FULL PAPER

## Solution-Processable n-Type Semiconductors Based on Unsymmetrical Naphthalene Imides: Synthesis, Characterization, and Applications in Field-Effect Transistors

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Abstract: A series of unsymmetrical naphthalene imide derivatives (1–5) with high electron affinity was synthesized and used in n-channel organic field-effect transistors (OFETs). They have very good solubility in common organic solvents and good thermal stability up to 320 °C. Their photophysical, electrochemical, and thermal properties were investigated in detail. They showed low-lying LUMO energy levels from -3.90 to -4.15 eV owing to a strong electron-withdrawing character. Solution-processed thin-film OFETs based on **1–4** were measured in

**Keywords:** electrochemistry • naphthalene imides • photophysics • semiconductors • thin films both  $N_2$  and air. They all showed ntype FET behavior. The liquid-crystalline compounds **1a**, **1b**, and **3** showed good performance owing to the selfhealing properties of the film in the liquid-crystal phase. Compound **3** has an electron mobility of up to  $0.016 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and current on/off ratios of  $10^4$ - $10^5$ .

## Introduction

Organic semiconductors are of great importance and interest from the viewpoints of their fundamental optoelectronic properties and potential applications, such as for organic field-effect transistors (OFETs).<sup>[1-9]</sup> After large success with hole-transporting (p-type) organic semiconductors,<sup>[10–13]</sup> recently there has been increasing attention on the development of high-performance electron-transporting (n-type) semiconductors, which are desirable for the fabrication of p-n junction diodes, bipolar transistors, and complementary integrated circuits.<sup>[14-19]</sup> Naphthalene diimide (NDI) is a promising building block, which has been widely employed to construct n-type semiconductors with high performance and good air stability. Based on core-expansion or core-substitution strategies,<sup>[20-27]</sup> considerable NDI derivatives with symmetrical structures have been designed and synthesized for n-channel OFETs. Some of them showed high electron mobility. Nevertheless, unsymmetrical naphthalene diimide derivatives have rarely been synthesized and used for nchannel OFETs.<sup>[28-30]</sup> A series of n-type semiconductors, 1,8naphthoylene(trifluoromethylbenzimidazole)-4,5-dicarboxylic acid imide (NTFBII) derivatives, were reported by Zhang et al., and they exhibited electron mobility up to 0.08 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> by means of vacuum deposition.<sup>[28]</sup> Marks

 [a] J. Shao, J. Chang, Prof. C. Chi Department of Chemistry National University of Singapore 3 Science Drive 3, 117543 (Singapore) Fax: (+65)6779-1691 E-mail: chmcc@nus.edu.sg et al. reported a series of unsymmetrical naphthalene imide derivative, naphthaleneamidinemonoimide-fused oligothiophenes, which showed electron mobility up to  $0.35 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  based on vapor-deposited thin films. However, the solution-processed films gave electron mobility of only  $4 \times 10^{-5}$  to  $3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  under vacuum.<sup>[30]</sup> When the length of the electron-donating oligothiophene fragment increases, the majority-carrier charge transport can be switched from n-type to ambipolar behavior.<sup>[29]</sup>

For large-scale fabrication of low-cost devices, solutionbased film-deposition processes with high charge-carrier mobility are highly desirable.<sup>[31-33]</sup> Herein, we report the synthesis of a family of unsymmetrical naphthalene imide derivatives 1a, 1b, and 2-5 with high electron affinity, and their applications in solution-processed n-channel OFETs. The unsymmetrical naphthalene imide derivatives were prepared here owing to the following reasons: 1) Based on previous reports,<sup>[34,35]</sup> some unsymmetrical molecules showed higher or comparable charge mobilities compared to the corresponding symmetric analogues. 2) Easier synthesis procedures compared with the symmetrical NDI derivatives. Only reflux in acetic acid (HOAc) is required in the last step; the palladium-catalyzed reaction is not necessary. 3) The formed structure has an electron-deficient imine (-N=) moiety, which will result in a lower LUMO energy level. 4) Compared to previous work,<sup>[28-30]</sup> one imide group in these unsymmetric naphthalene imides was annulated with benzoimidazole or an imidazole unit carrying various electronwithdrawing substituents (e.g., imide, cyano, and nitro groups). Thus these new molecules are expected to show extended  $\pi$  conjugation and high electron affinity with tunable LUMO energy levels, which are essential for air-stable nchannel OFETs. Their electronic, photophysical properties,

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thermal behavior, molecular packing, and OFET device performance are studied in this paper.



## **Results and Discussion**

## Synthesis

The synthesis of these electron-deficient organic semiconductors is shown in Scheme 1. The key reaction is the condensation between the naphthalene monoanhydride 6 and different diamines (7a, 7b, 9, 11–13). Naphthalene monoan-



Scheme 1. Synthetic route to 1a, 1b, and 2-5.

hydride 6 and diamines 7a, 7b, and 13 were prepared according to reported literature procedures.<sup>[31-33]</sup> To synthesize 4,5-diaminophthalonitrile (9), NaBH<sub>4</sub> was first employed to reduce benzothiadiazole-4,7-dicarbonitrile (8),<sup>[32]</sup> however, the yield was only 12%. Later Fe powder was applied to reduce 8 in acetic acid at reflux,<sup>[32]</sup> and 9 was obtained in 80% yield. Similarly, 2,3-diaminoterephthalonitrile (11) was prepared from 10 under the same conditions in 85% yield.<sup>[36]</sup> The naphthalene imide derivatives 1a, 1b, and 2–5 were then prepared by condensation between 6 and diamines 7a, 7b, 9, and 11–13, respectively, in 81–88% yields. Compounds 1a, 1b, and 2–5 showed good solubility in normal organic solvents such as dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and THF, which allows us to perform various characterizations in solution, and makes it possible to fabricate OFET

devices by convenient solution-processing techniques. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry (HRMS (EI) and MALDI-TOF MS), and elemental analysis were used to identify the chemical structure and purity of all the new compounds (see the Experimental Section).

### **Photophysical Properties**

The UV-visible absorption and photoluminescence (PL) spectra of compounds **1a**,**b** and **2–5** were recorded in chloroform and as solid films (Figure 1, Table 1, and the Support-



Figure 1. a) Absorption spectra  $(c=1\times10^{-5} \text{ M})$  and b) normalized emission spectra  $(c=1\times10^{-6} \text{ M})$  of solutions of **1a**, **1b**, and **2–5** in CHCl<sub>3</sub>. The emission spectra of **1a**, **1b**, and **2–5** were recorded under the excitation wavelength of 432, 432, 416, 416, 416, and 416 nm, respectively.

Table 1. Absorption and PL data for compounds 1a, 1b, and 2-5.

	$\lambda_{abs}^{[a]} [nm]$	$\varepsilon_{max}^{[b]} \left[ M^{-1} cm^{-1} \right]$	$\lambda_{em}^{[c]} [nm]$	QY <sup>[d]</sup> [%]
1a	432	42300	528	65
1b	432	42 000	528	66
2	416	41 000	500	81
3	416	40 500	500	45
4	416	41600	498	42
5	416	41 900	498	41

[a] UV-visible absorption maximum. [b] Molar extinction coefficient at the absorption maximum. [c] Photoluminescence maximum. [d] Fluorescence quantum yields by using fluorescein  $(QY=90\%)^{[37]}$  pH $\approx$ 11, NaOH aqueous solution) as a standard.

ing Information). In solution, for **1a** and **1b**, the alkyl chains had no effect on the spectra profiles, and both showed an absorption maximum  $(\lambda_{abs}^{max})$  at 432 nm and an emission maximum  $(\lambda_{em}^{max})$  at 528 nm. For **2** and **3**, the position of the two cyano groups has little effect on the absorption profiles, with the same  $\lambda_{abs}^{max}$  at 416 nm and  $\lambda_{em}^{max}$  at 500 nm. For **4**, although with one benzene ring less than **2**, it exhibited similar  $\lambda_{abs}^{max}$  at 416 nm and  $\lambda_{em}^{max}$  at 498 nm. For **5**, in which two cyano groups were replaced by two nitro groups relative to **2**, the absorption and emission maxima are almost the same as those of **2**. It is worth noting that all of these compounds show moderate-to-high photoluminescence quantum yields ranging from 41 to 81% in chloroform (Table 1). In the thin-film state, the absorption spectra of these compounds became much broader, and emission spectra are redshifted compared to that in solution. For compound **5** with two nitro groups, no emission was observed. These phenomena are due to the aggregation in the solid state.

### **Electrochemical Properties**

The electrochemical properties of solutions of **1a**, **1b**, and **2–5** in CH<sub>2</sub>Cl<sub>2</sub> were investigated by cyclic voltammetry and differential pulse voltammetry (Figure 2, Table 2). Three quasi-reversible reduction waves were observed for **1a** and **1b**, with the half-wave potential  $(E_{red}^{1/2})$  at -0.95, -1.35, and -2.41 V for **1a** (versus Fc<sup>+</sup>/Fc), and the different alkyl chains showed less effect on the redox behaviors. The LUMO energy level derived from the onset of the reduction



Figure 2. Cyclic voltammograms of **1a**, **1b**, and **2–5** in dry CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte, a gold disk electrode, a Pt wire, and an Ag/AgCl electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively, with a scan rate at 50 mV s<sup>-1</sup>.

Table 2. Cyclic voltammogram data for compounds 1a, 1b, and 2–5.

Compound		$E^{1/2}$	[1/]		Fonset [1/]			
Compound		L <sub>red</sub>	[•]		$L_{red}$ [V]	LUNIO	HOMO	$L_{g}$ [ev]
<b>1</b> a	-0.95	-1.35	-2.41	-	-0.90	-3.90	-6.43	2.53
1b	-0.96	-1.33	-2.51	-	-0.88	-3.92	-6.46	2.54
2	-0.88	-1.28	-	-	-0.80	-4.00	-6.68	2.68
3	-0.95	-1.35	-	-	-0.90	-3.90	-6.58	2.68
4	-0.75	-1.19	-	-	-0.65	-4.15	-6.73	2.68
5	-0.86	-1.24	-1.71	-1.99	-0.78	-4.02	-6.70	2.68

[a] The LUMO was calculated according to the equation,  $LUMO = -(4.80 + E_{red}^{noset})$ , in which  $E_{red}^{noset}$  is the onset potential of the first reduction wave, 4.8 eV is the energy level of ferrocene/ferrocenium (Fc<sup>+</sup>/Fc) below the vacuum level.<sup>[38,39]</sup> [b] HOMO was estimated according to the equation, HOMO = LUMO -  $E_{g}$ . [c]  $E_{g}$  was estimated from the absorption edge in solution.

potential ( $E_{\rm red}^{\rm onset}$ ) is -3.90 and -3.92 eV for **1a** and **1b**, respectively. Accordingly, the respective HOMO energy levels are deduced as -6.43 and -6.46 eV for **1a** and **1b**, respectively, based on the equation HOMO =  $LUMO - E_{\alpha}^{opt}$ , in which  $E_{\sigma}^{\text{opt}}$  is the optical energy gap determined from the lowest-energy absorption onset. For 2, 3, and 4, two quasireversible reduction waves were observed with  $E_{\rm red}^{1/2}$  at -0.88and -1.28 V for 2, -0.95 and -1.35 V for 3, and -0.75 and -1.19 V for 4. The LUMO energy level derived from  $E_{\rm red}^{\rm onset}$ was -4.00, -3.90, and -4.15 eV, respectively, and the HOMO energy level was calculated to be -6.68, -6.58, and -6.73 eV, respectively. By changing the position of the two cyano groups, the LUMO energy level was shifted by 0.10 eV (2 versus 3), and by removal of one benzene moiety from 2 to 4, the LUMO energy level was lowered by around 0.15 eV. For compound 5, four quasi-reversible reduction waves were observed with  $E_{\rm red}^{1/2}$  at -0.86, -1.24, -1.71, and -1.99 V. Hence the LUMO and HOMO were calculated to be -4.02 and -6.70 eV, respectively. For all compounds, no clear redox waves were observed upon oxidation up to 1.80 V. Because strong electron-withdrawing groups are fused to the naphthalene imide, the LUMO energy levels of these compounds between -3.90 and -4.15 eV are lower than those of reported naphthaleneamidinemonoimidefused oligothiophenes,<sup>[29,30]</sup> Some of them are even lower than those of trifluoromethylbenzene-fused derivatives.<sup>[28]</sup> The low-lying LUMO energy level (i.e., large electron affinity) of these compounds indicates that they can serve as promising candidates for n-channel OFETs with good air stability.<sup>[40]</sup>

### **Thermal Behavior**

The thermal behavior and self-assembly of **1a**,**b** and **2–5** in the solid state were investigated by a combination of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and powder X-ray diffraction (XRD) techniques (Figures 3 and 4, Table 3, and the Supporting Information). TGA measurements revealed that all compounds were thermally stable over 320 °C with 5 % weight loss (Figure 3, Table 3). Compounds **1a**, **1b**, and **3** show a crystalline-phase-to-liquid-crystalline-phase transition at 31, -0.5, and 64 °C, respectively, which can be confirmed by DSC (Figure 4) and POM (in

the Supporting Information) studies. The powder XRD measurements of **1a** and **1b** showed only one major reflection peak (in the Supporting Information), so their packing structures cannot be obtained. A clear XRD peak at 3.31 Å correlated to intermolecular  $\pi$ - $\pi$  stacking was observed for **3**, which indicates the existence of ordered  $\pi$  stacking. Compounds **2** and **4** are both crystal-

Chem. Asian J. 2014, 9, 253-260



Figure 3. TGA curves for compounds 1a, 1b, and 2-5 with a heating rate of 10 °C min<sup>-1</sup> under nitrogen.

Table 3. Thermal properties of 1a, 1b, and 2-5.

Compound	$T_{\rm d}$ [°C]	Phase transition during heating process <sup>[a</sup>
1a	430	$(Cr) \rightarrow 31 \degree C (LC) \rightarrow 362 \degree C (I)$
1b	458	$(Cr) \rightarrow -0.5 \text{ °C} (LC) \rightarrow 252 \text{ °C} (I)$
2	392	(Cr)→245 °C (I)
3	395	$(Cr) \rightarrow 64 ^{\circ}C  (LC) \rightarrow 320 ^{\circ}C  (I)$
4	359	(Cr)→200 °C (I)
5	329	217°C (I)

[a] Cr: crystal phase; LC: liquid-crystal phase; I: isotropic phase.

line materials at room temperature with a melting point at 245 and 200°C, respectively. The crystals can be observed under POM and many reflection peaks appeared in the XRD curves. Compound 5 turned out to be an amorphous solid at room temperature with a melting point at 197°C. The liquid-crystalline properties of 1a, 1b, and 3 may facilitate the formation of self-healed, ordered thin films in OFET devices.

## **OFET Characterization**

The charge-transport properties of **1a**, **1b**, and **2–5** were characterized by using OFETs. Bottom-gate top-contact OFETs were fabricated on  $p^+$ -Si/SiO<sub>2</sub> substrates by spincasting a 0.8–1.0 wt % chloroform solution onto octadecyltrimethoxysilane (OTMS)- or octadecyltrichlorosilane (ODTS)-treated substrates. The thin films were then annealed at selective temperatures for 30 min. Au source/drain electrodes (80 nm) were patterned on the organic layer through a shadow mask. All devices were characterized under both N<sub>2</sub> and ambient conditions. The typical transfer and output curves are shown in Figure 5 and in the Support-



Figure 5. a) Representative output and b) transfer ( $V_D = 70$  V) characteristics of OFET devices fabricated by solution-casting of **3** on OTMS-treated substrates.

ing Information. The thin film of **5** did not show any fieldeffect behavior in this study, presumably owing to its amorphous character in the solid state (in the Supporting Information). The devices of **1a**, **1b**, and **2–4** all operate in the n-



Figure 4. DSC curves for compounds a) 1a, b) 1b, c) 2, d) 3, e) 4, f) 5 with a heating/cooling scan rate of  $10^{\circ}$ Cmin<sup>-1</sup> under nitrogen (Cr=crystalline phase, LC=liquid crystal phase, I=isotropic phase).

Chem. Asian J. 2014, 9, 253-260

256

Table 4.	The optimized	OFET	characteristic	data	for	1 a.	1b.	and 2	2-4.

	Surface	Annealing		In N <sub>2</sub>			In air			
	treatment	temperature [°C]	$\mu_{\rm e}  [{\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}]$	$\tilde{V}_{ ext{T}}\left[ extbf{V} ight]$	$I_{ m on/off}$	$\mu_{\rm e}  [{\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}]$	$V_{\mathrm{T}}\left[\mathrm{V} ight]$	$I_{ m on/off}$		
1a	ODTS	as-spun	$6.3 \times 10^{-3}$	15	10 <sup>5</sup>	$5.6 \times 10^{-4}$	45	$10^{4}$		
	OTMS	as-spun	$1.2 \times 10^{-2}$	15	$10^{5}$	$2.1 \times 10^{-3}$	25	$10^{4}$		
1b	ODTS	as-spun	$6.4 \times 10^{-3}$	20	$10^{5}$	$5.7 \times 10^{-5}$	26	$10^{4}$		
	OTMS	as-spun	$1.0 \times 10^{-2}$	15	$10^{5}$	$2.4 \times 10^{-3}$	36	$10^{4}$		
2	ODTS	150	$1.1 \times 10^{-3}$	10	$10^{4}$	$3.6 \times 10^{-4}$	8	$10^{3}$		
	OTMS	150	$2.8 \times 10^{-3}$	10	$10^{4}$	$1.6 \times 10^{-3}$	12	$10^{4}$		
3	ODTS	150	$4.8 \times 10^{-3}$	10	$10^{4}$	$1.6 \times 10^{-3}$	20	$10^{5}$		
	OTMS	150	$1.6 \times 10^{-2}$	18	$10^{5}$	$6.1 \times 10^{-4}$	16	$10^{5}$		
4	ODTS	100	$3.2 \times 10^{-5}$	5	$10^{3}$	$5.4 \times 10^{-6}$	20	$10^{3}$		
	OTMS	100	$4.5 \times 10^{-4}$	5	$10^{4}$	$1.0 \times 10^{-4}$	20	10 <sup>3</sup>		

channel region, and their characteristic data are summarized in Table 4 and in the Supporting Information. Various annealing temperatures were employed to optimize the device performance. Under an N2 atmosphere, the as-spun thinfilm devices based on 1a and 1b on OTMS-treated substrates showed high electron mobilities of about 0.01- $0.012 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , which renders them attractive for low-temperature processes and facilitates device fabrication for organic electronics. However, upon thermal annealing, the device performance slightly decreases. In contrast, for thin films of 2 and 3, when annealing at 150°C, the devices exhibited relatively higher average electron mobilities  $(0.0028 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \text{ for } 2 \text{ and } 0.016 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \text{ for } 3 \text{ on an}$ OTMS-treated substrate) compared to the as-deposited devices under N2. These results are comparable to those previously reported owing to coplanarity of these series of derivatives.<sup>[29]</sup> Nonetheless, upon annealing at 100 °C, thin films of 4 showed much lower electron mobility (about  $4 \times$  $10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ). The current on/off ratio for all the devices is about  $10^4$ – $10^5$ , and the threshold voltage is around 10– 20 V. When the devices operated in air, a slight decrease of electron mobility and on/off ratio were observed (Table 4). As can be seen, the cyano-substituted compounds 2-4 showed less degradation compared to the alkyl-chain-substituted compounds (1a and 1b). The slightly better device stability of 2-4 relative to the alkyl-chain-substituted compounds (1a and 1b) might be ascribed to the low-lying LUMO energy levels and dense solid-state packing of these derivatives owing to cyano substitution.

Thin-film morphology and solid-state microstructure were characterized by tapping-mode atomic force microscopy (AFM) and XRD. The thin films of **1a**, **1b**, and **2–4** exhibited intense and sharp Bragg reflections in XRD patterns (Figure 6), which are correlated to a lamellar packing structure with interlayer distance of 3.15, 3.45, 2.28, 1.94, and 2.11 nm, respectively. AFM images of the thin films revealed polycrystalline or liquid-crystalline grains with different shapes (Figure 7 and the Supporting Information). Thin films of **2** and **4** exhibited a relatively larger grain boundary, and thus poor FET performance. However, the liquid-crystalline **1a**, **1b**, and **3** showed more continuous thin films and higher charge-carrier mobilities.



Figure 6. X-ray diffraction patterns for the thin films of 1a,b (as-spun); 2 and 3 (annealed at 150 °C); and 4 (annealed at 100 °C).



Figure 7. AFM height images  $(2 \ \mu m \times 2 \ \mu m)$  of the thin films of a) **1a** (asspun), b) **1b** (as-spun), c) **2** (annealed at 150 °C), d) **3** (annealed at 150 °C), and e) **4** (annealed at 100 °C).

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## Conclusion

In summary, a series of unsymmetric naphthalene imide derivatives **1a**, **1b**, and **2–5** were synthesized. They have very good solubility in common organic solvents, and good thermal stability up to 320 °C. Owing to their strong electronwithdrawing character, they have a low-lying LUMO energy level from 3.90 to 4.15 eV. These compounds can be easily processed from solution at low temperature. All of the OFETs showed n-type behavior under both N<sub>2</sub> and air conditions. It was found that liquid-crystalline compounds **1a**, **1b**, and **3** showed good performance owing to the self-healing properties of the film in the liquid-crystal phase. Compound **3** has electron mobility up to 0.016 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and current on/off ratios of  $10^4$ – $10^5$ . Therefore, these materials have promising applications in solution-processed organic electronics.

## **Experimental Section**

#### General Information

All NMR spectra were recorded on a Bruker AMX500 500 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub>, CDCl<sub>2</sub>CDCl<sub>2</sub>, and [D<sub>6</sub>]DMSO. All chemical shifts are quoted in ppm, using the residual solvent peak as a reference standard. MS was recorded in EI mode and high-resolution mass spectrometry was recorded with an EI source. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis was performed on a Bruker Autoflex IIIMAL-DI-TOF instrument by using 1,8,9-trihydroxyanthracene as matrix and Pepmix as internal standard or external standard. UV-visible absorption and fluorescence spectra were recorded on Shimadzu UV-1700 and RF-5301 spectrometers in HPLC pure solvents. Cyclic voltammetry was performed on a CHI 620C electrochemical analyzer with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate  $(Bu_4NPF_6)$  dissolved in dry  $CH_2Cl_2$  at a scan rate of 50 mV s<sup>-1</sup>. A gold disc electrode with a diameter of 2 mm, a Pt wire, and an Ag/AgCl electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively. The potential was calibrated against the ferrocene/ferrocenium couple. Thermogravimetric analysis (TGA) was carried out on a TA instrument 2960 at a heating rate of 10°C min<sup>-1</sup> under N2 flow. Differential scanning calorimetry (DSC) was performed on a TA instrument 2920 at a heating/cooling rate of 10°C min<sup>-1</sup> under N2 flow. The initial phase transitions and corresponding temperatures for these compounds were determined by the OLYMPUS BX51 polarizing optical microscope equipped with the Linkam TP94 programmable hot stage. XRD measurements were performed on a Bruker-AXS D8 DIS-COVER with GADDS powder X-ray diffractometer, both with  $Cu_{K\alpha}$  radiation.

### Synthesis

7-Octyl-1*H*-isochromeno[6,5,4-*def*]isoquinoline-1,3,6,8(7*H*)-tetraone (6), 5,6-diamino-2-(3,7-dimethyloctyl)isoindoline-1,3-dione (7**a**), 5,6-diamino-2-(2-decyltetradecyl)isoindoline-1,3-dione (7**b**), benzo[*c*]-[1,2,5]thiadiazole-5,6-dicarbonitrile (8), benzo[*c*][1,2,5]thiadiazole-4,7-dicarbonitrile (10), and 4,5-dinitrobenzene-1,2-diamine (13) were prepared according to a literature procedure.<sup>[31-33,36]</sup>

#### Synthesis of 4,5-Diaminophthalonitrile (9)

A mixture of benzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (8; 0.930 g, 5.0 mmol), iron powder (3.360 g, 60 mmol, 12 equiv), and glacial acetic acid (20 mL) was heated under reflux for around 30 min. The mixture was then cooled to room temperature, basified with a solution of NaOH, and extracted with diethyl ether. The combined ether extract was washed

with a solution of NaOH and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed to afford a yellow residue, which was purified by column chromatography (silica gel, hexanes (Hex)/THF=1:1) to give pure **9** as a white solid (0.632 g, 80 %). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =6.87 (s, 2H) 5.87 ppm (br, 4H); <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =139.06, 117.82, 115.52, 101.39 ppm; EIMS: *m*/*z* calcd for C<sub>8</sub>H<sub>6</sub>N<sub>4</sub>: 158.0592; found: 158.1.

### Synthesis of 2,3-Diaminoterephthalonitrile (11)

A mixture of benzo[c][1,2,5]thiadiazole-4,7-dicarbonitrile (**10**; 0.930 g, 5.0 mmol), iron powder (3.360 g, 60 mmol, 12 equiv), and glacial acetic acid (20 mL) was heated under reflux for around 30 min. The mixture was then cooled to room temperature, basified with a solution of NaOH, and extracted with diethyl ether. The combined ether extract was washed with a solution of NaOH and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed to afford a yellow residue, which was purified by column chromatography (silica gel, Hex/THF=1:1) to give pure **11** as a white solid (0.672 g, 85 %). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =6.71 (s, 2 H), 6.06 ppm (br, 4 H); <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =139.62, 118.48, 117.66, 95.05 ppm; HR EIMS: *m*/*z* calcd for C<sub>8</sub>H<sub>6</sub>N<sub>4</sub>: 158.0592; found: 158.0586 (error=-0.4 ppm); elemental analysis calcd (%) for C<sub>64</sub>H<sub>76</sub>N<sub>6</sub>O<sub>4</sub>: C 60.75, H 3.82, N 35.42; found: C 60.47, H 3.89, N 35.19.

# General procedure to synthesize 1–5 through condensation reaction between anhydride and diamine

A mixture of **6** (1.0 equiv) and diamine (1.0 equiv) was heated to reflux in acetic acid under a nitrogen atmosphere overnight. Upon cooling, the suspension was dissolved with  $CH_2Cl_2$  and water, and extracted with  $CH_2Cl_2$ . The combined organic phase was washed with saturated NaCl (aq), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to give a residue that was purified by column chromatography to give the pure product.

### Synthesis of 10-(3,7-Dimethyloctyl)-2-octyl-1H-

benzo[lmn]isoindolo[5',6':4,5]imidazo[2,1-b][3,8]phenanthroline-1,3,6,9,11(2H,10H)-pentaone (**1a**)

Compound **6** (152 mg, 0.4 mmol), diamine **7a** (127 mg, 0.4 mmol); **1a** was obtained as a golden yellow solid (230 mg, 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>2</sub>CDCl<sub>2</sub>, 373 K):  $\delta$ =9.07 (d, *J*=8.0 Hz, 2H), 9.01–8.98 (m, 2H), 8.88–8.83 (m, 2H), 8.34 (s, 1H), 4.26 (t, *J*=7.0 Hz, 2H), 3.81 (d, *J*=7.5 Hz, 2H), 1.87–1.81 (m, 2H), 1.64–1.23 (m, 20H), 1.05 (d, *J*=6.5 Hz, 3H), 0.96–0.92 ppm (m, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>2</sub>CDCl<sub>2</sub>, 373 K):  $\delta$ =167.10, 162.22, 162.05, 158.72, 150.44, 147.80, 135.25, 131.70, 131.19, 130.56, 130.26, 129.96, 128.28, 127.61, 127.24, 126.36, 125.79, 125.63, 124.35, 120.13, 116.02, 111.42, 40.88, 39.04, 36.84, 36.66, 35.28, 31.43, 30.76, 28.91, 28.77, 27.88, 27.59, 26.82, 24.23, 22.27, 22.22 ppm; MALDI-TOF-MS: *m*/z calcd for C<sub>64</sub>H<sub>76</sub>N<sub>6</sub>O<sub>4</sub>: C 72.70, H 6.71, N 8.48; found: C 72.57, H 6.61, N 8.61.

### Synthesis of 10-(2-Decyltetradecyl)-2-octyl-1 H-

benzo[*lmn*]isoindolo[5',6':4,5]imidazo[2,1-*b*][3,8]phenanthroline-1,3,6,9,11(2*H*,10*H*)-pentaone (**1b**)

Compound **6** (143 mg, 0.375 mmol), diamine**7b** (192 mg, 0.375 mmol); **1b** was obtained as a golden yellow solid (282 mg, 88%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 323 K):  $\delta$ =8.94–8.91 (m, 2H), 8.84 (s, 1H), 8.81–8.76 (m, 2H), 8.17 (s, 1H), 4.21 (t, *J*=8.0 Hz, 2H), 3.63 (d, *J*=7.0 Hz, 2H), 1.93 (br, 1H), 1.81–1.75 (m, 2H), 1.49–1.24 (m, 50H), 0.90–0.85 ppm (m, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 323 K):  $\delta$ =167.75, 167.73, 162.50, 162.34, 158.84, 150.52, 147.84, 135.33, 132.07, 131.52, 130.88, 130.31, 130.02, 128.45, 127.82, 127.42, 126.46, 125.91, 125.83, 124.43, 116.18, 111.73, 42.88, 41.15, 37.22, 31.92, 31.82, 29.98, 29.68, 29.65, 29.63, 29.59, 29.32, 29.28, 29.18, 28.16, 27.15, 26.45, 22.64, 22.61, 13.99 ppm; HR EIMS: *m/z* calcd for C<sub>54</sub>H<sub>72</sub>N<sub>4</sub>O<sub>5</sub>: 856.5503; found 856.5536 (error = 3.9 ppm); elemental analysis calcd (%) for C<sub>64</sub>H<sub>76</sub>N<sub>6</sub>O<sub>4</sub>: C 75.66, H 8.47, N 6.54; found: C 75.37, H 8.29, N 6.38.

## CHEMISTRY

## **AN ASIAN JOURNAL**

### Synthesis of 2-Octyl-1,3,6-trioxo-1,2,3,6-

*tetrahydrobenzo*[*lmn*]benzo[4,5]imidazo[2,1-*b*][3,8]phenanthroline-9,10-dicarbonitrile (**2**)

Compound **6** (190 mg, 0. 50 mmol), diamine **9** (79 mg, 0.50 mmol); **2** was obtained as a yellow solid (202 mg, 81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 273 K):  $\delta$ =9.08 (d, *J*=7.5 Hz, 1H), 9.04–9.02 (m, 2H), 8.91–8.88 (m, 2H), 8.35 (s, 1H), 4.22 (t, *J*=7.5 Hz, 2H), 1.79–1.73 (br, 2H), 1.56–1.28 (m, 10H), 1.49–1.24 (m, 50H), 0.88 ppm (t, *J*=6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 323 K):  $\delta$ =162.40, 162.25, 159.04, 152.45, 146.20, 134.06, 132.66, 131.65, 131.12, 128.97, 128.82, 127.58, 126.70, 126.64, 126.28, 126.05, 123.80, 121.82, 115.49, 115.33, 113.42, 112.58, 41.25, 31.80, 29.26, 29.16, 28.16, 27.12, 22.60, 13.96 ppm; HR EIMS: *m*/z calcd for C<sub>30</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>: 501.1801; found 501.1814 (error=2.6 ppm); elemental analysis calcd (%) for C<sub>64</sub>H<sub>76</sub>N<sub>6</sub>O<sub>4</sub>: C 71.84, H 4.62, N 13.96; found: C 71.99, H 4.89, N 13.68.

### Synthesis of 2-Octyl-1,3,6-trioxo-1,2,3,6-

*tetrahydrobenzo*[*lmn*]benzo[4,5]imidazo[2,1-*b*][3,8]phenanthroline-8,11-dicarbonitrile (**3**)

Compound **6** (190 mg, 0. 5 mmol), diamine **11** (79 mg, 0.5 mmol); **3** was obtained as a yellow solid (210 mg, 84%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 273 K):  $\delta$ =9.17 (d, *J*=8.0 Hz, 1H), 9.05 (d, *J*=7.5 Hz, 1H), 8.89–8.86 (m, 2H), 7.98 (d, *J*=8.0 Hz, 1H) 7.92 (d, *J*=8.0 HZ, 1H), 4.21 (t, *J*=7.5 Hz, 2H), 1.79–1.73 (br, 2H), 1.46–1.25 (m, 10H), 0.88 ppm (t, *J*=7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 273 K):  $\delta$ =162.42, 162.25, 158.73, 151.30, 146.49, 133.02, 132.59, 131.70, 131.18, 130.99, 130.05, 129.13, 128.64, 127.24, 126.36, 125.93, 125.76, 123.59, 115.83, 114.52, 109.13, 104.88, 41.15, 31.79, 29.27, 29.16, 28.09, 27.06, 22.62, 14.07 ppm; HR EIMS: *m*/*z* calcd for C<sub>30</sub>H<sub>23</sub>N<sub>5</sub>O<sub>3</sub>: 501.1801; found 501.1814 (error = 2.6 ppm); elemental analysis calcd (%) for C<sub>64</sub>H<sub>76</sub>N<sub>6</sub>O<sub>4</sub>: C 71.84, H 4.62, N 13.96; found: C 71.77, H 4.91, N 13.77.

Synthesis of 2-Octyl-1,3,6-trioxo-1,2,3,6-tetrahydrobenzo[lmn]imidazo[2,1b][3,8]phenanthroline-8,9-dicarbonitrile (**4**)

Compound **6** (190 mg, 0. 5 mmol), diamine **12** (54 mg, 0.5 mmol); **4** was obtained as a yellow solid (210 mg, 84 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 273 K):  $\delta$  = 9.04 (d, *J* = 7.5 Hz, 1H), 8.92 (d, *J* = 7.5 Hz, 1H), 8.90 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 4.20 (t, *J* = 7.5 Hz, 2H), 1.78–1.71 (m, 2H), 1.46–1.25 (m, 10H), 0.87 ppm (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 273 K):  $\delta$  = 162.12, 161.96, 156.68, 147.44, 134.29, 131.84, 131.10, 129.64, 128.75, 127.31, 127.14, 126.44, 125.09, 124.31, 122.37, 110.50, 109.38, 107.20, 41.23, 31.76, 29.22, 29.14, 28.05, 27.04, 22.60, 14.06 ppm; HR EIMS: *m*/*z* calcd for C<sub>30</sub>H<sub>23</sub>N<sub>5</sub>O<sub>3</sub>: 501.1801; found 501.1814 (error = 2.6 ppm); elemental analysis calcd (%) for C<sub>64</sub>H<sub>76</sub>N<sub>6</sub>O<sub>4</sub>: C 69.17, H 4.69, N 15.51; found: C 69.36, H 4.92, N 15.53.

### *Synthesis of 9,10-dinitro-2-octylbenzo[lmn*]benzo[4,5]imidazo[2,1*b*][3,8]phenanthroline-1,3,6(2*H*)-trione (5)

Compound **6** (228 mg, 0. 6 mmol), diamine **13** (118 mg, 0.6 mmol); **5** was obtained as a yellow solid (270 mg, 83%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 273 K):  $\delta$ =9.13 (s, 1H), 9.09 (d, *J*=8.0 Hz, 1H), 9.04 (d, *J*=8.0 Hz, 1H), 8.91–8.88 (m, 2H), 8.43 (s, 1H), 4.23 (t, *J*=8.0 Hz, 2H), 1.80–1.74 (br, 2H), 1.32–1.29 (m, 10H), 0.88 ppm (t, *J*=7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 273 K):  $\delta$ =162.36, 162.20, 158.90,153.41, 145.47, 142.02, 141.13, 132.94, 132.78, 131.64, 131.11, 129.02, 128.86, 127.55, 126.75, 126.21, 125.84, 123.66, 117.57, 113.32, 41.25, 31.80, 29.26, 29.16, 28.15, 27.11, 22.60, 13.97 ppm; HR EIMS: *m*/z calcd for C<sub>28</sub>H<sub>23</sub>N<sub>5</sub>O<sub>7</sub>: 541.1597; found 541.1617 (error=3.7 ppm); elemental analysis calcd (%) for C<sub>64</sub>H<sub>76</sub>N<sub>6</sub>O<sub>4</sub>: C 62.10, H 4.28, N 12.93; found: C 62.28, H 4.28, N 12.83.

### Device Fabrication

Top-contact, bottom-gate OFET devices were prepared on the  $p^+$  silicon wafer and a 200 nm thermally grown SiO<sub>2</sub> layer served as the gate dielectric. The SiO<sub>2</sub>/Si substrate was cleaned with acetone and isopropanol, then immersed in a piranha solution (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) for 8 min, and washed with deionized water. The octadecyltrimethoxysilane (OTMS) treatment was performed according to a modified procedure reported in

the literature<sup>[41]</sup>: the clean substrates were spin-casted with 10 mM OTMS solution in trichloroethylene and placed in an environment saturated with ammonia vapor for 7 h at room temperature, then washed with deionized water and toluene. The octadecyltrichlorosilane (ODTS) treatment was conducted by immersing the sample in a 3 mM solution of ODTS in hexadecane at RT for 16 h in N2. It was then rinsed with toluene and isopropyl alcohol (IPA). The semiconductor layer was deposited on top of the OTMS- or ODTS-modified dielectric surface by spin-coating or -casting from the solution of active component in chloroform (0.8-1 wt%). For ODTS-treated substrates, the solutions were deposited from spin-coating. However, for OTMS-treated substrates, owing to the poor wetting problem, only compounds 1a, 1b, and 3 have good thin-film formation; whereas, compounds 2 and 4 were processed from drop-casting. Subsequently, gold source/drain electrodes were deposited by thermal evaporation through a metal shadow mask to create a series of FETs (channel width (W) = 1 mm; channel length (L) = 50-100 um). The FET devices were then characterized by using a Keithley SCS-4200 semiconductor parameter analyzer in the N2 glovebox or in air. The FET mobility was extracted by using the following equation in the saturation regime from the gate sweep [Eq. (1)]:

# $I_{\rm D} = \frac{W}{2L} C_{\rm i} \mu (V_{\rm G} - V_{\rm T})^2$

in which  $I_{\rm D}$  is the drain current,  $\mu$  is the field-effect mobility,  $C_{\rm i}$  is the capacitance per unit area of the gate dielectric layer (SiO<sub>2</sub>, 200 nm,  $C_{\rm i}$ = 17 nF cm<sup>-2</sup>), and  $V_{\rm G}$  and  $V_{\rm T}$  are the gate voltage and threshold voltage, respectively.

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