



# Synthesis, characterization, and transistor applications of new linear small molecules: Naphthyl-ethynyl-anthracene-based small molecules containing different alkyl end group



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## ABSTRACT

A novel small molecule consisting of triple bond-bridged naphthalene-anthracene core was synthesized with either a pentyl or decyl end group. The linear and planar shape of naphthalene-anthracene core allowed herringbone packing pattern with enhanced conjugation length and close molecular packing structure. The film morphology of naphthalene-anthracene based small molecules was also affected by the pentyl and decyl groups. The pentyl substituted molecule exhibited more unified and ordered packing patterns than did the decyl substituted example, which showed at least two polymorphs. The p-type semiconducting properties of the two new molecules were characterized by organic field-effect transistor measurements. In annealed devices at 80 °C, the field-effect mobility of pentyl analogue was 0.045 cm<sup>2</sup>/(V·s), which was about 3 times higher than the decyl substituted compound.

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## 1. Introduction

In small molecules that contain aromatic rings, the effect of crystal structure on charge carrier transport has been studied by experimental [1,2] and theoretical [3] methods. In the solid state, charge carrier transport in small molecules is attributed to the packing patterns, crystal size, and inter-crystal connectivity of the film morphology [4–11]. Among these factors, the packing patterns of the small molecule should be subject to their interaction types. The small molecules usually have three energetically-attractive interaction types: parallel, T-shaped, and slipped-parallel [12].

The most energetically-stable conformation of small molecule is determined by van der Waals (VDW) dispersion and electrostatic interaction [13] caused by their geometrical and chemical structure of their conjugated core [14–16] and substituents [16–19].

Linear-shaped small molecules generally adopt a herringbone-type packing with T-shaped interactions because these interactions are stabilized by a number of short intermolecular C···C contacts and weak acid-base contacts between C–H bonds (weak hydrogen-bonds; soft acids) and  $\pi$ -systems (electron rich; soft bases) [12,13]. Additionally, the substituted alkyl group of linear-shaped small molecules can affect the film morphology by affecting VDW interaction and the steric hindrance between adjacent molecules [20] and also their solubility in a processing solvent.

In previous reports, our group has tried to reveal how the molecular structure of linear-shaped small molecules influences their film morphology and charge carrier transport of the corresponding OFETs [21–25]. Modification of the conjugated core of several series of linear-shaped small molecules can yield molecular structures which could fabricate favorable film morphology to charge carrier

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transport: a large fused or triple-bond-bridged conjugated core with planar geometrical structure produces improved intramolecular  $\pi$ -conjugated system as well as intermolecular interactions [26]. Moreover the shape and length of alkyl group have a strong influence on molecular ordering, particularly during formation of films by solution processing [1,2].

Previous work in our group has investigated the small molecules that have a triple-bond-bridged phenylene-anthracene conjugated core (phenylethynylantracene; PEA) which exhibited good charge carrier transport. For the PEA core, a pentyl end group was found to be most suitable alkyl end group for improving both solubility and molecular arrangement [27]. However, it is still necessary to discuss the packing patterns of the molecular assembly. Moreover, the further fine-tuning opportunity is allowed to extend conjugation length of PEA by simply substituting a larger fused conjugated core than that of the PEA core.

In this paper, we present two linear-shaped small molecules that contain a triple bond-bridged naphthalene-anthracene conjugated core (NEA) which has longer conjugation length than that of PEA. Therefore, the fine-tuned NEA-based small molecules are expected to provide improved carrier transport through their extended intramolecular  $\pi$ -conjugated system as well as increased intermolecular interaction in comparison to the PEA-based small molecules. The NEA core was substituted with two end groups of differing alkyl length: pentyl (2-(p-pentynaphthylethynyl)anthracene; **PNEA**) and decyl (2-(p-decynaphthylethynyl)anthracene; **DNEA**). We will discuss the film morphology including packing patterns of NEA-based small molecules, and the relationship between morphology and OFET properties depending on alkyl length.

## 2. Experimental section

### 2.1. Synthesis method

#### 2.1.1. Materials

2-Bromoanthracene, trimethylsilyl acetylene, copper(I) iodide, tetrabutylammonium fluoride were purchased from Aldrich. Pd(PPh<sub>3</sub>)Cl<sub>2</sub> catalyst purchased from Strem.

#### 2.1.2. Anthracen-2-ylethynyl-trimethyl-silane (**1**)

Compound **1** was synthesized according to the literature [27]. Yield: 25.28 g, 79%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 8.38 (s, 2H), 8.19 (s, 1H), 8.03–7.99 (m, 2H), 7.95–7.92 (d, J = 9 Hz, 1H), 7.52–7.45 (m, 3H), 0.33 (s, 9H).

#### 2.1.3. 2-Ethynyl-anthracene (**2**)

Compound **2** was synthesized according to the literature [27]. Yield: 2.5 g, 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 8.41 (s, 2H), 8.22 (s, 1H), 8.03–7.95 (m, 3H), 7.53–7.47 (m, 3H), 3.22 (s, 1H).

#### 2.1.4. 1-(6-Bromonaphthalen-2-yl)pentan-1-one (**3**)

Compound **3** was synthesized according to the literature [28]. Yield: 14.2 g, 60%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 8.46 (s, 1H), 8.10–8.07 (d, J = 9 Hz, 2H), 7.87–7.84 (t, J = 4.5 Hz, 2H), 7.66–7.63 (d, J = 9 Hz, 1H), 3.10–3.09 (t, J = 1.5 Hz, 2H), 1.82–1.80 (m, 2H), 1.61–1.52 (m, 2H), 0.89–0.87 (t, J = 3 Hz, 3H).

#### 2.1.5. 1-(6-Bromonaphthalen-2-yl)decan-1-one (**4**)

Compound **4** was synthesized according to the literature [28]. Yield: 11.0 g, 57%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 8.45 (s, 1H), 8.09–8.06 (d, J = 9 Hz, 2H), 7.87–7.81 (t, J = 9 Hz, 2H), 7.66–7.63 (d, J = 9 Hz, 1H), 3.10–3.09 (t, J = 1.5 Hz, 2H), 1.80–1.78 (m, 2H), 1.58–1.29 (m, 12H), 0.89–0.87 (t, J = 3 Hz, 3H).

#### 2.1.6. 2-Bromo-6-pentynaphthalene (**5**)

Compound **5** was synthesized according to the literature [28]. Yield: 0.6 g, 64%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 7.97 (s, 1H), 7.70–7.50 (m, 4H), 7.38–7.35 (m, 1H), 2.78–2.74 (m, 2H), 1.34–1.27 (m, 6H), 0.87–0.86 (t, J = 3 Hz, 3H).

#### 2.1.7. 2-Bromo-6-decynaphthalene (**6**)

Compound **6** was synthesized according to the literature [28]. Yield: 0.5 g, 52%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 8.04–8.02 (s, 1H), 7.70–7.58 (m, 4H), 7.38–7.35 (m, 1H), 2.84–2.82 (m, 2H), 0.131–1.27 (m, 16H), 0.87–0.86 (t, J = 3 Hz, 3H).

#### 2.1.8. 2-((6-Pentynaphthalen-2-yl)ethynyl)anthracene (**PNEA**)

2-Bromo-6-pentynaphthalene (1.0 g, 3.6 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (1.0 mg, 2 mmol), copper(I) iodide (2.0 g, 10.8 mmol), 20 mL triethylamine were dissolved in 20 mL toluene. 2-ethynyl-anthracene (0.8 g, 3.9 mmol) was added at room temperature. Mixture was refluxed 24 h at 90 °C. After cooled to room temperature, reaction mixture poured into water and then extracted with methylene chloride. The organic layer was separated and dried over MgSO<sub>4</sub>, and then the solvent was removed by using a rotary evaporator. The residue purified by column chromatography on silica gel with methylene chloride/hexane (1:5) to obtain the product. Yield: 0.8 g, 56%. mp: 212 °C, IR(KBr) cm<sup>-1</sup>: 3057–3021 (aromatic C–H), 2950–2843 (aliphatic C–H), 2301–2194 (triple bond). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 8.43 (s, 2H), 8.20 (s, 1H), 8.10 (s, 1H), 8.05–8.00 (m, 3H), 7.80–7.78 (d, J = 6 Hz, 2H), 7.65–7.63 (m, 3H), 7.50–7.41 (m, 2H), 7.38 (m, 1H), 2.82–2.78 (m, 2H), 1.77–1.71 (m, 2H), 1.41–1.37 (m, 4H), 0.95–0.91 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ : 141.680, 133.115, 132.185, 132.128, 131.844, 131.556, 131.347, 131.152, 130.698, 128.465, 128.379, 128.312, 128.280, 128.234, 128.211, 127.692, 127.584, 126.334, 126.269, 126.258, 125.823, 125.758, 120.167, 119.661, 91.017, 90.144, 36.163, 31.556, 30.986, 22.577, 14.036. C<sub>31</sub>H<sub>26</sub> Cal. C, 93.42; H, 6.584; Found: C, 93.94; H, 6.54 HRMS Cal. 398.2035, Found: 398.2033.

#### 2.1.9. 2-((6-Decynaphthalen-2-yl)ethynyl)anthracene (**DNEA**)

**DNEA** was prepared using the same method as described for compound **PNEA** using 2-bromo-6-nonylnaphthalene (1.0 g, 2.8 mmol), copper(I) iodide (1.6 g, 8.4 mmol), 2-ethynyl-anthracene (0.6 g, 3.1 mmol), 20 mL triethylamine. Yield: 0.8 g, 62%. mp: 202 °C, IR(KBr) cm<sup>-1</sup>: 3058–3026 (aromatic C–H), 2939–2840 (aliphatic C–H), 2316–2202 (triple bond). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 8.43 (s, 2H), 8.28 (s, 1H), 8.10 (s, 1H), 8.04–7.99 (m, 3H), 7.80–7.77 (d, J = 9 Hz, 2H), 7.64–7.61 (m, 3H), 7.52–7.50 (m, 2H), 7.40 (d, 1H), 2.82–2.77 (m, 2H), 1.75–1.70 (m, 2H), 1.36–1.12 (m, 14H), 0.92–0.87 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ : 141.700, 133.114, 132.184, 132.126, 131.850, 131.550, 131.355, 131.150, 130.698, 128.464, 128.320, 128.287, 128.243, 128.134, 127.780, 127.697, 127.587, 126.341, 126.270, 125.831, 125.765, 123.691, 120.164, 119.649, 91.019, 90.141, 36.206, 31.918, 31.326, 29.639, 29.610, 29.549, 29.382, 29.348, 22.701, 14.131. C<sub>36</sub>H<sub>36</sub> Cal. C, 92.26; H, 7.74; Found: C, 92.08; H, 7.76 HRMS Cal. 468.2817, Found: 468.2818.

## 2.2. Measurements

<sup>1</sup>H NMR spectra were recorded using a Bruker Advance-300 spectrometer. The thermal analyses were performed on a TA TGA 2100 thermogravimetric analyzer under N<sub>2</sub> atmosphere at a rate of 10 °C/min. Differential scanning calorimeter (DSC) was conducted under N<sub>2</sub> atmosphere using a TA instrument 2100 DSC. The sample was heated at 10 °C/min from 30 °C to 300 °C. UV–vis absorption spectra were measured using a UV-1650PC spectrophotometer. Cyclic voltammetry (CV) was performed on an EG and G Parc model 273 Å potentiostat/galvanostat system with a three-electrode cell in

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