Enhanced Photosensitive Schottky Diode Behavior of Pyrazine over 2-Aminopyrimidine Ligand in Copper(II)-Phthalate MOFs: Experimental and Theoretical Rationalization

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ABSTRACT: Two novel Cu(II)-based metal–organic frameworks [C_{18}H_{14}Cu_{2}N_{6}O_{18} (1) and C_{20}H_{18}CuN_{2}O_{10} (2)] have been synthesized using 2-aminopyrimidine or pyrazine ligands and phthalate ion and characterized spectroscopically and by X-ray single-crystal diffraction. Both 1 and 2 show electrical conductivity and photosensitivity, evidencing their potentiality in optoelectronic device applications. Experimental and theoretical investigations revealed that the electrical conductivity under irradiation of visible light increases compared to that under dark condition (photosensitive Schottky barrier diode behavior), especially in complex 2. Both 1 and 2 have been successfully applied in technologically challenging thin-film active devices.

INTRODUCTION

Assembly and functionalization of metal–organic frameworks (MOFs) are attractive and one of the crucial topics in crystal engineering. MOFs are crystalline coordination polymers comprising organic ligands as spacers and metal-containing inorganic clusters as secondary building units1–4 to create porous and open frameworks.5 Due to their high surface area, uniform yet tunable porosity, and rich chemical functionality, enormous attempts have been made for the synthesis of MOFs with a new structure with novel topology and potential applications in the emerging fields of storage, separation, sensing, catalysis, optoelectronic devices, etc.5–11 The promising class of MOF has strongly promoted the research of hybrid organic–inorganic solids comprising the association of metallic centers with organic O- and/or N-donor ligands for the formation of novel crystalline periodic networks.12,13 Syntheses of MOFs are influenced by various factors such as the reaction conditions that include nature of anions, coordination geometry of the central atom, temperature, solvent, and flexibility of the organic ligands, either singly or multiply.14–17 Therefore, it is extremely important to normalize the reaction conditions and design the organic ligands to achieve at the target frameworks with precise structures and functions. The analysis of topology for MOFs is not only an effective tool for simplifying the intricate structures but also plays a significant role in the design of MOFs with specific properties. So far, although enormous effort has been made on the rational design and controlled synthesis of MOFs,18–20 it is still an arduous challenge to predict the final architectures and properties of the obtained MOFs. On the other hand, technologically it is very challenging to successfully fabricate MOF devices by solution processing method. To optimize the performance of the devices, detailed analysis of the charge-transport properties is also of extreme significance.9

The hallmark of molecular solid-state materials is the attractive tailorability of their properties by judicious modification of the molecular architecture. The recognition and assembly of designer building blocks by fine-tuning of covalent and particularly weak noncovalent interactions like hydrogen bonding, π–π stacking, and hydrophobic interactions play a crucial role in directing the properties of materials.21–31 In the last few years, relevant people note an...
emergent interest in supramolecular processes for the
generation of novel materials with fascinating properties.32,33
In this context, MOFs offer a dynamic methodology that
provides bond energies between the strong covalent bonds and
the weak noncovalent interactions. Self-assembly via weak
interaction has been revealed as the most powerful protocol to
generate predesigned and well-defined structures.

The functional group of phthalic acid can adopt several
coordinated modes like terminal monodentate, chelating one
metal ion, and bridging two metal ions in a syn−anti, anti−anti, and tridentate form to construct fascinating
architecture. In continuation with our quest for MOFs,34
we have chosen phthalic acid as primary ligand, considering its
ability to get involved in metal centers that can promote
diverse structural and topological features. We report herein
the structural features of two new Cu(II) complexes based on a
suitable choice of combinations of the phthalic acid as primary
ligand and different diazine derivatives as secondary ligands.
Charge-transfer properties, which are invariably related to the
device applications, have been studied for both the complexes.
The applicability of the synthesized materials in optoelectronic
devices, behaving as a photosensitive Schottky barrier diode
(SBD), has been studied experimentally and explained on the
basis of theoretical calculation, which are useful to rationalize
the greater conductivity of complex 2 compared to 1 upon
illumination.

■ RESULTS AND DISCUSSION

Structural Description of 1. Single-crystal X-ray
diffraction study reveals that complex 1 has a discrete dinuclear
structure in which two Cu(II) ions are located in equivalent
sites with an octahedral coordination environment. The
ORTEP view of the title structure is presented in Figure 1.
The coordination environment is centrosymmetric as Cu(II)
occupies an inversion center and the coordination geometry
may be considered as a Jahn–Teller distorted octahedron.
Each metal center is coordinatively bonded with four
carboxylate oxygen atoms from four bridging phthalate groups,
one pyrimidine ring nitrogen atom, and the sixth position
occupied by another Cu(II) ion. The title structure consists of
phthalate-bridged centrosymmetric dinuclear units with a Cu–
Cu distance of 2.6820(9) Å. The four carboxylate groups
bridge the two Cu(II) atoms, generating a Cu2(OCO)4 paddle-
wheel-type cage with an almost orthogonal arrangement of the
chelate rings. The Cu–O(phthalate) distances are within the
normal range (from 1.964(3) to 1.971(3) Å), whereas the axial
Cu−N distance is 2.201(3) Å. Selected bond lengths and
angles are listed in Table S2. A detailed account on the
supramolecular forces that govern the crystal packing of
compound 1 is given in the Supporting Information.

Structural Description of 2. The asymmetric unit of
complex 2 is shown in Figure 2. The pyrazine ring and the

Figure 1. ORTEP view and atom numbering scheme of complex 1 with
displacement ellipsoid at 30% probability. The unlabeled atoms
are generated by the symmetry operation (−x + 2, −y + 1, −z + 1).
Hydrogen atoms have been omitted for clarity.

Figure 2. ORTEP view and atom numbering scheme of complex 2 with
displacement ellipsoid at 30% probability. The unlabeled atoms
are generated by the symmetry operation (−x + 1, y, −z + 1/2) and
(−x + 1, −y, −z). Hydrogen atoms have been omitted for clarity.

Cu(II) position on a 2-fold axis, and the phthalate and one
water molecule on an inversion center. The Cu(II) is six-
coordinated by two carboxylate oxygen atoms from two
phthalate ligands, two nitrogen atoms from pyrazine ligands,
and two oxygen atoms from solvent water molecules exhibiting
a slightly distorted CuO6N2 octahedral coordination geometry.
Table S2 lists selected bond parameters.

Complex 2 is a two-dimensional (2D) supramolecular
framework based on one-dimensional (1D) zigzag polymeric
chain along the [001] direction (see Figure 3). The parallel 1D
zigzag chains are interconnected through O−H···O hydrogen
bonds, as further described in the Supporting Information to
generate 2D assemblies in the solid state.

Optical Characterization. In this study, the optical
spectra of complexes 1 and 2 (inset Figure 4) have been
recorded for the deposited thin films of our synthesized
materials by preparing a well dispersion in dimethylformamide,
in the range of 250–800 nm. The absorption spectrum of both
1 and 2 exhibits absorption in the visible region, and optical
band gaps have been estimated using Tauc equations (eq 1).37

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

(1)

where “α” is the absorption coefficient, “E_g” is the band gap,
“h” is Planck’s constant, “ν” is the frequency of light, and the
exponent “n” is the electron transition process-dependent
constant. “A” is a constant, which is taken as 1 for ideal case.
To calculate direct optical band gap, the value of \( n \) has been considered as 1/2. Using the above equation, from the extrapolation of \( (\alpha h\nu)^2 \) vs \( h\nu \) plot (Figure 4), the direct optical band gap \( (E_g) \) has been evaluated as 2.27 and 1.92 eV for our synthesized complexes 1 and 2, respectively.

**Dielectric Characterization.** The estimated optical band gap has fallen right well within the semiconductor limit that motivated us to check the electrical conductivities of the synthesized complexes in terms of dielectric study. Impedance spectroscopy is one of the widely used powerful tools for the characterization of electrical properties of semiconducting materials. In this study, we have evaluated the capacitance \( (C) \), impedance \( (Z) \), and phase angle \( (\theta) \) of the sample as a function of frequency. The dielectric study has been performed as a function of frequency at room temperature using a computer-controlled Agilent precision 4294A LCR meter in the frequency range of 40 Hz to 11 MHz.

**Figure 4.** UV−vis absorption spectra (inset) and Tauc’s plots for complexes 1 and 2, respectively.

**Figure 5A** represents the complex plane impedance plot, i.e., the Nyquist plot, for complexes 1 and 2, from which it can be clearly seen that the impedance reveals prominent arc of semicircle for both materials. The semicircle in the high-frequency region may be contributed by semiconducting grains and generated resistance at the electrode. The semicircle also represents the charge-transfer resistance at the electrode/composite interface, and the bulk resistance \( R_b \) (direct current (DC) resistance) of the complexes has been calculated from the radius of the corresponding semicircle. In Figure 5A, it can be seen that complex 2 shows small semicircular arc, which signifies small bulk resistance \( R_b \) rather than complex 1. This observation primarily suggests the better conducting nature of complex 2. The estimated values of bulk resistance for both the complexes are listed in Table 1.

To extend the dielectric study, we have plotted Bode phase diagrams of our complexes (Figure 5B). The Bode phase plot
represents the characteristic peak position of the complexes from which the recombination lifetime or electron lifetime \( \tau_n \) can be determined using eq 2.58

\[
\tau_n = \frac{1}{2\sigma_{\text{min}}}
\]  

(2)

The calculated electron lifetimes \( \tau_n \) of both 1 and 2 are listed in Table 2. From this study, it can be easily concluded that the characteristic frequency is related to the electron lifetime. The longer electron lifetime corresponds to a smaller frequency.

The interior-related information of the semiconductor can be achieved from the analysis of alternating current (AC) conductivity. It is the most preferable study in the case of low conductivity analysis and when the conduction process is electrode-limited.59

The frequency vs AC conductivity plot of our synthesized complexes (1 and 2) is presented in Figure 6A. If the conductivity is governed by the free carriers, then it decreases with increase in frequency.40 In this case, the conductivity obeyed the frequency-dependent empirical law and is given by the power law of the form

\[
\sigma(\omega) = \sigma_{\text{DC}} + \sigma_{\text{AC}}
\]  

(3)

where \( \sigma(\omega) \), \( \sigma_{\text{DC}} \) and \( \sigma_{\text{AC}} \) are the total conductivity, DC conductivity, and AC conductivity, respectively. In the above equation, the frequency-dependent part is the AC conductivity, which obeys the relation

\[
\sigma_{\text{AC}} = A\omega^s
\]  

(4)

where \( A \) is a constant and \( s \) is a number at room temperature. The number \( s \) depends on the frequencies. The frequency \( (f) \)-dependent variation of the capacitance (C) at constant bias potential is shown in Figure 6B. At room temperature, the capacitance of the complexes (1 and 2) decreases in the low-frequency region. In the high-frequency region, the capacitance of the complexes (1 and 2) becomes saturated. From that saturated region, the relative permittivity of the complexes (1 and 2) can be calculated employing the following equation

\[
\varepsilon_r = \frac{1}{\varepsilon_0} \times \frac{C_d}{A}
\]  

(5)

where \( \varepsilon_0, \varepsilon_r, C, d, \) and \( A \) are the permittivity of free space, dielectric constant of the synthesized material, capacitance of the synthesized material (at saturation), and thickness and effective area of the thin film, respectively. The dielectric constants \( \varepsilon_r \) of 1 and 2 are calculated (Table 1) using eq 5.

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**Table 1. Dielectric Parameters of Complexes 1 and 2**

| sample  | bulk resistance (KΩ) | DC conductivity (S m⁻¹) | electron lifetime (10⁻⁸ s) | dielectric constant (F m⁻¹) |
|---------|----------------------|-------------------------|-----------------------------|-----------------------------|
| complex 1 | 78.73                | 1.79 \( \times 10^{-6} \) | 7.5                         | 1.18                        |
| complex 2 | 44.05                | 3.21 \( \times 10^{-6} \) | 2.3                         | 1.45                        |

**Table 2. Schottky Device Parameters of Complexes 1 and 2-Based Thin-Film Devices**

| sample  | condition | on/off | photosensitivity | conductivity (S m⁻¹) | ideality factor | barrier height (eV) | \( R_c \) from \( dV/dI \) (KΩ) | \( R_s \) from \( H \) (KΩ) |
|---------|-----------|--------|------------------|----------------------|----------------|-------------------|-----------------------------|-----------------------------|
| complex 1 | dark      | 8.46   | 2.27             | 2.02 \( \times 10^{-6} \) | 2.78           | 0.47              | 81.79                       | 84.36                       |
|         | light     | 13.98  |                  | 4.34 \( \times 10^{-6} \) | 1.85           | 0.43              | 42.35                       | 46.24                       |
| complex 2 | dark      | 8.49   | 3.77             | 2.34 \( \times 10^{-6} \) | 2.08           | 0.44              | 50.15                       | 53.17                       |
|         | light     | 20.06  |                  | 7.60 \( \times 10^{-6} \) | 1.13           | 0.41              | 18.55                       | 19.51                       |

**Electrical Characterization.** The impedance analysis and the observed direct optical band gap of the complexes represent the semiconductor behavior of our synthesized complexes. This encourages us to investigate the electrical properties of complexes 1 and 2. To perform this study, metal (Al)–semiconductor (synthesized complexes 1 and 2) (MS) junction thin-film devices have been fabricated because of the easy solution processability of our complexes. The thin-film device has been fabricated in indium tin oxide (ITO)/complex (1 or 2)/Al sandwich structure. To assure that our complexes construct a junction with metal (Al), multiple devices have been fabricated for analyzing the electrical properties. The current–voltage \( (I–V) \) measurements of complexes 1 and 2-based multiple devices have been carried out with a Keithley 2635B sourcemeter under dark and under AM1.5G photoirradiation at different applied bias voltages within the limit \( \pm 2 \) V.

With the ITO/complex (1 or 2) ohmic contact, the representative \( I–V \) characteristics of the Al/complex (1 or 2) under dark and illumination conditions are displayed in Figure 7. The conductivity of the synthesized complexes under dark condition has been measured as \( 2.02 \times 10^{-6} \) and \( 2.34 \times 10^{-6} \) S m⁻¹ for complexes 1 and 2-based thin films, respectively. However, with photon irradiation, the conductivities of complexes 1 and 2 have improved to \( 4.34 \times 10^{-6} \) and \( 7.6 \times 10^{-6} \) S m⁻¹, respectively, which is a recognizable improvement from the nonirradiated conditions.

The representative \( I–V \) characteristics (Figure 7) of our synthesized complexes-based devices exhibit nonlinear rectifying nature signifying it as Schottky barrier diode (SBD). Moreover, these \( I–V \) characteristics demonstrate the highly influencing rectifying nature under illumination condition. Hence, the photosensitivities of the complexes 1 and 2 have been calculated as 2.27 and 3.77, respectively. At \( \pm 2 \) V under dark condition, the rectification ratios \( (I_{\text{on}}/I_{\text{off}}) \) of the complexes 1 and 2-based SBD have been found to be 8.46 and 8.49, respectively, whereas the same have been found to be 13.98 and 20.06 after light soaking for complexes 1 and 2, respectively. This result represents an enhancement of rectification ratios after light soaking.

The \( I–V \) characteristics of complexes 1 and 2-based Schottky diode have been further analyzed by thermionic emission theory. To extract important diode parameters, Cheung’s method has been employed here.57 In this regard, considering the following standard equations, we have started \( I–V \) analysis quantitatively\(^{57,61}\)

\[
I = I_0 \exp \left( \frac{qV}{\eta KT} \right) \left[ 1 - \exp \left( -\frac{qV}{\eta KT} \right) \right]
\]  

(6)

\[
I_0 = AA^*T^2 \exp \left( -\frac{q\Phi_a}{KT} \right)
\]  

(7)

where \( I_0, q, k, T, V, A, \eta, \) and \( A^* \) denote saturation current, electronic charge, the Boltzmann constant, temperature in
Kelvin, forward-bias voltage, effective diode area, ideality factor, and the effective Richardson constant, respectively. Here, the effective diode area has been estimated as $7.065 \times 10^{-2} \text{ cm}^2$ and the effective Richardson constant has been considered as $32 \text{ A K}^{-2} \text{ cm}^{-2}$ for all of the devices. Linearity in current has been observed at low bias, which is consistent with eq 6. As the diode series resistance changes at higher bias voltage, a deviation from linearity in the $I$–$V$ curve takes place.

From Cheung, in terms of series resistance, the forward-bias $I$–$V$ characteristics can be expressed as

$$I = I_0 \exp \left( \frac{q(V - IR_S)}{\eta kT} \right)$$  \hspace{1cm} (8)

where $IR_S$ is the voltage drop across series resistance of device. In this context, the values of the series resistance can be determined from the following functions using eq 8.42

$$\frac{dV}{d\ln(I)} = \left( \frac{\eta kT}{q} \right) + IR_S$$  \hspace{1cm} (9)

Equation 9 also can be expressed as a function of $I$ as

$$H(I) = IR_S + \eta \phi_{B}$$  \hspace{1cm} (10)

The series resistance ($R_S$) and ideality factor ($\eta$) for all devices under dark and illumination condition have been estimated from the slope and intercept of $dV/d\ln I$ vs $I$ plot (Figure 8A) and are listed in Table 2. Estimated nonideal ($\sim 1$) values of ideality factor depict the nonideal formation of MS junction. This deviation may be due to the presence of inhomogeneities at the barrier of Schottky junction. The existence of interface states and series resistance also causes that type of deviation at the barrier of junction.43,44 However, the important observation is that the value of ideality factor of both the complexes approached more ideal (closer to 1) after light soaking. This generally indicates the less interfacial charge recombination.
and better homogeneity at the barrier of Schottky junctions. That observation illustrates that under photoirradiation condition, our synthesized complexes possess less carrier recombination at the junction, which signifies better barrier homogeneity. The value of series resistance $R_s$ has been determined from the slope of the $dV/dlnI$ vs $I$ plot (Figure 8A).

The values of barrier height ($\phi_B$) have been determined from the slope and intercept of $H(I)$ vs $I$ plot (Figure 8B) using the just obtained ideality factor ($\eta$) values in eq 10 and are listed in Table 2. For all of the complexes-based SBDs, the potential barrier height is found to be reduced when they are exposed to illumination. This decrement in the barrier potential height may be due to the effect of the generation of photoinduced charge carriers and their accumulation near the conduction band. The measured potential height ($\phi_B$), ideality factor ($\eta$), and series resistance ($R_s$) under dark and illumination condition for the metal (Al)—semiconductor (synthesized compounds) (MS) junctions are listed in Table 2. Using Cheung’s functions, the series resistance obtained from both the processes (eqs 9 and 10) shows good consistency, which is found to decrease upon light illumination (Table 2). All of the parameters represent a better performance for complex 2-based SBDs even under illumination condition than complex 1-based SBDs, which signifies its applicability in the field of optoelectronics devices.

Metal–organic frameworks (MOFs), also known as porous coordination polymers, represent an interesting type of solid crystalline materials that can be straightforwardly self-assembled through the coordination of metal ions/clusters with organic linkers. Compared to conventional light-harvesting organic polymers, MOFs possess long-range order. This long-range crystalline order of MOFs implies that charge transport through delocalized conduction and valence bands typical of crystalline inorganic semiconductors is possible. Emergence of delocalized bands in MOFs will require that the $\pi$ orbitals in the linker groups overlap effectively with the metal $d$ orbitals. The dispersion in ground- and excited-state electronic band structures is the resultant of the semiconducting nature of MOFs. The modification of the linker structure could lead to better charge transfer between the linker and the metal cations of the framework. The long-range crystalline order also could lead to higher charge mobility and energy-transfer rates by minimizing traps, dead ends, and defects.

To date, three types of charge-carrier transport mechanisms have been identified in hybrid organic—inorganic structure: (i) through-bond conduction, (ii) by guest molecules, and (iii) through-space conduction (charge delocalization due to the close approach of adjacent aromatic linkers). In this study, the mechanism for light-induced charge-carrier transport would be through-bond conduction. In through-bond conduction, charge moves through continuous chains of covalent and coordination bonds in the material. Typically, this mechanism involves the so-called “hopping transport”. When the excited photoelectrons migrate from the highest occupied molecular orbital to the lowest unoccupied molecular orbital, it generates the transient photocurrent response. The conductance value and the number of free carriers produced at the time of light irradiation in the semiconductor are mainly evaluated by the transient photocurrent response.

For a better investigation of the charge-transport behavior, the $log I$ vs $log V$ plot has been analyzed under both conditions (Figure 9A).

Figure 9A reveals that there are two distinguishable slopes with different values, which have been marked as region I and region II. The current and voltage show a proportional relation, i.e., a Ohmic relation ($I \propto V$), in region I. In this regime, the slope of the plot is $\sim 1$. After a certain voltage, the slope of the plot becomes $\sim 2$ (region II, Figure 9A). In this regime, the relation of current and voltage turns into $I \propto V^2$, which signifies the trap free space charge limited current (SCLC) regime. In this region, the quantity of injected carriers is higher than that of the background carriers, which generates a space charge field. Hence, this space charge field controls the flow of current and thus they are known as SCLC. The SCLC theory, which has recently drawn popular attention, was adopted here to estimate the mobility of materials.

Following this model, the effective carrier mobility has been estimated from higher-voltage region of the $I$ vs $V^2$ plot (Figure 9B) by Mott–Gurney equation

$$I = \frac{9\varepsilon_0^2e^2A}{8\varepsilon_f}\left(\frac{V^2}{d^3}\right)$$

where $d$ is the thickness of the film, which was considered about $\sim 1 \mu m$ for our device. Transit time ($\tau$) and diffusion length ($L_D$) of the charge carriers are few more key parameters that have also been estimated to analyze charge transport across the junction. For this purpose, $\tau$ has been evaluated.
from eq 12, by using the slope of the SCLC region (region II) in logarithmic representation of forward $I$–$V$ curve, shown in Figure 9A. The diffusion length of the charge carriers has been further extracted from eq 13

$$\tau = \frac{9e\varepsilon F^2 A}{8d} \frac{V}{I}$$  \hspace{1cm} (12)$$

$$L_D = \sqrt{2D\tau}$$  \hspace{1cm} (13)

where $D$ is the diffusion coefficient. Carrier lifetime has been extracted from the slope of the region II in log $I$ vs log $V$ graph, which has been shown in Figure 9A. Using the Einstein–Smoluchowski equation, the diffusion coefficient has been calculated as

$$\mu_{eff} = \frac{qD}{kT}$$  \hspace{1cm} (14)

Diffusion length ($L_D$) and the density of states (DOS) at the Fermi level of charge carriers are two important parameters that play an influential role in device performance after formation of an MS junction. The DOS distribution of the active films around the Fermi level $N(E_F)$ has been extracted from $I$–$V$ characteristics by using the simple relation

$$N(E_F) = \frac{2e\varepsilon F^2\Delta V}{q^2\Delta E_F}$$  \hspace{1cm} (15)$$

where

$$\Delta E_F = kT \ln \left( \frac{I_{V_1}}{I_{V_2}} \right)$$  \hspace{1cm} (16)$$

where $N(E_F)$ is the density of localized states near the Fermi level and other parameters are described earlier. The calculated values of all of the parameters in the SCLC region are listed in Table 3. The increase of effective mobility under irradiation condition depicts the higher transport rate of the charge carrier. The number of generating charge carriers also increased under photoirradiation condition. Under illumination condition, the charge carrier voyages more paths before being recombined, i.e., the diffusion length of the charge carriers increases. As a result, the current of the devices eventually increases under illumination condition. From these obtained values, it can be clearly stated that the charge-transport properties of our synthesized materials improved after light soaking (Table 3). All of the diode parameters of the complex 2-based SBDs demonstrate much enhanced charge-transfer properties after light soaking than complex 1. So, this kind of material can pave the way for a very promising future in device applications.

All of the parameters from electrical characterization show better result for complex 2-based devices rather than complex 1-based ones. This may be due to the polymeric nature of complex 2, which affects the electrical conductivity at a given

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**Table 3. Charge Conducting Parameters of Complexes 1 and 2-Based Thin-Film Devices**

| Complex | Condition | Effective Mobility $(\mu_{eff})$ $(m^2 V^{-1} s^{-1})$ | Transit Time $(\tau)$ (s) | $\mu_{eff}$ | Diffusion Coefficient $(D)$ $\times 10^{-13}$ m$^2$ s$^{-1}$ | Diffusion Length $(L_D)$ (m) | Density of States $N(E_F)$ $(eV^{-1} m^{-3})$ |
|---------|-----------|---------------------------------|-----------------|-------------|--------------------------|-----------------|---------------------|
| 1       | Dark      | $3.22 \times 10^{-12}$          | $1.01 \times 10^{-1}$ | $3.25 \times 10^{-13}$ | $8.05 \times 10^{-14}$ | $1.27 \times 10^{-7}$ | $2.26 \times 10^{26}$ |
|         | Light     | $6.54 \times 10^{-12}$          | $5.29 \times 10^{-2}$ | $3.46 \times 10^{-13}$ | $1.63 \times 10^{-13}$ | $1.31 \times 10^{-7}$ | $2.47 \times 10^{25}$ |
| 2       | Dark      | $2.46 \times 10^{-12}$          | $1.33 \times 10^{-1}$ | $3.27 \times 10^{-13}$ | $6.15 \times 10^{-14}$ | $1.28 \times 10^{-7}$ | $3.51 \times 10^{25}$ |
|         | Light     | $8.45 \times 10^{-12}$          | $4.59 \times 10^{-2}$ | $3.87 \times 10^{-13}$ | $2.11 \times 10^{-13}$ | $1.39 \times 10^{-7}$ | $3.71 \times 10^{24}$ |

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Figure 10. Left: electronic band structure of complex 1. Points of high symmetry in the first Brillouin zone are labeled as follows: $Z = (0, 0, 0), Y = (0, 0.5, 0), A = (-0.5, 0.5, 0), B = (-0.5, 0, 0), D = (-0.5, 0.5, 0), E = (-0.5, 0.5, 0), C = (0, 0.5, 0.5)$. Right: electronic band structure of complex 2. Points of high symmetry in the first Brillouin zone are labeled as follows: $L = (-0.5, 0, 0), M = (-0.5, -0.5, 0.5), A = (-0.5, 0, 0), G = (0, 0, 0), Z = (0, -0.5, 0.5), V = (0, 0, 0.5)$.

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photons absorption energy. In this study, discrete complex 1 forms 1D chain by involving noncovalent hydrogen-bonding interactions, but complex 2 is a coordination polymer. The electron-transfer mechanism in complex 1 is mediated by hydrogen bonds, whereas it is facilitated by regular periodicity of conjugated π system with intervening Cu(II) metal center in complex 2. This regular periodicity for complex 2 leads to the improvement in device performances.

It might be mentioned here that a comparison of the conductivities of recently reported Cu-MOFs with our synthesized compounds 1 and 2 (Table S6) shows that our materials have sufficient potentiality in optoelectronic applications.

An essential property of any active material used for light harvesting is that it must absorb solar radiation in the critical visible to near-IR region that comprises most of the photons incident upon earth. Since MOFs consist of both a metal ion and an organic linker, there are numerous possibilities for designing frameworks that can achieve this. Beyond light absorption, the advantageous property of MOFs’ use as active materials in electronic and optoelectronic devices is their charge mobility. Most MOFs exhibit localized electronic structure with little mixing between the metal-ion atomic orbitals and the linker molecular orbitals. The modification of the electronic structure of the linker is probably a better strategy for tailoring the light absorption properties. MOF-based optoelectronic devices could be made to optimally absorb the photoirradiation by introducing a range of appropriate sensitizing molecules; they could be made extremely thin, flexible, and light due to their porosity and structural stability; and they will likely be solution-processable, which substantially decreases their cost of production, a major factor in the low rate of usage and availability of photovoltaics.

**Computational Study.** The calculations were carried out by using the standard band theory and the partial density of states (PDOS) calculation (see Supporting Information for detailed theoretical methods). The results from these calculations evidence that both complexes 1 and 2 are semiconductors with band gap values of 2.26 and 1.62 eV, respectively (Figure 10). The band gap values are in good accordance with the experimentally obtained values of 2.27 and 1.92 eV, demonstrating that these materials belong to the semiconductor family and corroborated by the DOS calculations, which are depicted in Figures 11 and 12. In both compounds 1 and 2, the PDOS calculation shows that the valence bands are mainly dominated by Cu 3d states. In addition, the main contributors to the conduction band are p-orbitals, that is, the p-component of the pyrazine ligand in complex 2 and the p-component of the pyrimidine and phthalate ligands in complex 1. The representation of the electronic band structure in compounds 1 and 2 along with the PDOS analyses reveal the existence of deeply isolated intermediate bands, which mainly consist of Cu 3d orbitals and the p-orbitals of phthalate ligand (Figures 10–12). The presence of intermediate levels has been experimentally characterized in other inorganic semiconductors and has been attributed to orbital interactions between Cu and N.

However, in our case, these levels are not found experimentally because they are very weakly populated. For this reason, we have not considered these intermediate levels for the calculation of the band gap in both crystals.

To properly understand the electronic structure of the solid-state material, it is important to compute and analyze the optical properties (shown in Figure 13), since they provide some information regarding the character of the bands. In a given material, the frequency dependence of an incident photon can be studied by computing the dielectric function \( \varepsilon(\omega) \). Its imaginary part (Im) is computed taking into account the interband optical transitions. It is necessary to calculate the momentum matrix elements between the occupied and unoccupied wave functions. Moreover, the real part (Re) is acquired by using the Kramer–Kronig transform. The Re part of \( \varepsilon(\omega) \) gives information about the polarization degree of the material upon the application of an electric field. The Im part is a good indicator of the absorption in the material of the incident photon. We have used the computed band structure to measure the optical response. To do so, we have selected a photon energy range of 0–16 eV. Figure 13A shows that the Re component of \( \varepsilon(\omega) \) in the low-energy region increases with the photon energy reaching a maximum at 3.7 eV. This increment of the dielectric function is higher for the case of the complex 2, which agrees with its higher conductivity. The imaginary parts of dielectric functions have two main peaks for complex 2 at 4.1–5.0 eV.
while for 1, a main peak at 4.2 eV and one shoulder at 4.8 eV are observed. Finally, in Figure 13B, we represent the optical conductivity for complexes 1 (dashed line) and 2 (solid line). The optical conductivity is useful to analyze how the conductivity of the material changes upon illumination. The electrical conductivity and, concomitantly, the photoconductivity of the material increase as a consequence of photon absorption. As can be seen in the graph, the shape of the real part of conductivity in complex 2 is greater than that presented by complex 1. This fact explains the greater conductivity of complex 2 (Experimental Section) upon illumination. This is likely due to the polymeric nature of complex 2, which affects the electrical conductivity at a given photon absorption energy.

■ CONCLUSIONS

This report illustrates some emerging opportunities of MOFs in electronic and optoelectronic devices. The combination of long-range order and synthetic flexibility manifested by the presence of both metal ions and organic linkers in a predetermined spatial orientation of the MOFs enables a wide range of tunable properties useful in functional devices. In this work, we have illustrated two new photosensitive Cu-based MOFs that exhibit Schottky diode character. The electrical conductivity of both the complexes in the Al/(1 or 2)/ITO configuration shows that it increases under illumination, indicating its photosensitivity under visible light exposure. The Schottky barrier diode parameters obtained experimentally for complex 2 (coordination polymer) demonstrate much enhanced charge-transfer properties after light soaking than complex 1 (discrete complex). Theoretical studies have been used to rationalize the experimental observations and to provide an explanation to the greater conductivity of 2. Since these complexes are easy to synthesize, they are promising candidates to have applications in MOF semiconducting industries and in the fabrication of optoelectronic devices.

■ EXPERIMENTAL SECTION

Physical Measurements. IR spectra (KBr pellet) were recorded on a PerkinElmer RXI FT-IR spectrophotometer in the range of 4000–400 cm⁻¹. PerkinElmer 240C elemental analyzer was used for elemental analysis (C, H, N).

Materials. All reactions were carried out in aqueous medium under aerobic condition. Phthalic acid, copper(II) nitrate trihydrate, 2-aminopyrimidine, and pyrazine were purchased from Sigma-Aldrich Chemical Co. and used without further purification.

Synthesis of Complex 1. Cu(NO₃)₂·3H₂O (0.241 g, 1.0 mmol) dissolved in 25 mL of water was allowed to react with phthalic acid (0.332 g, 2.0 mmol) in water (25 mL) at 60 °C, resulting in a clear blue solution. A warm aqueous solution (20 mL) of 2-aminopyrimidine (0.190 g, 2.0 mmol) was added dropwise to the above solution with stirring. The reaction mixture thus obtained was further heated at 60 °C for an hour and then cooled to room temperature, filtered, and kept undisturbed for crystallization. After a few days, block-shaped dark green single crystals suitable for X-ray analysis were obtained. The crystals were collected by filtration, washed with cold water, and dried in air (yield: 65%). Anal. calc’d for CuHₓCu₂NₓO₁₀: C, 47.39; H, 3.38; N, 8.29%. Found: C, 47.34; H, 3.43; N, 8.22%. Main IR absorption bands observed for 1 (KBr pellet, cm⁻¹): 3445 (s), 3326 (s), 3208 (s), 2657 (b), 1876 (b), 1709 (s), 1647 (s), 1626 (s), 1578 (s), 1486 (s), 1452 (s), 1409 (s), 1361 (s), 1298 (s), 1260 (s), 1224 (s), 1195 (s), 1163 (s), 1138 (s), 1084 (s), 1005 (s), 977 (s), 919 (b), 876 (s), 854 (s), 804 (s), 789 (s), 747 (s), 711 (s), 689 (s), 654 (s), 610 (b), 592 (s), 574 (s), 524 (s), 485 (s), 475 (s).

Synthesis of Complex 2. The synthesis of complex 2 was achieved using methods identical to those for complex 1. Here, Cu(NO₃)₂·3H₂O (0.241 g, 1.0 mmol) dissolved in 25 mL of water was allowed to react with phthalic acid (0.332 g, 2.0 mmol) in water (25 mL) at 60 °C, resulting in a clear blue solution. A warm aqueous solution (20 mL) of pyrazine (0.160 g, 2.0 mmol) was added dropwise to the above solution with stirring. This solution was then heated at 60 °C for an hour and then cooled to room temperature, filtered, and kept undisturbed for crystallization. Block-shaped blue single crystals suitable for X-ray analysis were obtained after a few days, which were collected by filtration, washed with cold water, and dried in air (yield: 62%). Anal. calc’d for CuHₓCu₂NₓO₁₀: C, 47.11; H, 3.56; N, 5.49%. Found: C, 47.05; H, 3.51; N, 5.53%. Main IR absorption bands observed for 2 (KBr pellet, cm⁻¹): 3535 (s), 3411 (s), 2916 (b), 2793 (b), 1876 (b), 1709 (s), 1647 (s), 1626 (s), 1578 (s), 1486 (s), 1452 (s), 1409 (s), 1361 (s), 1298 (s), 1260 (s), 1224 (s), 1195 (s), 1163 (s), 1138 (s), 1084 (s), 1005 (s), 977 (s), 919 (b), 876 (s), 854 (s), 804 (s), 789 (s), 747 (s), 711 (s), 689 (s), 654 (s), 610 (b), 592 (s), 574 (s), 524 (s), 485 (s), 475 (s).
The authors declare no competing financial interest.

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