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## Application of a novel 2D cadmium(II)-MOF in the formation of a photo-switch with substantial on–off ratio

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 Sumit Roy<sup>a</sup>, Arka Dey<sup>b</sup>, Partha Pratim Ray<sup>b,\*</sup>, Joaquín Ortega-Castro<sup>c</sup>, Antonio Frontera<sup>c,\*</sup> and Shouvik Chattopadhyay<sup>a,\*</sup>

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**A novel thiocyanate bridged 2D MOF, [CdL(μ-1,3-SCN)<sub>2</sub>]<sub>n</sub>, [HL = 2-(2-(ethylamino)ethyliminomethyl)-6-ethoxyphenol] has been synthesized and characterized by X-ray crystallography. The band gap of the synthesized material in solid state has been determined by experimental measurement and compared with the theoretical value found from DFT calculation. For the 1st time the single crystal X-ray crystallography of a MOF has been reported along with its applicability in photosensitive devices.**

The significance of the synthesis of multinuclear d<sup>10</sup> cadmium(II) complexes lies in their interesting photochemical and photophysical properties, with potential applications as light-emitting diodes, luminescent probes, and photovoltaics.<sup>1–5</sup> They have also received considerable attention in coordination chemistry because of the exciting structural features of cadmium(II) acting as nodes and different pseudo-halides/organic ligands as linkers in the construction of multidimensional coordination networks, sometimes referred as metal–organic frameworks (MOF).<sup>6–9</sup> These MOFs represent a class of hybrid materials comprising metal-based vertices (nodes) and organic ligands (linkers) that connect the vertices into two or three-dimensional periodic structures.<sup>10–13</sup> Instead of a bare metal ion, suitable metal–ligand complexes are also used as nodes.<sup>14–17</sup> The structures and properties of MOFs can be carefully tailored by judicious selection of nodes and linkers. A hallmark property of MOFs is their intrinsic porosity, which renders them potentially useful for gas storage, separations, catalysis, and a variety of additional applications that rely on highly specific host–guest interactions. Their promising properties coupled with the ease by which their structures can be modified make MOFs one of the most exciting, diverse, and rapidly growing areas of modern chemistry research. The use of MOFs for light harvesting and energy

transfer is also a promising area of research. Formation of such photoconductive MOFs requires generation and transportation of photoinduced charge carriers within the network. In this study, we have demonstrated photosensitivity of the synthesized semiconducting MOF with an appreciably high on–off ratio. Though several MOFs are reported to harvest visible light and trigger photocurrent generation with a quick response to irradiation with visible light,<sup>18,19</sup> probably no such systems are characterized by single crystal X-ray crystallography till date. In the present work, we have prepared and characterized by X-ray crystallography a novel Cd(II)-MOF, which is photoconductive probably as a result of exciton migration over the lattice followed by charge separation at the molecule–electrode interface.

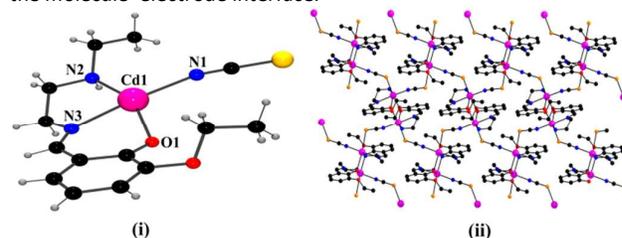


Fig. 1 (i) A perspective view of the asymmetric unit of the complex with selective atom numbering scheme (ii) Two-dimensional layer of the complex. Ethyl groups and hydrogen atoms are omitted for clarity.

The complex crystallizes in the orthorhombic space group *Pbca*. The asymmetric unit contains one cadmium(II), one SCN group and one deprotonated Schiff base (L<sup>−</sup>) {Fig. 1(i)}. The cadmium(II) is coordinated by one amine nitrogen atom, N(2), one imine nitrogen atom, N(3) and one phenoxo oxygen atom, O(1) of the deprotonated Schiff base (L<sup>−</sup>) and one nitrogen atom, N(1) of a μ-1,3-thiocyanate. A symmetry related oxygen atom, O(1)<sup>a</sup>, (symmetry transformation <sup>a</sup> = 1-x, -y, 1-z) of phenoxo group coordinates the cadmium(II) to form a pseudo-dimer, as shown in Figure S1 in the Electronic Supporting Information (ESI). Another symmetry related sulphur atom, S(1)<sup>b</sup>, (symmetry transformation <sup>b</sup> = 3/2-x, 1/2+y, z) of a μ-1,3-thiocyanate coordinates cadmium(II) to

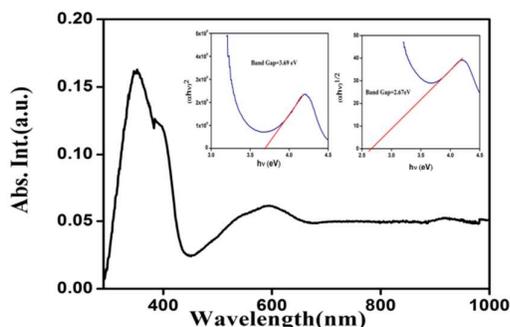
<sup>a</sup> Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata 700032, India.

<sup>b</sup> Department of Physics, Jadavpur University, Kolkata 700032, India.

<sup>c</sup> Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca (Balears), Spain.

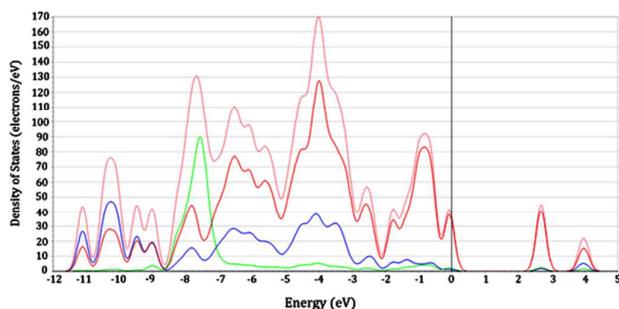
Electronic Supplementary Information (ESI) available: Details of the Synthesis, elemental and spectral analyses, PXRD, crystallographic data in CIF format, data, H-bonding interactions, Device fabrication, Hirshfeld Surface Analysis, Theoretical methods, Tables S1–S3, Fig.s S1–S9. CCDC 1400219.

completes its distorted octahedral geometry. The pseudo-dimeric bridging unit  $\text{Cd}_2\text{O}_2$  describes a rhombohedral plane. The saturated five member ring  $\text{Cd}(1)-\text{N}(1)-\text{C}(3)-\text{C}(4)-\text{N}(2)$ , present an envelope conformation with puckering parameters  $q(2) = 0.426(4) \text{ \AA}$  and  $\phi(2) = 259.3(4)^\circ$ .<sup>20</sup> Selected bond lengths and angles are presented in Tables S1 and S2, (ESI). Each cadmium(II) center of the pseudo-dimer is connected to two neighboring cadmium(II) centers of two different pseudo-dimers via two  $\mu$ -1,3-thiocyanates to form a 2D polymeric layer {Figure 1(ii)}. A 2D flat four connected net based on (4,4) square grid topology produced (Figure S2, ESI) with dimeric cadmium(II) unit occupying the nodes and  $\mu$ -1,3-thiocyanate connectors take part in the formation of edges. It forms a H-bonded dimer (Figure S3, ESI).



**Fig. 2** The absorbance spectra of synthesized material with Tauc's plots (inset).

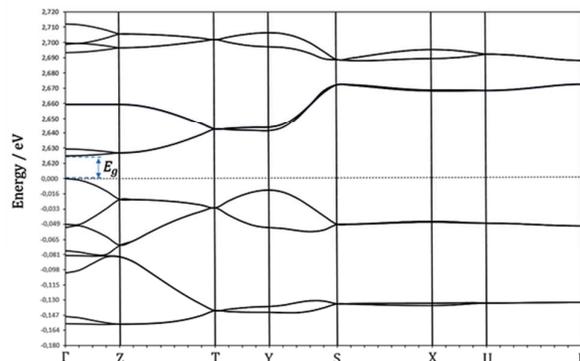
In this study, optical spectrum of the complex (Fig. 2) was recorded for the deposited thin films of as synthesized material by preparing a well dispersed solution in DMSO, in the range 200–1000 nm. The absorption spectrum of the synthesized material illustrates energy absorption in UV region at  $\sim 348 \text{ nm}$ . The optical band gap of the film was estimated using the fundamental absorption, which corresponds to electron excitation from the valence band to conduction band.<sup>21</sup> The band gap of the film was calculated using the following equation<sup>22</sup>:  $\alpha h\nu = A \cdot (h\nu - E_g)^n$  Where ' $\alpha$ ' is the absorption coefficient, ' $E_g$ ' is the band gap,  $h$  is Planck's constant, ' $n$ ' is the nature of transition dependent constant and ' $A$ ' is an energy-independent constant. Considering  $n = 2$  and  $0.5$  in the above equation, the value of optical band gap of the synthesized material was evaluated at 3.69 and 2.67 eV.



**Fig. 3** Calculated total (pink line) and partial DOS (s-orbital: blue

line, p-orbital: red line, d-orbital: green line) of  $[\text{CdL}(\mu\text{-}1,3\text{-SCN})_2]_8$  crystal.

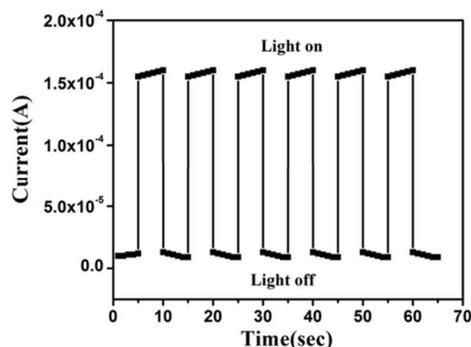
The analysis of the crystal structure was performed by standard band theory and total/partial density of states calculation which shows that  $[\text{CdL}(\mu\text{-}1,3\text{-SCN})_2]_8$  crystal has two semiconductor band gaps of 2.61 eV and 3.94 eV (Figs 3 and 4).



**Fig. 4** Electronic band structure of  $[\text{CdL}(\mu\text{-}1,3\text{-SCN})_2]_8$  crystal. Points of high symmetry in the first Brillouin zone are labelled as follows:  $\Gamma=(0,0,0)$ ,  $Z=(0,0,0.5)$ ,  $T=(-0.5,0,0.5)$ ,  $Y=(-0.5,0,0)$ ,  $S=(-0.5,0.5,0)$ ,  $X=(0,0.5,0)$ ,  $U=(0,0.5,0.5)$ , and  $R=(-0.5,0.5,0.5)$ .

Generally the DFT band gaps tend to be lower than experimentally determined band gaps,<sup>23</sup> however, in our case, DFT band gap values are unexpectedly in good agreement with the experimental values (2.67 eV and 3.69 eV). The electronic states distribution in both valence and conduction bands can be characterized with the PDOS (Fig. 3). The d-states and s-states of Cd and H atoms control the contribution in the valence band. The s-state and p-state of C, O and N atoms also contribute to the valence band, being the p-state of these atoms the greatest contribution in the conduction band. Compared to conventional light-harvesting organic polymers, MOFs possess long-range order and are comprised of metal ions or clusters that are connected by electron-donating "linker" groups to create a networked structure with well-defined pores.<sup>24</sup> This framework itself can serve as an "active" material and contributes in exciton migration followed by charge separation through the network at the molecule–electrode interface. The synthesized complex exhibits strong absorbance at the wavelength region 345–390 nm, which predicts some impact of incident radiation on the charge transport phenomena. For better understanding of charge transport phenomenon the electrical characterization was accomplished by coating thin film on top of ITO coated glass substrates. The conductivity of the thin film was measured under dark and illumination (irradiance  $\sim 80 \text{ mWcm}^{-2}$ ) from the current-voltage characteristic curve. Also the photosensitivity at +10V of the material was computed as 14.36. The obtained results exhibit synthesized Cd(II) based MOF harvests photons (345–390 nm) and generates photocurrent with a fast response to irradiation with visible light. The conductivity of the thin film was calculated as  $1.01 \times 10^{-8} \text{ Scm}^{-1}$  and  $2.16 \times 10^{-8} \text{ Scm}^{-1}$  for dark and light. In MOF, high order molecules produce unit cell like structures. These unit cells can be assembled together to form high surface area arrays for

photon collection.<sup>25</sup> As the material has photo-response, with the above result in mind the electric current of the material was measured many times at constant bias voltage 10V by switching the light on and off repeatedly and sequentially.



**Fig. 5** Current vs Time plot when the light was turned on or off

Fig. 5 represents the corresponding array, which indicates that the material has good sensitivity to light source switched on/off. This exhibits that the photocurrent can be switched many times repeatedly without deterioration of on/off ratio and might find application in photo-switch nano devices. This unique property is exceptional and represents an important step toward the use of synthesized sample in optoelectronics and photovoltaics. A likely explanation for this behaviour may be given based on the dual donor-acceptor properties of the organic-inorganic hybrid material. That is, in this system, the organic ligand behaves as an electron donor upon photoexcitation, while inorganic CdSCN part acts as an electron acceptor.<sup>26-28</sup>

In conclusion, we have synthesized a photoconductive Cd(II)-MOF which has two band gaps as demonstrated both from experimental measurement and DFT calculations. The present investigation reports for the first time the X-ray structure of a MOF, showing response to irradiation with visible light, thereby enabling repetitive switching of the photocurrent displaying substantial on-off ratio. Work is in progress to get better yield of the reaction and to synthesize other photoconductive thiocyanate bridged Cd(II)-MOF based on this strategy to generalize the concept.

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