Designing of Pb(II)-Based Novel Coordination Polymers (CPs): Structural Elucidation and Optoelectronic Application

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Supporting Information

ABSTRACT: [Pb2(bdc)1.5(aiz)], (1) and [Pb2(bdc)1.5(aiz)-(MeOH)]n (2) (H2bdc = 1,4-benzenedicarboxylic acid, aiz = (E)-N’-(thiophen-2-ylmethylene)isonicotinohydrazide) have been synthesized, and structural characterization has been established by X-ray analysis and thermogravimetric analysis (TGA). Here, bdc2− links two Pb(II) centers and the aiz ligand binds the metal centers in two different manners: chelating and monodonating. Thus, polymerizations have taken place from the combination of mixed ligand system. Optical band gaps have been studied via UV measurements. Again, the experimental and calculated (from density functional theory (DFT)) band gaps agree well and the semiconducting properties of synthesized polymeric materials have been approved. Thus, optoelectronic and photonic devices can be made by this type of coordination polymers (CPs). The I−V representative curves of 1 (device-A) and 2 (device-B) in both dark and illuminated conditions show that device-A has a higher magnitude of current than device-B. Dark- and photo-conductivity values of device-A are calculated as 2.94 × 10−6 and 6.12 × 10−6 S m−1, respectively, whereas for device-B, the values of dark- and photo-conductivity are 2.92 × 10−7 and 3.66 × 10−7 S m−1, respectively, at room temperature.

INTRODUCTION:

Lead(II), a heavy toxic metal, is affecting almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery. The coordination chemistry of lead is not as popular unlike transition metals as Pb(II), d10, neither is so flexible almost every organ in the body.1 Still, lead is used worldwide because of its application in energy storage devices for their reliability and cost-efficiency such as lead-acid batteries and lead-carbon batteries2 along with lithium-ion battery.

The insulating properties of semiconductors, photovoltaics, photoluminescent, and optoelectronic devices have been investigated widely. Nonmetallic insulating materials can also be used as semiconductors for their photovoltaic properties, but the thermal and chemical instability of these materials is a major drawback. Hence, metal-organic frameworks (MOFs) have been introduced as hybrid materials to overcome these problems. In this aspect, the self-assembly (via secondary interactions) of metal−organic coordination polymers (MOCPs) allows for the construction of different materials from the combination of mixed ligand systems. Optical band gaps have been calculated from UV measurements, and the experimental and calculated (from density functional theory (DFT)) band gaps agree well and the semiconducting properties of synthesized polymeric materials have been approved. Thus, optoelectronic and photonic devices can be made by this type of coordination polymers (CPs). The I−V representative curves of 1 (device-A) and 2 (device-B) in both dark and illuminated conditions show that device-A has a higher magnitude of current than device-B. Dark- and photo-conductivity values of device-A are calculated as 2.94 × 10−6 and 6.12 × 10−6 S m−1, respectively, whereas for device-B, the values of dark- and photo-conductivity are 2.92 × 10−7 and 3.66 × 10−7 S m−1, respectively, at room temperature.
[Pb_{2}(bdc)_{1.5}(aiz)(MeOH)]_{n} (2) have been synthesized (Scheme 1), and electrical conductivity has been studied. A higher magnitude of current is observed in the $I$–$V$ characteristic curves for 1 than 2, in both dark and irradiated conditions. Dark- and photo-conductivity values of 1 are calculated as $2.94 \times 10^{-6}$ and $6.12 \times 10^{-6}$ S m$^{-1}$, respectively, whereas for 2, the values of dark- and photo-conductivity are $2.92 \times 10^{-7}$ and $3.66 \times 10^{-7}$ S m$^{-1}$, respectively. Thus, these compounds may be possible options for optoelectronic device fabrication.

## RESULT AND DISCUSSION

**Crystal Structures.** The confirmatory molecular arrangements of 1 and 2 are obtained by single-crystal X-ray diffraction (SCXRD). The asymmetric unit in 1 contains two metal centers (Pb01 and Pb02), and they are in the distorted pentagonal geometry with a PbO$_4$N coordination sphere. In Pb01, the center metal ion binds through bdc$^{2-}$ in two different manners, chelating (by two O-atoms from a carboxylic acid group) and bridging (by two O-atoms, one is $\mu$-O and another is $\mu^2$-O, from two different carboxylic acid groups), and resulted in polymerization. Again, there is a monodonation of pyridyl-N atom from the “aiz” ligand. Thus, every Pb(II) center is coordinated with three bdc$^{2-}$ and one aiz ligands. The Pb–O and Pb–N bond lengths (Pb01–O004, 2.435(10); Pb01–O2, 2.943(10); Pb01–O005_d, 2.763(9); Pb01–O006, 2.285(10); and Pb01–N00A_c, 2.533(12) Å) also confirm the distorted nature of the geometry (Figure 1a).

The similar PbO$_4$N geometrical atmosphere also appears around the Pb02 center. In this case, the central metal ion is chelated from both the ligands: dicarboxylic acid and aiz along with bridging-O of the second bdc$^{2-}$ unit. The Pb02–O and Pb02–N bond lengths are Pb02–O1, 2.322(10); Pb02–O2_a, 2.651(10); Pb02–O3, 2.392(12); Pb02–O005, 2.890(9); and Pb02–N1, 2.447(15) Å (Figure 1a). Due to presence of two types of Pb(II) centers and two kinds of bridging units (bdc$^{2-}$ and aiz), 1 adopts a 1D ribbon-like polymorphic structure (Figure 1b), and the 2D square-grid arrangement is achieved by the chelating and monodonating nature of aiz with Pb(II) (Figure 1c). During the formation of structural architecture, there are a few prominent supramolecular hydrogen-bonding (intramolecular: N2–H2A···S1 = 2.07 Å ($\angle$N2–H2A···S1 = 143°), C3–H3···O2 = 2.59 Å ($\angle$C3–H3···O2 = 131°), and C00S–H00S···O004 = 2.42 Å ($\angle$C00S–H00S···O004 = 127°) along with intermolecular: C4–H4···O1 = 2.56 Å ($\angle$C4–H4···O1 = 159°) and C00X–H00X···O005 = 2.51 Å ($\angle$C00X–H00X···O005 = 134°) interactions, which play a crucial role in maintaining the molecular structure. As a result, 1 produces a three-dimensional (3D) structure assisted from $\pi$–$\pi$ interactions (Figure 2). The asymmetric unit of 2 also holds two metal centers (Pb1 and Pb2) of hexa-coordinated geometry with a PbO$_4$N coordination sphere. In the Pb1 center, the metal ion binds in a chelating manner by two different bdc$^{2-}$ units along with bridging-O ($\mu^2$-O) with another bdc$^{2-}$ unit and monodonation of the pyridyl-N atom from the aiz ligand and satisfies the hexa-coordinating (Pb1–O3d, 2.638(9); Pb1–O4c, 2.500(7); Pb1–O5c, 2.526(7); Pb1–O6, 2.532(8); Pb1–O7, 2.711(8); and Pb1–N4, 2.449(9) Å) geometrical arrangement (Figure 3a).

But in the Pb2 environment, two solvent molecules (MeOH) are coordinated with the metal center and it is also chelated by aiz and bdc$^{2-}$ ligands (Pb2–O1, 2.301(8); Pb2–O2, 2.414(7); Pb2–O3, 2.795(8); Pb2–O9, 2.788(12); Pb2–O10b, 2.808(9); Pb2–N2, 2.425(9) Å). Again, the monomeric unit

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**Scheme 1. Synthesis of Compound 1 and 2 upon the Reaction of Pb(NO$_3$)$_2$ with Aiz and H$_2$bdc Ligands**

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Figure 1. (a) View of the repeating dimeric unit of I, (b) one-dimensional (1D) ribbon-like polymeric arrangement of the molecule along the “b” axis, and (c) two-dimensional (2D) square-grid net of I viewed along the “a” axis.

Figure 2. (a) Supramolecular π···π interactions in I along the b axis. (b) Supramolecular 3D aggregated netlike structure along the a-axis.
undergoes polymerization from dicarboxylic acid along with aiz and is supported from the π···π supramolecular interaction (Figure 3b) to form 2D arrangements (Figure 3c).

The hydrogen bonding, intermolecular (O(9)−H(9)···O(4) = 1.97 Å (∠O(9)−H(9)···O(4) = 168°) and C(26)−H(26B)···O(6) = 2.50 Å (∠C(26)−H(26B)···O(6) = 164°)) and intramolecular (C(3)−H(3)···O(3) = 2.50 Å, ∠C(3)−H(3)···O(3)133), is responsible for the formation of assembly of the molecules and constructs a 3D supramolecular structure (Figure 4).

**Thermal Stability of 1 and 2.** Thermogravimetric analyses (TGA, 30−700 °C) revealed that 1 is more stable (150 °C) than 2 (120 °C) (Figure S1) and the loss in weight may be due to the release of coordinated solvent molecules. Finally, the network breaks after 225 °C for 1 and 270 °C for 2. To verify the phase purity of 1 and 2, the powder X-ray diffraction (PXRD) test was also undertaken (Figures S2 and S3).

**DFT Computation.** The experimental UV−vis spectra of 1 and 2 in dimethyl sulfoxide (DMSO) have sharp absorption at ~323 and 360 nm, respectively. The time-dependent density functional theory (TD-DFT) calculation in the triplet spin state (using the DMSO solvent and conductor-like polarizable continuum model (CPCM) model) was performed to investigate the cause of UV−vis transitions in 1 and 2.
TD-DFT-calculated energies of the specific bands along with the nature of transitions, theoretical lambdas, and oscillation strengths ($f$) are listed in Table S1. Some molecular orbital diagrams with energy are also listed (Tables S2–S5). The $\lambda$ (calcd) values for 1 and 2 are 327.72 and 360.09 nm, respectively, and these may be interligand charge transfer transitions (ILCTs) and the experimental wavelengths are 323 and 362 nm correspondingly. For compound 1, the transition from HOMO $\rightarrow$ LUMO + 1 ($\beta$) has contributions mainly due to the absorption bands at 323 nm. However, 2 shows the absorption peaks at 362 nm, and this may be due to the HOMO $- 1 \rightarrow$ LUMO + 1 ($\alpha$) transition. The energy difference between HOMO and LUMO, $\Delta E = E_{LUMO} - E_{HOMO}$ (eV), is also obtained from DFT computation in the triplet state (Figure 5), and it is correlated with the obtained band gap (normally considered as the difference between conduction and valence

Figure 5. Energy difference between HOMO and LUMO of 1 and 2 in the triplet state (DFT).

Figure 6. Tauc’s plots of 1 and 2; inset: UV–vis absorption.

Figure 7. $I$–$V$ plots (a) device-A and (b) device-B under dark and illumination conditions.
follows, eqs 2 according to this theory, the current of a diode may be stated as

$$I = I_0 \exp \left( \frac{qV}{\eta kT} \right) \left[ 1 - \exp \left( \frac{qV}{\eta kT} \right) \right]$$  \hspace{1cm} (2)

where

$$I_0 = A \alpha T^2 \exp \left( - \frac{\phi_B}{kT} \right)$$  \hspace{1cm} (3)

$$\phi_B = \frac{kT}{q} \ln \left( \frac{A \alpha T^2}{I_0} \right)$$  \hspace{1cm} (4)

Table 1. Schottky Diode Parameters

| compound | measured condition | conductivity (\(\delta\)) \((\text{S m}^{-1})\) | \(d(V)/d(\ln J)\) vs \(J\) graph | \(H(J)\) vs \(J\) graph |
|----------|-------------------|-----------------------------|---------------------------------|---------------------|
|          |                   | ideality factor \((\eta)\) | series resistance \((R_s)\) \((\Omega)\) | barrier height \((\phi_B)\) \((\text{eV})\) | series resistance \((R_s)\) \((\Omega)\) |
| 1        | dark              | 2.94 \times 10^{-6}        | 1.32                            | 5.35 \times 10^4   | 0.76                             | 5.34 \times 10^4   |
|          | light             | 6.12 \times 10^{-6}        | 1.11                            | 2.25 \times 10^4   | 0.73                             | 2.15 \times 10^4   |
| 2        | dark              | 2.92 \times 10^{-7}        | 0.93                            | 4.48 \times 10^5   | 0.80                             | 4.32 \times 10^5   |
|          | light             | 3.66 \times 10^{-7}        | 0.97                            | 3.64 \times 10^5   | 0.78                             | 3.44 \times 10^5   |

bands) from Tauc’s plot by the UV spectrum. Minor discrepancy between experimental and calculated band gaps is obtained in the triplet than in the singlet spin state (Figure S4). The band gaps (Tauc’s plot) of the synthesized 1 and 2 were estimated as 3.46 and 3.01 eV, respectively, while band gaps from DFT computation are 2.84 and 2.52 eV (\(\beta\) spin), respectively.

**Optical Characterization.** The optical characterization was studied \((\lambda, 300–600 \text{ nm})\). Figure 6 (inset) exhibits normalized optical absorbance spectra of 1 and 2. The optical band gap of the compounds resembles the excitation of an electron to the conduction band from the valence band (obtained using Tauc’s equation).42,43

\[
(a\nu) = \Delta(h\nu - E_g)^n
\]

where \(\alpha\) is the absorption coefficient; \(E_g\) is the band gap energy, \(h\) is Planck’s constant, \(\nu\) is the frequency of light, \(n\) is the electron transition process-dependent constant (in direct transition, \(n = 1/2\)), and \(A\) is the constant, which is considered as 1 for the common case.44,45 The \((a\nu)^2\) vs \(h\nu\) plot of compounds under investigation is shown in Figure 6. In the \((a\nu)^2\) vs \(h\nu\) plot, the linear region of both the plots is extrapolated and the direct optical band gap energies of 1 and 2 are calculated as 3.46 and 3.01 eV, respectively.

**Electrical Characterization.** Figure 7 shows \(I-V\) characteristics of device-A (Al/1/ITO) and device-B (Al/2/ITO) under dark and illuminated conditions, and it shows that device-A has a higher magnitude of current than device-B. At room temperature (RT), dark- and photo-conductivity values of device-A are calculated as 2.94 \times 10^{-6} and 6.12 \times 10^{-6} \text{ S m}^{-1}, respectively, whereas for device-B, the values of dark- and photo-conductivity are 2.92 \times 10^{-7} and 3.66 \times 10^{-7} \text{ S m}^{-1}, respectively. The inset of Figure 7 shows the logarithmic presentation of current as a function of voltage.

For better understanding of the charge transport mechanism in devices, the thermionic emission (TE) theory is used,46 and according to this theory, the current of a diode may be stated as follows, eqs 2–4

From the \(dV/d(\ln J)\) vs \(J\) plot, the series resistance, \(R_s\), and ideality factor, \(\eta\), for all of the devices in dark- and photo-conditions are determined by the slope and intercept, respectively (Figure 8). Using the y-axis intercept of the \(H(J)\) vs \(J\) curve, the potential barrier height (\(\phi_B\)) for the devices is
calculated, and the slope of this plot provides a second determination of the series resistance. Obtained $R_S$, $\eta$, and $\phi_b$ are listed in Table 1.

The value of $\eta$ in dark conditions deviates from ideal behavior, and the difference may arise for the presence of inhomogeneities of the Schottky barrier height, hole recombination in the depletion region, series resistance, and existence of interface states.55,56 The ideality factor, $\eta$, value moves toward unity upon illumination of light. After absorbing light, the series resistance, $R_S$, of the compounds in both cases decreases and signifies its applicability in the field of optoelectronic devices.

By using the power law ($I \propto V^m$), the current conduction mechanism is described, where $m$ refers to the slope of the $I$ vs $V$ curve. The current–voltage plot (Figure 9) exhibits two different regions under forward bias. At low bias voltage, region-I, the sample exhibits an Ohmic nature, i.e., the current is directly proportional to the applied bias voltage ($I \propto V$). The region II corroborates the variation of current with square of forward bias voltage ($I \propto V^2$), and in this region the conduction mechanism is explained by the space-charge-limited current (SCLC) mechanism dominated by the discrete trapping level.55,56

The injected carriers spread and make a space charge field when it is more than that of background carriers, and the currents are controlled by the field and known as SCLC.55 The performance of the device greatly depends on the mobility and transit time of carriers. Thus, from the $I$ vs $V^2$ plot, the mobility has been evaluated (Figure 9) taking the Mott–Gurney space-charge-limited current (SCLC)55,56 (eq 9)

$$I = \frac{9\mu_{eff}\varepsilon_0\varepsilon_r A}{8d} \frac{V^2}{d^3}$$

Figure 9. Logarithmic plots of the $I$–$V$ characteristic curves in dark and light conditions: (a) device-A and (b) device-B.

\[
\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{10}
\]

The values of mobility for 1 and 2 are $8.31 \times 10^{-7}$ and $2.25 \times 10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$ under dark conditions and $1.43 \times 10^{-5}$ and $2.57 \times 10^{-6}$ m$^2$ V$^{-1}$ s$^{-1}$ under photo conditions, respectively. This has been admirable compared to some other materials of this type. Some examples of semiconducting materials and their corresponding photosensitivities are listed in Table S6.

The transit time, $\tau$, is the time required by a carrier to travel to the cathode from anode, and it may be stated as a summation of the average time spent by each electron (as a free carrier) plus the total time spent in the trap.57 The transit time of the charge carrier is calculated using eq 11

$$\tau = \frac{9\varepsilon_r A}{8d} \frac{V}{I} \tag{11}$$

In dark conditions, the effective mobility values of the carriers are estimated as $8.31 \times 10^{-7}$ and $2.25 \times 10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$ for 1 and 2, respectively. Effective carrier mobility ($\mu_{eff}$) values, after irradiation of light, improve to $1.43 \times 10^{-5}$ (1) and $2.57 \times 10^{-6}$ m$^2$ V$^{-1}$ s$^{-1}$ (2), respectively. In dark conditions, the transit time ($\tau$) is longer, which leads to higher trapping probabilities, but the situation is reverse after illumination of light, which may be due to the higher carrier mobility.\textsuperscript{59} The values of $\mu_{eff}$ and $\tau$ of 1 and 2 are presented in Table 2.

Impedance Spectroscopic Measurement. The impedance spectroscopic study is carried out within the frequency range 40 Hz to 10 MHz taking the oscillating voltage of 200 mV by an Agilent 4294A LCR meter at room temperature. Nyquist
Table 2. Charge Transport Parameters

| Compound | Measured Condition | Effective Carrier Mobility ($\mu_{eff}$) \((m^2/V⋅s)\) | Transit Time \((\tau)\) \((s)\) |
|----------|--------------------|---------------------------------------------|-------------------------------|
| 1        | Dark               | 8.31 × 10^{-6}                             | 1.06 × 10^{-6}                |
|          | Light              | 1.38 × 10^{-6}                             | 6.34 × 10^{-7}                |
| 2        | Dark               | 2.52 × 10^{-7}                             | 3.51 × 10^{-6}                |
|          | Light              | 3.67 × 10^{-7}                             | 2.15 × 10^{-6}                |

plots for two compounds 1 and 2 are shown in Figure 11. The higher-frequency semicircular arc represents the bulk contribution, and the intermediate- or low-frequency semicircular arc represents the grain-boundary or electrode-specimen effect. The bulk resistance $R_b$ (dc resistance) of the sample is obtained from the intercept of the semicircle on real axis $Z'$, and from this figure, it is clearly specified that 1 possesses lower resistance than that of 2. This lower bulk resistance of 1 results in enhanced possibility of charge transfers and reduces the charge recombination chances.

**CONCLUSIONS**

Here, two coordination polymeric compounds with Pb(II) as node, bdc$^{2-}$ and aiz as linkers, were isolated. The Pb(II) coordination systems have been synthesized, structurally elucidated, and well characterized. Isostructural compounds are utilized for studying electrical conductivity. The $I$-$V$ characteristics are determined for 1 and 2 in dark and illuminated conditions. From this study, at room temperature, dark- and photo-conductivity values of 1 are calculated as 2.94 × 10^{-6} and 6.12 × 10^{-6} S m$^{-1}$, respectively, whereas for 2, the values of dark- and photo-conductivity are 2.92 × 10^{-7} and 3.66 × 10^{-7} S m$^{-1}$, respectively. In the absorption of light, the compounds show increased electrical conductivity. Thus, the compounds may be the potential alternative for optoelectronic device fabrication. Higher distortion and greater polarization in the structure of 1 may be the reason for the faster charge mobility and higher conductivity than those of 2.

**EXPERIMENTAL SECTION**

The experimental details that include materials and physical methods used in this work, general X-ray crystallography, device fabrication, and characterization are added in the corresponding Supporting Information.

**Synthesis of 1.** (E)-N'-(Thiophen-2-ylmethylene)-isonicotinohydrazide (aiz) was prepared by stirring of isonicotid and thiophene-2-carbaldehyde in dry MeOH solution for 6 h. A solution of aiz (0.046 g, 0.2 mmol) in dimethylformamide (DMF)/MeOH (1:10 v/v) (2 mL) was gently and sensibly layered in a solution of Pb(NO$_3$)$_2$ (0.066 g, 0.2 mmol), in 2 mL of H$_2$O taking 2 mL of DMF buffer solution followed by layering with H$_2$bdc (0.033 g, 0.2 mmol, neutralized with Et$_3$N, 0.04 g, 0.4 mmol) in 2 mL of EtOH. Brown needle-shaped crystals of 1 were found after 2 weeks (0.123 g, yield 69%). Elemental analysis (calcd %) for C$_{23}$H$_{15}$N$_3$O$_7$Pb$_2$S: C 30.97, H 1.70, N 4.71; found: C 30.91, H 1.63, N 4.78. IR (KBr disk, cm$^{-1}$): 1586 $\nu$(COO$^-$), 1360 $\nu$(COO$^-$), and 1646 $\nu$ (−C=O−) (Figure S5).

**Synthesis of 2.** 2 was prepared following the same technique as for the synthesis of 1, except the use of buffer solution, H$_2$O/MeOH (1:1, v/v) instead of DMF. The red prismatic crystals of [Pb$_2$(bdc)$_{1.5}$(aiz)(MeOH)$_2$]$_n$ (2) were acquired after seven days (0.142 g, yield 74%). Elemental analysis (calcd %) for C$_{25}$H$_{15}$N$_3$O$_7$Pb$_2$: C 31.44, H 2.32, N 4.40; found: C 31.41, H 2.38, N 4.45. IR (KBr disk, cm$^{-1}$): 1578 $\nu_{as}$(COO$^-$), 1352 $\nu_{as}$(COO$^-$), and 1654 $\nu$ (−C=O−) and 3209 $\nu$ (−OH, methanol) (Figure S6).

**Theoretical Calculations.** The Gaiassian-09 program with the DFT-B3LYP hybrid function was used to carry out DFT computations for determining the correlation between theoretically and experimentally obtained band gaps. For C, H, and N, the 6-31G (d) basis set was allocated, and for Pb, LanL2DZ was used. The SCXRD coordinates were taken for the compounds during the calculations. In the experimental spectra, low-lying electronic transitions of the compounds were acquired from TD-DFT calculations. GaussSum was used to calculate the fractional contribution in the metal-ion-centered molecular orbital and ligand-based molecular orbital.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02899.

TGA graph (Figure S1); PXRD measurement (Figures S2 and S3); DFT calculation (Figure S4 and Tables S1–S5); literature report of some semiconducting materials (Table S6); the crystal data, refinement parameters, and some selected bond lengths and angles of 1 and 2 (Tables S7–S9); IR spectra (Figures S5 and S6); materials and physical methods, general X-ray crystallography, and device fabrication and characterization procedures (PDF)

AI-Z-Pb1 (CIF)

AI-Z-Pb2 (CIF)

**Accession Codes**

For this work, CCDC 1945643 (1) and 1945657 (2) contains the supporting crystallographic data.

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**Notes**

The authors declare no competing financial interest.
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