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Cd(II) based metal–organic framework behaving as a Schottky barrier diode†

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Biswajit Bhattacharya,[a] Animesh Layek,[b] Md. Mehboob Alam,[c] Dilip Kumar Maity,[a] Swapan Chakrabarti,*[c] Partha Pratim Ray*[b] and Debajyoti Ghoshal*[a]

A metal–organic framework (MOF) of cadmium(II) is reported here which is the first example of an experimentally achieved MOF based electronic device, and in the present case it is a Schottky diode.

Searching for a system with performance-tailored functionality is the ‘holy grail’ of state-of-the art synthetic chemistry research and in this context, metal–organic frameworks (MOFs) are the new rising stars whose possible applications are just endless.[1] MOFs are an assembly of inorganic and organic moieties with a crystalline network.[2] Extensive studies on this class of material have already been done which essentially exploit the high surface area and porosity of their architecture, with the number of reports escalating rapidly on the conducting behavior of protons in MOF channels, and on their magnetism, drug delivery, catalysis and sensing applications.[3–9] However, the most tantalizing prospect of these highly ordered crystalline materials is that electronic device fabrication using MOFs, is still not even at its rudimentary stage. In MOFs, metal atoms are separated by organic linkers and these linkers play the most pivotal role in determining their overall electronic and electrical properties.[10] Thus, like other functionalities of MOFs, their electronic properties can also be customized by the appropriate choice of organic linkers. Therefore the electronic properties of MOFs are a promising area of research, which has the immense prospect of opening up the door of a new El Dorado of tailor-made Schottky barrier diodes, solar cells, light emitting diodes and memory devices.[11]

In the recent past, organic semiconductors and their derivatives have become more popular than conventional inorganic semiconductors in designing electronic devices such as diodes and field-effect transistors.[12–15] This has been made possible due to their easy fabrication, modulation capabilities, low cost, and the large area of device characterization compared to inorganic semiconductors. However, the key limitation of organic semiconductors is their poor thermal stabilities compared to conventional inorganic semiconductors. In this context, MOFs can be made to strike a balance between the ease of their fabrication and their thermal stability. Moreover, most MOFs are insoluble in common organic solvents, which can further facilitate their use in designing plastic electronics. Hence, one of the major challenges and potentially rewarding endeavours in this rapidly developing field is to synthesize conductive MOFs, particularly ones which can be used for the fabrication of electronic devices, such as those mentioned above. In this communication, we present an experimentally synthesized MOF, which shows substantially high electrical conductivity and exhibits Schottky barrier diode behaviour at the metal–MOF junction, which is the first example of its kind.

Single crystals of $\{[\mathrm{Cd_2(azbpy)_2(HO\text{-}1,3\text{-}bdc)_2](azbpy)\cdot(H_2O)}\}_n$, Cd-MOF (**1**) were obtained by slow diffusion of 4,4′-azobispyridine (azbpy) and disodium 5-hydroxyisophthalate (HO-1,3-bdc) with $Cd(NO_3)_2\cdot 4H_2O$ in an EtOH–H_2O medium at room temperature. X-ray single crystal structure determination revealed that the Cd-MOF (**1**) crystallizes in the triclinic $P\bar{1}$ space group and has a 2D bipillared structure connected by the bridging HO-1,3-bdc and azbpy ligands. In the asymmetric unit there are two different crystallographically independent hexacoordinated Cd(II) centres, two HO-1,3-bdc ligands, two azbpy linkers, one lattice azbpy and one guest water molecule.

Here each hexacoordinated Cd(II) adopts a distorted octahedral geometry with a CdO_4N_2 core (Fig. 1a), which is reflected by the cisoid and transoid angles (Table S2, ESI†), and the coordination is furnished by the four carboxylate oxygen atoms of three different HO-1,3-bdc ligands and the two pyridyl nitrogen atoms of the two bridging azbpy linkers. The two Cd(II) centers are propagated along the *c*-direction with the bridging dicarboxylate to form a 1D ladder like structure (Fig. 1b). This 1D ladder is pillared with the azbpy ligands, perpendicularly forming a 2D-grid like structure (Fig. 1c).

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[a] *Department of Chemistry, Jadavpur University, Jadavpur, Kolkata, 700 032, India. E-mail: dghoshal@chemistry.jdvu.ac.in; Fax: +91 3324146223*

[b] *Department of Physics, Jadavpur University, Jadavpur, Kolkata, 700 032, India. E-mail: parthapray@yahoo.com; Fax: +91 3324138917*

[c] *Department of Chemistry, University of Calcutta, Kolkata, 700 009, India. E-mail: swapanchem@yahoo.co.in; Fax: +91 3323519755*

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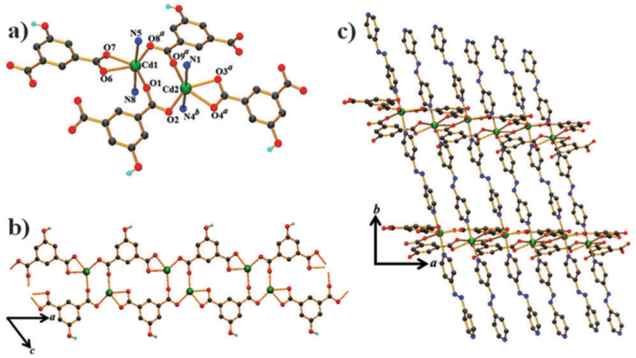


Fig. 1 (a) View of the coordination environment with the atom numbering scheme of the Cd-MOF (**1**). (b) The metal–carboxylate linkages create an infinite one dimensional ladder arrangement in the Cd-MOF (**1**) [the azbpy ligands have been omitted for clarity]. (c) The two dimensional grid structure constructed by the joining of the one dimensional ladder with the azbpy linker in the Cd-MOF (**1**) [lattice azbpy ligands have been omitted for clarity].

In the solid state structure, these 2D grids are self-assembled through π–π interactions between the lattice azbpy and bridging azbpy ligands (centroid–centroid distances are in the range of 3.860–4.255 Å). The bridging HO-1,3-bdc ligands are also involved in intermolecular π–π interactions. Furthermore, the lattice water molecules, along with the HO-1,3-bdc bridging ligands are involved in H-bonding (Fig. S2, ESI†) and these cooperative π-interactions and H-bonds fabricate a 3D supramolecular arrangement by locking the 2D grids together (Fig. S3, ESI†).

Thermogravimetric analysis (TGA) in a nitrogen atmosphere of 1 atm, and powder X-ray diffraction (PXRD) measurements were carried out to examine the thermal stability and the phase purity of the Cd-MOF (**1**) even at high temperature (170 °C). The TGA trace for the as-synthesized Cd-MOF (**1**) (Fig. S5, ESI†) shows a gradual weight-loss step of 2.5% (30–60 °C), which corresponds to the escape of the guest water molecule from the framework. The Cd-MOF (**1**) is stable up to ∼330 °C and then decomposes to unidentified products. In order to confirm the phase purity of the bulk material, powder X-ray diffraction (PXRD) experiments were carried out on the Cd-MOF (**1**). All of the major peaks of the experimental PXRD patterns of the Cd-MOF (**1**) match quite well with those of the simulated PXRD patterns from their single crystal data, indicating their reasonable crystalline phase purity. The PXRD pattern of the dehydrated framework of the Cd-MOF (**1**), obtained on removal of the guest water molecules by heating at 70 °C for 3 h in vacuum, indicates that the evacuated species has the same framework structure, which remains unaltered even at 170 °C (Fig. S6, ESI†).

The good thermal stability, along with the retention of the high quality crystalline phase of the Cd-MOF (**1**) even in powdered form, raised our interest to check its electrical properties first. To this end, our investigation begins with the estimation of the electrical conductivity of the studied MOF. The measured conductivity of the Cd-MOF (**1**) (drawn as a thin film from the microcrystalline powder as a suitable single crystal for the conductivity measurements was not obtained) was found to be 1.86 S cm^{-1} at room temperature and 1 bar, which indicates that the material is a semiconductor. Many of the MOFs and coordination polymers synthesized so far, show electrical conductivity, but very few of them have conductivity values lying in the higher semiconductor range as exhibited by the Cd-MOF (**1**). For example, some platinum dithiocarboxylate based one dimensional coordination polymers have conductivity values ranging from 2 × 10^{-3} to 83 S cm^{-1}, and the 1D-coordination polymer $[\{Cu(TANC)\}F_{0.5}]_n$ showed a conductivity value of 50 S cm^{-1} at room temperature.[10] However, in both of these cases, the conductivity was measured using a single crystal. To the best of our knowledge, the reported MOFs with 2D or 3D structures, did not show such high values of conductance even in the cases where their single crystals were used for the measurements.[10]

The appealing electrical conductivity of the Cd-MOF (**1**) certainly deserves a thorough inspection of the prospects of this material in electronic device fabrication. To give a proper judgment on this issue, at first, we estimated the band gap of the Cd-MOF (**1**) and this was done with the selective fit of the tail of the UV-VIS absorption spectra using Tauc's equation, the details of which are presented in the ESI† (Fig. S8 and S9). The band gap of the Cd-MOF (**1**) was found to be 2.0 eV, which is well in agreement with the theoretically evaluated band gap (E_g = 2.07 eV) between the valence band (VB) and conduction band (CB) at both the '*Γ*' and '*X*' points of the Brillouin zone. The theoretical band structure confirms that the Cd-MOF (**1**) is an n-type semiconductor since the Fermi level (E_F = −1.97 eV) is inclined more towards the CB and is quite evident from Fig. 2. The dispersion of the calculated band structure also evidently demonstrates that the Cd-MOF (**1**) will be a direct band gap semiconductor at the '*X*' point of the Brillouin zone, given that the bottom of the CB and the top of the VB lie at −1.21 eV and −3.28 eV, respectively. We have also examined the nature of the eigenfunctions in the momentum space, commonly known as the Bloch orbitals (BOs). The BOs corresponding to the VB and CB are presented in Fig. 2. In the VB, the electron density is completely localized over the organic moiety of the Cd-MOF (**1**), while the corresponding density in the CB is mostly constrained over the Cd atoms only. This clearly illustrates that the Cd-MOF (**1**)

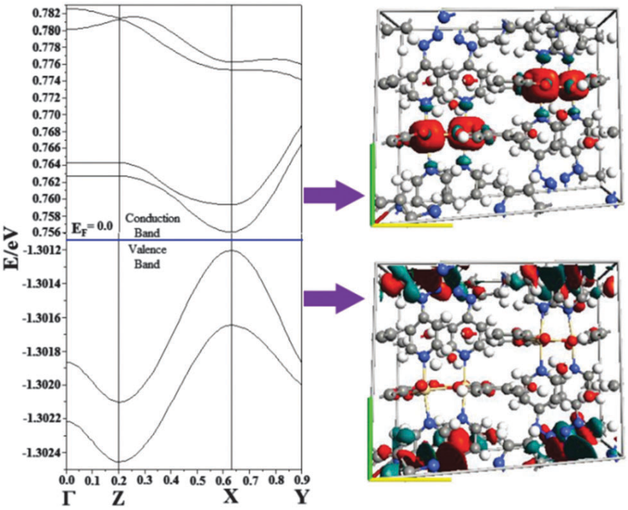
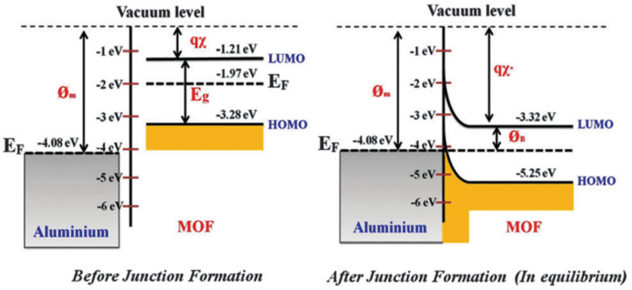


Fig. 2 Band structure of the Cd-MOF (**1**): the right hand panel of this figure describes the nature of the orbitals that correspond to the VB and CB. The details of the diagram are given in the ESI.†



Scheme 1 Energy band diagram of aluminium and Cd-MOF (**1**) before and after contact is made.

is intrinsically a charge transfer system which indeed is responsible for the moderately large electrical conductivity of the system.

The work function of the aluminium electrode (Φ_{Al}) is 4.08 eV, and obviously it is much larger than that of the n-type Cd-MOF (**1**) (Φ_{MOF} = 1.97 eV), which basically creates an ideal background for a rectifying Schottky barrier when the two systems are in contact with each other. Nevertheless, when the MOF comes into contact with the Al electrode, the electrons will flow from the CB of the MOF to the E_F of the Al electrode and this process will continue until equilibrium is reached, leading to a constant Fermi level throughout the system. To ensure the constant E_F of the metal–semiconductor junction, the VB and CB of the Cd-MOF (**1**) at the '*X*' point of the Brillouin zone will no longer be able to retain their own positions, which ultimately results in the further bending of the bands as depicted in Scheme 1. Following the Schottky–Mott theory,[11a] the calculated barrier height (Φ_B) of the Al/Cd-MOF (**1**) junction is 0.76 eV. However, the actual value of Φ_B may deviate from this theoretically predicted value due to the surface states induced Fermi level pinning of the Al/Cd-MOF (**1**).[11] This relatively small barrier height will indeed provide us with a very desirable small cut-in voltage during the rectification process.

Having ascertained the band gap and conductivity values of the Cd-MOF (**1**), along with the computational foray into the possible rectification scheme, it seems reasonable to believe that the present MOF may, under suitably devised conditions, behave as a Schottky barrier diode. In general metal–semiconductor contacts which show rectifying behavior are labeled as Schottky barrier diodes.[11a] To verify this alluring *in silico* anticipation of the Cd-MOF (**1**), we have studied the probable charge transportation phenomenon of the metal–MOF junction by monitoring the current (*I*)–voltage (*V*) characteristics of the MOF based device, fabricated in a sandwiched configuration, indium tin oxide (ITO)/Cd-MOF (**1**)/aluminium (Al).

We were delighted to find our presumption corroborated by a graphical plot which proves the rectifying nature of the fabricated Al/Cd-MOF (**1**)/ITO based device. The current–voltage (*I*–*V*) characteristics of this device (Fig. 3) exhibit a non-linear behavior with an on/off current ratio in the order of $\sim 10^2$ (at ±10 V) signifying a sound rectification behavior. Recently Dalapati *et al.* reported a porous organic molecule behaving as a Schottky barrier diode, with a rectifying current ratio of 4.7 at ±2 V.[16] As a result, our observation appears to be pretty much up to the mark. Following the thermionic emission–diffusion model, significant parameters such as series resistance (R_S), ideality factor (n), and barrier potential (Φ_B), were determined to be 413 kΩ, 1.44, and 0.41 eV by Cheung's equations, and the details of these calculations can be found in the ESI† (Fig. S10 and S11). The values of these diode parameters are excellent in comparison to the Schottky diodes fabricated from semiconducting organic single crystals.[17]

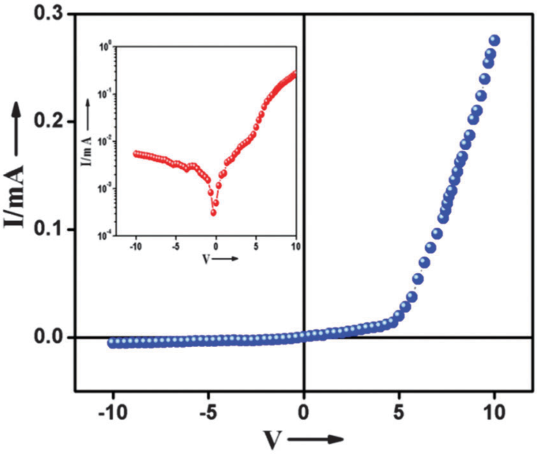


Fig. 3 Current (*I*)–voltage (*V*) characteristics of the ITO/Cd-MOF (**1**)/Al device on linear and logarithmic (inset of the figure) scales.

Based on our discussion, we conclude that the studied Cd-MOF (**1**), which has a 2D grid structure, is thermally stable up to 330 °C and shows a high quality crystalline behaviour even in powdered form. The room temperature electrical conductivity of this MOF is at least 10^3 times larger than that of the hitherto existing 2D/3D MOFs, like $Ag_2(CA)$,[18] MET-3,[19] $K_{1.2}Ru_{3.6}[Ru(CN)_6]_3 \cdot 16H_2O$[20] *etc.* Meticulous computational investigations revealed that the mode of conduction in this semiconducting material is n-type due to the alignment of the Fermi level more towards the conduction band. Moreover, the work functions of the Cd-MOF (**1**) and a metal, like aluminium ($\Phi_{\text{Cd-MOF (1)}} < \Phi_{\text{Al}}$), are such that when we bring them (metal–semiconductor junction) together, the combined system under the influence of the applied bias, should offer us current rectification. Remarkably, the experimental *I*–*V* characteristics of the MOF in the ITO/Cd-MOF (**1**)/Al structure exhibit substantial rectification with I (+10 V)/I (−10 V) lying in the order of $\sim 10^2$. The calculated diode parameters of Cd-MOF (**1**) are really exciting, embracing the signature of the first MOF based electronic device as a Schottky barrier diode.

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