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Fluorinated 1,8-naphthalimides: Synthesis, solid structure and properties

ABSTRACT

n-type semiconductor.

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1. Introduction

In recent years, organic semiconductors have drawn significantly more attention, compared to the traditional inorganic materials such as amorphous or crystalline silicon. They displayed several advantages such as their adaptability to low-temperature processing on flexible substrates, low cost, amenability to highspeed fabrication, and tunable electronic properties [1–3]. Organic semiconductors become a promising technology for large-area electronic applications including electronic paper displays, radio frequency identification tags, smart cards, and large-area sensors [4,5]. Organic semiconducting materials are commonly classified as p-type (hole-conducting) or n-type (electron-conducting), depending on which type of charge carrier is more efficiently transported through the material. So far, a large number of high performance p-type organic semiconductors have been studied, and stable organic p-type semiconductors have fulfilled many of the requirements in diverse applications. However, high performance n-type organic semiconductors are relatively rare, mainly owing to synthetic difficulties and poor air stability [6].

In view of the requirements for the fabrication of organic complementary circuits, n-type organic semiconductor has evoked increasing interest recently [7]. To afford air stable n-type organic semiconductors, the common strategy is to introduce strong

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electron-withdrawing groups to a conjugated system, such as 31 cyano, imide or fluorine groups [8,9]. Among all kinds of n-type 32 organic semiconductors, naphthalene diimide (NDI) was consid-33 ered one of the most promising candidates due to its good air-34 stability and film-forming ability [10]. Fluorine atoms can lower 35 both the HOMO and LUMO energy levels to facilitate the electron 36 injection and stabilize the materials to display a greater resistance 37 against the degradative oxidation processes [11]. Moreover, the 38 C-H...F interactions play an important role in the solid state 39 supramolecular organization, originating a typical π -stack ar-40 rangement that enhances the charge carrier mobility [12]. Herein, 41 we report three fluorinated 1,8-napthalimides. Their structures 42 were characterized and their optoelectronic properties were 43 investigated. 44

2. Experimental

Three fluorinated 1,8-napthalimides were synthesized from acenaphthene. Their structures were

characterized by NMR and EI-MS analyses. The structures of compounds 1b and 1c were also confirmed

by X-ray diffraction analysis, which showed that they possessed different packing models. Their

optoelectronic properties were investigated. The results indicated that all of the naphthalimides possess

good solubility and low LUMO energy level, which make them good solution processing candidates in

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Compounds **3**, **4**, **5** and **6a** have been reported in the literature 46 [13,14]. Unless otherwise mentioned, all commercially available 47 starting materials were used as received without further purifica-48 tion. DMSO was dried with CaH₂ and then distilled under reduced 49 pressure. ¹H NMR and ¹³C NMR spectra were collected on an 50 American Varian Mercury Plus at 400 spectrometer 400 MHz or 51 52 600 MHz. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. MS spectra were collected on a Thermo DSQ II. 53 UV-vis spectra were obtained on a U-3310 UV Spectrophotometer. 54 55 Fluorescence spectra were obtained on a FluoroMax-P. The crystal 56 structure was recorded on a Bruker SMART CCD area-detector 57 X-ray diffraction spectrometer.

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Scheme 1. Synthesis of compounds 1a-c.

58 2.1. General synthetic procedures for **6b** and **6c**

A mixture of 4,5-dibromo-1,8-naphthoic anhydride 5
(2.8 mmol), amine (2.8 mmol) in ethanol (50 mL) was stirred
overnight under nitrogen at 78 °C. The reaction mixture was then
cooled and the solvent was removed under vacuum. The residue
was purified by column chromatography using dichloromethane/
petroleum ether (1:3, v/v) as an eluent to afford pure product as a
yellow solid.

66 Compound **6b**. Yield: 0.49 g, 40%. ¹H NMR (400 MHz, CDCl₃): δ 67 8.40 (d, 2H, *J* = 5.6 Hz), 8.21 (d, 2H, *J* = 8 Hz), 4.14 (t, 2H, *J* = 7.6 Hz), 68 1.73–1.68 (m, 2H), 1.41–1.25 (m, 6H), 0.89 (t, 3H, *J* = 4 Hz). ¹³C 69 NMR (100 MHz, CDCl₃): δ 163.00, 136.04, 131.36, 131.02, 127.97, 70 127.52, 123.01, 40.71, 31.46, 27.85, 26.71, 22.52, 14.02. EI-MS: *m/z* 71 439.00; calcd. for C₁₈H₁₇Br₂NO₂: 439.14.

72Compound **6c**. Yield: 0.42 g, 35%. ¹H NMR (600 MHz, CDCl₃): δ738.38 (d, 2H, J = 7.8 Hz), 8.21 (d, 2H, J = 8.4 Hz), 5.01–4.96 (m, 1H),742.24–2.17 (m, 2H), 1.93–1.87 (m, 2H), 0.89 (t, 6H, J = 7.8 Hz). ¹³C75NMR (100 MHz, CDCl₃): δ 158.50, 136.20, 131.37, 131.00, 128.02,76127.75, 127.55, 57.55, 24.10, 10.90. EI-MS: m/z 424.82; calcd. for77 $C_{17}H_{15}Br_2NO_2$: 424.94.

2.2. General synthetic procedures for 1a-c

A mixture of 4,5-dibromo-1, 8-naphthalimide (0.5 mmol), anhydrous powered CsF (3.3 mmol) in dry DMSO (50 mL) was stirred for 1 h under nitrogen at 95 °C. The reaction mixture was then cooled and poured into ice and the yellow solid was collected by filtration. The residue was purified by column chromatography using dichloromethane/petroleum ether (1:3, v/v) as an eluent to afford the pure product.

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Compound **1a**. Yellow solid; yield: 36 mg, 25%. ¹H NMR (400 MHz, CDCl₃): δ 8.63 (d, 2H, *J* = 8.4 Hz), 7.45–7.28 (m, 2H), 4.16 (t, 2H, *J* = 7.6 Hz), 1.72–1.68 (m, 2H), 1.25–1.46 (m, 2H), 0.97 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 162.86, 162.59, 162.48, 159.76, 159.65, 133.68, 131.41, 118.79, 112.88, 40.23, 30.00, 20.26, 13.75. EI-MS: *m*/*z* 289.03; calcd. for C₁₆H₁₃F₂NO₂: 289.09.

Compound **1b**. Yellow solid; yield: 33 mg, 21%. ¹H NMR (400 MHz, CDCl₃): δ 8.63 (d, 2H, *J* = 7.6 Hz), 7.49–7.42 (m, 2H), 4.14 (t, 2H, *J* = 7.6 Hz), 1.75–1.67 (m, 2H), 1.41–1.33 (m, 6H), 0.89 (t, 3H, *J* = 6.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 162.96, 162.71, 162.60, 159.89, 159.78, 133.75, 131.91, 131.56, 127.11, 126.78,



Fig. 1. (a) Normalized UV-vis absorption and photoluminescence spectra of **1a** in $CH_2Cl_2(1.0 \times 10^{-5} \text{ mol } L^{-1})$ and in thin film; (b) **1b** in $CH_2Cl_2(1.0 \times 10^{-5} \text{ mol } L^{-1})$ and in thin film; (c) **1c** in $CH_2Cl_2(1.0 \times 10^{-5} \text{ mol } L^{-1})$ and in thin film; (d) Cyclic voltammogram (CV) of **1a-c** in dry DCM with 0.1 mol L^{-1} Bu₄NPF₆ as supporting electrolyte.

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Optical and electrochemical data of 1a-c.

χ_{max} (11)	HOMO ^a (ev) E_g^c (' (eV)
1a 338, 353 (solution); 350, 365 (film) 388 (solution); 419 (film) 26,000 -1.67 -1.63 -3.17 1b 338, 352 (solution); 341, 358 (film) 388 (solution); 421 (film) 14,400 -1.66 -1.62 -3.18 1c 338, 352 (solution); 340, 359 (film) 388 (solution); 426 (film) 22,800 -1.73 -1.69 -3.11	-6.52 3.35 -6.53 3.35 -6.49 3.38	35 35 38

 $^a\,$ The wavelength of absorption and photoluminescence in CH_2Cl_2 (1.0 $\times\,10^{-5}\,mol\,L^{-1}$).

^b The molar extinction coefficient.

^c LUMO energy levels was calculated from the onset of the first reduction according to equation: $LUMO = -(4.8 + E_r^{onset}) eV$.

^d HOMO = LUMO – E_{g} .

^e E_g was calculated from the low-energy absorption onset in the absorption spectra according to equations: $E_g = 1240 / \lambda_{onset}$ [15].

118.93, 112.93, 112.19, 40.52, 31.46, 27.93, 26.70, 22.50, 13.98. EI MS: *m*/*z* 317.18; calcd. for C₁₈H₁₂F₂NO₂: 317.12.

100Compound 1c. White solid; yield: 22 mg, 15%. ¹H NMR101(400 MHz, CDCl₃): δ 8.61 (d, 2H, J = 9.3 Hz), 7.46–7.41 (m, 2H),1025.15–4.87 (m, 1H), 2.25–2.18 (m, 2H), 1.98–1.92 (m, 2H), 0.88 (t,1036H, J = 7.4 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 162.56, 162.43,104133.85, 131.74, 119.21, 119.03, 113.02, 112.91, 112.81, 57.48,10524.52, 10.82. EI-MS: m/z 303.09; calcd. for C₁₇H₁₅F₂NO₂: 303.10.

106 **3. Results and discussion**

107 The synthesis of **1a-c** was outlined in Scheme 1. Acenaphthene 108 was bromated using NBS to give 3. Subsequently, a two-step 109 oxidation reaction was performed to afford **5**. Then naphthoic 110 anhydride was treated with different amine in ethanol to afford the 111 corresponding bromo-1,8-naphthalimide. The targeted com-112 pounds were prepared from bromo-1,8-naphthalimide in dry DMSO using CsF. These compounds showed very good solubility in 113 common solvents, such as dichloromethane, chloroform and 114 115 acetone. This good solubility allowed them to be processed in 116 solution and allowed the formation of thin films. The optical 117 properties were investigated by UV-vis absorption and fluores-118 cence spectrometry. Fig. 1a showed the UV-vis absorption and 119 fluorescence spectra of **1a** in CH₂Cl₂. Two characteristic absorption peaks at 338 nm and 353 nm were observed, compared with the 120 121 absorption bands at 334 nm and 344 nm of non-substituted 1,8-122 naphthalimide [16], which suggested that the introduction of the 123 two fluorine atoms led to a slight red shift. Compound 1a had a 124 wavelength of 388 nm for the maximum fluorescence emission in

solution in Fig. 1a and Table 1, which represented a 50 nm Stokes 125 shift (excited at 338 nm). 126

The UV-vis absorption and fluorescence spectra of **1a** were also measured in the thin-film state as shown in Fig. 1a. The UV-vis absorption spectra and fluorescence spectra collected in the thin films were broader than those spectra collected in solutions and showed a large bathochromic shift, indicating that the chromophore had a strong tendency to aggregate in the solid state. 132

As can be seen in Fig. 1b and c and Table 1, similar phenomena 133 were also observed on the absorption and emission spectra of **1b** 134 and **1c** in the solution and in the film state, indicated that the 135 different alkyl chain had little effects on their optical properties. 136 The values of optical energy gaps (E_g) (\sim 3.35–3.38 eV) were 137 calculated from the low-energy absorption onset in the absorption 138 spectra, as shown in Table 1. 139

Subsequently, the electrochemical properties of these naphtha-140 limides were investigated by cyclic voltammetry (CV). The 141 measurements were carried out in dry dichloromethane at room 142 temperature under nitrogen atmosphere. As shown in Fig. 1d, one 143 pair of irreversible reduction waves were observed. For example, 144 compound **1a** showed a reduction wave at -1.67 V and no obvious 145 oxidation waves were observed. The LUMO energy level of -3.17, 146 -3.18, -3.11 eV were estimated for **1a-c** based on the onset 147 potential of the first reduction wave. The HOMO energy levels of 148 **1a-c** were also calculated based on the equation described in 149 Table 1. From these calculations, we found that these compounds 150 had similar HOMO and LUMO energy levels. The HOMO and LUMO 151 energy levels of **1a-c** were much lower, in comparison with those 152 of non-substituted 1,8-naphthalimide. These data demonstrated 153 that fluorine atoms lowered not only the LUMO energy level but 154



Fig. 2. The single crystal structures and packing views of 1b (a), 1c (b). (Top, side, and packing view from left to right. Hydrogen atoms have been omitted in packing views.).

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also the HOMO energy level, which was significant to afford airstable n-type organic semiconductors.

157 Single crystals of 1b and 1c suitable for crystallographic 158 analysis were grown by slow diffusion of n-hexane to their 159 dichloromethane solutions. As depicted in Fig. 2, C-H···O 160 hydrogen bonds made 1b pack into one-dimensional planar 161 structures. Compound 1c displayed lamellar packing promoted by the C–H \cdots O hydrogen bonds and C–H \cdots F hydrogen bonds. The 162 slight structural change induced by alkyl chain resulted in an 163 obvious change of packing form. It is well-known that molecular 164 165 stacking is very important for the properties of a material [17]. 166 Hence, these results afforded an alternative approach to explore 167 organic optoelectronic materials by decorating of their structures.

168 **4. Conclusion**

169 In summary, three fluorinated 1,8-napthalimides were suc-170 cessfully synthesized. The structures of compounds 1b and 1c were 171 confirmed by single crystal X-ray diffraction analysis. It should be 172 noted that compounds **1b** and **1c** had different packing motifs in 173 the solid state. This work affords an alternative approach to the 174 exploration of organic optoelectronic materials with good perfor-175 mance in devices, using only minor structural decorations. Their 176 optoelectronic properties indicated that the introduction of 177 fluorine atoms could lower the LUMO and HOMO energy level. 178 Their good solubility and optoelectronic properties make them 179 potential solution-processable candidates for organic devices.

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