Electronic Supplementary Material for CrystEngComm

The Illustrative use of Thiosulfate in the Formation of New Three-dimensional Hybrid Structures: Synthesis, Structure, Transformation Studies and Sunlight Assisted Photocatalytic Behavior

Avijit Kumar Paul[a], Giridhar Madras[b*] and Srinivasan Natarajan[a*]

[a] Framework Solids Laboratory, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India. E-mail: snatarajan@sscu.iisc.ernet.in

[b] Department of Chemical Engineering, Indian Institute of Science, Bangalore-560012, India. E-mail: giridhar@chemeng.iisc.ernet.in

ELECTRONIC SUPPLEMENTARY INFORMATION

Photocatalytic Experiment

Photocatalytic activity was studied using mercury vapor lamp of 125 W (λ=365 nm). Water was circulated through the annulus of the reactor to avoid heating of the solution and to maintain the temperature at 30 ºC. The solution was continuously stirred to ensure that the catalyst was suspended uniformly. Samples were collected at regular intervals, filtered through Millipore membrane filters and centrifuged to remove the catalyst and analyzed using UV-Vis spectrometer (Perkin-Elmer, Lambda-32). Control experiments without the catalyst were also carried out which does not show any degradation under UV light.

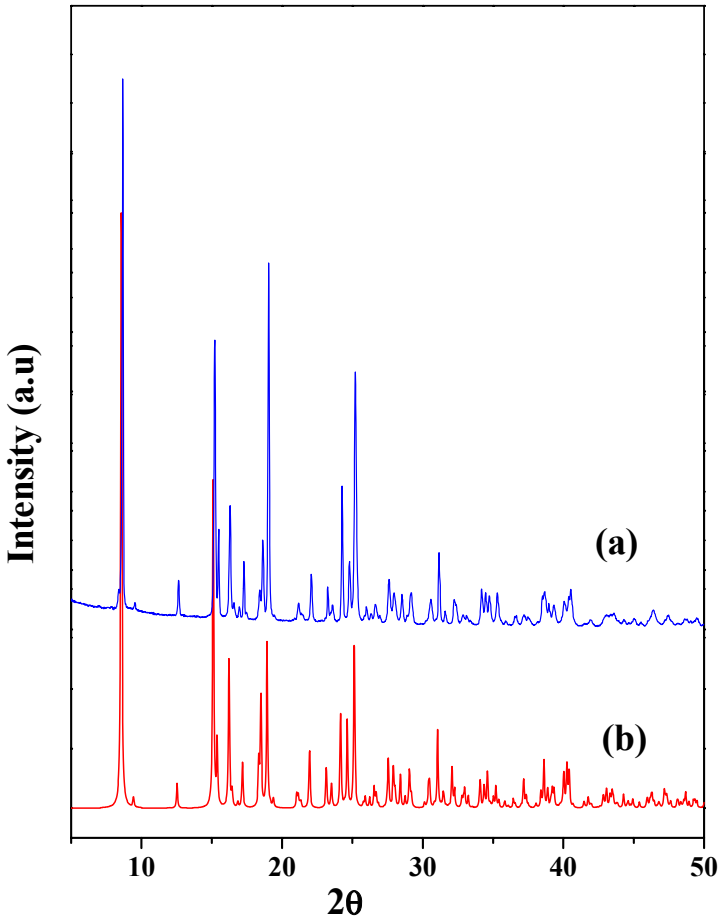


Fig. S1: Powder XRD (CuKα) pattern of **I**, (a) experimental and (b) simulated

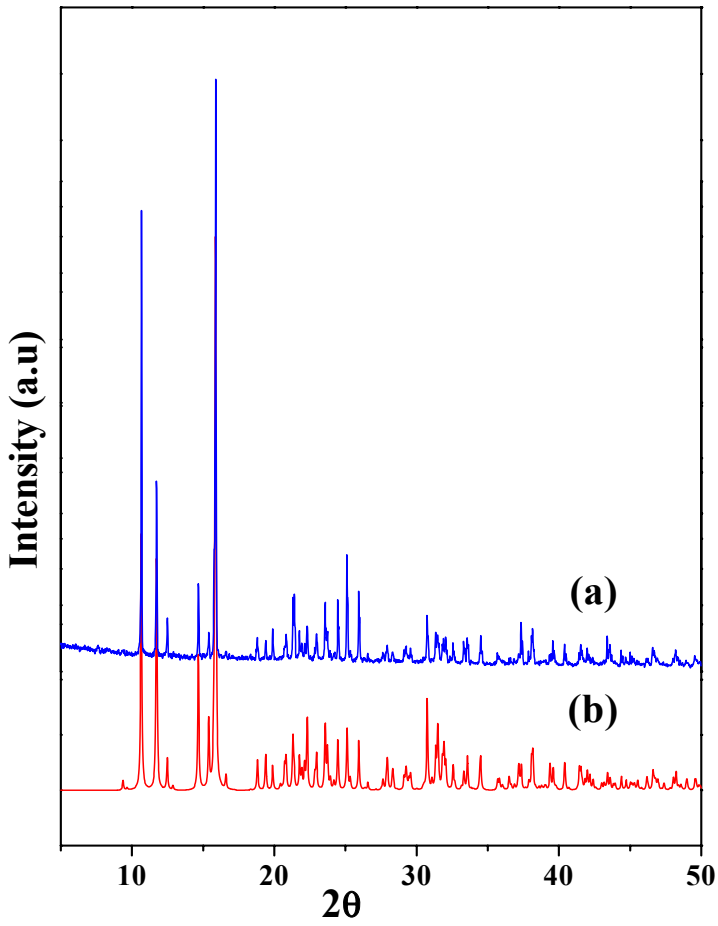


Fig. S2: Powder XRD (CuKα) pattern of **II**, (a) experimental and (b) simulated

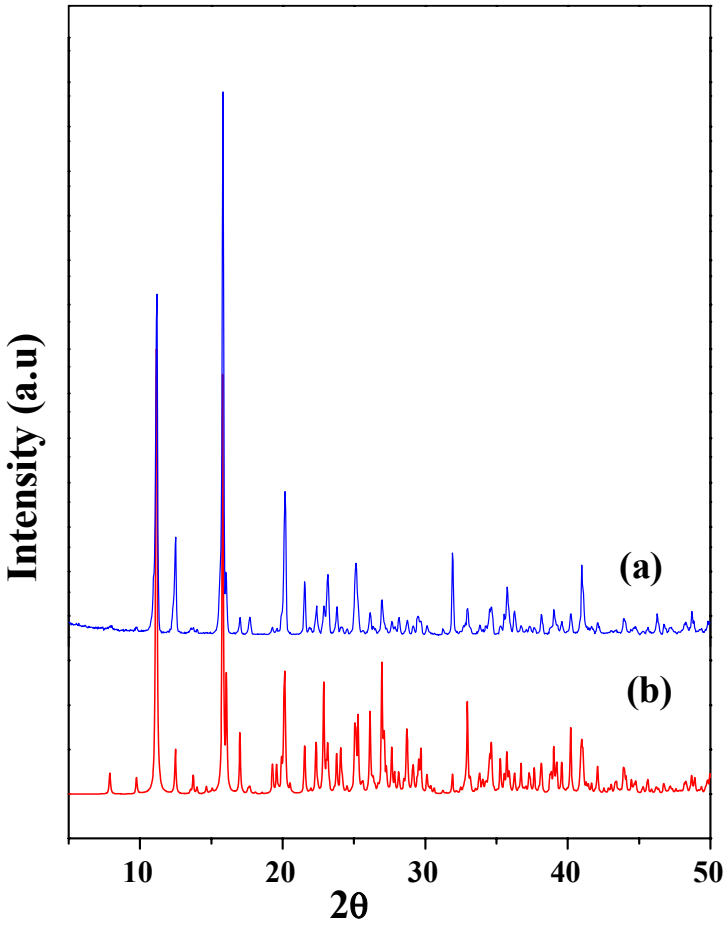


Fig. S3: Powder XRD (CuKα) pattern of **III**, (a) experimental and (b) simulated

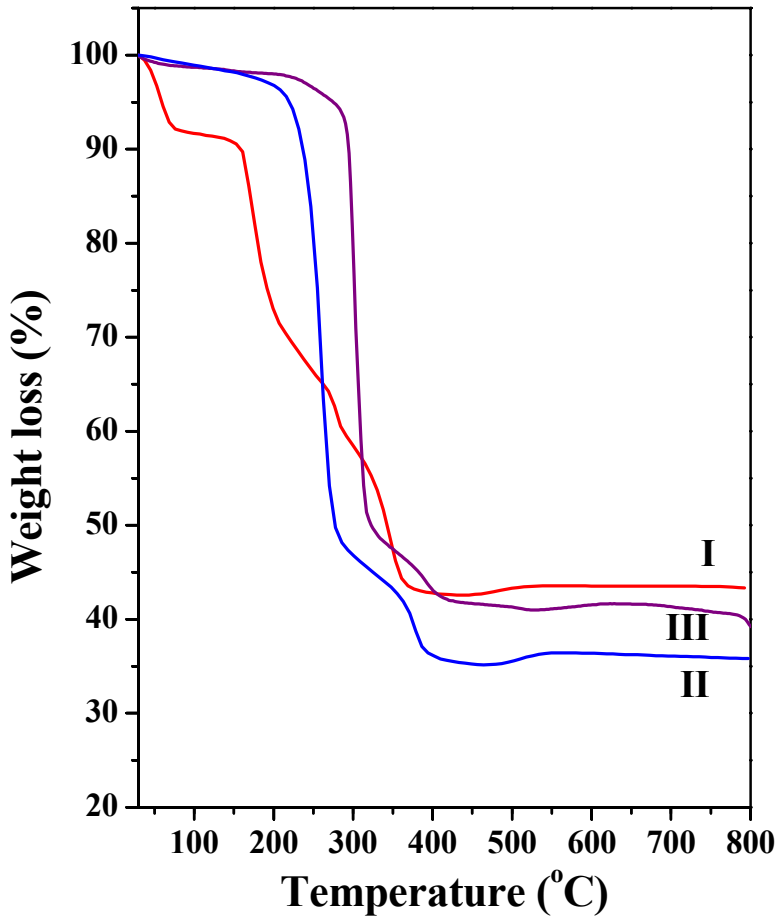


Fig. S4: TGA studies (in oxygen) of **I**, **II** and **III**.

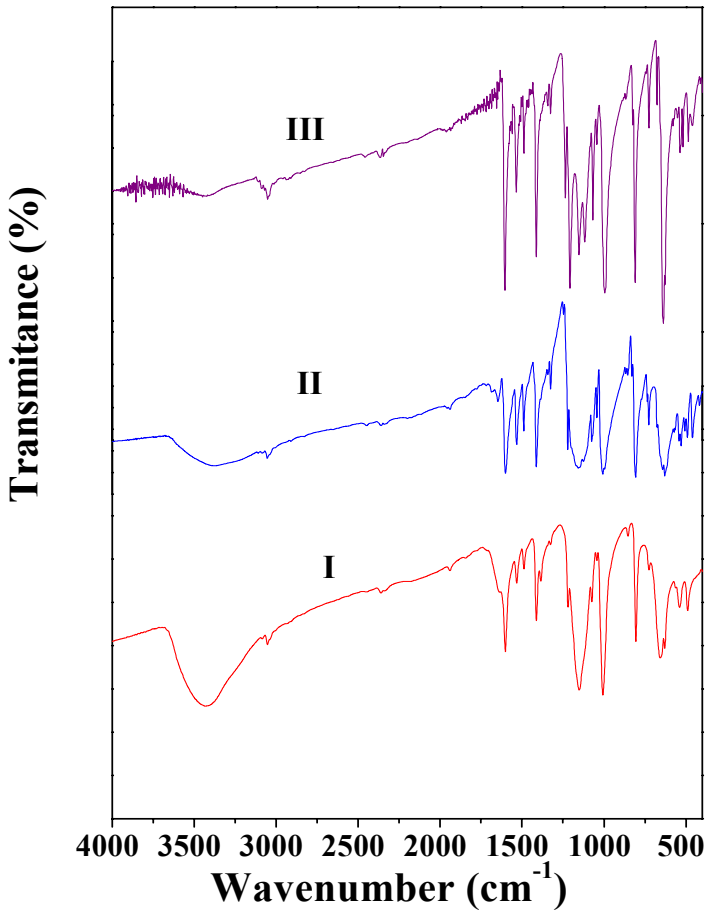


Fig. S5: IR spectra of **I**, **II** and **III.**

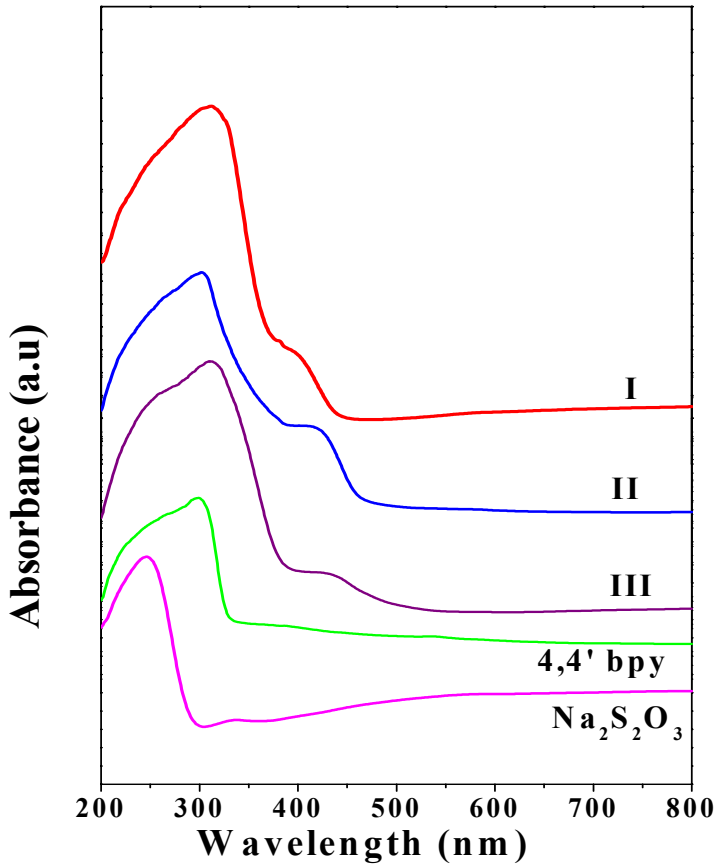


Fig. S6: Solid state absorbance spectra (UV-visible) of compound **I-III**, 4,4'-bipyridine and $Na_2S_2O_3$.

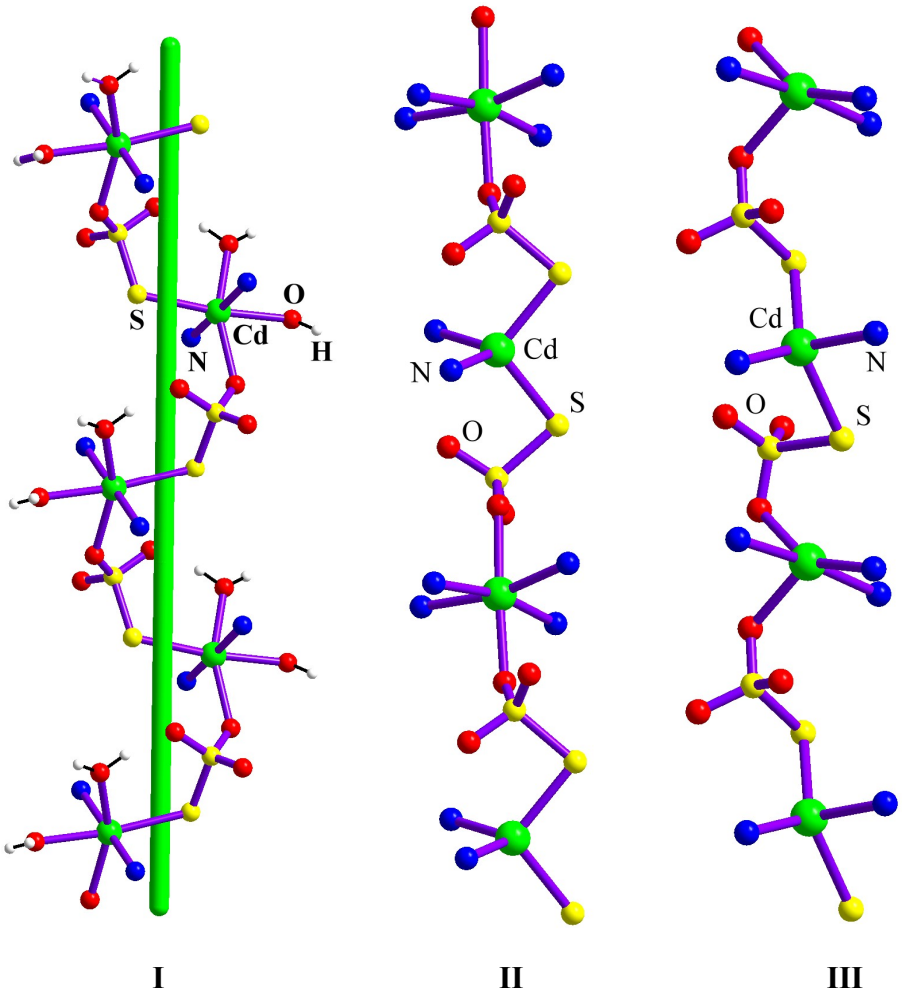
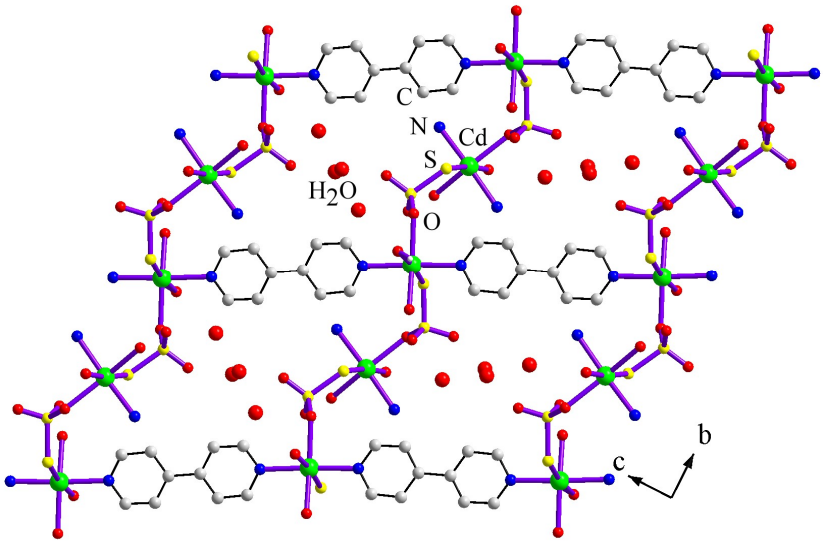
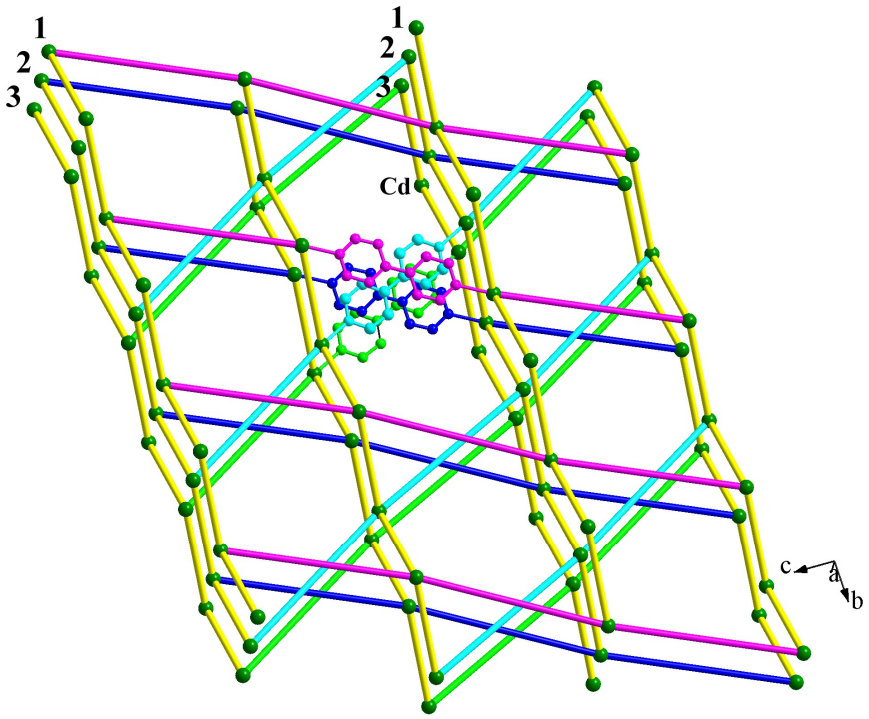


Fig. S8: One dimensional metal-thiosulfate chains in compound **I**, **II** and **III.**

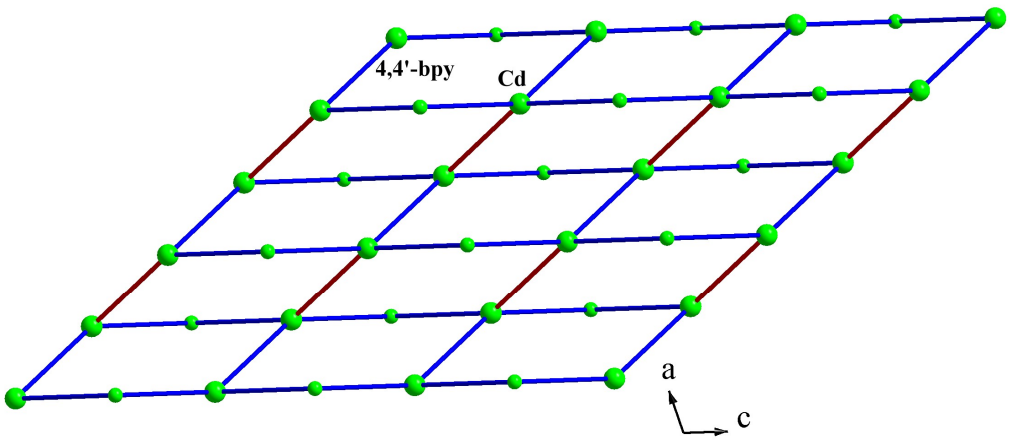


(a)

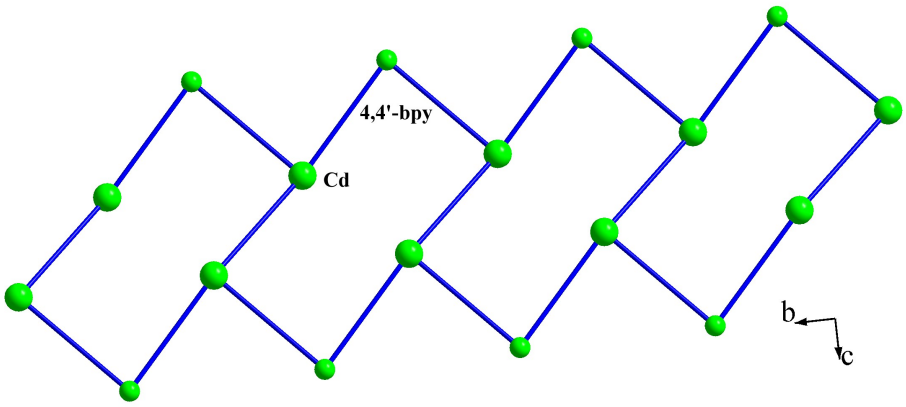


(b)

Fig. S9: (a) Two-dimensional layer view of cadmium-thiosulfate with *bpy*, containing lattice water of compound **I**. (b) Three-dimensional interpenetrating structure of compound **I**. Purple, blue, cyan and green lines show that the different layer of *bpy*. Yellow line corresponds the thiosulfate chain.

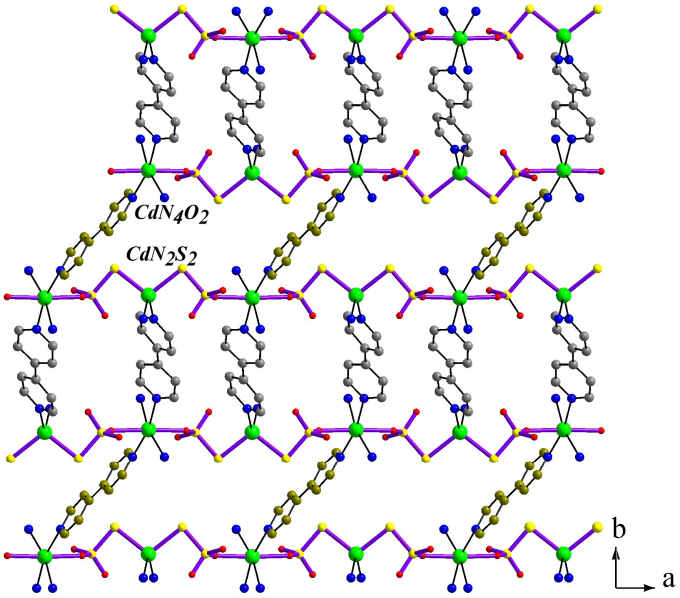


(a)

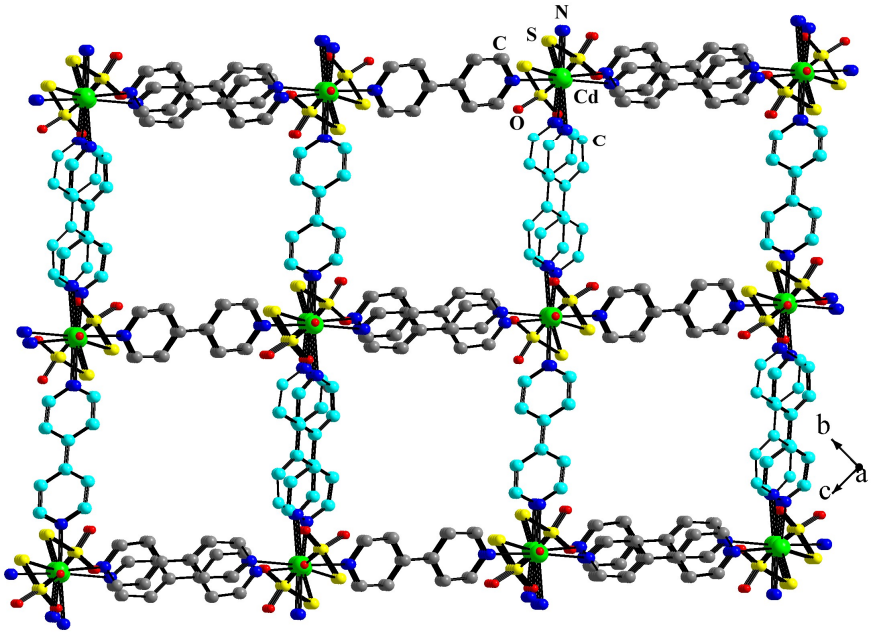


(b)

Fig. S10: (a) Two-dimensional layer of Cd and bpy in Compound **II**. (b) One-dimensional edge-sharing rectangular box in compound **III**. Linear lines are *bpy* unit and green spheres are Cd.

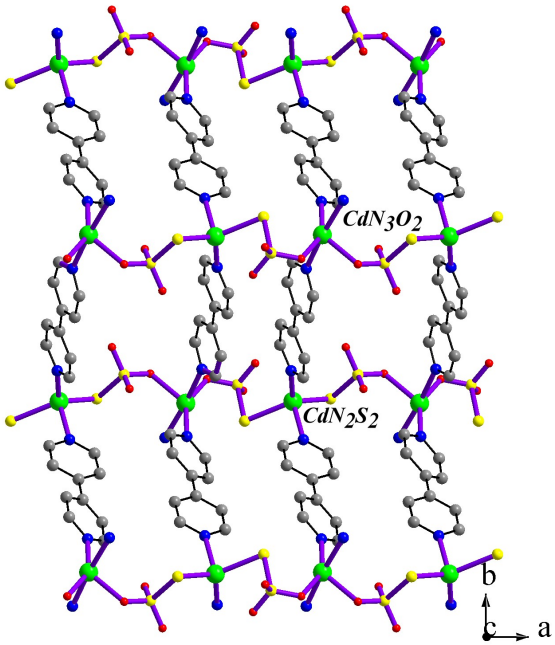


(a)

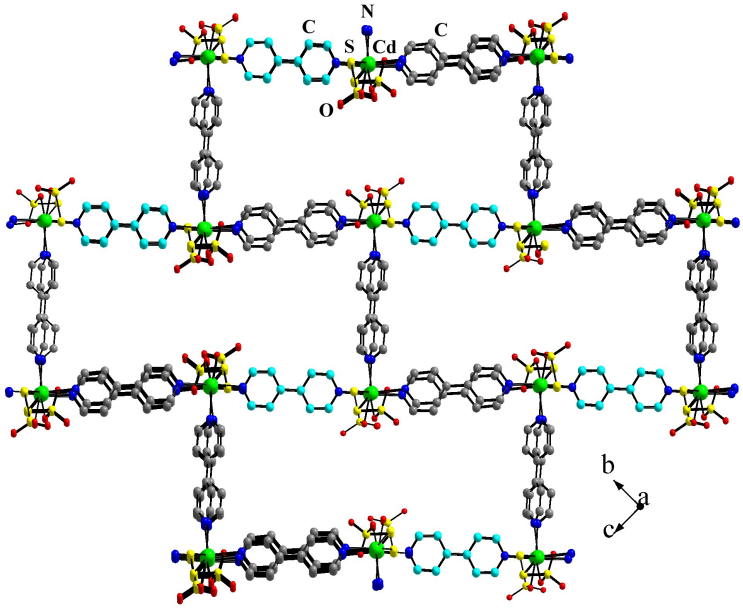


(b)

Fig. S11: (a) Two-dimensional layer view of compound **II** with metal-thiosulfate and *bpy*. Two coordination of octahedral cadmium with *bpy* is missing here which forms the three-dimensional structure. (b) The three-dimensional architecture of compound **II**.



(a)



(b)

Fig. S12: (a) Two-dimensional layer view of compound **III** with metal-thiosulfate and *bpy*. One coordination of trigonal bipyramidal cadmium with *bpy* is missing here which forms the three-dimensional structure. (b) The three-dimensional architecture of compound **III**.

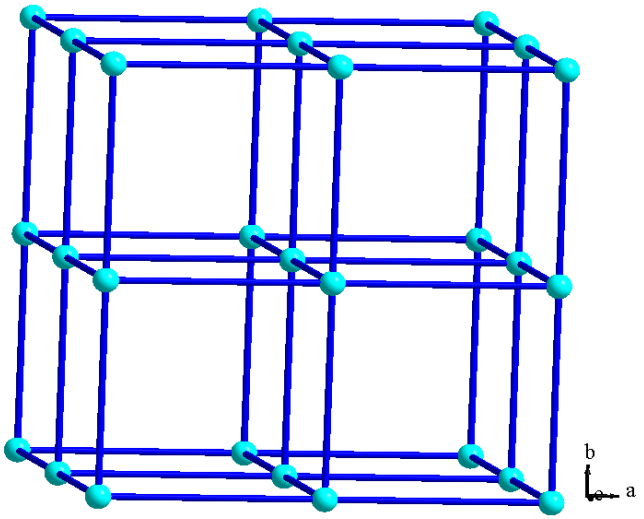


Fig. S13: (a) Schematic diagram of **pcu** net.

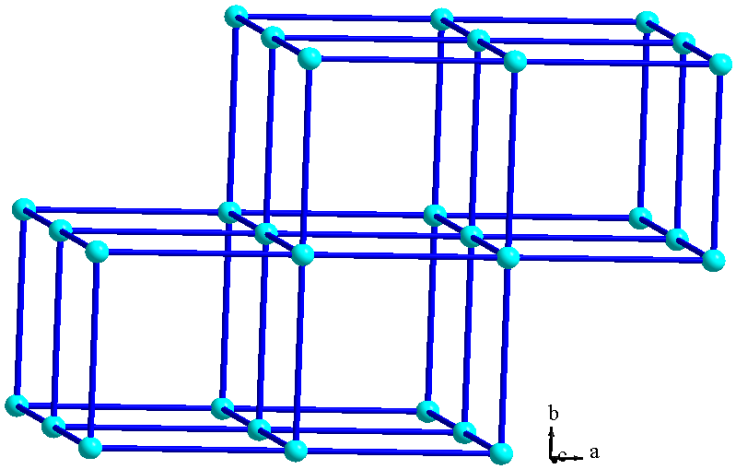


Fig. S13: (b) Schematic diagram of **pcu** net in another view.

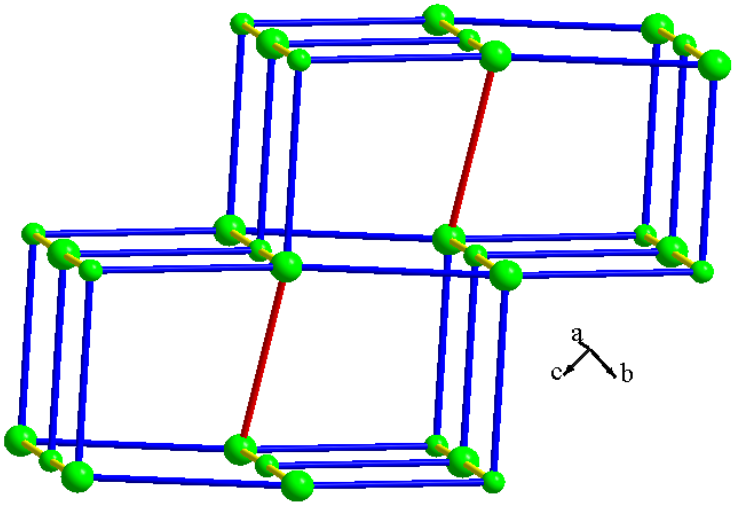


Fig. S14: (a) Schematic diagram of compound **II.** Big green spheres are octahedral and small green spheres are tetrahedral cadmium centers which are connected by thiosulfate ion (yellow lines) and 4,4'-*bpy* (blue and red lines) unit.

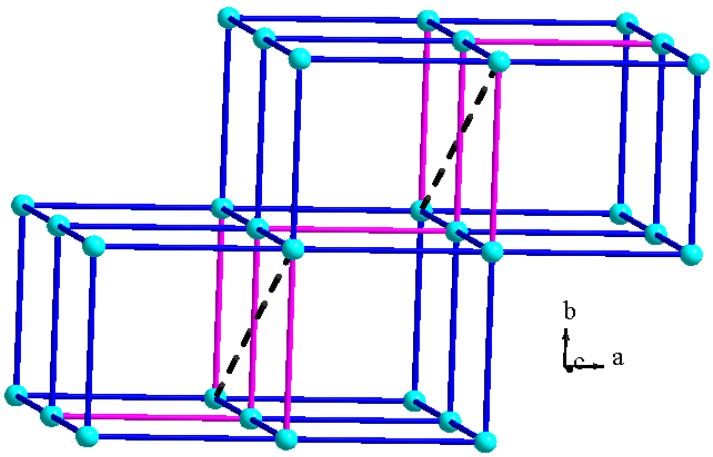


Fig. S14: (b) Schematic diagram of **pcu** net. Purple bonds show the bonds that are absent in **II** and black dotted lines are extra bonds in **II**.

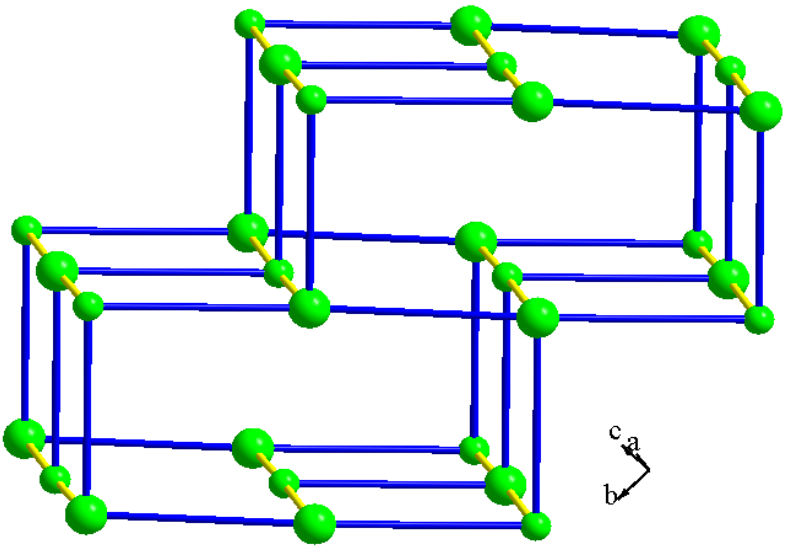


Fig. S15: (a) Schematic diagram of compound **III.** Big green spheres are trigonal bipyramidal and small green spheres are tetrahedral cadmium centers, respectively, connected by thiosulfate ion (yellow lines) and 4,4'-*bpy* (blue lines) unit.

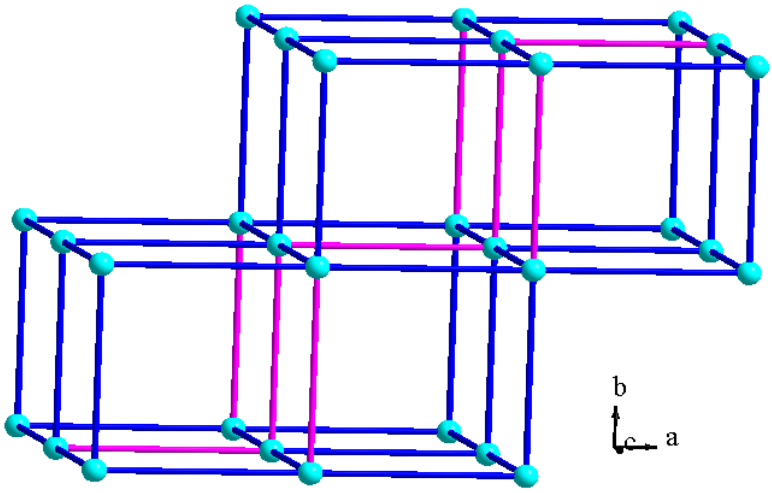


Fig. S15: (b) Schematic diagram of **pcu** net. Purple bonds represent the bonds that are absent in **III.**

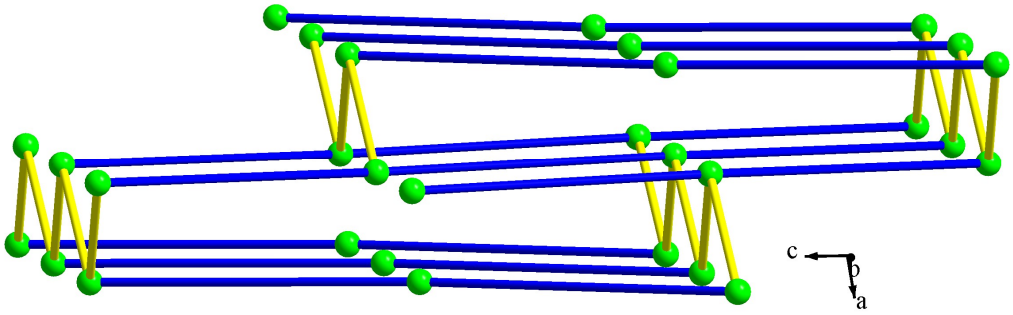


Fig. S16: (a) Schematic diagram of compound **III.** Green spheres are tetrahedral cadmium centers (avoiding two terminal water molecules) which are connected by thiosulfate ion (yellow lines) and 4,4'-*bpy* (blue lines) unit.

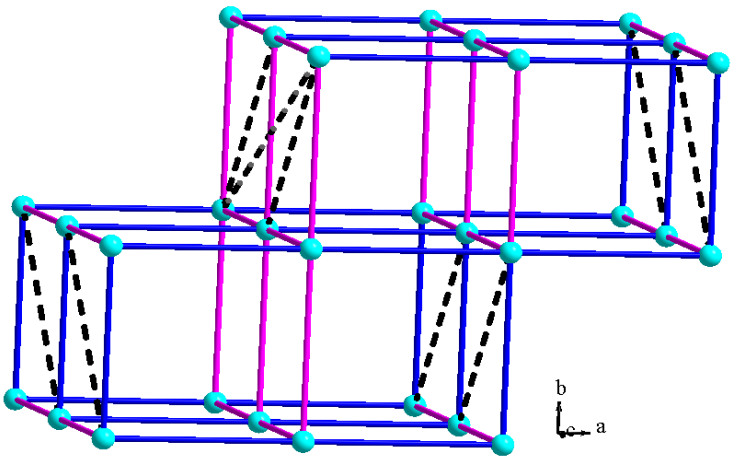


Fig. S16: (b) Schematic diagram of **pcu** net. Purple bonds represent the bonds that are absent in **I** and black dotted lines are the extra bonds present **I**.

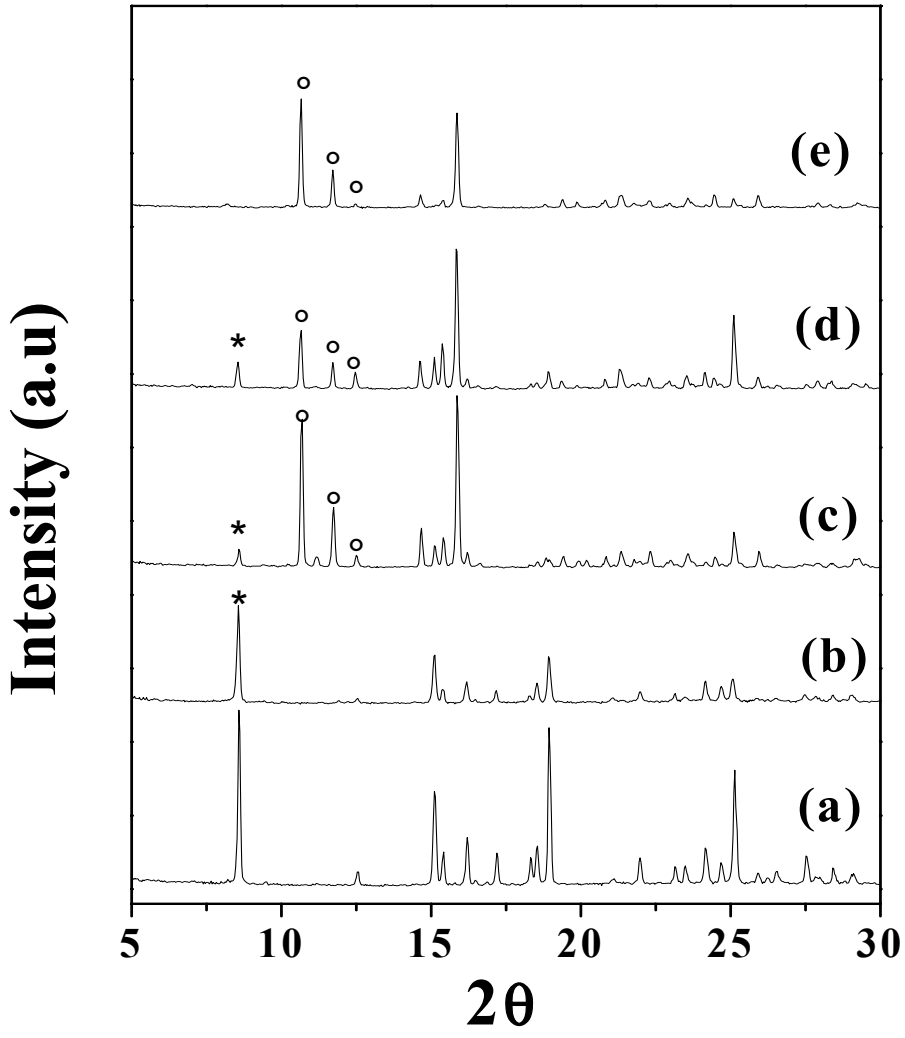


Fig. S17: Transformation of **I** to **II** by reaction of **I** and *bpy* (1: 0.50) at 45 ^{0}C at different times (a) pure **I**, (b) after 4 hrs, (c) after 8 hrs, (d) after 12 hrs and (e) after 20 hrs (pure **II**) The symbol * shows the peak of **I** and the symbol o represents **II.**

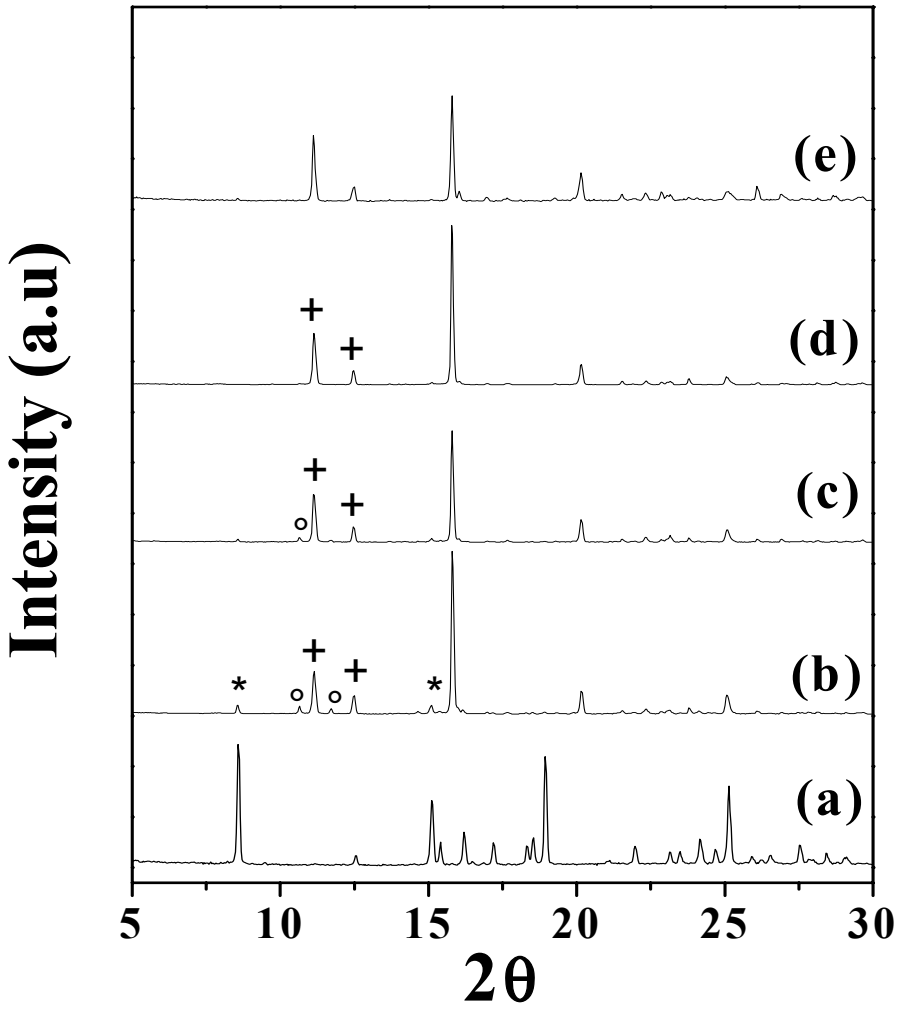


Fig. S18: Transformation of **I** to **III** by the reaction of **I** and *bpy* (1: 0.25) at 60 ^{0}C in different times (a) pure **I**, (b) after 4 hrs, (c) after 8 hrs, (d) after 12 hrs and (e) after 20 hrs (pure **III**). The symbol * represent the peaks of **I**, the symbol o represents the peaks of **II** and the symbol + represents the peaks of **III**.