



## Electron-transporting naphthalimide-substituted derivatives of fluorene



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### ABSTRACT

Naphthalimide-substituted derivatives of fluorene were synthesized by Suzuki–Miyaura coupling reactions. Most of the synthesized materials were found to constitute glasses with glass transition temperatures ranging from 30 to 76 °C as characterized by differential scanning calorimetry. Their initial weight loss temperatures range from 315 to 466 °C. Dilute solutions of the naphthalimide-substituted derivatives of fluorene in nonpolar solvents were found to emit in the blue region with high quantum yield ranging from 0.47 to 0.69, while in the solid state fluorescence quantum yields were found to be in the range of 0.06–0.25. Fluorenes possessing two naphthalimide moieties exhibited higher values of the fluorescence quantum yield due to enhanced oscillator strength of the transition. The derivatives of fluorene containing naphthalimide moieties exhibited pronounced positive solvatochromic behaviour in polar solvents indicating on charge-transfer character of the lowest excited states. Fluorescence red shift in dimethylsulfoxide is found of 94 nm, while the fluorescence quantum yield is increasing with polarity from 0.47 in cyclohexane to 0.84 in dimethylsulfoxide. Such untypical enhancement of fluorescence quantum yield is accounted to reduced intersystem crossing in polar solvents, which is proved by almost 10 fold increase in the values of nonradiative decay rate for compounds dissolved in polar solvents. Time-of-flight electron drift mobilities of the layer of 2,7-di(*N*-octyl-1,8-naphthalimide)-4-yl)-9,9-dioctyl-9*H*-fluorene in air at 25 °C approach  $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at an electric field of  $6.4 \times 10^5 \text{ Vcm}^{-1}$ .

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### 1. Introduction

Low-molar-mass organic semiconductors with electron-transporting property have received great deal of research interest in recent years due to their potential applications in the field of (opto)electronics [1–3]. Solution processable amorphous molecular materials with appealing photoelectrical and operational stability are particularly interesting in the standpoint of possible applications in cost-effective large-area electronic devices [4–6]. However, practical devices based on organic semiconductors possessing air-stable electron-transporting properties are limited due to the lack of ambient stability of charge carriers, i.e. electrons [7,8]. Therefore, the development of soluble electron-transporting materials that can operate in air is of considerable interest for the device applications.

Naphthalimides have been of interest in organic electronics research for many years as n-type semiconductors due to their capability to be reduced into stable radical anions [3,9]. The derivatives of naphthalimide are also known as photochromic materials [10,11]. Moreover wide possibility of functionalization via imide moiety and carbocyclic core using non chromophore or chromophore substituents in order to improve the processability or electronic properties have also driven research interest extensively on naphthalimides and their derivatives [9,12]. The substitutions may change glass transition temperatures, shift photoluminescence (PL) wavelengths, change PL quantum yields, shift redox potentials and/or improve photoelectrical characteristics [13–15]. It is known that absorption, emission, electrochemical and/or photoelectrical properties of naphthalimides and their analogues can be varied by extending the  $\pi$ -conjugation at the carbocyclic core using electron-donor chromophores which affect the electronic structure of the derivatives [9,16–18]. However, the substitutions at the imide position have little or no influence on the electronic properties of the derivatives [9,16–19].

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Fluorene and its derivatives are proven to be useful building blocks for the preparation of luminescent and charge-transporting materials [20–22]. They are applied extensively in the design and synthesis of polymers, low-molar-mass compounds, and dendrimers for electronic and optoelectronic applications [20–24]. The possibility of functionalization at 2, 7 and 9 positions, of fluorene moiety not only improves the solubility of its derivatives but also influences the molecular properties like glass transition, absorption or emission.

Formation of donor-acceptor (D-A) combinations represents an important methodology for the preparation of semiconducting materials with the tunable properties [25]. Low-band-gap copolymers containing electron-accepting naphthalene bisimide moieties and fluorene derivatives as electron-donor moieties for organic solar cell applications have been reported [26]. We recently reported low-molar-mass D-A derivatives exhibiting hole-transporting and glass forming abilities in which naphthalimide-acceptor moieties are functionalized with triphenylamino donor chromophores via hydrazine linkages or ethenyl spacers [14,15].

In the present study, we report on the synthesis and thermal, photophysical, electrochemical, and charge-transporting properties of naphthalimide-substituted fluorene derivatives containing different alkyl substituents.

## 2. Experimental section

### 2.1. Materials

The starting compounds, i.e. 2-bromofluorene, 2,7-dibromofluorene, 4-bromo-1,8-naphthalic anhydride, 9,9-(2-ethylhexyl)-9H-fluorene-2-yl-boronic acid (**2b**), [9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl]bisboronic acid (**3b**) were purchased from Sigma Aldrich and used as received. The reagents and the required materials, i.e. iodoethane, 1-bromo 2-ethylhexane, 1-bromooctane, 2-ethylhexylamine, *n*-octylamine, *n*-butyllithium, potassium *tert*-butoxide, tetrabutylammonium hydrogen sulfate, sodium sulfate, potassium carbonate, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, bis(triphenylphosphine)palladium(II) dichloride and tetrabutylammonium hexafluoroborate (Bu<sub>4</sub>NBF<sub>6</sub>) were also purchased from Sigma Aldrich and used as received.

4-Bromo-*N*-(2-ethylhexyl)-1,8-naphthalimide (**1a**) (lit. [15] m.p.: = 82–83 °C), 9,9-diethylfluorene-2-boronic acid (**2a**) (lit. [27] m.p.: = 118–120 °C), 9,9-dioctylfluorene-2,7-diboronic acid (**3c**) (m.p.: = > 400 °C, lit. [28] > 400 °C), 9,9-dioctylfluorene-2-boronic acid (**2c**) (m.p.: = 72–74 °C, lit. [29] 70.1–77.3 °C) were prepared according to the published procedures.

#### 2.1.1. 4-Bromo-*N*-octyl-1,8-naphthalimide (**1b**)

A solution of 4-bromo-1,8-naphthalic anhydride (1 g, 3.61 mmol) in 25 ml of dimethylformamide (DMF) was added to a 100 mL three neck round bottom flask equipped with a reflux condenser and a magnetic stirrer. Then *n*-octylamine (0.60 g, 3.61 mmol) was added drop-wise and the reaction mixture was heated up to 120 °C and stirred under nitrogen for 24 h. The reaction mixture was concentrated using rotary evaporator and then the product was precipitated out into 1M HCl solution, filtered off and washed with 1M HCl solution. The crude product was purified by silica gel column chromatography using hexane/ethylacetate, 8:1 as an eluent. Yield: 1.03 g (74%) of white crystals; m.p.: = 74–75 °C. <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 8.67 (d, 1H, *J* = 8.4 Hz, 5-H<sub>Naphthalene</sub>), 8.57 (d, 1H, *J* = 7.5 Hz, 7-H<sub>Naphthalene</sub>), 8.43 (d, 1H, *J* = 7.9 Hz, 2-H<sub>Naphthalene</sub>), 8.05 (d, 1H, *J* = 7.9 Hz, 3-H<sub>Naphthalene</sub>), 7.87 (tr, 1H, *J*<sub>1</sub> = 7.3 Hz, *J*<sub>2</sub> = 15.8 Hz, 6-H<sub>Naphthalene</sub>), 4.21–4.13 (m, 2H, –CH<sub>2</sub>, –H<sub>aliphatic</sub>), 1.80–1.69 (m, 2H, CH<sub>2</sub>, –H<sub>aliphatic</sub>), 1.51–1.18 (m, 10H, CH<sub>2</sub>), 0.89 (tr, 3H, *J*<sub>1</sub> = 6.7 Hz,

*J*<sub>2</sub> = 13.7 Hz, CH<sub>3</sub>, –H<sub>aliphatic</sub>). IR (KBr, ν cm<sup>-1</sup>): (arene C–H) 3068; (aliphatic C–H) 2958, 2927, 2871, 2852; (imide C=O) 1699; (Ar C=C) 1585, 1512, 1458; (imide C–N) 1351, 1234; (C–Br) 665, 560. <sup>13</sup>C NMR spectrum (75.5 MHz, CDCl<sub>3</sub>, δ, ppm): 163.61, 133.21, 132.01, 131.21, 131.09, 130.62, 130.19, 129.02, 128.08, 123.16, 122.30, 40.65, 31.83, 29.29, 28.10, 27.14, 22.66, 14.12. Anal. Calcd. for C<sub>20</sub>H<sub>22</sub>BrNO<sub>2</sub>: C, 61.86; H, 5.71; Br, 20.58; N, 3.61; O, 8.24%. Found: C, 61.78; H, 5.77; N, 3.59%. MS (APCI<sup>+</sup>, 20 V), *m/z*: 389 [(M + H)<sup>+</sup>].

### 2.2. General procedure for Suzuki–Miyaura reactions

4-bromo-*N*-(2-ethylhexyl)-1,8-naphthalimide or 4-bromo-*N*-octyl-1,8-naphthalimide (300 mg, 0.77 mmol) and 9,9-dialkyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9H-fluorene (0.85 mmol) or 9,9-dialkyl-2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9H-fluorene (0.38 mmol) were taken in a 100 mL Schlenk flask. A solvent mixture of 20 mL of tetrahydrofuran (THF) and 2 mL of water and powdered potassium carbonate (2.7 mmol) was added. The reaction mixture was purged with nitrogen for 5 min. The reaction flask was degassed and then again purged with nitrogen for 2 min. Bis(triphenylphosphine)palladium(II) dichloride (0.04 mmol) was added into it and stirred for 12–16 h at 80 °C under nitrogen. The reaction mixture was allowed to cool down to the room temperature, diluted with water and extracted using ethyl acetate. The organic layers were dried over sodium sulfate and evaporated at reduced pressure. The crude products were purified by silica gel column chromatography (the details are given below).

#### 2.2.1. 2-((*N*-(2-ethylhexyl)-1,8-naphthalimide)-4-yl)-9,9-diethyl-9H-fluorene (**1**)

The crude product was purified by column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 9:1. Yield = 73% (370 mg); Yellow crystals (FW = 529.73 g/mol); m.p.: 133–134 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 8.69 (t, *J* = 5.3 Hz, 2H), 8.38 (d, *J* = 3.2 Hz, 1H), 7.92 (d, *J* = 2.6 Hz, 1H), 7.85–7.72 (m, 3H), 7.53–7.50 (m, 2H), 7.46–7.40 (m, 3H), 4.26–4.14 (m, 2H, NCH<sub>2</sub>), 2.13 (q, *J* = 7.3 Hz, 4H, CH<sub>2</sub><sub>Fluorene</sub>), 2.04–1.97 (m, H, CH<sub>Naphthalimide</sub>), 1.49–1.32 (m, 8H, CH<sub>2</sub><sub>Naphthalimide</sub>), 1.01–0.90 (m, 6H, CH<sub>3</sub><sub>Naphthalimide</sub>), 0.45 (t, *J* = 4.9 Hz, 6H, CH<sub>3</sub><sub>Fluorene</sub>). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, δ, ppm): 165.0, 164.8, 150.7, 150.4, 147.7, 142.2, 140.9, 137.7, 132.8, 131.5, 131.1, 130.5, 129.1, 128.2, 127.9, 127.3, 127.0, 124.7, 123.3, 121.8, 120.2, 120.0, 56.5, 44.4, 38.2, 32.9, 31.0, 29.0, 24.3, 23.3, 14.4, 10.9, 8.9. IR (KBr, ν cm<sup>-1</sup>): (arene C–H) 3063; (aliphatic C–H) 2961, 2929, 2853; (imide C=O) 1698; (Ar C=C) 1659, 1588; (imide C–N) 1353, 1231. Anal. Calc. for C<sub>37</sub>H<sub>39</sub>NO<sub>2</sub>: C, 83.89; H, 7.42; N, 2.64; O, 6.04%. Found: C, 83.82; H 7.36; N, 2.69%. MS (APCI<sup>+</sup>, 20 V), *m/z*: 530 [M + H]<sup>+</sup>.

#### 2.2.2. 2-((*N*-(2-ethylhexyl)-1,8-naphthalimide)-4-yl)-9,9-di(2-ethylhexyl)-9H-fluorene (**2**)

The product was purified by column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 8:1. Yield = 78% (180 mg); Yellow crystals (FW = 698.03 g/mol); m.p.: 55–56 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 8.74–8.66 (m, 2H), 8.45 (d, *J* = 7.9 Hz, 1H), 8.37 (dd, *J*<sub>1</sub> = 1.1 Hz, *J*<sub>2</sub> = 8.5 Hz, 1H), 7.94–7.88 (m, 1H), 7.85–7.81 (m, 2H), 7.79–7.72 (m, 1H), 7.54–7.49 (m, 2H), 7.47–7.40 (m, 2H), 4.26–4.13 (m, 2H, NCH<sub>2</sub>), 3.56–3.47 (m, 1H, CH), 2.18–2.07 (m, 4H, CH<sub>2</sub><sub>Fluorene</sub>), 2.05–1.93 (m, 2H, CH<sub>Naphthalimide</sub>), 1.55–1.27 (m, 24H, CH<sub>2</sub><sub>Naphthalimide</sub>, CH<sub>2</sub><sub>Fluorene</sub>), 1.07–0.80 (m, 12H, CH<sub>3</sub><sub>Naphthalimide</sub>, CH<sub>3</sub><sub>Fluorene</sub>), 0.47 (t, *J* = 7.3 Hz, 6H, CH<sub>3</sub><sub>Fluorene</sub>). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, δ, ppm): 164.9, 164.3, 150.8, 150.4, 147.6, 142.2, 141.0, 137.8, 133.4, 132.9, 132.3, 131.5, 131.2, 130.4, 129.1, 128.1, 127.9, 127.3, 127.1, 124.7, 123.3, 121.8, 120.2, 119.8, 56.5, 44.5, 44.4, 38.2, 38.2, 33.0, 31.1, 29.0, 24.4, 23.5, 23.3, 14.4, 11.0, 10.9,

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