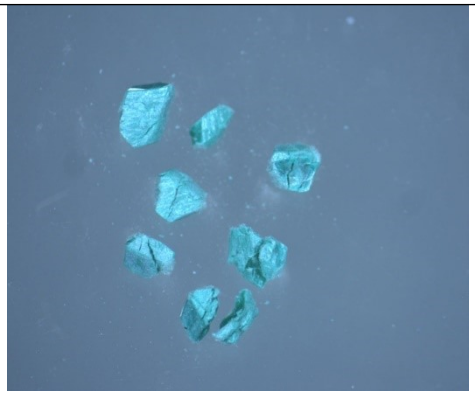
@ 0 min



@ 10 min

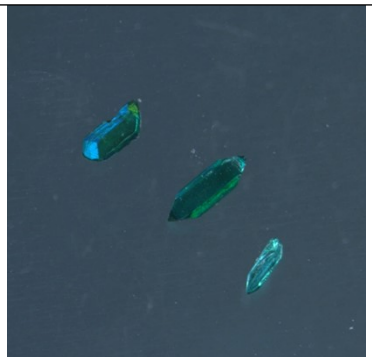


@ 20 min

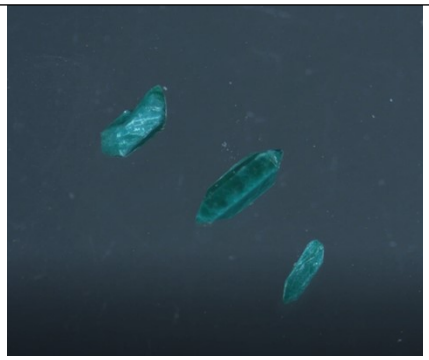


@ 30 min

Figure S9b. Crystal cracking in time intervals, $[Cu_2(benzoate)_4(24F\text{-}4spy)_2]$ form I. Different size and shape crystals of form I.

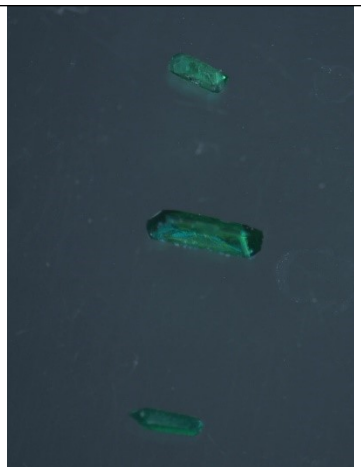


Before UV irradiation, Complex **4**

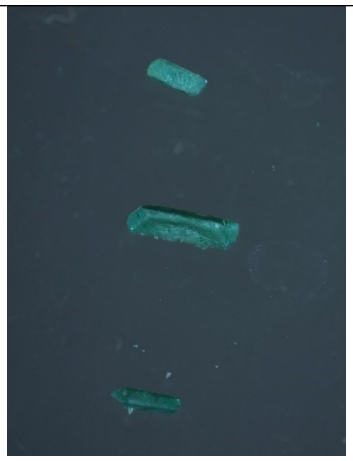


After UV irradiation 3 min, Complex **4**

Figure S10a. Crystal cracking in time intervals, $[Cu_2(benzoate)_4(26F\text{-}4spy)_2]$, complex **4**. Different size and shape crystals of **4**.

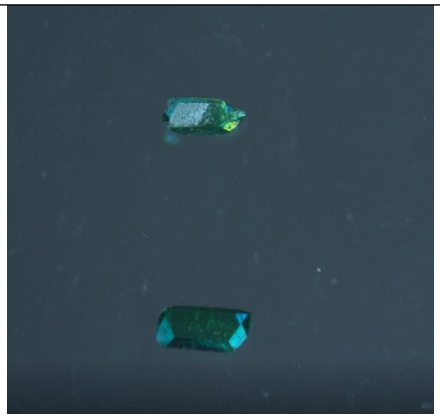


Before UV irradiation, Complex **4**

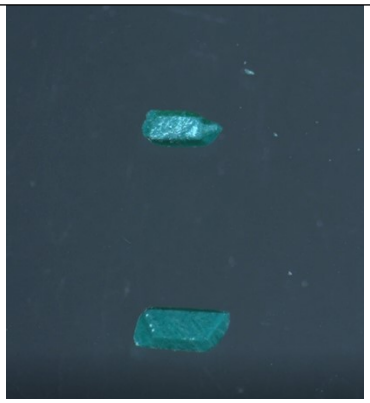


After UV irradiation 5 min, Complex **4**

Figure S10b. Crystal cracking in time intervals, $[Cu_2(benzoate)_4(26F\text{-}4spy)_2]$, complex **4**. Different size and shape crystals of **4**.

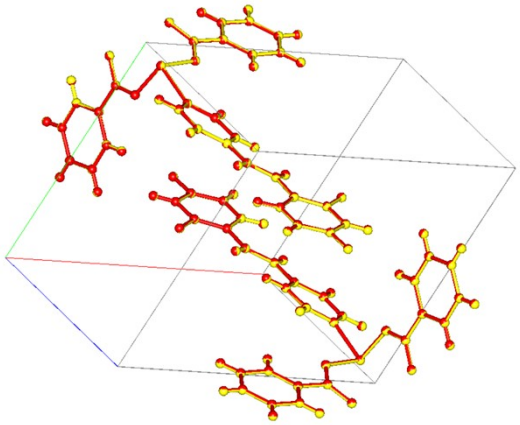


Before UV irradiation, Complex **4**



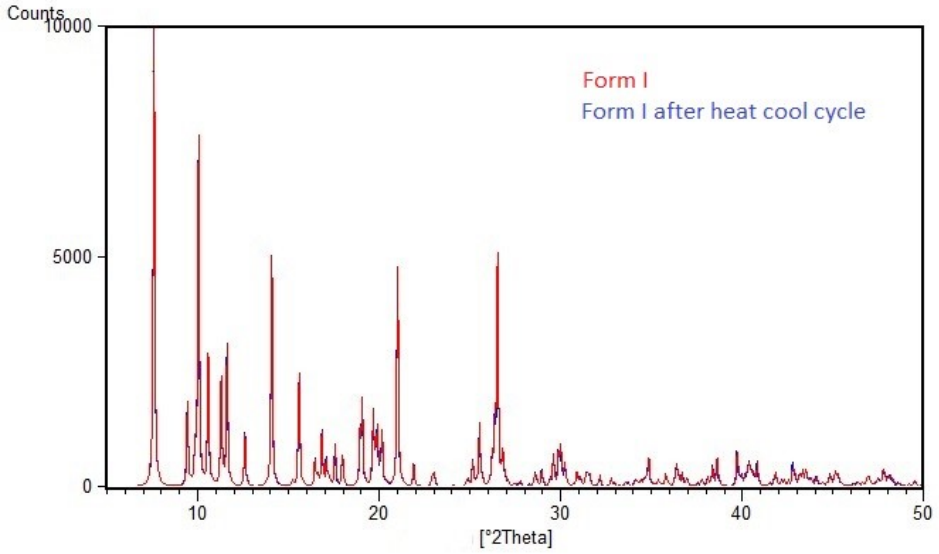
After UV irradiation 5 min, Complex **4**

Figure S10c. Crystal cracking in time intervals, $[Cu_2(benzoate)_4(26F\text{-}4spy)_2]$, complex **4**. Different size and shape crystals of **4**.

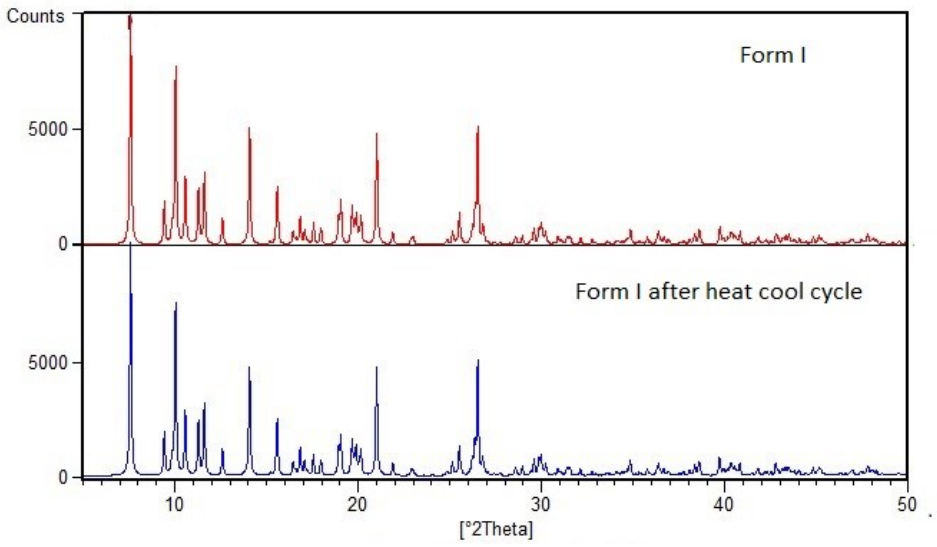


(a) Structure overlay of the form I crystal structure before heating (Red color) and after the heat cool cycle (yellow). Which clearly showed that they are same structures.

(b) Isostructural study of the form I crystal structure before heating and after the heat cool cycle (yellow). All the values are zero, which clearly showed that they are same structures. To further establish the packing similarity along unit cell similarity, CrystalCMP[1-2] has been used.



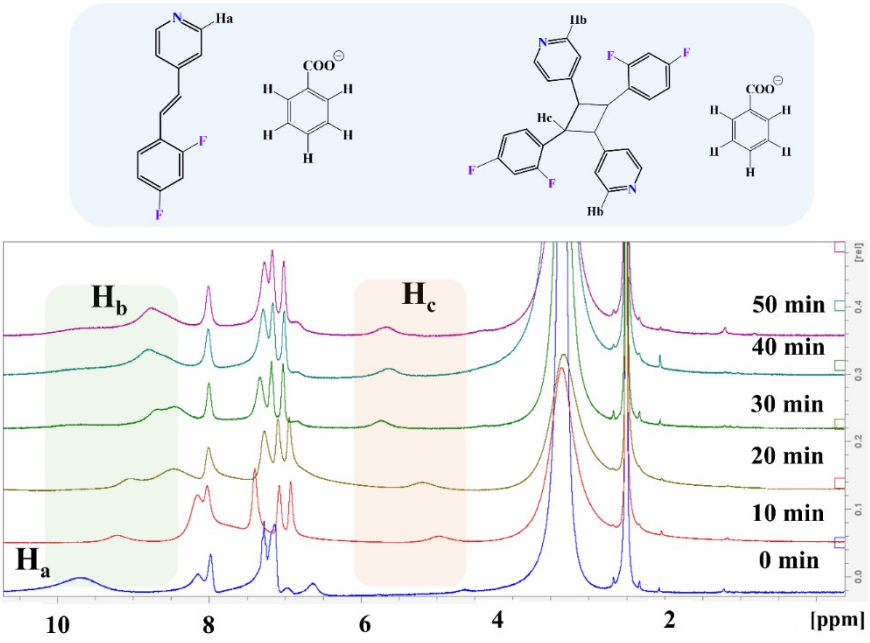
(c) Overlay powder patrons of the both the crystal structures form I before heating and form II after heat cool cycle. A complete matching of the 2 theta values confirmed that both the structures are same.



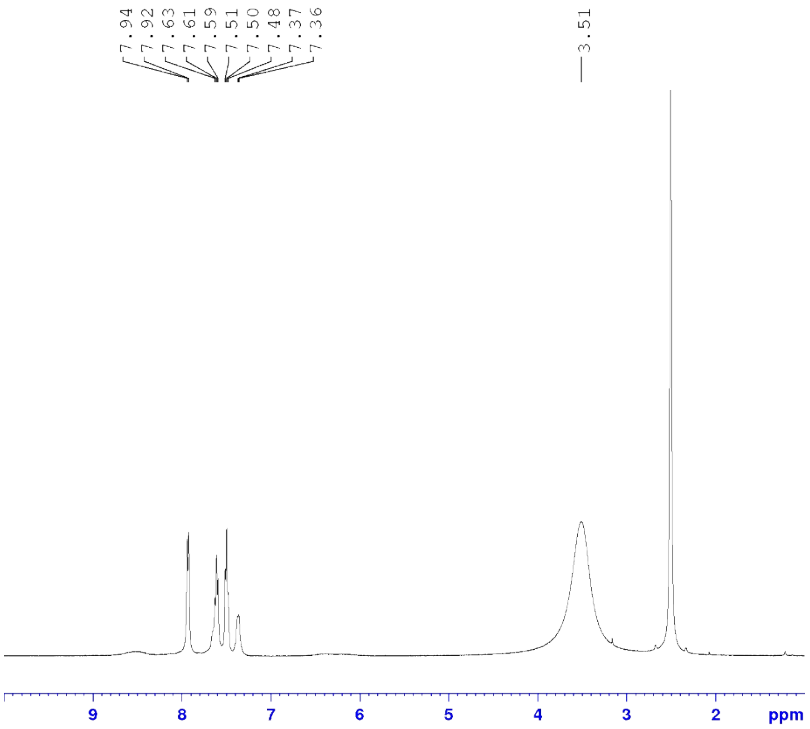
(d) Comparison powder patrons of the both the crystal structures form I before heating and form II after heat cool cycle. A complete matching of the 2 theta values confirmed that both the structures are same.

Figure S11. Structural comparison of the both form I before heating and after heat cool cycle.

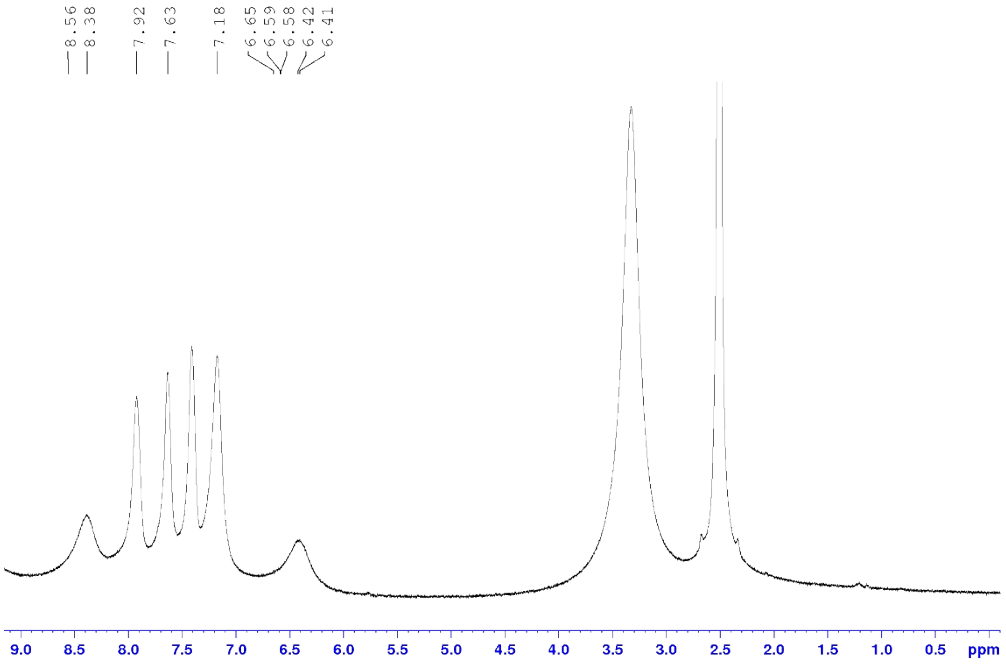
5. NMR spectrums ^{1}H NMR of the complexes.



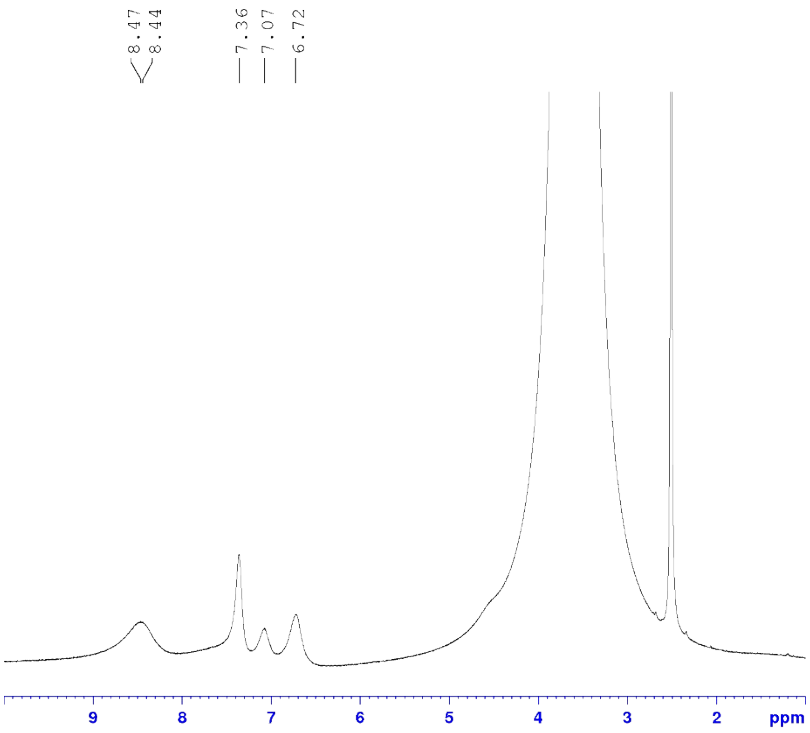
(a) Time dimerization study of **form I**.



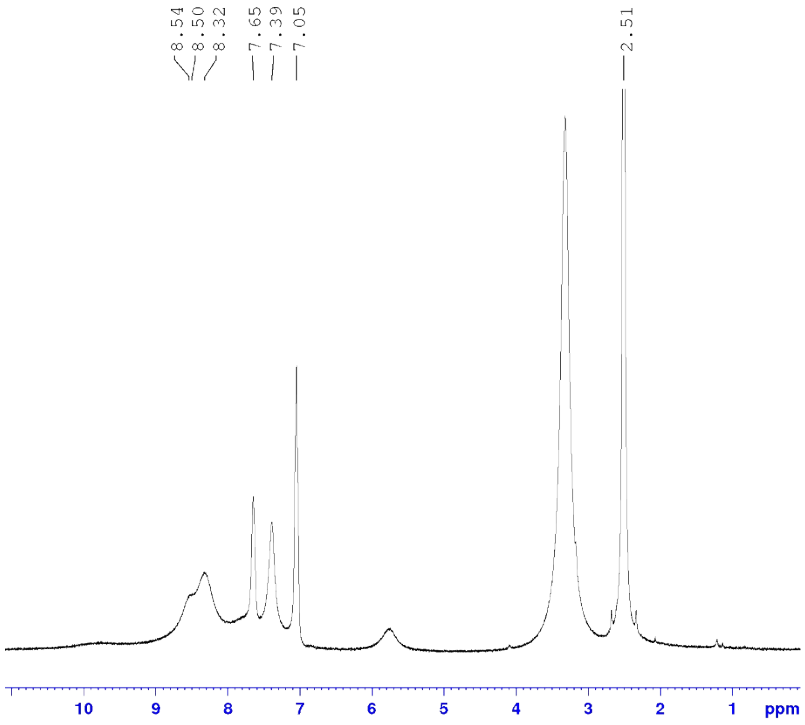
(b) ^{1}H NMR of the **form II**.



(c) ^{1}H NMR of the Complex **4**



(d) ^{1}H NMR of the Complex **5**



(e) ^{1}H NMR of the Complex **6**

Figure S12. Solution NMR (^{1}H) of the **form I**, **II**, **3, 4**, **5,** and **6** along with photoproducts.

References.

[1] J. Rohlíček, E. Skořepová, M. Babor, J. Čejka, CrystalCMP: an easy-to-use tool for fast comparison of molecular packing. *App. Cryst.*, **2016**, *49*, 2172–2183.

[2] J. Rohlíček, E. Skořepová, CrystalCMP: automatic comparison of molecular structures. *App. Cryst.*, **2020**, *53*, 841–847.