In quest of New Energy Material: 3D Mn (II)-Coordination Polymer, The Schottky Device and Theoretical Interpretation

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Abstract

Single crystal X-ray structure of amino-isophthalate bridged Mn (II) coordination polymer, [[Mn(asp)][H₂O]],(H₂O)₂]n (compound 1) [H₂asp = 5-amino isophthalic acid] is determined to support previously characterized structure of the polymer. The Tauc plot obtained from UV-Visible spectra has determined the optical band gap, 2.53 eV, which corroborates the semiconducting nature. Mn(II) center is coordinated by four carboxylate-O (one chelated carboxylate-O,O and two monodentate carboxylate-O), one H₂O, and one -NH₂ (of asp²⁻) to constitute MnO₃N distorted octahedral geometry. Bridging carboxylates constitute a 2D coordination polymer and have been assembled through strong noncovalent interactions to form a 3D supramolecular aggregate. The determination of various weak interactions in the compound is also supported by Hirshfeld surface analysis. The 3D assembly of compound 1 shows electrical conductivity in the semiconducting region (barrier height, 0.59 eV) and follows a non-ohmic relation (I α V²), and the conductivity is 4.02 × 10⁻⁴ Sm⁻¹ which constitutes Schottky Diode Barrier.

Keywords: Dicarboxylato Mn(II) 3D coordination polymer; Noncovalent interactions; Hirshfeld surface analysis; Schottky diode barrier; Semiconducting optical band gap 2.53 eV.

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1. Introduction

Molecules are the building blocks of materials.1,2 These engineered materials with multifunctional properties introduce advanced technological platforms to solve many complex issues, including health and environment-related problems. Over the past few decades, Coordination Polymers (CP)/Metal-Organic Frameworks (MOFs) serve as potential materials for diverse applications such as gas sorption, storage, and separation, catalysis, sensing, magnetism, drug delivery, etc.3-11 Structural dimensionality of the CPs is largely influenced by the nature of metal-ligand interaction, temperature, solvent, and synthetic procedure.12 One of the challenging research fields is the search for new energy materials for sustainable development.13,14 CPs are applied in the design of electronic devices like Schottky barrier diodes (SBD).15 The efficiency of SBD is guided by electrical conductivity, charge mobility, and band gap of the CPs which are predominantly dependent on the nature of metal ions, bridging organics as well as structural aspects of the CPs.16 Judicious choice of the appropriate organic linker between metal centers can effectively harmonize the energy gap and thereby the electrical devices can be efficiently used depending on the chemical functionality of such ligands.17-19 Dicarboxylic acids exhibit potential bridging ability for designing coordination polymers which can be utilized for the formation of Schottky diode barrier devices.20 Metal ions like Mn(II), having the highest number of unpaired electrons (d⁵) may be suitable for procuring high-conducting materials. In this work, we have revisited the Mn(II) complex of 5-amino isophthalic acid which makes a three-dimensional Mn(II) coordination polymer (Mn-CP). The electrical conductivity studies of Mn-CP reveal its Schottky diode behavior with a conductivity of 4.02×10⁻⁴ Sm⁻¹. Charge transportation has been a common criterion in this area of electrical conductivity and has been a direct function of structural factors. The direct connections between structure, property, and applications are well known. Theoretical optimization of the structure has been performed by using Density Functional Theory (DFT) computation and the calculated band gap (2.46 eV) serves as the guideline in the designing of the Schottky Diode barrier.

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2. Experimental section
Materials and general method, Hirshfeld surface (HS) analysis are logically described in Supplementary Information.

2.1 Synthesis of compound 1
An ethanol solution (5 mL) of 5-aminooisophthalic acid (0.036 g, 0.2 mmol) neutralized with Et$_3$N (0.042 g, 0.4 mmol) in the same solvent (EtOH, 2 mL) with a buffer layer of DMF-MeOH (1:1, v/v, 2 mL) was slowly and carefully layered onto an aqueous solution (2 mL) of MnCl$_2$·4H$_2$O (0.040 g, 0.2 mmol). Yellow-colored block-shaped crystals of [(Mn(aspy)$_2$·2 MeOH (1:1, v/v, 2mL) was slowly and carefully layered onto an aqueous solution (2 mL) of MnCl$_2$·4H$_2$O (0.040 g, 0.2 mmol). Yellow-colored block-shaped crystals of \([\text{Mn(aspy)}]_2\cdot2\text{MeOH} + 2\text{H}_2\text{O}\) (compound 1), were obtained after a week (yield, 0.284 g, 65%). Microanalytical data (％) calcd for C$_8$H$_{11}$MnNO$_4$: C 33.35, H 3.85, N 4.86; found: C 33.43, H 3.92, N 4.77. IR (cm$^{-1}$): 1687 $\nu_{as}$(COO$^-$), 1544 $\nu_{sys}$(COO$^-$) (Fig. S1).

2.2 Electrical measurements
The synthesized material, Mn-CP (compound 1) was used to fabricate a thin film semiconducting device. Metal-Semiconductor (MS) junction was prepared by employing Mn-CP as the semiconductor component and Al as the connecting metal in the device. To investigate the electrical characteristics of the synthesized material, a thorough analysis of the characteristics of the device was conducted. Keithley 2635B source meter equipment was used to record Current - Voltage (I-V) data for the device for electrical characterization (using two probe method) at ambient temperature (303K). The device, Al/compound/ITO, was subjected to a bias voltage range of -1V to +1V, and corresponding current values were recorded.

2.3 DFT computation
Density Functional Theory (DFT) was employed to perform the structural optimization of the gas phase geometry of Mn-CP using the GAUSSIAN 09 Program Package.$^{[21-23]}$ The coordinates obtained from Single Crystal X-Ray Structure were used for the optimization following the B3LYP method for C, H, O, N, and LanL2DZ basis set for Mn. Theoretical Electronic Transitions of the Mn-CP were computed by Time-Dependent Density Functional Theory (TD-DFT) using Conductor Like Polarizable Continuum Model (CPCM) where the vibrational frequency calculations represent local minima and only positive eigenvalues.$^{[24]}$ The fractional contribution of the different orbitals was calculated using GaussSum.

3. Results and discussion
3.1 Structure description
The structure analysis of compound 1 shows that the crystal system belongs to the triclinic with space group P -1 and Z = 2; D$_x$ = 1.849 g·cm$^{-3}$ and is analogous to the reported structure.$^{[25]}$ Organic linker, 5-aminooisophthalate (aspy$^2$) has two carboxylate -COO groups and one -NH$_2$ to coordinate Mn (II). Here aspy$^2$ is connecting three Mn(II) nodes through monodentate -NH$_2$, bidentate bridging -COO, and chelating carboxylate-O, O centers. There are four coordinated 5-aminooisothalates (aspy$^2$) around Mn(II) to constitute the distorted octahedral coordination MnO$_6$N unit where two coordinated aspy$^2$ serve as monodentate carboxylate-O donor, one aspy$^2$ turns as O, O chelator and another aspy$^2$ is an amine-N donor along with coordinated H$_2$O (Fig. 1a).

![Fig. 1](image)

Fig. 1 (a) Monomeric unit of 3D coordination polymer of 1; (b) The 2D network formed by continuous coordinate of aspy and Mn(II).
been identified by the color depth; the darker the color, the relatively strong the interaction between neighboring atoms, and vice versa.\[27\] The fingerprint region is grey, and the blue part is the short-range interaction (Fig. 4) amongst the O···H (34.1%), H···H (22.2%), and C···H(17.3%).

In the 2D fingerprint graphs of the surface of the molecule in relation to the inside and outside two distance parameters, di and de, are considered. First, a complete fingerprint plot is created to show all potential interactions within the crystal structure. A small portion (34.1 % only) of the HS is accounted for the specific atom interactions, such as O···H/H···O. The top spike (di = 1.1, de = 0.6) in the plot illustrates the O···H interaction, while the bottom spike (di = 0.8, de = 1.1) represents the O···H interaction (Fig. 4). There is 17.3% C···H interaction (bottom: di = 1.7, de = 1.2; top: di = 0.8, de = 1.1), and the H···H interaction comprises 22.2% of the HS area. Thus, the result confirms the importance of contacts in determining molecular crystal packing, which is then supplemented with the help of various secondary connections (Fig. 5).

The crystalline consistency of Mn-CP (compound 1) is confirmed by Powder X-ray diffraction (PXRD) at room temperature. The peaks in the as-synthesized of 1 have matched well with the experimental spectrum (Fig. S2).

Thermogravimetric analysis (TGA) of 1 at 30°C - 800°C in the N\(_2\) environment shows initial weight loss at 100°C and the second loss at 150°C. This may be ascribed to the evaporation of water molecules present on the surface and also in the molecular structure of compound 1. The weight loss at about 400°C can be attributed to the loss of coordinated carboxylate followed by the formation of residual MnO\(_2\) (residue experimental: 31.34%; calculated 30.17%) above 500 °C (Fig. S3).

3.2 Optical Characterization
The UV Visible absorption spectrum (Fig. 6, inset) of compound 1 within 300-700 nm shows a sharp peak at 340 nm is assigned to n-\(\pi^*\) transition.\[28\] The optical band gap has been calculated following Tauc’s plot\[29\] using Eq. 1 (Fig. 6).

\[
(\alpha h\nu)^2 = A [h\nu - E_g]
\]

where \(\alpha\) stands for the absorption coefficient, \(E_g\) is the band gap, \(h\) is Planck’s constant, and \(\nu\) is the frequency of light respectively. After plotting \((\alpha h\nu)^2\) vs \(h\nu\) and extrapolating the linear region of the plot, the optical band gap is 2.53 eV for compound 1.

3.4 Electrical Characterization
The bias voltage of the device, Al/compound/ITO, is adjusted

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Fig. 2 (a) H bonding interactions in compound 1; (b) \(\pi\cdots\pi\) interactions between aryl rings of two asp\(^2\) moieties.

Fig. 3 Hirshfeld surfaces for compound 1 are plotted above (a) dnorm, (b) shape index, and (c) curvedness.
Fig. 4 The areas of intermolecular interactions are simply visible in a 2D fingerprint plot.

Fig. 5 The relative contribution to Hirshfeld surface area from different intermolecular interactions (O, H, C, and N) in compound 1.

in the range of -1 to +1 V to record the current. The J-V plot (J = Current/Area) (Fig. 7) is nonlinear with a rectification ratio of 16.92 which confirms the Schottky barriers are formed at the Metal-Semiconductor (MS) junction.

The lnJ - lnV plot has been interpreted to explain the carrier transport mechanism through the interface (Fig. 8a). The slope value of 1, $I \propto V$, denotes the charge transport follows the ohmic rule.\(^{[30]}\)

Device characteristics such as the ideality factor ($\eta$), barrier height ($\Phi$), and series resistance ($R_s$) were extracted using a set of Cheung's equations (Eqs. 2 and 3).\(^{[31, 32]}\)

According to the Cheung model,\(^{[33]}\) the ideality factor and

Fig. 6 Absorption spectroscopy and Tauc's plot (Inset) of compound 1.

Fig. 7 Current Density-Voltage (J-V) measurement of the fabricated structure in (a) linear scale and (b) log scale.
series resistance for the Schottky device were calculated using the dV/dlnJ vs J plot (Fig. 8b).

\[
\frac{dV}{d\ln(J)} = \frac{n k T}{q} + JAR_s
\]  

and

\[
H(J) = V - \left(\frac{n k T}{q}\right) \ln \left(\frac{J}{A T^2}\right) = R_s A j + n \phi_b
\]

The linear area of the dV/dlnJ vs J curve has been fitted at the lower bias voltage component. The Rs and \(\eta\) were calculated from the slope and intercept of the curve (Table 1). The Schottky barrier height was calculated using the H(J) vs J graphs (Fig. 8b). The plot also demonstrated linearity for the low voltage area, similar to dV/dlnJ vs J graphs. The series resistances (Rs) obtained from two different methods are comparable. The ideality factor (\(\eta\)) is 1.48 and its deviation from 1 may be due to the presence of tunneling current, the possibility of electron and hole recombination in the depletion zone, inhomogeneity, etc. The device characteristics are significantly influenced by the metal and semiconductor interface properties and surface conditions. At the Ohmic area (Region I), the bulk-generated electrons are primarily responsible for the current, while the injected free carriers play a smaller role in the conduction mechanism.

In Region II the relation is \(J\) vs \(V^2\) (Fig. 8a) obtained from the Mott-Gurney equation (Eq. 4)

\[
J = \frac{\eta \mu_{\text{eff}} \varepsilon_0 \varepsilon_r V^2}{8 A^3}
\]

where \(J\) is the current density, \(\varepsilon_0\) is the permittivity of the free space, \(\varepsilon_r\) is the relative dielectric constant of the synthesized material and \(\mu_{\text{eff}}\) is the effective mobility.

The graph of capacitance (F) vs log f at a constant bias voltage was used to determine the relative dielectric constant for the compound (Fig. 9a). The saturated capacitance value was entered into the following equation (Eq. 5) in order to determine the relative dielectric constant of the film made from synthesized material

\[
\varepsilon_r = \frac{1}{\varepsilon_0} \frac{C d}{\varepsilon_r A^2}
\]

where C is the capacitance at saturation, d is the thickness of the film.

Table 1. Schottky diode parameters of the device.

<table>
<thead>
<tr>
<th>Conductivity (S m(^{-1}))</th>
<th>Ideality factor ((\eta))</th>
<th>Barrier height (eV)</th>
<th>Rs from dV/dlnJ ((\Omega))</th>
<th>Rs from H(J) ((\Omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.02\times10^{-4}</td>
<td>1.48</td>
<td>0.59</td>
<td>305.73</td>
<td>302.90</td>
</tr>
</tbody>
</table>
the film, $\varepsilon_0$ is the free space permittivity and $A$ is the effective area. The relative dielectric constant was derived as 0.1657 for the compound. The carrier concentration ($N$) and transit time ($\tau$) were calculated from the equations (Eqs. 6 and 7):\(^{[39,40]}\)

$$N = \frac{\sigma_{SCLC}}{4\mu_{eff}}$$

(6)

and,

$$\tau = \frac{9\varepsilon_0\varepsilon_r}{8d} \left(\frac{V}{T}\right)$$

(7)

### Table 2. Schottky device parameter for SCLC region.

<table>
<thead>
<tr>
<th>$\mu_{eff}$ (m$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\tau$ (s)</th>
<th>$\mu_{eff} \tau$</th>
<th>$N$ (m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6.94 \times 10^{-4}$</td>
<td>$9.33 \times 10^{-10}$</td>
<td>$6.47 \times 10^{11}$</td>
<td>$1.69 \times 10^{19}$</td>
</tr>
</tbody>
</table>

**Fig. 10** HOMO-LUMO of the optimized geometry of Mn-CP.

### 3.4 Theoretical band gap calculation

Molecular energy labels have been computed from optimized structure using crystallographic coordinates by DFT. The energy gap between the valence band and conduction band directs the applicability of the CP toward the construction of optoelectronic devices. The calculated HOMO-LUMO energy gap is 2.46 eV which is very close to the experimental data, 2.53 eV (Fig. 10). The observed theoretical energy gap shows resemblances with that obtained experimentally from the Tauc’s Plot which is 2.53 eV (Fig. 6). A small deviation from the experimental value may be accounted due to the geometrical strain which is not included in the optimization of the monomeric unit. Selected orbitals along with their energy are listed in Table S1. From Time-Dependent Density Functional Theory (TD-DFT) calculation, some selected transitions comparable to the UV absorption spectra are listed in Table 3.

**Table 3.** Some Selected Transition obtained from TD-DFT calculation.

<table>
<thead>
<tr>
<th>Excitation energy (eV)</th>
<th>Experimental Wavelength (nm)</th>
<th>Theoretical Wavelength (nm)</th>
<th>Oscillation Frequency (f)</th>
<th>Key Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2871</td>
<td>290</td>
<td>289.20</td>
<td>0.54349</td>
<td>HOMO-5–LUMO+1</td>
</tr>
<tr>
<td>4.2788</td>
<td>290</td>
<td>289.77</td>
<td>0.47864</td>
<td>HOMO-3–LUMO+5</td>
</tr>
</tbody>
</table>

4. Conclusion

Energy is key to civilization. Making energy materials is thus the foremost importance in this power-crazy civilization. In this regard, hybrid materials having appropriate molecular architecture, suitable stability, and smooth charge transportation will be highly acceptable in this application arena. Keeping in mind this fact, we have synthesized an amine appended isophthalic acid bridged-Mn(II) Coordination Polymer which is semiconducting (optical band gap, 2.53 eV). The CP is used for the fabrication of the Schottky device and has measured the electrical conductivity, $4.02 \times 10^{-4}$ Sm$^{-1}$. The compound is crystalline; shows high phase purity and is thermally stable. DFT computed theoretical energy difference ($E_{\text{HOMO}} - E_{\text{LUMO}}$) is 2.46 eV which is closer to the experimental data. In view of the literature survey, it can be ascribed that Mn(II) based MOFs are very rarely reported as electrically conducting material. Therefore, this compound may be an ornament for material researchers and can be highly appreciated for the laboratory to land applications.

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**Conflict of Interest**

There is no conflict of interest.

**Supporting Information**

Applicable.

**References**


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