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1. Introduction

Over the last few decades, organic thin-film transistors (OTFTs) have attracted widespread interest and huge progress has been achieved on their application in versatile electronic devices.¹ Accordingly, significant efforts have been targeted toward the development of a wide variety of organics/polymers for the ultimate goal of generating inexpensive organic devices.² In organic small-molecule-based TFTs, polycyclic aromatic compounds are preferentially used as the semiconducting materials;3 e.g., acene derivatives4 and diketopyrrolopyrrole (DPP) derivatives⁵ as the p-channel components and fullerene derivatives⁶ and rylene diimide derivatives⁷ as the n-channel semiconductors. Recently, we demonstrated that easily accessible, small molecular DPPs could be used for p-channel OTFTs.8 In contrast to p-channel small molecules, where a large variety of chemical structures have been presented, there remains a need to explore easily derivable, inexpensive small molecule-based n-channel semiconductors.

n-Type small aromatic core diimides flanked with electron donating thienylethyl moieties and electrical responses in organic devices[†]

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We report n-type small aromatic core diimide derivatives functionalized with electron donating heteroaromatic ring bearing moieties, *N*,*N'*-bis[2-(2-thienyl)ethyl]-benzene-1,2,4,5-tetracarboxylic diimide and *N*,*N'*-bis[2-(2-thienyl)ethyl]-napthalene-1,4,5,8-tetracarboxylic diimide. The synthesis, and characterization of the newly synthesized diimide based organic semiconductors and electrical responses in electronic devices are investigated in detail. The structure, and electrochemical and optical properties of the diimide derivatives were determined using ¹H NMR, ¹³C NMR, mass spectrometry, UV-visible spectroscopy and cyclic voltammetry. The electron density distribution of the materials was also studied using density functional theory calculations to relate the structure and device's characteristics. The materials were employed for the preparation of organic thin-film transistors with inorganic and polymeric gate dielectrics at various substrate temperatures, and the device's electrical characteristics have been analyzed in detail. We also further explore its applicability in advanced electronic devices by fabricating a resistance load-type organic inverter, and the dynamic response behavior was investigated.

Rylene diimide derivatives are well-known aromatic electrontransport materials that are used in a variety of organic electronic devices because of their excellent thermal and environmental stability.9 In particular, pyromellitic diimide (PMDI), naphthalene diimide (NDI) and perylene diimide (PDI) are the most extensively studied organic semiconductor (OSC) materials for n-channel OTFTs owing to their relatively high electron affinities and the versatile tunability of their optical and electrochemical properties via parent core extension or functionalization.¹⁰ Unlike the core alteration, chemical structure engineering through a functionalization at the N-position of imide is a simple one-pot synthetic approach to a variety of aromatic derivatives for n-channel OTFTs.11 The relatively facile synthesis of pyromellitic diimide (PMDI) and NDI derivatives in comparison to that of PDI derivatives enables more efficient large-scale production. Hence, a large number of N-functionalized PMDI and NDI derivatives with various side chains have been reported as a channel layer material for OTFTs.9^a A series of NDI derivatives with alkylthienyl moieties have been reported and their spectroscopic, electrochemical, electronic, and structural properties were investigated in detail.12 The Asha's group also prepared a series of amidefunctionalized NDIs for improved charge-carrier mobility, and described the effect of hydrogen bonding on the self-assembly of NDIs.13 Lee et al. investigated two n-type soluble NDI derivatives with phenylmethyl and (trifluoromethyl)benzyl groups in the N-position of NDI.¹⁴ An alkylphenyl functionalized NDI¹⁵ and a 2-phenylethyl functionalized PDI derivative (BPE-PTCDI)¹⁶

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for a high performance n-channel OTFTs have been reported by Katz's and Bao's group, respectively. It is also reported that the aromatic/heteroaromatic ring bearing side chains in the rylene diimide derivatives have a potential role in controlling molecular packing and optoelectronic properties.¹⁷

Here, we report the synthesis and characteristics of new small aromatic core diimide derivatives which have different core size and are functionalized with heteroaromatic ring (thienylethyl group) at the *N*-position of the core. We also report the electrical characteristics of the aromatic core diimide derivatives based organic electronic devices with inorganic/ organic dielectric fabricated at different substrate temperature.

2. Experimental

Details of the materials and instruments used in the synthesis and characterization are described in the Materials and instruments section of the ESI.[†]

2.1 Synthesis of *N*,*N*[']-bis[2-(2-thienyl)ethyl]-benzene-1,2,4,5-tetracarboxylic diimide (3a)

Benzene-1,2,4,5-tetracarboxylic dianhydride (500 mg, 2.29 mmol) was dissolved in dimethylformamide (DMF; 10 mL). 2-Thiophene ethylamine (640.8 mg, 5.04 mmol) was added and the resultant mixture was stirred at 110 °C overnight under a nitrogen atmosphere. After cooling to ambient temperature, the mixture was filtered and washed with methanol. A white flake like solid (920 mg) was obtained with a yield of 92%. The material was purified by vacuum sublimation. ¹H NMR (CDCl₃, 400 MHz): δ = 8.25 (s, 2H), 7.15 (m, 2H), 6.91 (d, 2H), 6.86 (d, 2H), 4.04 (t, 4H), 3.28 (t, 4H). ¹³C (CDCl₃, 100 MHz): δ = 165.91, 139.39, 137.13, 127.08, 125.83, 124.40, 118.37, 39.99, 28.31. Mp: 276.4 °C.

2.2 Synthesis of *N*,*N*[']-bis[2-(2-thienyl)ethyl]-naphthalene-1,4,5,8-tetracarboxylic diimide (3b)

1,4,5,8-Naphthalene-1,4,5,8-tetracarboxylic dianhydride (200 mg, 0.745 mmol) was dissolved in dimethylformamide (DMF; 6 mL). 2-Thiophene ethylamine (208.7 mg, 1.64 mmol) was added and the resultant mixture was stirred at 110 °C overnight under a nitrogen atmosphere. After cooling to ambient temperature, the mixture was filtered and washed with methanol. A yellowish brown solid (300 mg) was obtained with a yield of 83%. The material was purified by vacuum sublimation. Mp: 277.1 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.76$ (s, 4H), 7.14–6.92 (m, 6H), 4.48 (t, 4H), 3.29 (t, 4H). ¹³C (CDCl₃, 100 MHz): $\delta = 162.67$, 140.16, 131.08, 127.08, 127.01, 126.59, 125.71, 124.13, 42.05, 28.11. HRMS [M + H]⁺, *m*/z calcd for C₂₆H₁₈N₂O₄S₂: 487.562, found: 487.3613.

2.3 Thin-film transistor fabrication and characterization

Three types of gate dielectric were used for the fabrication of OTFTs with the synthesized aromatic diimide small molecules: (i) p-doped Si/bare SiO₂ (300 nm) (capacitance (C_i) = 100 pF mm⁻²), (ii) p-doped Si/OTS-treated SiO₂ (300 nm) (C_i = 110 pF mm⁻²), and (iii) ITO/cross-linked poly(4-vinylphenol) (CL-PVP) (C_i = 61.04 pF mm⁻²). A metal-insulator-metal (MIM, active area of 0.203 cm²) device was used to measure the capacitance

of the gate dielectrics. The Si/SiO2 and glass/ITO substrates were cleaned as per a previously reported procedure.8 An n-octadecyltrichlorosilane self-assembled monolayer was deposited over Si/SiO₂ by spin-coating (3000 rpm, 10 s) a 0.05 M OTS solution (in toluene) immediately after UV-ozone treatment; the OTStreated substrate was then baked at 80 °C for 3 min. Using our previously reported method, a robust uniform thin-film of cross-linked poly(4-vinylphenol) (CL-PVP) on a glass/ITO substrate was obtained as a gate dielectric.18 The active layer (50 nm) of 3a or 3b was deposited by thermal vacuum evaporation on top of the dielectrics at varied substrate temperatures $(25, 45, \text{and } 60 \degree \text{C})$ at a fixed rate of 0.2 Å s^{-1} . Finally, gold source and drain electrodes (50 nm) were thermally deposited under high vacuum (6 \times 10⁻⁶ Torr) at a rate of 0.3 Å s⁻¹. During Au deposition, a shadow mask was used to define the channel length (L) and width (W) of 50 and 1000 µm, respectively. An HP 4156A semiconductor analyzer was used to determine the electrical characteristics of the OTFTs under vacuum.

2.4 Organic inverter fabrication and characterization

A resistive-load-type inverter was constructed by connecting the **3b** OTFT fabricated at $T_{\rm s}$ of 45 °C with the OTS-treated SiO₂ and an external resistive load (100 M Ω). To characterize the dynamic response of the transistor, a function generator (maximum 60 MHz; Rigol DG4062) was used to supply the input voltage. The output voltage response was detected using a digital oscilloscope (100 MHz; Rigol DS2102). A high-voltage amplifier (1 MHz, 400 Vp-p, Pintek HA-405) was used to amplify the signal and a Keithley 6517A was used as the power supply.

3. Results and discussion

The synthetic schematic (Scheme 1) of thienylethylfunctionalized pyrromelittic (3a) and naphthalene diimides



Scheme 1 Synthesis scheme of new small core aromatic diimides.



Fig. 1 Structures of 4a and 4b, are taken from ref. 19.

(3b) are shown in Fig. 1. The materials were successfully prepared using an amine/DMF/110 $^{\circ}$ C protocol¹⁹ with a high yield (92% for 3a and 83% for 3b). The chemical structures were identified by spectroscopic analysis (ESI, Fig. S1 and S2†) and the corresponding data are provided in the Experimental section.

DFT calculations [B3LYP/6-31G(d,p) level] of the energy levels using SPARTAN10,20 predicted a LUMO energy level of -3.21 eV for 3a and -3.47 eV for 3b in vacuum and their respective HOMO energy levels are at -6.30 and -6.17 eV, respectively. Electron density distribution of the LUMO (a and b) and HOMO (c and d) of 3a and 3b is depicted in Fig. 2. It is found that the lowest unoccupied molecular orbital (LUMO) density is distributed mainly on the core of the molecule and the highest occupied molecular orbital (HOMO) density is localized on thiophene unit (side chain) suggesting that the core of the material is electron accepting in nature. Similar predominant localization of the LUMO and HOMO wave functions on the acceptor and donor units, respectively, has been reported for a set of rylene and related diimide derivatives.^{21,22} The LUMO energy of 3a and 3b was also experimentally calculated by cyclic voltammetry (Instrument section of the ESI for details†), as shown in inset of Fig. 2 (right side) and Fig. S3a,† respectively. The LUMO value of 3a and 3b, calculated by E_{LUMO} $= -[4.8 - E_{1/2,Fc/Fc^{+}} + E_{red,onset}] eV^{23}$ were found to be -3.29 and -3.91 eV, respectively. The onset potential of the first reduction wave of 3a and 3b are -1.13 and -0.51 V (3b), respectively, where $E_{1/2}$ of ferrocene is 0.38 V. The optical properties of 3a and 3b in chloroform were investigated via UV-visible spectroscopy and the corresponding absorption spectra are shown in Fig. S3.[†] The absorption bands for 3a are centered at 320 and 310 nm where as for 3b the peaks are at 362 and 382 nm



Fig. 2 Electron density distribution in (a and b) LUMO and (c and d) HOMO of **3a** and **3b**, respectively. Left inset: the theoretically calculated energy level diagram of synthesized material compared with reported diimides. * These are taken from ref. 19. Right inset: the CV curve of **3b** in DCM (scan rate: 50 mV s⁻¹).

respectively. Optical bandgaps calculated from absorption cut off values are 3.65 and 3.05 eV for **3a** and **3b**, respectively. The thermal properties of the materials were investigated through a thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal decomposition temperatures with a 5% weight loss were calculated to be 328 °C and 395 °C for **3a** and **3b**, respectively (Fig. 3a). Differential scanning calorimetry (DSC) analysis revealed that the materials showed clear exothermic crystallization and endothermic melting temperature at 267 and 277.1 °C for **3b** (Fig. 3b) and at 273 and 276.4 °C for **3a** (inset, Fig. 3b), respectively. These results reveal that their thin-film could be easily prepared through a thermal vacuum evaporation over a broad range of substrate temperatures

without any thermal degradation during the film formation. The OTFTs based on 3b show well-defined n-channel characteristics (discussed in the later part). On the other hand, the device based on 3a showed no such characteristics. It is clearly different observation from other diimide derivatives with pyromellitic diimide core (4a and 4b, Fig. 1) exhibiting n-channel transport behavior.¹⁹ The reported diimides (4a and 4b) have fluorinated side chain that stabilizes the LUMO energy level. However, in our pyromellitic diimide (3a), electron donating thienylethyl group is introduced as a side chain, resulting in the higher LUMO energy level. The higher LUMO level of 3a may increase charge injection barrier (1.99 eV) from Au electrode ($\phi_m = 5.2 \text{ eV}$),²⁴ that is relatively higher than those of 4a (1.74 eV) and 4b (1.66 eV) (See the left inset of Fig. 2). On the other hand, the 3b with an extended diimide core shows lower lying LUMO energy compared to 3a, and the devices based on 3b showed good n-channel OTFT properties. It can be inferred from the above reasons that the electrical characteristics of small aromatic core diimide derivatives could be affected by the core size and the type of introduced side group. The theoretically calculated LUMO energy levels of all the discussed materials are depicted in inset of Fig. 2 (left side). Based on the results, we further investigated in detail the performance of OTFTs with 3b deposited on different gate dielectrics such as OTS-treated SiO₂, and cross-linked poly(4-vinylphenol) at various substrate temperature in order to explore its potential applicability as an organic semiconductor in advanced OTFTs.

It could be inferred from the device results (discussed in the later section) that the electron mobilities of the device are dependent on the type of gate dielectric and T_{s} .^{11b,25,26} Atomic force microscopy (AFM) and X-ray diffraction (XRD) analysis were performed on the 3b thin-film to understand the variation in the performance of the OTFTs with different gate dielectrics and $T_{\rm s}$. Fig. 4a–c show the AFM height profiles of the 3b thinfilm deposited at a T_s of 45 °C onto bare SiO₂, OTS-treated SiO₂, and CL-PVP, respectively, while those on the various gate dielectrics at T_s of 25 and 60 °C are depicted in Fig. S5.† The images reveal that the grain size increases slightly with increasing T_s but retains an almost identical crystal shape. Although there are many reports on the increased charge-carrier mobility with increasing grain size,16c,19,27 our initial studies showed the opposite trend; the mobility decreased with increasing grain size that are also observed by Park group.28 It has been suggested by them that interconnection and improved



Fig. 3 (a) Thermogravimetric analysis (TGA) of synthesized materials and (b) differential scanning calorimetry (DSC) curve of 3a and 3b in nitrogen with a heating and scanning rate of 10 °C min⁻¹, respectively.

contact between grains results in the enhancement of mobility, while the layer with larger voids could reduce the carrier mobility inspite of the formation of large grains. In our study we also observed larger grains of **3b** with bigger voids at higher T_s (60 °C) in the film that may lead the decrease in the hole mobility. The AFM image of the **3b** thin-film on OTS-treated SiO₂ (Fig. 4b) prepared at T_s of 45 °C revealed improved contact between the grains with needle-like crystals, which were not observed on bare SiO₂ and CL-PVP. In addition, the device fabricated with OTS-treated SiO₂ at T_s of 45 °C showed the best device performance. This improvement in electron mobility may also be because of an increase in the crystallinity of the **3b** thin-film, which was evident from the XRD analyses. Fig. 4d shows the XRD patterns of the **3b** thin-films prepared at T_s of 45 °C on bare SiO₂, OTS-treated SiO₂, and CL-PVP. The XRD patterns reveal that the **3b** on OTS-treated SiO₂ gives the highest diffraction intensity, which indicates improved crystallinity. Similar observations were reported by the Bao's group regarding BPE-PTCDI thin films on an OTS-treated SiO₂.^{16c} The XRD patterns of **3b** film (50 nm) on bare SiO₂, CL-PVP and OTStreated SiO₂ substrates at various T_s are also depicted in Fig. S6.† For all samples a diffraction peak at $2\theta = 6.47^{\circ}$ was detected and the corresponding *d*-spacing was calculated to be 1.364 nm using Bragg's equation $[n\lambda = 2d \sin \theta$, where λ is the incident X-ray wavelength ($\lambda = 1.540598$ Å)].

We have investigated the characteristics of the OTFTs with **3b** (naphthalene diimide core) as channel layer material on bare SiO₂, OTS-treated SiO₂, and CL-PVP at different substrate temperatures (T_s) of 25, 45, and 60 °C and a schematic structure of a bottom-gate, top-contact OTFT is shown in Fig. 5a.



Fig. 4 Tapping-mode atomic force microscopy (AFM) images of **3b** thin-film (50 nm) on (a) bare SiO₂, (b) OTS treated SiO₂ and (c) CL-PVP at T_s = 45 °C. (d) Corresponding out-of-plane XRD patterns at the same substrate temperature.



Fig. 5 (a) Schematic diagram of bottom gate, top-contact OTFT devices. Transfer characteristics of OTFTs with **3b** at different substrate temperature (T_s) ($V_{DS} = 80$ V) on various gate dielectrics: (b) bare SiO₂, (c) OTS-treated SiO₂ and (d) cross-linked polymer gate dielectric (CL-PVP).

Fig. S4(a–c)[†] show the representative output characteristics of the OTFTs prepared on bare SiO₂, OTS-treated SiO₂, and CL-PVP, respectively at T_s of 25 °C. The output characteristic curves for all the devices clearly showed typical n-type characteristics. The transfer curves of all the devices fabricated with different gate dielectrics and T_s are shown in Fig. 5b–d, and the device performance parameters are listed in Table 1. Fig. 5b shows the transfer characteristics of the OTFT fabricated on a bare SiO₂ at various T_s . The electron mobility extracted from the saturation regime were 6.2×10^{-4} , 5.5×10^{-4} , and 5.9×10^{-6} cm² V⁻¹ s⁻¹ for the devices prepared at T_s of 25, 45, and 60 °C, respectively. Similarly, OTFT devices based on an OTS-treated SiO₂ (Fig. 5c) at T_s of 25, 45, and 60 °C, exhibited charge carrier motilities of 1.2×10^{-2} , 1.7×10^{-2} , and 3.8×10^{-3} cm² V⁻¹ s⁻¹, respectively. The OTFT devices with an OTS-treated SiO₂ showed much better performance with respect to chargecarrier mobility and $I_{\rm on}/I_{\rm off}$ than that of devices with bare SiO₂. Devices with an OTS-treated SiO₂ exhibit $I_{\rm on}/I_{\rm off}$ values in the range 10^4-10^5 and electron mobilities varying from 10^{-2} to 10^{-3} cm² V⁻¹ s⁻¹, which is almost 100 times higher than that of devices with a bare SiO₂. The enhanced performance may be caused by lower charge-carrier trap density at the interface between the gate dielectric and semiconducting channel. The effect of treatment of the SiO₂ surface with a self-assembled monolayer has been discussed in literature both for p-type²⁹ and n-type^{16c,30} semiconductors. The highest mobility ~0.02 cm² V⁻¹ s⁻¹ was achieved for the device fabricated at a substrate temperature of 45 °C on an OTS-treated SiO₂ gate dielectric. We also have analyzed devices with a polymer gate dielectric, poly(4-vinylphenol) (CL-PVP) (Fig. 5d) fabricated at $T_s = 25$, 45,

| Table 1 Summary of performance of OTFTs with 3b | | | | | |
|---|----------------------|---|------------------------------|------------------|----------------------|
| Gate dielectric | Substrate temp. (°C) | Mobility (cm ² V ⁻¹ s ⁻¹) | $I_{ m on}/I_{ m off}$ ratio | $V_{\rm th}$ (V) | S.S (V dec $^{-1}$) |
| Bare SiO ₂ | 25 | $6.2	imes10^{-4}$ | $3.8	imes10^3$ | 44.8 | 2.4 |
| Bare SiO ₂ | 45 | $5.5	imes10^{-4}$ | $7.5	imes10^{1}$ | 70.7 | 2.5 |
| Bare SiO ₂ | 60 | $5.9	imes10^{-6}$ | $1.6	imes10^1$ | 50.0 | 13.9 |
| OTS-SiO ₂ | 25 | $1.2	imes10^{-2}$ | $1.2	imes 10^5$ | 51.0 | 1.3 |
| OTS-SiO ₂ | 45 | $1.7	imes10^{-2}$ | $3.1	imes10^4$ | 48.2 | 2.1 |
| OTS-SiO ₂ | 60 | $3.8	imes 10^{-3}$ | $2.5	imes10^4$ | 50.1 | 3.4 |
| CL-PVP ^a | 25 | $3.6	imes10^{-4}$ | $5.8	imes10^2$ | 26.7 | 5.6 |
| $CL-PVP^{a}$ | 45 | $1.9	imes 10^{-4}$ | $3.4	imes10^3$ | 26.5 | 5.6 |
| CL-PVP ^a | 60 | 7.6×10^{-5} | $1.2	imes 10^2$ | 28.5 | 15.4 |

^a CL-PVP: cross-linked poly(4-vinylphenol).

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Fig. 6 (a) Schematic diagram of resistance-load type inverter based on **3b** OTFT (OTS treated SiO₂ substrate, $T_s = 45$ °C), (b) dynamic behavior of the corresponding device operated under a supply voltage $V_{DD} = 50$ V, resistor R = 100 M Ω and input voltage pulse = 0.5 Hz.

and 60 °C. The devices showed mobilities of 3.6×10^{-4} , 1.9×10^{-4} , and 7.6×10^{-5} cm² V⁻¹ s⁻¹, respectively, which are comparable or higher than those of bare SiO₂ devices. It indicates that the newly synthesized NDI derivative is potential active candidate for device with inorganic as well as organic gate dielectrics and flexible substrates.

To demonstrate the potential of the synthesized material for application in advanced organic electronics, load-type inverters were fabricated and characterized. The inverter, which is the fundamental logic element in an integrated circuit (IC) that converts low input (logic 0) to high output (logic 1) or vice versa, was constructed using a 3b based OTFT fabricated at $T_{\rm s}$ of 45 °C with an OTS-treated SiO2. A schematic diagram of the resistiveload inverter with an external resistive load (100 M Ω) is shown in Fig. 6a. We measured the dynamic response characteristics of the inverter at frequencies of 1 (Fig. S7a[†]), 0.5 (Fig. 6b), and 0.1 Hz (Fig. S7b[†]), with a fixed $V_{DD} = 50$ V. As shown in Fig. 6b, when a square wave of $V_{\rm IN}$ switching from 0 to 50 V at a fixed frequency, V_{OUT} exhibits a dynamic switching response to V_{IN} with a transient behavior just after the changes in the $V_{\rm IN}$.³¹ However, it does not generate square-like output waves because of a large overlap capacitance,32 which could be avoided by using a high dielectric insulator and/or designing an appropriate device structure. Similar dynamic behavior was reported by Lee et al. in a resistance load-type organic inverter.³³

4. Conclusions

In summary, we adopted the simplest one-pot synthetic procedure to obtain small aromatic core diimide molecules **3a** and **3b**. The best performance was observed from the **3b** device prepared using an OTS-treated SiO₂ substrate. The AFM images and XRD patterns reveal that the morphology and crystalline nature of the **3b** film varies according to the surface properties and substrate temperature during deposition. The highest electron mobility of ~0.02 cm² V⁻¹ s⁻¹ with an I_{on}/I_{off} of 3.14×10^4 was achieved for the **3b** TFT. We also demonstrated decent dynamic inverter action from our **3b**-TFT-based resistive load-type organic inverter. Moreover, the synthesized NDI derivative is compatible with polymer gate dielectric and hence could be used for advanced flexible organic electronic device applications.

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