Modulation of Weak Interactions in Structural Isomers: Positional Isomeric Effects on Crystal Packing and Physical Properties and Solid-State Thin-Film Fabrication

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1 Supporting Information

ABSTRACT: Selective formation of positional isomers and accordingly tuning the physicochemical properties of small conjugated organic molecules through structural isomers is an effective crystal engineering for a fascinating successful delivery of thermally stable and photophysically exciting compounds. By small structural skeleton changes, the single crystal of the naphthalenemaleonitrile isomers is found to exhibit a drastic change in crystal packing array, which in turn is found to tune the thermal and physicochemical properties. The α-isomer (A) forms the “herringbone packing” (HP) due to peri-interaction-sensitive C–H···(Ar)π (Ar = naphthalene ring) interactions, and the β-isomer (B) forms the “bricklayer packing” (BP) due to π(C≡N)···π(Ar) stacking interactions. These two positional isomers have revealed insight of molecular packing-dependent structure–property relationship. In this report, we show that a simple modification of relatively less common weak interactions, such as C–H···π(Ar) ↔ π(C≡N)···π(Ar), through the preparation of isomers, can lead to a drastic change in crystal packing (HP ↔ BP). Also, this report demonstrates that by a small structural diversity, one can obtain significant changes in the physicochemical properties like melting behavior, enthalpy, entropy, and electrical properties in the solid state. Therefore, it transpires from this study that structural isomer provides a useful complement to intermolecular nonbonding interactions as a tool to design new promising materials.

1. INTRODUCTION

Modulation in the molecular packing of organic materials has sparked intensive research in the field of crystal engineering. The intermolecular interaction is found to be the controlling factor for crystal packing with different molecular shapes.1–5 For example, intermolecular interactions in solid-state packing give an idea to improve the electrical characteristics of the materials based on different packings.1–5 Therefore, growing interest in crystal engineering, which accommodates various aspects of chemistry, biology, physics, engineering, material science, and pharmaceuticals,6 has become the need for the development of new materials for technological applications.9,10 As crystal engineering is to design and tune intermolecular interactions through changing functional group and conjugated backbone, some important packing motifs like herringbone (HP),11,12 bricklayer (BP) π-stacked,13,14 and lamellar (LP) slipped π-stacked15–17 in organic crystals play an important role in organic electronic devices and have been of intense research in current years (see Table 1).18–20 As documented in Table 1, an interchange between two different interesting crystal packings through modulation of weak intermolecular interactions has been of great interest among crystal engineers in the last decade.

Among them, Curtis and co-workers discussed the correlation between solid-state packing and carrier transport to explain organic semiconductors.21–23 Theoretically, a co-facial π stacking structure is expected to provide effective orbital overlaps, leading to better carrier transport. Although pentacene, which shows HP packing mode with C–H···π intermolecular interactions in spite of π–π stacking, is the classical example showing high organic field-effect transistor (OFET) performance, when π–π stacking is taken into consideration, it is found to be much more efficient for the transporting of charge carriers than HP.20,21 Rubrene22 and 6,13-bis-(triisopropylsilylethynyl)pentacene23 are good examples of π–π stacking materials in the literature that are used to enhance the OFET efficiency. Several efforts have been made to promote the self-assembly process in such a way to prevent C–H···π interactions and to obtain π–π stacking interaction or lamellar packing.24–26

Crystal structure modification with desired properties as well as with the desired packing can be achieved, not only by the
functionalization of the molecules but also by choosing different isomer configurations.27,28 Studies of isomeric compounds are important as discussed by Takimiya and co-workers for transistor performances.29 It has been reported in the literature that the molecules which have similar chemical structures and electronic properties but different crystal structures are more efficient in charge transportation.30 Ghiassi et al. studied four bio-based cyanate ester isomers and described the crystal structure and thermodynamic characteristics of melting, as well as showed a considerable variation in enthalpy, entropy, and melting points despite their high level of chemical similarity.31 However, it is challenging to predict the solid-state order of the crystals but quite interesting to make small changes in structural skeleton which directly affect crystal packing drastically by complex intermolecular interactions.32 Anthony and co-workers carried out this beautiful task by substitution at the peri-position of acenes.33 Modificiation at the peri-position may be responsible for obstructing the edge-to-face interaction with a favorable π−π stacking arrangement, improved ambient stability, and excellent carrier mobility.24 Moreover, the crystal structure and intermolecular interactions greatly influence the physicochemical and mechanical properties like thermal stability and solubility.34,35 Katritzky and co-workers explained well that crystal packing significantly affects the physicochemical properties.36 The physicochemical properties of organic conjugated molecules are expounded through molecular formulas, crystal

Table 1. Compilation of Important Literature in Which Transformations in Crystal Packings due to Change in Intermolecular Interactions Are Reported

| Transformation between packing modes | Molecules studied | Transformation of packing | Change in intermolecular interaction | References |
|--------------------------------------|------------------|--------------------------|--------------------------------------|------------|
| HP ↔ CP                              | ![Molecule Image] | ![Transformation Image] | C-H⋯π \(\downarrow\) \(\pi(Ar)\)−π(Ar) | J. Am. Chem. Soc. (2001), 123, 9482-9483. |
| HP ↔ LP                              | ![Molecule Image] | ![Transformation Image] | C-H⋯π \(\downarrow\) \(\pi(Ar)\)−π(Ar) | Cryst. Growth Des. (2010), 10, 4155-4160 |
| CP/LP ↔ HP                           | ![Molecule Image] | ![Transformation Image] | S⋯N, S⋯S \(\downarrow\) C⋯C | J. Am. Chem. Soc. (2004), 126, 4318-4328 |
| HP ↔ LP, CP                          | ![Molecule Image] | ![Transformation Image] | C-H⋯π \(\downarrow\) C-H⋯F, C-H⋯C | Cryst. Growth Des. (2016), 16, 5822–5830 |
| HP ↔ BL, LP, CP                      | ![Molecule Image] | ![Transformation Image] | C-H⋯H-C \(\downarrow\) C-H⋯π | Chem. Eur. J. (2018), 24, 8679–8685 |
| SP ↔ HP                              | ![Molecule Image] | ![Transformation Image] | Edge to face π−π interaction \(\downarrow\) Face to face π−π interactions | Cryst. Growth Des. (2013), 13, 4418–4427 |
| HP ↔ BL                              | ![Molecule Image] | ![Transformation Image] | N⋯X interaction | Chem. Commun. (2015), 51, 8825-8828 |
packing, and crystal compositions.\textsuperscript{37,38} In relation with the study of the physicochemical properties, examination of the structure and the accordingly changing properties\textsuperscript{39} of novel $\pi$-conjugated materials is an exciting option to develop organic sensors,\textsuperscript{40} OFETs,\textsuperscript{41a,c} and organic light-emitting diodes (OLEDs).\textsuperscript{41b,d}

Efforts in the direction of crystal packing pattern modification through intermolecular interaction and the accordingly tuning physicochemical and thermophysical properties are being devoted both theoretically and experimentally.\textsuperscript{42−44} Therefore, the architecture of essential building blocks by desired crystal packing array with desired material properties is demanding.

In this paper, we use a careful selection of peri-position substitution in naphthalene moiety-based derivatives (Chart 1) to demonstrate the powerful effect of weak intermolecular interactions, which directly control the different crystal packing of $\alpha$- and $\beta$-isomers. This report points to the involvement of C–H–$\pi$(Ar) $\leftrightarrow$ $\pi$(C≡N)–$\pi$(Ar) weak interactions in the alteration of crystal packings in two molecular isomers.

The main points discussed in this paper are (i) different interaction preferences in isomers which leads to significantly different packing modes and (ii) its effect on the thermophysical properties, resistivity, and other properties. Single-crystal X-ray diffraction (SCXRD), two-dimensional (2D) nuclear magnetic resonance (correlation spectroscopy, COSY), nuclear over-hauser effect spectroscopy (NOESY), thermogravimetric analysis with differential scanning calorimetry (TGA-DSC), and electrical conductivity measurement are presented here. Hirshfeld surface analysis is also used to substantiate the SCXRD data and help us in quantifying different modes of interactions.\textsuperscript{45}

2. RESULTS AND DISCUSSION

2.1. Crystal Structure Analysis. The crystal structures of the two isomers of 2-amino-3-(((E)-naphthalen-1-ylmethylene)amino) maleonitrile (A) and 2-amino-3-(((E)-naphthalen-2-ylmethylene)amino)maleonitrile (B) have been determined by SCXRD. A crystallizes in the monoclinic with space group $P2_1/c$, while B crystallizes in triclinic with $P\overline{1}$ space group. In both cases, the asymmetric unit of the crystal lattice contains two crystallographically independent molecules, which are held together by the N8H–N3 hydrogen bond in A and the N4H–N7 hydrogen bond in B, as shown in Figure 1 and Table 2.

The crystal structures of A and B, therefore, are stabilized by intermolecular NH–N hydrogen bonding (N8–H8B–N3 = 2.138 Å for A; N8–H8B–N4 = 2.154 Å for B), in which the two units are found to be closer in A compared to B as revealed by the shorter H-bonding distance. In addition to these classical H-bonding interactions, several other weak intermolecular interactions are found to contribute signific-
are two kinds of main packing motifs as shown in Figures 3 and 4.

Molecular packing in A shows predominant C−H⋯π (edge-to-face: 2.89 Å) noncovalent binding intermolecular interactions. In A, molecules are arranged in an antiparallel slip-stacked manner where units are connected through an edge-to-face fashion and a loosely bound interaction, which is termed as herringbone packing (Figure 3a). The other H-bonding distances which interconnect two asymmetric units are N4−H4A⋯N′4 = 2.215 Å and N8−H8A⋯N′6 = 2.634 Å.

In contrast, (C≡N)π···π(AR) = 3.38 Å intermolecular interaction predominates in B, leading to a planar molecular arrangement as depicted in Figure 4. The other interconnected hydrogen bonds in B which stabilized the moiety are N8−H8A⋯N′4 = 2.248 Å, N8−H8A⋯N′6 = 2.341 Å. Several other shorts contacts with the conjugated ring that help to pack the molecules in a bricklayer fashion are C13⋯C′17 (Ar), C5(AR)⋯C′28 = 3.382 Å. Hydrogen-bonded planar sheets are arranged on top of each other by stronger (C≡N)π···π(AR) stacking having a separation of 3.38 Å with a head-to-tail-type arrangement (Figure 4a). The π···π interaction occurs in the entire packing that arranges the molecule in a planar sheets (2D bricklayer packing). With these kinds of different intermolecular interactions (C−H⋯π in A vs C≡N−π in B), distinct crystal packings are observed (schematic representation given in Supporting Information (SI) Figure S5).

A closer look at the molecular orientation in A reveals that the peri-interaction (i.e., C11−H11⋯C1−H interaction) tilts the naphthalene ring with respect to the DAMN moiety about 11.4° dihedral angle, as depicted in Figure 5a.

This distorted structure of A can now afford a minimized interaction between the electron-deficient groups (C28≡N6⋯C′23=H23 = 2.629 Å) of the naphthalene ring. This type of interaction, in principle, leads to loose packing of HP type. Though scanty, a similar HP packing via edge-to-face (in C−H⋯π) interaction is reported only for trimethylsilyle derivative.40 B is almost planar having a 0.3° dihedral angle, as shown in Figure 5b, due to the absence of any peri-interaction steric factor. A consequence of this planar structure leads to the absence of C28N6⋯C′23=H23 interaction in B. Introduction of a functional group is reported to modulate the packing, as shown in the case of anthradithiophene having an acenes-type central ring, by Anthony and co-workers,46 Yamashita et al.,14a and Wurthner et al.14b Our investigation suggests that simply by changing the position of the functional group, one can modulate the interaction to a large extent, which leads to a drastic change in overall packing (SI Figure S5) and furthermore their unit cell volume presented in (SI Figure S6). Further, a comprehensive collection of reports...
depicting weak interactions leading to popular crystal packings (such as HP, BP, etc.) published in high-impact journals in recent times are tabulated in SI Table S4.

2.2. Hirshfeld Surface Analysis. SCXRD structure analysis clearly indicates that the difference of weak interaction brings drastic changes in overall packings. Hirshfeld surface analysis helps us to understand the intermolecular interactions in depth. It also contributes toward better cognition of packing interactions and contribution of molecular interactions quantitatively, which are responsible for molecular architecture in a crystal. Hirshfeld surface is mapped over the $d_{\text{norm}}$ (interatomic distances normalized by the size of the atoms via the van der Waals radii) properties, as shown in Figure 6 along with their full two-dimensional fingerprint plots. Relative percentage contributions of various intermolecular interactions to the Hirshfeld surface areas for both isomers are also presented in SI Figure S7.

Hirshfeld surfaces of an asymmetric unit of A and B show close contacts as a function of color contour. The surfaces are represented as transparent for the visualization of the molecule. The white color on the surface represents distances equal to van der Waals radii, while the red and blue colors represent the shorter and longer distances of the sum of van der Waals radii, respectively, on the Hirshfeld surfaces. The large red

1. $\text{N}^\prime - \text{H}^\prime \cdots \text{N6} \equiv \text{C28} / \text{C28} \equiv \text{N6} \cdots \text{H} - \text{N}$,
2. $\text{N}^\prime - \text{H}^\prime \cdots \text{N3} \equiv \text{C15} / \text{C15} \equiv \text{N3} \cdots \text{H} - \text{N}^\prime$,
3. $\text{N}^\prime - \text{H}^\prime \cdots \text{N2} \equiv \text{C13} / \text{C13} \equiv \text{N2} \cdots \text{H} - \text{N}^\prime$

regions in both isomers represent hydrogen-bonding interactions, which are relevant in the $d_{\text{norm}}$ maps for these two isomers. These interactions in the fingerprint can be seen as symmetrical spikes at $d_e + d_i \geq 2.13 \text{ Å}$ for A, and a center spike

Figure 4. Bricklayer packing for B isomer. (a) Close look at the (C=N)$\pi \cdots \pi$(Ar) intermolecular interaction between molecules of two successive layers leading to bricklayer packing. (b) Overall 2D bricklayer packing (down the b axis) in B due to interlayer $\pi \cdots \pi$ stacking interaction.

Figure 5. Dihedral angle between the naphthalene ring and DAMN moiety: (a) 11.4° for A and (b) ~0.3° (planar) for B.

Figure 6. View of Hirshfeld surfaces of A and B mapped with $d_{\text{norm}}$ (left) and full 2D fingerprint plots derived from the same surfaces (right). The numbers 1, 2, and 3 show close contact (N–H···N≡C) in both isomers and are discussed in the text.
is observed at a $d_1 + d_d$ distance of $\sim 2.2$ Å, which indicates the H···H contact observed in B, as expected for the strong hydrogen bond in B. It is found that H···H, N···H/N···N, and C···C weak intermolecular interactions are more in B compared to A, while the C···H/H···C, N···C/C···N, and N···N interactions are dominant in A. Four small red spots are labeled for $\alpha$-isomer, while only three red spots are labeled for B. There is no C28···N6···H$^-$C interaction in $\beta$-isomer (planar molecule). The N$^-$H$^-$H$^-$N$^-$ contacts shown by the red spot 2 and N$^-$H$^-$N$^-$N$^-$C13/C13···N2···H$^-$N$^-$ shown by the red spot 3 are dominant for both the isomers, with highest contributions of 12.6% in B and 10.0% in A, of the total Hirshfeld surface area. Moreover, B has (C$\equiv$N)\$π\cdots π$(Ar) stacking interaction, which is stronger than the weak C···H$\cdots$π interaction in A. Therefore, we can conclude from Hirshfeld analysis that B has a higher contribution of intermolecular interactions compared to A. Perhaps, this might be a predominant reason for why B has a higher melting point, which will be discussed shortly.

2.3. Correlation Spectroscopy (COSY) and Nuclear Over-Hauser Effect Spectroscopy (NOESY) NMR Studies. So far, we have examined the single-crystal structures of two isomers using SCXRD, a direct experimental observation. The interaction analysis by Hirshfeld surface also provides same inferences. However, it is also interesting to study the behavior of the molecules in solution. The 2D NMR spectroscopy gives an understanding of long-range coupling interactions in the molecule. Particularly, the coplanarity, conformational aspects (such as gauche, trans, etc.), and bond proximity are studied well by this spectroscopy. Long-range coupling interactions of A and B isomers in solution were investigated by $^1$H COSY, and NOESY spectroscopy studies, as shown in Figure 7. The chemical shifts of Ca$^-$$H$ protons are found to be at 8.98 and 8.36 ppm in COSY in CDCl$_3$ for A and B, respectively. This significant difference in the chemical shift ($\Delta \delta \sim 0.62$ ppm) from $\alpha$- to $\beta$-isomer is quite informative. The shifting of Ca$^-$$H$ proton toward downfield in the case of A indicates that it is more deshielded and therefore gives a clear indication about the different orientations of naphthalene ring even in solution. As we have discussed in the SCXRD study, the naphthalene ring in A is found to be twisted $\sim 11.4^\circ$ with respect to the DAMN moiety (see Figure 5a). This makes the Ca$^-$$H$ proton less hindered and therefore deshielded. This Ca$^-$$H$ proton in both isomers gives no off-diagonal peak, which means that this proton does not couple with any adjacent proton. Moreover, all of the aromatic protons of B isomer are upfield in comparison to A. The reason for this shifting can be explained that B is a planar molecule so that there is proper conjugation and more electron density on the naphthalene ring part in the case of B.
But in A, due to its distorted structure or peri-interaction hindrance, there is no proper conjugation and less electron density on naphthalene ring, therefore protons are deshielded as shown in the COSY spectra (Figure 7). Hirshfeld surface analysis shows that number 4 interaction (vide Figure 7a) in A, not present in B, is also reflected in the COSY NMR spectra as the aromatic protons are also deshielded in A. We have observed from the NOESY spectra of A that there were strong interactions between C8−H and C8−H protons. Moreover, no interaction between C8−H and C8−H can be explained that these protons are not in the same plane, which indicates the peri-steric hindrance in solution also. In the case of the NOESY spectra of B, an interaction between the C8−H and C8−H protons occurs and no interaction occurs between C8−H and C8−H protons, which supports the planar structure of B. Therefore, it appears from the solution-state 2D NMR studies that the interaction observed in the solid-state is present in solution as well.

2.4. Thermal Studies (DSC and TGA Analyses). To understand the impact of the difference in crystal packing and the consequence of variation in weak interactions on the thermal properties, detailed thermal studies are performed. Thermal studies allow deeper insights about the stability, melting point, and phase behavior of these structural isomers. Our SCXRD studies established that α- and β-isomers possess a small change in the molecular structure, which leads to a significant difference in molecular packing, resulting in a big difference in melting points as will be discussed here. The equilibrium melting temperature of A is found to be 170 °C, while that of B is much higher (248 °C), as can be seen in the DSC endotherm provided in Figure 8.

Despite the similarity of these compounds, a difference of 78 °C in melting points is exciting and deserves a detailed analysis. Our group reported several examples in which thermal behaviors of compounds are found to depend on packing in crystal and intermolecular interactions. Lian et al. also described the effect of molecular geometry on melting-point-related properties like enthalpy and entropy, while Ghiasi et al. reported the relation of melting behavior with crystal packing for the isomer of cyanate ester. From the DSC thermogram, we have calculated the thermodynamic parameters associated with the melting process, according to eq 1, and the data are presented in Table 3.

\[
\Delta H_m = \Delta S_m \times T_m \tag{1}
\]

where \(\Delta H_m\) and \(\Delta S_m\) stand for enthalpy and entropy changes of the melting process, respectively.

According to eq 1, higher melting point of a crystal is because of the higher enthalpy change of melting, smaller entropy change of melting, or both. Table 3 shows that there is a significant difference in entropy of melting. In the case of A, \(\Delta H_m\) and \(\Delta S_m\) are obtained from DSC results as 30.7 kJ/mol and 6.92 \(\times\) 10\(^{-2}\) kJ/K\(^{-1}\), respectively. However, there is a considerable decrement observed in \(\Delta H_m\) (24.14 kJ/mol) and \(\Delta S_m\) (4.63 \(\times\) 10\(^{-2}\) kJ/K\(^{-1}\)) for B. A smaller entropy change of melting is directly related to the crystal packing. B has a strong head-to-tail packing (bricklayer packing) and therefore in a more compacted form. In contrast to β-isomer, A has higher entropy change of melting (6.92 \(\times\) 10\(^{-2}\) kJ/K\(^{-1}\)) and has a low melting point as the α-isomer has a comparatively less compact herringbone packing. By consideration of \(\Delta S_m\) data, we can conclude that B is more ordered and stable, which is also further supported by SCXRD and Hirshfeld surface analysis data. Thermogravimetric analysis was also performed to find the thermal stability of A and B isomers (Figure 8b). The decomposition temperatures of A and B were found to be 230 and 260 °C, respectively, indicating that B is more stable than A. However, very close values for decomposition and melting temperature for B are further interesting, indicating the temperature sensitiveness of the B isomer. This significant difference in melting point and thermal stability is due to the different type of packing and interactions in the crystal packing of A and B isomers.

2.5. Thin-Film Fabrication from the Precursors of A and B Isomers. Since electrical resistivity is an anisotropic property (i.e., depends on the orientation of the molecule in solid), it is expected that these two isomers will have different responses considering the fact that they have predominantly different molecular packing. It was reported that the physical properties like electrical resistivity and magnetic properties are governed by dimensional control of intermolecular inter-
actions.\(^\text{48}\) The thin films of A and B isomers of 2-aminonaphthalenemaleonitrile can therefore contribute to design various microelectronic, optoelectronic devices.

### 2.6. Two-Probe-Based Current (I)–Voltage (V) Characteristics

The two-probe I–V measurements for both these films were carried out by taking bottom-most contact on fluorine-doped tin oxide (FTO) glass substrates and top contacts made onto the material. Contacts having an area of 1 cm × 1 cm with graphite paste-conducting carbon tape were used. Figure 9 shows the two-probe I–V plots for two different films, which show the typical weak diode nature between FTO and A/B-isomers.

![Figure 9. Two-probe dark and light I–V characteristic of A/B-isomers/FTO films with experimental setup.](image)

The contacts were therefore made by the spring action of the four probes (see inset of Figure 10).

![Figure 10. Four-probe I–V measurement with experimental setup.](image)

The four-probe technique (DFP-RM, SES Instruments, India) was utilized for resistivity measurement of two different films. About 0.2 cm spacing was kept between these adjacent probes. Two probes are used to apply current across the samples, while voltage changes with respect to current have been noted through the other two probes in the four-probe setup. A linear relationship between current and voltage for the fabricated films of A and B isomers is found to be observed and is shown in Figure 10.

The deposited films of A or B isomers have thickness much lesser than 0.25 mm, and the correction factor is applied to obtain exact values of resistivity, which are found to be 1.2048 × 10\(^6\) and 1.4710 × 10\(^6\) Ω cm for ρ\(_A\) and ρ\(_B\) films, respectively. Results of a comparative study of the electrical and other physical parameters of the two isomers are indicated in Table 4.

| compound | A (α-isomer) | B (β-isomer) |
|----------|--------------|--------------|
| empirical formula | \(\text{C}_{30}\text{H}_{20}\text{N}_8\) | \(\text{C}_{30}\text{H}_{20}\text{N}_8\) |
| crystal system | monoclinic | triclinic |
| \(D_\text{calc}\) | 1.291 g/cm\(^3\) | 1.278 g/cm\(^3\) |
| film thickness | \(2.685 \times 10^{-5}\) cm | \(3.129 \times 10^{-5}\) cm |
| resistivity | \(1.2048 \times 10^6\) Ω cm | \(1.4710 \times 10^6\) Ω cm |
| diode nature | weak | strong |

The lower electrical resistivity or the higher conductance associated with the stability of compound can be explained in relation to the melting temperature. Therefore, we can clearly say that crystal packing is of great importance and profoundly affects the electrical properties like resistivity or conductivity.

### 3. CONCLUSIONS

We present here a strategy to realize a high degree of control over molecular packing using peri-interaction-sensitive positional isomers. Just by changing the position of a functional group from \(\alpha\) to \(\beta\) position on naphthalene ring, one could alter the molecular packing array from herringbone packing (HP) to bricklayer packing (BP). This is attributed to the peri-interaction which distorts the \(\alpha\)-isomer from planarity by about 11.4°, and the absence of peri-interaction is responsible for the planar structure for the \(\beta\)-isomer. Further in-depth studies of intermolecular interactions in these two isomers by combined SCXRD and Hirshfeld surface analysis reveal that C–H···π(Ar) is the primary interaction responsible for HP crystal
packing for A, while π(C≡N)⋯π(Ar) stacking is the dictating interaction in B leading to the bricklayer packing (BP). To the best of our knowledge, we have not come across where such less common weak interactions (i.e., C–H⋯π(Ar) ⇔ π(C≡N)⋯π(Ar)) alter a crystal packing from a fundamentally important packing mode HP to BP or vice versa. Further, these positional isomers are found to have drastically different thermophysicalchemical and electrical properties, which correlate with the different crystal packing arrangement. A large difference in melting point reveals a significant difference in both the enthalpy and entropy of these two isomers. Furthermore, thin film of these isomers shows significantly different electrical conductivity properties; while A shows a weak diode nature, B shows a strong diode nature. The result provided here enhances the understanding toward how the effect of packing pattern can control the thermodynamic and electrical conductivity properties, which leads to the development of compounds with desired characteristics of high-performance application.

4. EXPERIMENTAL SECTION

4.1. Materials and Method. Starting materials such as α-naphthaldehyde, β-naphthaldehyde, and diaminonapthalenonitrile (DAMN) were purchased from Sigma-Aldrich and used as received, while all solvents were of AR grade and procured from either Sigma-Aldrich or TCI. 1H and 13C NMR spectra were recorded on 500 MHz NMR (JEOL-500L) spectrometers, and the spectra are given in SI Figures S1 and S2. Fourier transform infrared spectra were recorded on a PerkinElmer Spectrum-2 FTIR spectrometer using KBr pellets in the 400−4000 cm−1 region, and the spectra are given in SI Figure S3. Thermogravimetric analysis (TGA) experiments were done using a PerkinElmer STA 6000 instrument under the nitrogen atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) experiments were performed on Mettler STAR SW10.00 instrument under the nitrogen atmosphere. The instrument was calibrated with indium before measurement of samples. The samples were heated to 100 °C first at a rate of 10 °C/min to remove moisture, then cooled to room temperature, and again heated below its decomposition temperature at a heating rate of 10 °C/min.

4.2. Electrical Conductivity Measurements. The spin-coating method has been used for the preparation of thin films, which has several merits such as convenience, low-cost equipment, and faster operating system. The precursor’s sols were stirred for 30 min at room temperature with a constant speed without any agitation. The fluoride-doped tin oxide (FTO) glass substrates were cleaned in the usual manner for the deposition of thin films by a spin coater.49 It is found to be a suitable and convenient machine for obtaining uniform films on the glass substrate surface. For conductivity measurement, the two different films of A and B isomers were fabricated onto FTO glass substrate having an area of 3.5 cm × 1.5 cm (l × b) by using sol precursors prepared with acetonitrile in the ratio of 1:10, at 2000 rpm for 2 min using a rotating vacuum pump. About 10 drops of ligand sols in acetonitrile were taken carefully with the help of a 0.5 mL syringe onto the center of a stationary conducting glass substrate. This glass substrate was held firmly in position by an ambient pressure. Due to the influence of the centrifugal force, drops spread out across the substrate and the corresponding solvents from the solution evaporated out to have a smooth continuous film. The resulting films were annealed at ~65 °C in air for 25 min to remove the residual solvent, if any. These processes were successively done to obtain uniform and pinhole-free films on the FTO glass substrate (sheet resistance ~ 10 Ω/sq). The film thickness was determined by the trivial gravimetric method using the formula t = (W2 − W1)/Ad, where, “t” is the thickness of the film, ‘A’ is the area covered by the film, ‘d’ is the density of ligand isomers (dA = 1.291 gcm−3, dB = 1.278 gcm−3), and W1 and W2 are the weight of the FTO glass substrate before and after deposition, respectively.50 The coated films (tA = 2.685 × 10−3 and tB = 3.129 × 10−3 cm) of different ligand isomers were studied for resistivity as well as semiconducting behavior of electrical measurement done by semiconducting characterization unit (KEITHLEY-4200 SCS). Therefore, the prepared thin films have two different structures: A isomer sol/FTO and B isomer sol/FTO were subjected to studies of diode characteristics in the dark and light by the current−voltage measurement.

4.3. Synthesis of Compounds (A and B). A and B were synthesized by dissolving DAMN (1 mmol, 108 mg) in ethanol, and then α-naphthaldehyde (1 mmol, 156.18 mg) or β-naphthaldehyde (1 mmol, 156.18 mg) was added and stirred (Scheme 1). The reaction mixture was then refluxed for 10 h for A and stirred at room temperature for 12 h for B, following a clear brown-colored solution in A (80% yield) while the precipitate form in B (82% yield). Progress of the reaction was monitored by TLC. The reaction mixture was filtered and kept for crystallization (in ethanolic solution) by a slow evaporation method at low temperature around 10−15 °C in a fridge. Brown-colored crystals for both the isomers were obtained, suitable for SCXRD within a week. The detailed characterization data and CHN analysis reports are provided in SI Table S1. To study the crystallinity and pure phase, powder X-ray diffraction (PXRD) of the two compounds was also performed, and the results are presented in SI Figure S4.

4.4. Crystallographic Data Collections and Refinements. Crystal data for A were collected on an Oxford Diffraction XCALIBUR EoS diffractometer using graphite monochromatized Mo Kα radiation at 296 K (λ = 0.71073 Å), while those for the B isomer were collected on a Bruker Kappa APEX II diffractometer having the same source of radiation at 200 K. The PXRD data were collected on a Bruker D8-ADVANCE diffractometer equipped with Cu Kα1 (λ = 1.5406 Å; 1600 W, 40 kV, 40 mA) at a scan speed of 5° min−1. The structures were solved by direct methods and refined by fullmatrix least squares on F2 using SHELX-2016.50 While nonhydrogen atoms were refined with anisotropic thermal parameters, all of the hydrogen atoms were geometrically fixed
and were allowed to refine using a riding model. The refinements were converged to final values of $R_1$ and $wR_2^2$ 0.1056, 0.0987 and 0.1692, 0.2861, respectively, for A and B isomer. The reason for relatively higher $wR_2^2$ for B was found to be the presence of twinning in crystal system, and also higher angle reflections were found to be weak. The crystal data of B belong to a nonmerohedrally twinned crystal. The twin law $[-1 0 0, 0.463 1 0, 0 0 -1]$ was identified by the "TwinRotMat" program and is used for refinement of HKL5 reflection format, which was used for refinement. The percentage of twin is given by a batch scale factor (BASF) of 0.17. This might be a reason for the higher value of $wR_2^2$. The small residual peaks in the electron density map are due to outliers as a result of twinning, which are omitted from refinement. The final refinement of these data gives a negligible residual peak. Also we have tried a disorder model but did not provide better result. Relevant crystal data are presented in Table 2, whereas other selected crystallographic data like bond distance and bond angles are given in SI (Tables S2 and S3). Drawings were made using ORTEP-III, OLEX2.

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