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New core-expanded naphthalene diimides with different functional groups for air-stable solution-processed organic n-type semiconductors⁺

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Among the reported organic n-type semiconductors, naphthalene diimide (NDI) derivatives have received increasing attention. In this paper, we report four non-symmetric core-expanded NDI derivatives **1–4**. Electrochemical, absorption spectral and theoretical calculation studies show that LUMO energies of **1–4** are lower than that of parent NDI without substitution. OFET devices based on thin films of **1–4** which can be easily solution-processed are fabricated with conventional techniques and they show n-type semiconducting behaviours. Moreover, the performance of OFET devices of **1–4** can be significantly improved by annealing their thin films. OFETs of **3** exhibit electron mobility up to 0.17 cm² V⁻¹ s⁻¹ with high on/off ratio (under ambient conditions) after annealing.

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Introduction

Organic semiconducting materials have received increasing attention in recent years because of their promising applications in various areas such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic light-emitting transistors (OLETs), organic solar cells (OSCs) and sensors.¹ Until now, various organic semiconductors bearing p-type, n-type or ambipolar properties have been disclosed in large numbers.²⁻⁶ For instance, Takimiya et al. described a series of thiophene-containing conjugated molecules for p-type semiconductors which exhibit high hole mobilities and good air stabilities.⁷ However, air-stable n-type organic semiconductors with high electron mobilities are still limited mainly because of the fact that anions of normal conjugated molecules are sensitive to oxygen and water.8 Naturally, the OFETs that can work in air are desirable for future applications. Thus, organic n-type semiconductors which are stable under OFETs working conditions are demanding. It is known that organic conjugated molecules with low LUMO energies are potential candidates for air-stable n-type semiconductors.

1,4,5,8-Naphthalene diimide (NDI) and its derivatives have been intensively investigated for n-type semiconductors.9-11 However, the LUMO energy of NDI itself is around -3.9 eV which is not low enough to enable efficient electron injection from electrodes and increase the air stability of the NDI anion.¹⁰ In order to lower the LUMO energy, various functional groups are connected to an NDI core. Previous studies manifest that the fusion of functional groups at core positions of NDI can efficiently tune the energy levels of front orbitals.¹¹ For instance, Gao et al. introduced two 2-(1,3-dithiol-2-ylidene)malonitrile (electron withdrawing) groups to the NDI core, and the LUMO energy was significantly lowered; the resulting OFETs exhibited electron mobilities up to 1.2 cm² V⁻¹ s⁻¹ in air.¹² An alternating NDI-bithiophene polymer was reported by Facchetti et al., and the top gate bottom contact OFETs showed electron mobilities up to 0.85 cm² V⁻¹ s⁻¹ under ambient conditions.9 Some of us have very recently described NDI derivatives entailing 1,3-dithole-2-thione (-one) moieties, and they showed n-type semiconducting behaviour with electron mobility up to 0.05 cm² V⁻¹ s⁻¹ in air.¹³ Alternatively, incorporation of electron donating groups into an NDI core can change the semiconducting behaviour from n-type to ambipolar and even to p-type. For instance, we described ambipolar and p-type semiconductors based on NDI with tetrathiafulvalene groups.¹⁴ Würthner et al. also reported p-type and ambipoar semiconductors based on core-expanded NDI.15

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In this paper, we report four NDI derivatives **1–4** (Scheme 1) with thiazole, 1,3-dithole-2-thione and 2-(1,3-dithiol-2-ylidene)-malonitrile moieties at the core positions. The molecular design

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 $[\]dagger$ Electronic supplementary information (ESI) available: TGA analysis, cyclic voltammograms, UV-Vis spectra, DFT calculation data, XRD patterns and AFM images of thin films of 2 and 4, transfer and output characteristics for OFET of 2 and 4, ¹H NMR and ¹³C NMR spectra of all new compounds. See DOI: 10.1039/c3nj00050h



Scheme 1 Chemical structures of 1, 2, 3 and 4 and their synthetic approaches

is based on the following considerations: (1) connection of thiazole, 1,3-dithole-2-thione and 2-(1,3-dithiol-2-ylidene)malonitrile moieties to the NDI core can lower the LUMO energy to different extents according to previous reports;^{12–14,16} (2) non-symmetric substitution of these groups to the NDI core may be able to finely tune the LUMO/HOMO energies to match well with the work function of electrodes. Such non-symmetric substitution will allow the introduction of different functional groups to the NDI core, and thus the intermolecular interactions can be further tuned;¹⁷ (3) connection of these groups to the NDI core may be beneficial for extending pi-conjugation and increasing intermolecular interactions; (4) these NDI derivatives are easily accessible as to be discussed below. The results reveal that new NDI derivates 1–4 behave as air-stable n-type semiconductors and electron mobility of OFETs based on 3 can reach 0.17 cm² V⁻¹ s⁻¹ in air.

Results and discussion

Synthesis and characterization

The synthesis of compounds **1–4** started from 2,3,6,7-tetrabromo-NDI (4BrNDI), as depicted in Scheme 1. As reported previously by us, dithiazole-fused NDI derivatives could be

Table 1 Absorption and electrochemical data, HOMO/LUMO energies and band gaps of 1–4

yielded in high yields from 4BrNDI and thioamide derivatives without catalysts.¹⁶ After properly adjusting the reaction conditions, mono-thiazole-fused NDI derivatives **5** and **6** were obtained in more than 70% yield. Further separate reactions of **5** and **6** with (n-Bu₄N)₂Zn(dmit)₂ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) or sodium 2,2-dicyanoethene-1,1-bis(thiolate) led to **1**, **2**, **3** and **4** in 94, 96, 71 and 82% yields, respectively, under mild conditions.

The chemical structures and purities of compounds 1–4 were established and confirmed by spectroscopic data and elemental analysis (see Experimental section). Compounds 1–4 show good solubilities (>10 mg mL⁻¹) in common solvents such as CH₂Cl₂, CHCl₃, THF and dichlorobenzene. Based on TGA analysis (see Fig. S1, ESI[†]) compounds 1 and 2 show an early weight loss at around 270 °C. This may be due to the decomposition or loss of the 1,3-dithiole-2-thione moiety within 1 and 2. However, 3 and 4 are thermally stable below 370 °C.

Cyclic voltammograms of 1–4 were measured and their reduction potentials were determined (see Table 1). As examples, Fig. 1 and S2 (ESI[†]) show cyclic voltammograms of 1–4. 1 and 2 show two quasi-reversible reduction waves, whereas 3 and 4 exhibit three quasi-reduction waves. Based on the respective onset reduction potentials, the respective LUMO energies of 1–4 were estimated to be -4.16, -4.15, -4.35 and -4.35 eV, respectively, by employing the equation:¹⁸ LUMO = $-(E_{\text{ordset}}^{\text{red1}} + 4.41)$ eV. Compared to that of unsubstituted NDI, LUMO energies of 1–4 are obviously lowered. This may be caused by the following effects: (1) elongation of conjugation; and (2) electron-induction due to the functional groups in 1–4. Moreover, 3 and 4 exhibit lower LUMO energies than 1 and 2. This is likely due to the strong electron-withdrawing characteristics of 2-(1,3-dithiol-2-ylidene)malonitrile moieties in 3 and 4.

Fig. 2 shows the absorption spectra of solutions as well as thin films of **1** and **3**. Compared to those of their solutions, the onset absorptions of thin films of **1** and **3** were obviously redshifted. This is probably owing to the intermolecular interactions within thin films of **1** and **3**. The band gaps of **1** and **3** were estimated to be 1.64 and 2.02 eV, respectively, according to the respective onset absorption wavelengths of thin films of **1** and **3**. Therefore, HOMO energies of **1** and **3** were estimated to be -5.80 and -6.37 eV, respectively. Similarly, band gaps of **2** and **4** (based on Fig. S3, ESI[†]) were determined and their HOMO energies were estimated to be -5.77 and -6.38 eV, respectively (see Table 1).

 λ_{\max} (nm)

Compounds	Solution ^a	Film	$E_{1/2}^{\operatorname{red1}b}\left(V\right)$	$E_{1/2}^{\operatorname{red2} b}\left(\mathbf{V}\right)$	$E_{1/2}^{\operatorname{red3} b}\left(V\right)$	LUMO (eV) Exp^{c} (Cal) ^d	HOMO (eV) $\operatorname{Exp}^{c} (\operatorname{Cal})^{d}$	$E_{\rm g}$ (eV) Exp ^c (Cal) ^d
1 2 3 4	456, 546 442, 558 334, 546 322, 532	464, 590 451, 604 356, 578 349, 573	$-0.35 \\ -0.35 \\ -0.14 \\ -0.15$	-0.77 -0.77 -0.30 -0.30	-0.69 -0.69	$\begin{array}{c} -4.16 \ (-3.70) \\ -4.15 \ (-3.71) \\ -4.35 \ (-3.92) \\ -4.35 \ (-3.94) \end{array}$	$\begin{array}{c} -5.80 \ (-5.95) \\ -5.77 \ (-5.97) \\ -6.37 \ (-6.42) \\ -6.38 \ (-6.49) \end{array}$	$\begin{array}{c} 1.64 \ (2.25) \\ 1.62 \ (2.26) \\ 2.02 \ (2.50) \\ 2.03 \ (2.55) \end{array}$

^{*a*} Measured in CH₂Cl₂ solutions of 1–4 (1.0×10^{-5} M). ^{*b*} Measured in CH₂Cl₂ solutions containing *n*-Bu₄NPF₆ (0.1 M) at a scan rate of 100 mV s⁻¹. ^{*c*} Estimated from the following equations: LUMO = -($4.41 + E_{onset}^{red1}$), HOMO = LUMO - E_g (Exp.). ^{*d*} Based on the DFT calculations.



Fig. 1 Cyclic voltammograms of **1** and **3** in CH_2CI_2 (1.0×10^{-3} M) at a scan rate of 100 mV s⁻¹, with Pt as the working and counter electrodes and Ag/AgCl electrode (saturated KCl) as the reference electrode, and *n*-Bu₄NPF₆ (0.1 M) as supporting electrolyte.



Fig. 2 The normalized absorption spectra of the solutions and thin films of $1 \mbox{ and } 3.$

DFT calculations

The chemical structures of 1–4 were investigated with theoretical calculations based on density functional theory (DFT). The alkyl chains in 1–4 were replaced by methyl groups in the calculations. As depicted in Fig. 3 and S4 (ESI[†]), the NDI core and the thiazole ring are coplanar with each other in 1–4. Also, NDI cores are coplanar with 2-(1,3-dithiol-2-ylidene)malonitrile moieties in 3 and 4. The 1,3-dithiole-2-thione unit forms a dihedral angle of about 128° with the NDI core in 1 and 2. HOMO orbitals of 1 and 2 are mainly localized on the 1,3-dithiole-2-thione moiety, while the LUMO orbitals are delocalized throughout the NDI core and the thiazole ring (see Fig. 3 and S4, ESI[†]). The corresponding two sulfur atoms attached to the NDI core also contribute slightly to the respective LUMO orbitals of 3 and 4 are more delocalized. LUMO/HOMO energies of 1, 2, 3 and 4 were calculated to be



Fig. 3 LUMO, HOMO orbitals and structures of compounds 1 (A) and 3 (B) obtained by DFT calculations; the alkyl chains were replaced by methyl groups in the calculations.

-3.70 eV/-5.95 eV, -3.71 eV/-5.97 eV, -3.92 eV/-6.42 eV and -3.94 eV/-6.49 eV, respectively. The solvent effects were not included in the theoretical calculations and thus there were differences between the LUMO/HOMO energies calculated theoretically and those obtained based on the electrochemical and spectroscopic data (see Table 1).^{14,19} But, these results do indicate that the introduction of functional moieties to the NDI core can effectively tune their LUMO/HOMO levels.

OFETs based on thin films of 1-4

Bottom gate bottom contact OFETs (organic field effect transistors) with thin films of 1-4 were fabricated with conventional techniques. All of the thin films show typical n-type semiconducting behaviours in the air, and their performances increase after annealing thin films of 1-4 at different temperatures. Fig. 4 depicts the transfer and output characteristics for OFETs with thin films of 1 and 3 after annealing at 180 °C. The electron mobilities and on/off ratios as well as threshold voltages for OFETs of 1-4 were deduced accordingly and listed in Table 2. The electron mobility of the OFETs with thin films of 1 is 0.019 cm² V⁻¹ s⁻¹ after annealing at 120 $^{\circ}$ C and it increases to 0.034 $\mbox{cm}^2\ \mbox{V}^{-1}\ \mbox{s}^{-1}$ after annealing at 160 $\ ^\circ\mbox{C}.$ After further annealing at 180 °C, μ_e reaches 0.043 cm² V⁻¹ s⁻¹. Simultaneously, the on/off ratio increases, whereas the threshold voltage decreases for OFETs of 1 after annealing (see Table 2). The electron mobility and on/off ratio for OFETs of 3 also increase after annealing the thin films. The maximum mobility reaches 0.069 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for OFETs of 3 after annealing at 180 °C, as listed in Table 2. As shown in Table 2, electron mobilities of OFETs of 2 and 4 increased from 1.8 \times 10⁻² to 3.8 \times $10^{-2}~cm^2~V^{-1}~s^{-1},$ and from 3.8 \times 10^{-3} to 8.0 \times 10^{-2} cm² V⁻¹ s⁻¹, respectively, after temperature annealing from 120 to 180 °C. This significant increase in μ_e for OFETs of 1–4 after annealing is in agreement with the respective morphological changes within their thin films as to be discussed below.



Fig. 4 Transfer and output characteristics for OFETs of **1** (A and B) and **3** (C and D) after annealing at 180 °C; the channel width (*W*) and length (*L*) were 1440 and 50 μ m, respectively.²¹

Furthermore, the electron mobility for OFETs of **3** can be further enhanced after modification of drain-source Au electrodes with pentafluorothiophenol, reaching 0.17 cm² V⁻¹ s⁻¹ after annealing at 180 °C. This is probably due to the modification of interfacial properties and the work function of Au electrodes according to previous reports.²⁰ Note that efforts were also made to increase the electron mobilities of OFETs with **1**, **2** and **4** by modifying the drain-source Au electrodes with pentafluoro-benzenethiol. However, obvious increases of μ_e were not achieved.

Additionally, air-stabilities of OFETs of **1–4** were examined by leaving the devices in air and measuring their performances at different times. As depicted in Fig. S6 (ESI[†]), their electron mobilities decreased by various degrees after the first three

Table 2 The electron mobilities (μ_e), threshold voltages (V_{th}), and on/off ratios ($l_{on/off}$) for bottom contact OFET devices based on thin films of **1–4** after annealing at different temperatures

Compound	$T/^{\circ}\mathbf{C}$	$\mu_{\rm e}{}^a\!/{\rm cm}^2~{\rm V}^{-1}~{\rm s}^{-1}$	$V_{\rm th}/{\rm V}$	I _{on/off}
1	120	0.011 (0.019)	30-36	$6.7 imes10^{5}$ – $1.2 imes10^{6}$
	160	0.026 (0.034)	20-27	$3.5 imes10^6$ – $8.3 imes10^6$
	180	0.035 (0.043)	14 - 18	$5.7 imes10^6$ – $1.0 imes10^7$
2	120	0.0080(0.018)	28-32	$4.2 imes10^4$ – $1.1 imes10^5$
	160	0.018 (0.027)	14-18	$2.4 imes10^4$ – $1.8 imes10^5$
	180	0.027 (0.038)	14-17	$3.6 imes10^4$ – $3.1 imes10^5$
3	120	0.011 (0.018)	12-18	$7.1 imes10^4$ – $1.5 imes10^5$
	160	0.043 (0.051)	9-14	$2.7 imes10^{5}$ – $5.6 imes10^{5}$
	180	0.062 (0.069)	4-6	$5.8 imes10^{5}$ – $1.0 imes10^{6}$
3 (modified Au)	120	0.016 (0.031)	8-15	$1.4 imes10^{5}$ – $3.2 imes10^{5}$
. ,	160	0.073 (0.083)	5-9	$6.4 imes10^{5}$ – $3.6 imes10^{6}$
	180	0.13 (0.17)	-5-0	$1.0 imes10^6$ – $7.6 imes10^6$
4	120	0.0027 (0.0038)	16-18	$8.3 imes10^3$ – $5.6 imes10^4$
	160	0.009 (0.014)	12 - 14	$3.4 imes10^4$ –7. $2 imes10^4$
	180	0.073 (0.080)	0-6	7.4 $ imes$ 10 ⁴ –2.1 $ imes$ 10 ⁵

^{*a*} The mobilities were provided in "average (highest)" form, and the performance data were obtained based on more than 10 different OFETs.

days and then remained almost unaltered after an additional seven days. The electron mobilities and $I_{\rm on/off}$ of OFETs of 3 and 4 were decreased to *ca.* 70% and *ca.* 80% of the respective initial ones after 10 days. However, for OFETs of 1 and 2, their electron mobilities and $I_{\rm on/off}$ decreased more significantly after being left in air for 10 days (see Fig. S6, ESI[†]). Therefore, compounds 3 and 4 show more air-stable semiconducting behavior than 1 and 2. This agrees well with the fact that 3 and 4 exhibit lower LUMO energies than 1 and 2 (see Table 1).

XRD and AFM investigations

In order to understand the enhancement of electron mobility of OFETs of 1-4 after annealing their thin films, XRD and AFM studies were carried out. Thin films of 1-4 exhibit typical lamellar structures because of the presence of integral multiple diffraction peaks as depicted in Fig. 5 and S7 (ESI⁺). As shown in Fig. 5(A), diffraction peaks at 4.0 and 7.9°, corresponding to d-spacings of 2.2 and 1.1 nm, respectively, were detected for the thin film of 1 after annealing at 120 °C. After further annealing at 160 and 180 °C, the intensity of the diffraction peaks increased. Meanwhile, more diffraction peaks at 11.9 and 15.9°, corresponding to d-spacings of 0.74 and 0.56 nm, respectively, emerged. These XRD data clearly manifest that molecules of 1 are more orderly arranged and crystallinity is improved for the thin film of 1 after annealing. This agrees well with the observation that electron mobility of OFETs increases after annealing the thin films of 1 (see Table 2).²² Similarly, intensities of diffraction peaks at 3.8 and 7.4° (corresponding to *d*-spacing of 2.3 nm and 1.2 nm, respectively) were largely enhanced and new peaks at 11.1 and 14.7° (corresponding to *d*-spacings of 0.80 and 0.60 nm, respectively) appeared after annealing of thin films of 3 at 160 and 180 °C. Note that the diffraction patterns of thin films of 1 and 3 after annealing at 160 °C are similar to the respective ones after annealing at 180 °C. The XRD patterns of thin films of 2 and 4



Fig. 5 XRD patterns of thin films of 1 (A) and 3 (B) after annealing at 120, 160 and 180 $^\circ\text{C},$ respectively.

vary in a similar way as for those of 1 and 3 after annealing (see Fig. S7, ESI⁺).

Fig. 6 and S8 (ESI[†]) show AFM images of thin films of **1–4** after annealing at different temperatures. The surface morphologies were changed after annealing. As depicted in Fig. 6, the surface structure of the thin film of **1** became more uniform after annealing at 180 °C. The respective height profiles are displayed in Fig. S9 (ESI[†]). After annealing at 180 °C, the corresponding height variation became less frequent across the thin film of **1**. This surface structural change is consistent with the slight enhancement of mobility after annealing at 180 °C for the thin film of **1** (see Table 2). As shown in Fig. 6, molecular domains within the thin film of **3** emerged and boundary areas decreased after increasing the annealing temperatures from



Fig. 6 AFM images of thin films of 1 (A) and 3 (B) after annealing at 120, 160 and 180 °C, respectively.

120 to 160 and 180 °C. Furthermore, as depicted in Fig. S9 (ESI[†]), the corresponding height variation for the thin film of **3** became less obvious after annealing at 160 and 180 °C. This indicates the formation of a more continuous and flat thin-film of **3** after annealing at high temperature. Similar morphological changes were also observed for the thin films of **2** and **4** (see Fig. S8, ESI[†]). Such morphological transformation is beneficial for improving the performances of OFETs of **1–4** according to previous studies.^{12–14}

Conclusions

In summary, we describe four non-symmetric core-expanded NDI derivatives 1-4 which can be easily synthesized in high yields. The incorporation of 1,3-dithiole-2-thione-4,5-dithiolate and 2-(1,3-dithiol-2-ylidene) malonitrile moieties into monothiazole-fused NDIs modifies the electronic structures of the NDI core significantly, and LUMO energies of 1-4 are lower than that of NDI which enable them to be used as air-stable n-type semiconductors. OFET devices based on thin films of 1-4 which can be easily solution-processed are fabricated with conventional techniques. Interestingly, the performance of OFET devices of 1-4 can be significantly improved by annealing their thin films at high temperatures. This is likely due to the intermolecular rearrangements in thin films of 1-4 based on the XRD and AFM studies. OFETs of 3 exhibit electron mobility up to 0.17 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ with a high on/off ratio (under ambient conditions) after annealing. These results and others clearly indicate that it is possible to generate new air-stable and solution-processed n-type semiconductors by appropriate chemical modifications of NDI, and further studies using thiazole-fused NDI as building blocks are in progress.

Experimental

General

All chemicals were purchased from Alfa Aesar and Sigma-Aldrich, and used as received. Solvents and other common reagents were obtained from Beijing Chemical Co. 4BrNDI, $(n-Bu_4N)_2Zn(dmit)_2$ and sodium 2,2-dicyanoethene-1,1-bis(thiolate) were synthesized according to the literature.^{12,23}

Melting points were measured with Büchi B540. ¹H NMR and ¹³C NMR spectra were recorded on Bruker ADVANCE III 400 MHz and Bruker ADVANCE III 600 MHz spectrometers. MALDI-TOF MS spectra were recorded with a BEFLEX III spectrometer. Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. TGA (SHIMADZU DTG-60) measurements were performed under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Solution and thin films absorption spectra were measured with a JASCO V-570 UV-Vis spectrophotometer. Cyclic voltammetric measurements were carried out in a standard three-electrode cell using a Pt working electrode, a Pt counter electrode and a Ag/AgCl (saturated KCl) reference electrode on a computer-controlled CHI660C instrument. The scan rate was 100 mV s⁻¹, and n-Bu₄NPF₆ (0.1 M) was used as the supporting electrolyte. Paper

X-Ray diffraction (XRD) measurements were carried out in the reflection mode at room temperature, using a 2 kW Rigaku X-ray diffraction system. The thin film surfaces were examined by tapping-mode AFM using a Digital Instruments Nanoscope V atomic force microscope in ambient air conditions in the dark. AFM samples and microscopic images were identical to those used in organic filed effect transistors. The molecular structures of the compounds were calculated with the DFT method at B3LYP/6-31G (d, p) level. All calculations were performed with the Gaussian 09 program.

Fabrication of OFET devices

Bottom gate bottom contact OFETs were fabricated with conventional techniques. Briefly, a heavily doped n-type Si wafer and a layer of dry oxidized SiO₂ (300 nm, with roughness lower than 0.1 nm and capacitance of 11 nF cm⁻²) were used as a gate electrode and gate dielectric layer, respectively. The drain-source (D-S) gold contacts were fabricated by photo-lithography. The channel length and width are 50 and 1440 μ m, respectively. The substrates were cleaned in water, deionized water, alcohol, and rinsed in acetone. Then, the surface was modified with *n*-octadecyltrichlorosilane (OTS). The Au electrodes were modified by immersing the OFETs in 0.1% (volume fraction) ethanol solution of pentafluorothiophenol. Compounds 1–4 were dissolved in CHCl₃ (about 10 mg mL⁻¹) and spin-coated on the above substrates at 2000 rpm. The annealing processes were carried in vacuum conditions for 1.0 h at each temperature.

Field-effect characteristics of the devices were determined in air by using a Keithley 4200 SCS semiconductor parameter analyzer. The field-effect mobility of electrons (μ_e) was calculated by fitting a straight line to the plot of the square root of $I_{\rm DS}$ vs. $V_{\rm G}$ (saturation region), according to the expression $I_{\rm DS} =$ $(W/2L)\mu_{\rm e}C_i(V_{\rm G} - V_{\rm TH})^2$.

Synthesis and characterization

Synthesis of 5. Under N₂ atmosphere, a mixture of 4BrNDI (457 mg, 0.4 mmol) and thiophene-2-carbothioamide (57 mg, 0.4 mmol) in EtOH (50 mL) was refluxed for 8 h. Then the mixture was filtrated after cooling to room temperature. The residue was subjected to column chromatography with petroleum ether (60 °C–90 °C)/CH₂Cl₂ (1:1, v/v) as eluent to give 5 as a red solid (342 mg) in 76% yield (based on 4BrNDI). M.p. 161.2–162.4 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.00 (br, 1H), 7.81 (d, 1H), 7.29 (br, 1H), 4.22 (d, 4H), 2.04 (br, 2H), 1.36–1.23 (m, 64H), 0.86-0.84 (m, 12H). 13 C NMR (100 MHz, CDCl₃) δ 173.09, 161.83, 161.11, 160.67, 159.96, 155.07, 142.39, 136.52, 135.03, 134.80, 134.16, 132.61, 129.17, 126.72, 126.63, 124.56, 124.00, 117.50, 115.67, 46.02, 45.84, 36.52, 36.35, 31.92, 31.65, 31.58, 30.16, 29.66, 29.36, 26.42, 26.33, 22.69, 14.12. MALDI-TOF: 1121.6 (M⁺); elemental analysis: calcd for $C_{59}H_{85}Br_2N_3O_4S_2$: C, 63.03; H, 7.62; N, 3.74; S, 5.70; found: C, 63.13; H, 7.64; N, 3.76; S, 5.68.

Synthesis of 6. Compound 6 was prepared similarly with 4BrNDI and benzothioamide. A yellow solid was obtained after purification in 83% yield (based on 4BrNDI). M.p. 154.4–155.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, 2H), 7.64-7.58 (m, 3H),

4.28 (d, 4H), 2.09 (br, 2H), 1.34–1.22 (m, 64H), 0.85 (br, 12H). 13 C NMR (100 MHz, CDCl₃) δ 180.36, 161.80, 161.13, 160.71, 160.13, 155.15, 142.30, 135.36, 134.95, 133.59, 132.35, 129.45, 129.03, 126.80, 126.51, 124.67, 124.05, 117.85, 116.33, 46.00, 45.89, 36.52, 36.41, 31.92, 31.66, 31.60, 30.11, 29.65, 29.36, 26.43, 26.33, 22.68, 14.11. MALDI-TOF: 1115.7 (M⁺); elemental analysis: calcd for C₆₁H₈₇Br₂N₃O₄S: C, 65.52; H, 7.84; N, 3.76; S, 2.87; found: C, 65.83; H, 7.80; N, 3.74; S, 2.82.

Synthesis of 1. To the solution of compound 5 (112 mg, 0.10 mmol) in 50 mL of THF was added (*n*-Bu₄N)₂Zn(dmit)₂ (104 mg, 0.11 mmol). The reaction mixture was stirred at room temperature for 1.0 h and then concentrated by rotary evaporation. The residue was subjected to column chromatography with petroleum ether (60–90 $^{\circ}$ C)/CH₂Cl₂ (1:1, v/v) as eluent to give 1 as a dark green solid (109 mg) in 94% yield. M.p. 240.0-241.2 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.90 (br, 1H), 7.75 (d, 1H), 7.22 (br, 1H), 4.23-4.20 (m, 4H), 2.05 (br,2H), 1.36-1.24 (m, 64H), 0.85–0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 210.30, 172.69, 162.68, 162.52, 161.77, 159.83, 154.81, 142.74, 142.44, 141.94, 136.38, 134.29, 132.61, 130.45, 129.74, 129.18, 125.39, 123.80, 122.56, 121.96, 116.96, 114.74, 45.77, 45.61, 36.61, 36.37, 31.93, 31.56, 30.19, 29.69, 29.39, 26.35, 26.28, 22.70, 14.13. MALDI-TOF: 1159.8 (M⁺); elemental analysis: calcd for C₆₂H₈₅N₃O₄S₇: C, 64.15; H, 7.38; N, 3.62; S, 19.34; found: C, 64.12; H, 7.39; N, 3.68; S, 19.31.

Synthesis of 2. Compound **2** was prepared similarly with compound **6** and $(n-\text{Bu}_4\text{N})_2\text{Zn}(\text{dmit})_2$. A solid was obtained after purification in 96% yield. M.p. 211.4–212.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, 2H), 7.62–7.57 (m, 3H), 4.27 (m, 4H), 2.12–2.09 (br, 2H), 1.40–1.23 (m, 64H), 0.86–0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 210.24, 179.93, 162.69, 162.55, 161.73, 159.98, 154.85, 143.08, 142.55, 141.82, 133.61, 132.06, 130.35, 129.71, 129.41, 128.95, 125.27, 123.81, 122.62, 121.99, 117.31, 115.35, 45.75, 45.68, 36.62, 36.43, 31.93, 31.60, 30.20, 29.68, 29.38, 26.37, 26.29, 22.69, 14.12. MALDI-TOF: 1154.0 (M⁺); elemental analysis: calcd for C₆₄H₈₇N₃O₄S₆: C, 66.57; H, 7.59; N, 3.64; S, 16.66; found: C, 66.42; H, 7.66; N, 3.61; S, 16.43.

Synthesis of 3. To the solution of compound 5 (112 mg, 0.10 mmol) in 50 mL of THF was added sodium 2,2-dicyanoethene-1,1-bis(thiolate) (20.5 mg, 0.11 mmol). The reaction mixture was stirred at room temperature for 1.0 h and then concentrated by rotary evaporation. The residue was subjected to column chromatography with petroleum ether (60-90 °C)/ CH_2Cl_2 (2:3, v/v) as eluent to give 3 as a dark red solid (78 mg) in 71% yield. M.p. 271.6–272.4 °C. ¹H NMR (400 MHz, CD_2Cl_2) δ 7.90-7.88 (m, 2H), 7.33 (br, 1H), 4.28-4.23 (m,4H), 2.09 (br, 2H), 1.41-1.23 (m, 64H), 0.85-0.84 (m, 12H). ¹³C NMR (100 MHz, $\mathrm{CDCl}_3)\,\delta$ 183.85, 172.08, 162.63, 162.55, 161.73, 159.19, 154.71, 144.18, 143.82, 141.70, 136.24, 135.39, 133.08, 129.67, 125.09, 122.54, 118.68, 117.52, 117.11, 114.19, 111.95, 111.89, 69.74, 46.23, 45.83, 36.71, 36.32, 31.92, 31.60, 31.54, 30.19, 29.68, 29.38, 26.41, 22.69, 14.11. MALDI-TOF: 1103.2 (M⁺); elemental analysis: calcd for C₆₃H₈₅N₅O₄S₄: C, 68.50; H, 7.76; N, 6.34; S, 11.61; found: C, 68.43; H, 7.81; N, 6.35; S, 11.56.

Synthesis of 4. Compound 4 was prepared similarly with compound 6 and sodium 2,2-dicyanoethene-1,1-bis(thiolate).

A red solid was obtained after purification in 82% yield. M.p. 267.3–268.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, 2H), 7.74–7.72 (m, 1H), 7.66–7.64 (m, 2H), 4.29 (br, 4H), 2.10 (br, 2H), 1.38–1.22 (m, 64H), 0.85 (br, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 183.56, 179.15, 162.66, 162.55, 161.65, 159.32, 154.51, 144.31, 144.16, 141.18, 134.23, 131.45, 130.02, 128.84, 124.86, 122.55, 118.70, 117.51, 117.38, 114.73, 111.81, 69.98, 46.21, 45.86, 36.73, 36.37, 31.92, 31.64, 31.57, 30.20, 29.67, 29.38, 26.41, 22.68, 14.11. MALDI-TOF: 1097.3 (M⁺); elemental analysis: calcd for C₆₅H₈₇N₅O₄S₃: C, 71.06; H, 7.98; N, 6.37; S, 8.76; found: C, 70.45; H, 7.93; N, 6.24; S, 8.49.

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