

# **One-dimensional Coordination Polymers of Bis-(3-pyridyl-acrylamido)ethane: Influence of Anions and Metal Ions on Their Solid State [2+2] Photochemical Polymerization and Dimerization Reactions**

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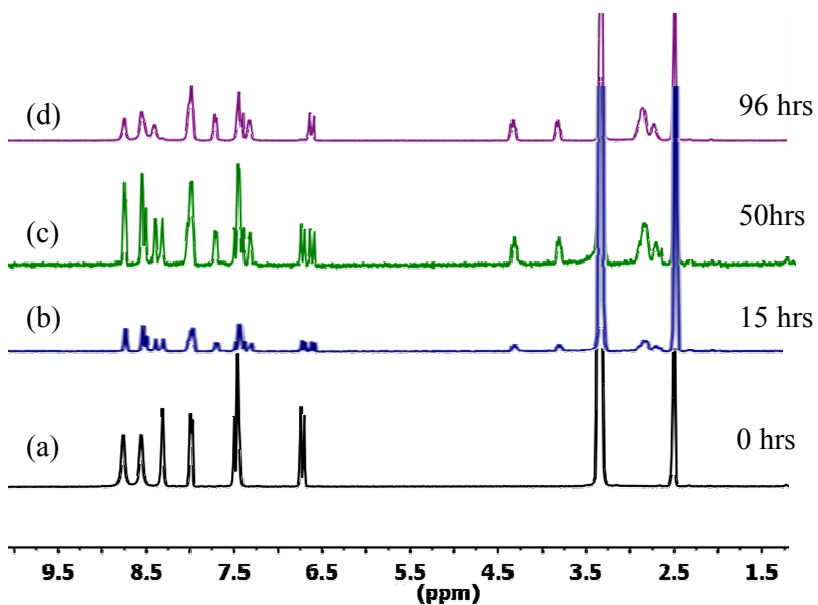
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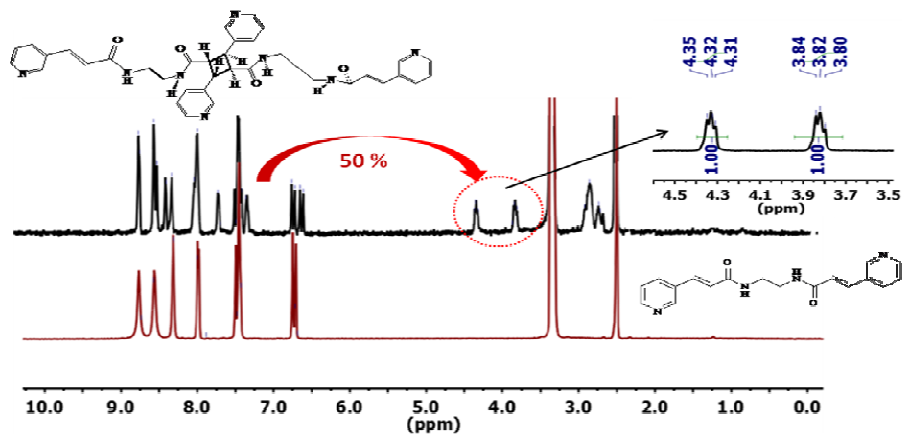
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## <sup>1</sup>H NMR Spectra



**Figure S1.** <sup>1</sup>H-NMR spectra recorded at various stages of irradiation of complex 1 after separation (a) before irradiation, (b-c) intermediate stages of irradiation and (d) after full irradiation (400MHz, D<sup>6</sup> DMSO).



**Figure S2.** <sup>1</sup>H NMR spectra of irradiated complex 4 after separation in 50% conversion (400MHz, D<sup>6</sup> DMSO).

## FTIR Spectra

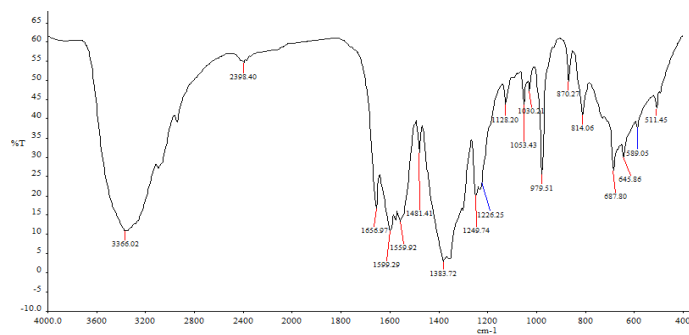


Figure S3. FTIR spectra of 1.

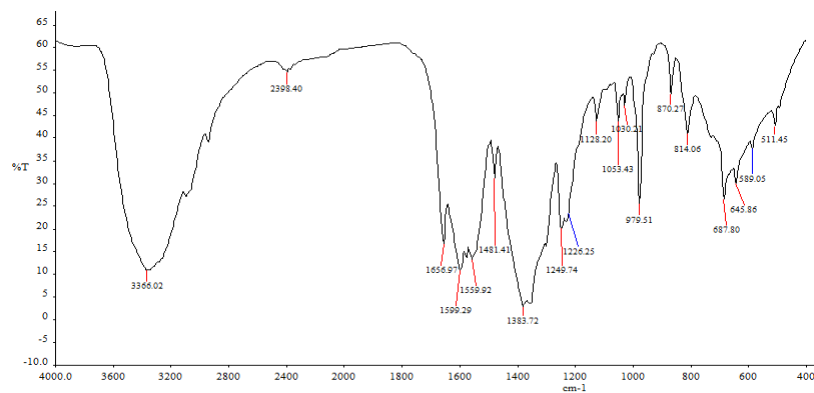


Figure S4. FTIR spectra of 2.

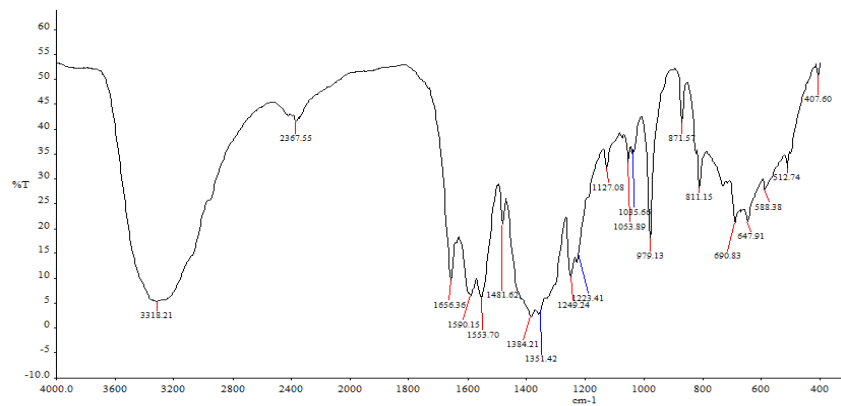


Figure S5. FTIR spectra of 3.

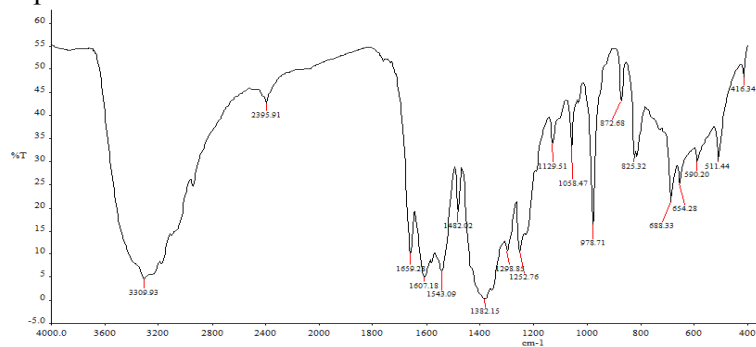
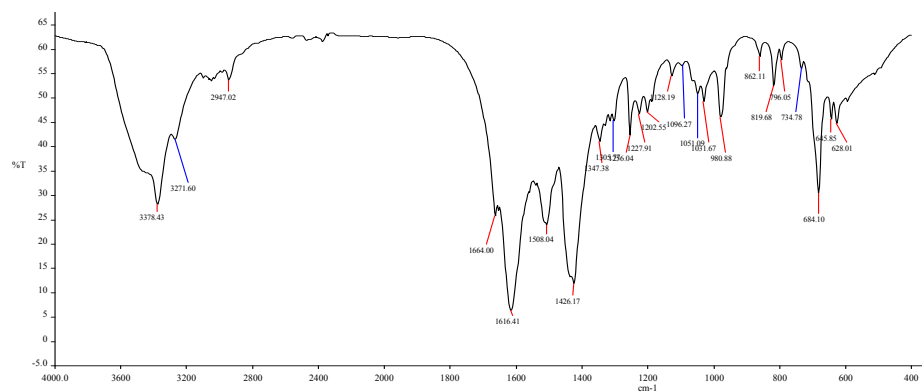
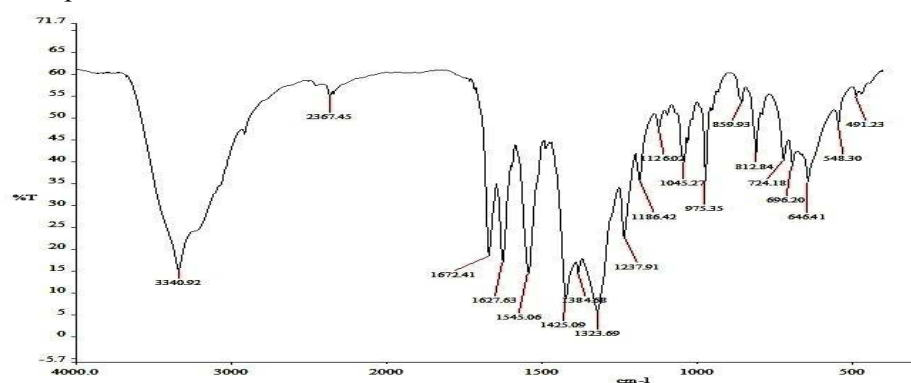


Figure S6. FTIR spectra of 4.

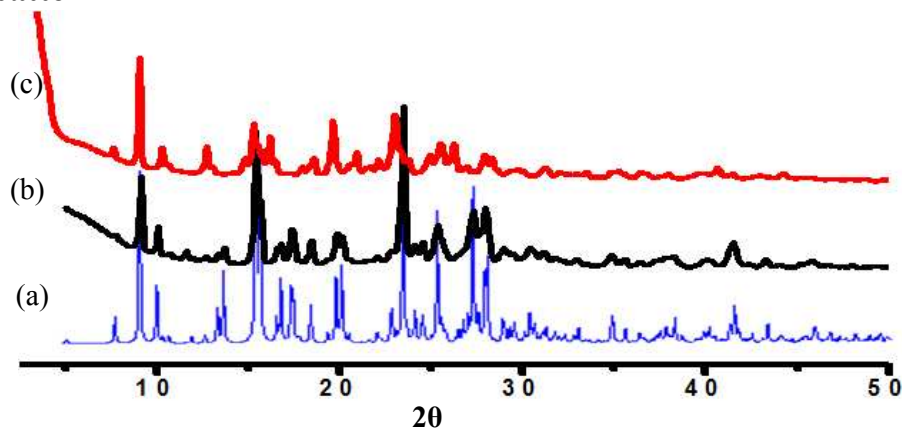


**Figure S7.** FTIR spectra of **5**.

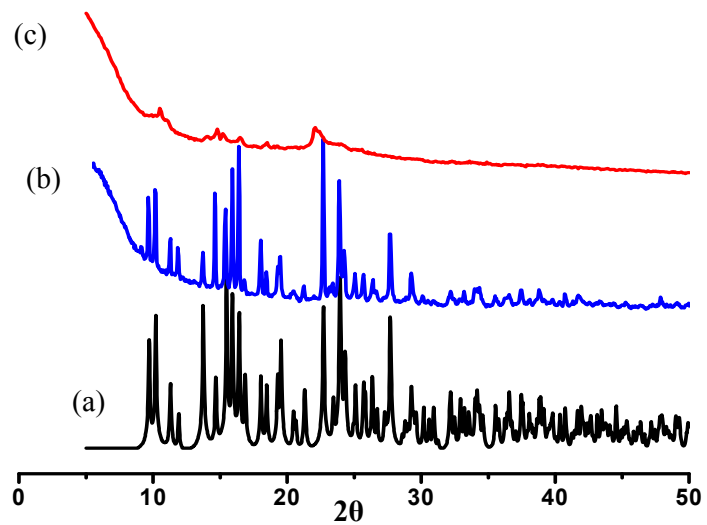


**Figure S8.** FTIR spectra of **6**.

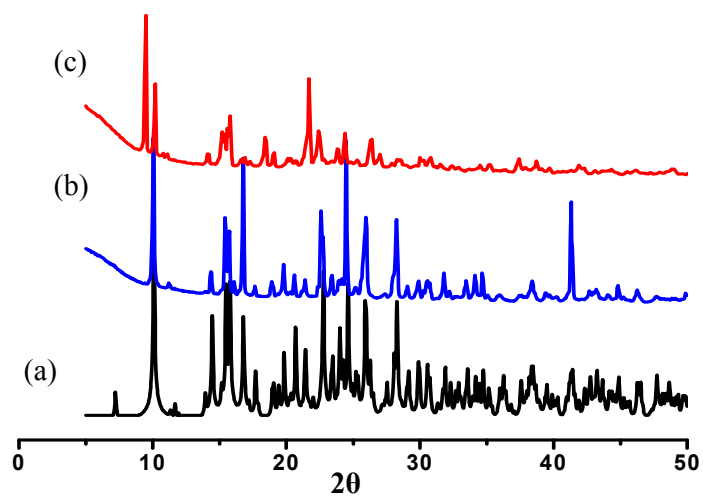
### XRPD pattern



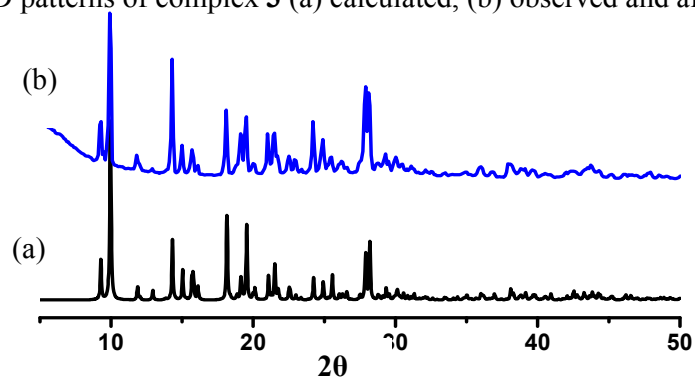
**Figure S9.** XRPD patterns of complex **1** before irradiation (a) calculated, (b) observed and after irradiation (c) observed.



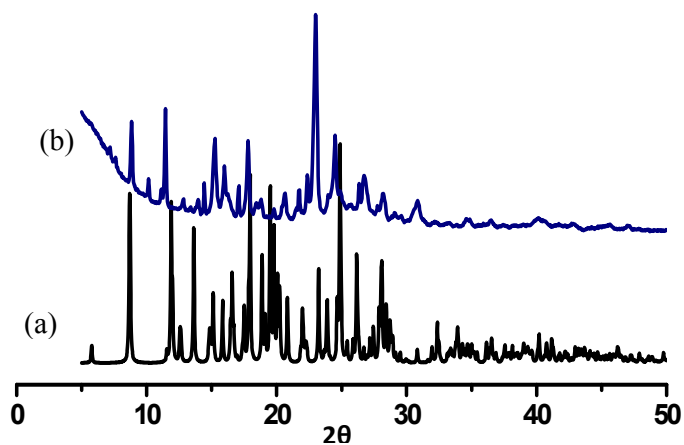
**Figure S10.** XRPD patterns of complex **2** (a) calculated, (b) observed and after irradiation (c) observed.



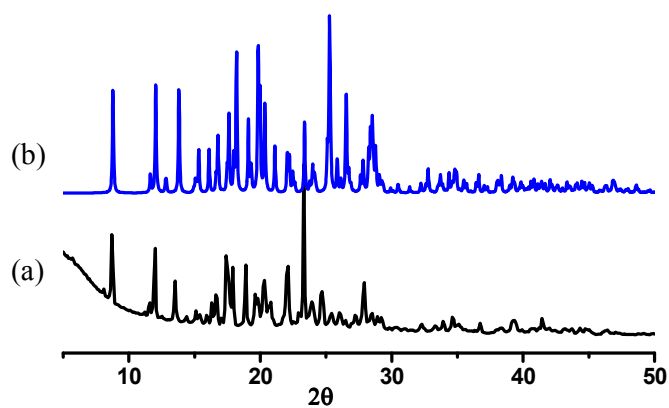
**Figure S11.** XRPD patterns of complex **3** (a) calculated, (b) observed and after irradiation (c) observed.



**Figure S12.** XRPD patterns of complex **4** (a) calculated, (b) observed.



**Figure S13.** XRPD patterns of complex **5** (a) calculated, (b) observed.

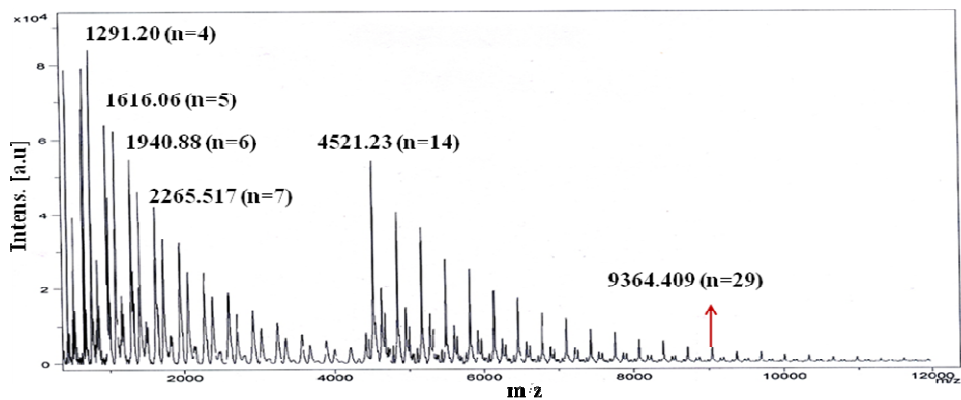


**Figure S14.** XRPD patterns of complex **6** (a) calculated, (b) observed.

## MALDI-TOF mass spectra

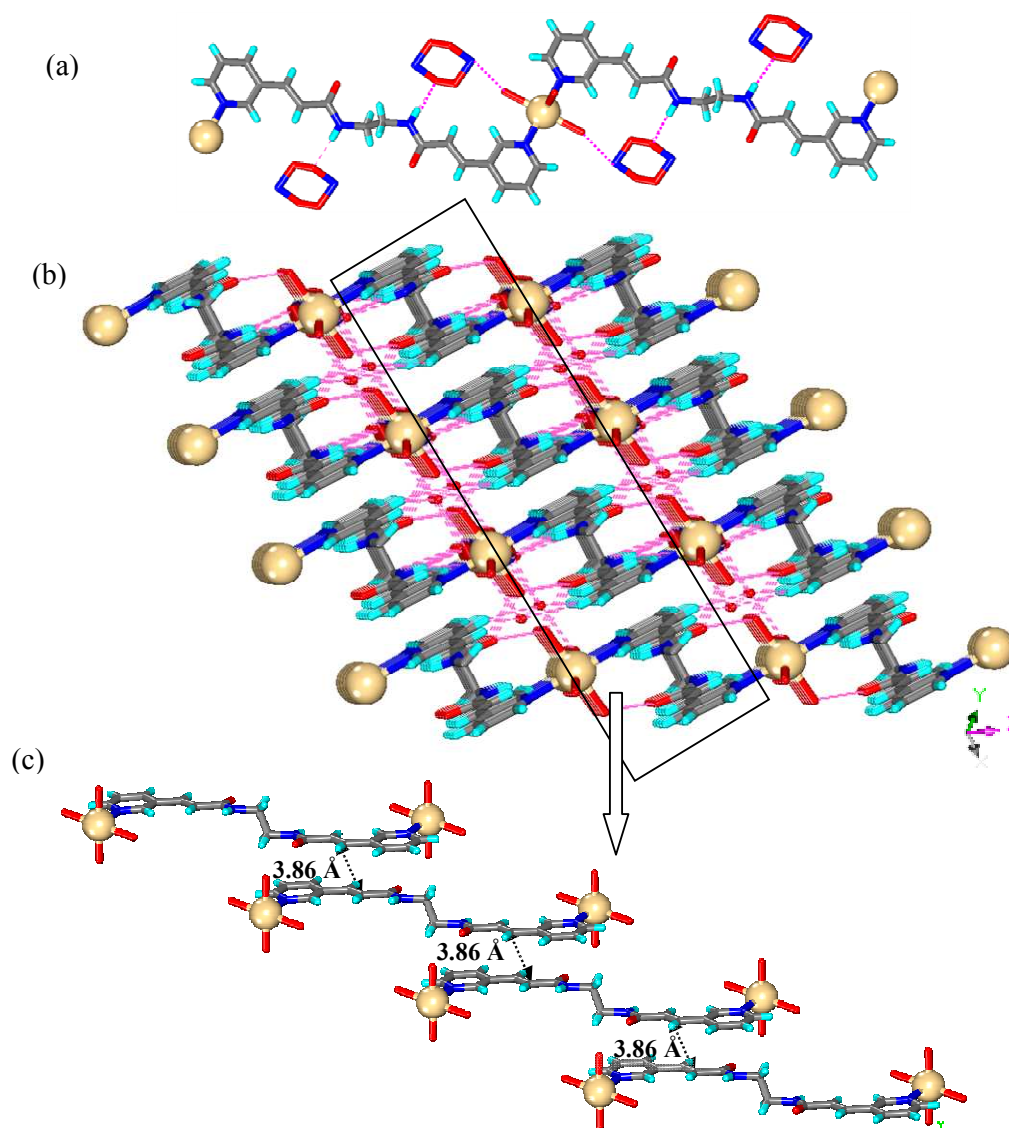
### Sample preparation for MALDI-TOF analysis:

2 mg irradiated materials were homogenously dispersed in 1 ml of ethanol and added 2, 5 di-hydroxy benzoic acid (DHB) as a matrix. Then, prepared sample was drop casted on the plate and dried in room temperature.

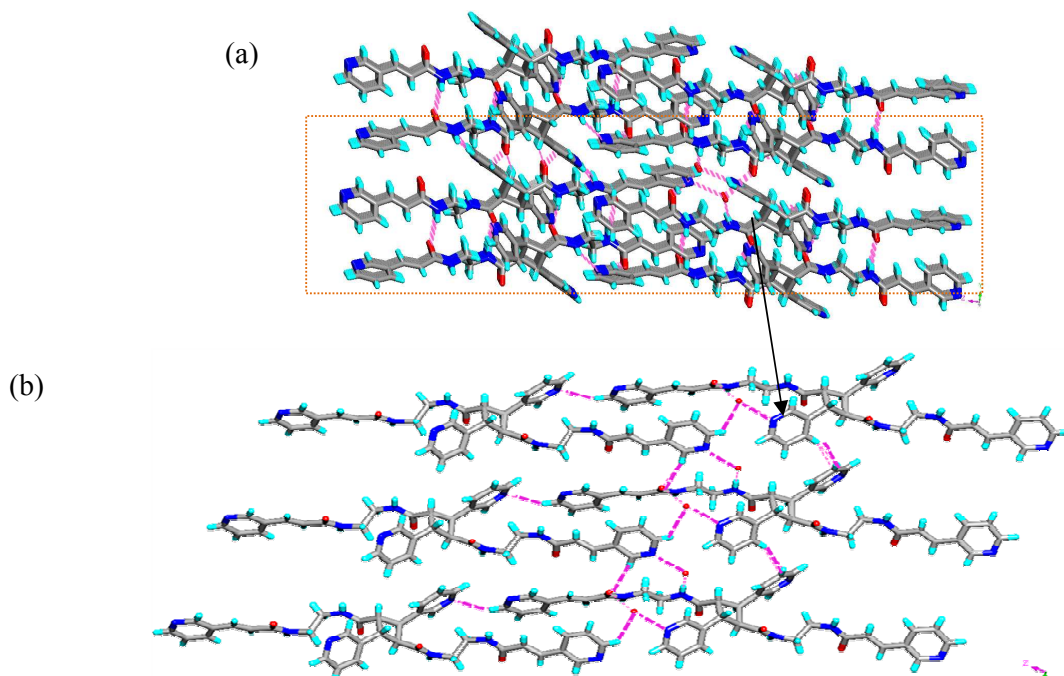


**Figure S15.** MALDI-TOF mass spectra of irradiated complex **2**.

## Crystal structure analysis



**Figure S16.** Illustrations for the crystal structure of **2**: (a) one-dimensional CPs, notice the hydrogen bonded nitrate ion with coordinated water and amide N-H groups; (b) packing of the 1D-chains in the lattice via hydrogen bonding between amides, water and nitrate ions; (c) alignment of 1D-chains for polymerization reaction.



**Figure S17.** Illustrations for the crystal structure of **7**: (a) packing of the dimers in the lattice via hydrogen bonding between amides and waters; (b) two-dimensional hydrogen bonded layer of dimers.

**Table S1. Bond lengths around M(II) centers**

CPs	M-N (Å)	M-O (Å)
<b>1</b>	2.007, 2.012, 2.015	1.978, 2.007, 2.015, 2.295 2.490, 2.584
<b>2</b>	2.306(7)	2.267(16), 2.326(13)
<b>3</b>	2.150(3), 2.204(3)	2.074(2), 2.078(2), 2.109(2), 2.140(3)
<b>4</b>	2.026(4), 2.036(4)	1.929(4), 1.954(4), 2.353(4)
<b>5</b>	2.322(2)	2.267(2), 2.322(2)
<b>6</b>	2.159(3)	2.097(3), 2.148(3)



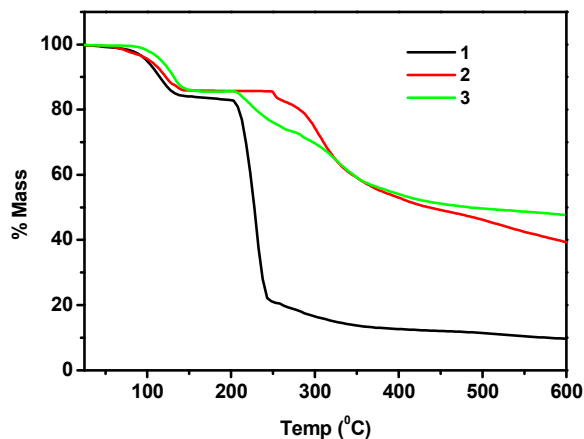
## Elemental analysis of irradiated complexes **2** and **3**

Irradiated **2**,  $\{[\text{Cd}(\text{L})(\text{H}_2\text{O})_4] \cdot 2(\text{NO}_3)\}_n$  Anal. Calc.(%) for  $\text{C}_{18}\text{H}_{26}\text{CdN}_6\text{O}_{12}$  (630.84): calc. (%) C, 34.27; H, 4.15; N, 13.32; found (%) C, 35.39; H, 4.86; N, 13.47.

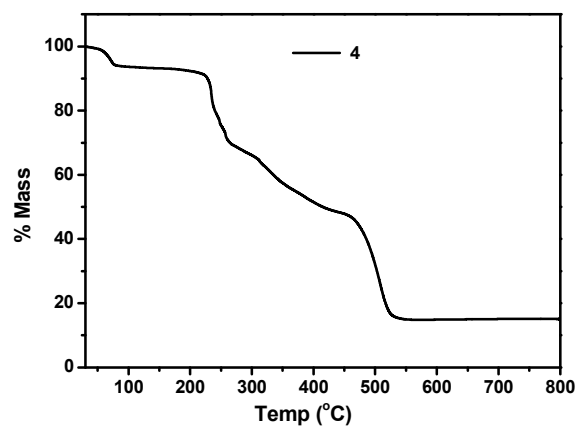
Irradiated **3**,  $\{[\text{Zn}(\text{L})(\text{H}_2\text{O})_4] \cdot 2(\text{NO}_3) \cdot 2(\text{H}_2\text{O})\}_n$  Anal. Calc.(%) for  $\text{C}_{18}\text{H}_{30}\text{CdN}_6\text{O}_{14}$  (619.85) calc.(%) C, 34.88; H, 4.88; N, 13.56; found (%) C, 34.83; H, 4.68; N, 13.27.

## TGA analysis

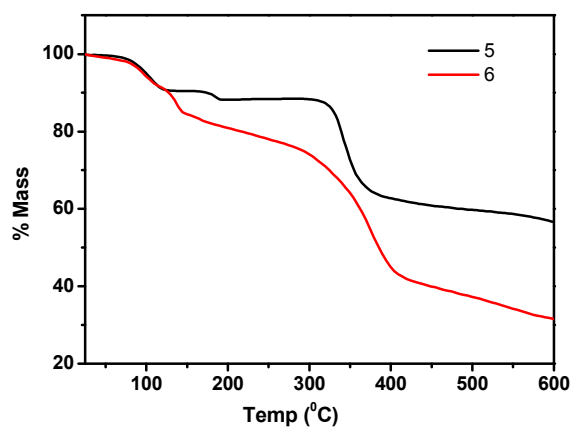
The thermal analyses of CPs (**1-6**) were performed in  $\text{N}_2$  atmosphere to investigate their thermal stability. The CPs **1**, **2** and **3** exhibits similar type of thermal decomposition. For all three complexes, initially 13-14% weight loss occurred range of 89-100 °C due to loss of coordinated and free water molecules. The complex **1** found to have fast decomposition in the temperature range of 200-245 °C, complex **2** slowly decomposes from 248 °C onwards and complex **3** also slowly decomposes 207 °C onwards (Fig. S18). The complex **4** exhibits 7% weight loss 77 °C that corresponds to the loss of water molecules and 25% weight loss occurred gradually in between 220-300 °C corresponding to acetate ions. From 310 °C onwards the gradual degradation started and continued up to 530 °C (Fig. S19). The complexes **5** and **6** show three steps degradations. Initial 9% weight loss occurs (77 °C to 122 °C) due to four coordinated and one free water molecules. Second loss occurs at 166-186°C and 126-143 °C for **5** and **6**, respectively, corresponding to the loss of perchlorate ions. The final degradation of the complexes **5** and **6** started at temperatures 320 °C and 324 °C respectively (Fig. S20).



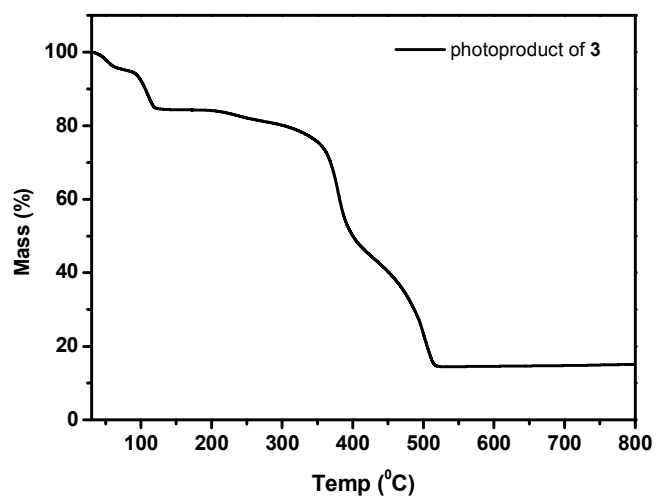
**Figure S18.** Thermal gravimetric analysis for **1**, **2** and **3**.



**Figure S19.** Thermal gravimetric analysis for **4**.



**Figure S20.** Thermal gravimetric analysis for **5** and **6**.



**Figure S21.** Thermal gravimetric analysis for irradiated materials of **3**.