

# Solution-processed single-crystal perylene diimide transistors with high electron mobility



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## ABSTRACT

We have successfully demonstrated a single-crystal field-effect transistors (FETs) based on an asymmetric perylenetetracarboxylic diimide (*a*-PDI) compound with polystyrene (PS)/SiO<sub>2</sub> bilayer as gate dielectric. The single crystals are in-situ grown on substrate from simple solution evaporation method, thus may be suitable for large area electronics applications. The PS modified gate dielectric could minimize charge trapping by the hydroxyl groups of the SiO<sub>2</sub> surface. The resulting solution processed single crystal transistors are characterized in ambient air, and exhibited maximum electron mobility of ca. 1.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and high  $I_{on}/I_{off} > 10^5$ .

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## 1. Introduction

Solution processed organic field-effect transistors (OFETs) have attracted a great deal of attention as promising components for low-cost, flexible and large area electronics applications [1–3]. A variety of  $\pi$ -conjugated organic molecules of both p- and n-type have been developed for the fabrication of complementary integrated circuits offering low-power operation, higher operating speed, and more stable device performance [4–13]. Unfortunately, the performance of n-type organic semiconductors has dawdled by that of the p-type materials due to poor electron mobility of the film and the lack of device stability operated under ambient conditions [14–18]. To date, the charge mobility of solution processed p-type OFETs has reached up to 10 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, while only a few solution processed n-type devices have mobility exceeding 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [19–27]. Additionally, single-crystal OFETs are far more interesting to estimate ultimate charge transport efficiencies and the greatest charge mobilities are reported for single crystal organic films. Therefore the development of solution processable high performance n-type OFETs is necessary for realization of low-cost organic electronics applications.

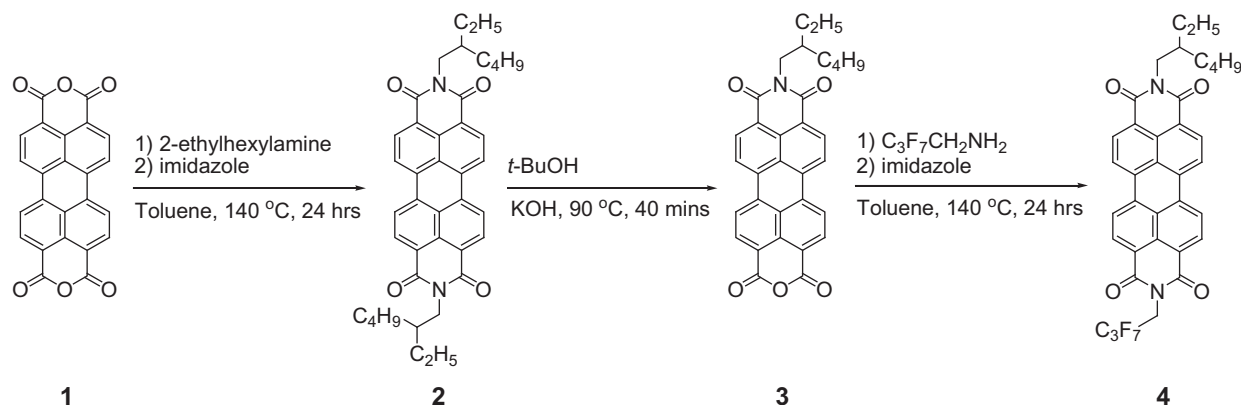
Perylene diimide (PDI) is an interesting material and many high mobility examples have been reported [28]. Among the best n-type

organic semiconductor, PDIs and their derivatives show air-stable electron mobility values up to 6.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, when single crystals are embedded in OFETs [29]. However, the vacuum deposited or solution processed PDIs exhibit lower electron mobility values of typically <1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> due to polycrystalline or granular film morphologies on the substrate [30–33]. It is believed that the greater structural order of single-crystal materials facilitate with superior device performance. Among the PDI molecules successfully explored in such high electron mobility devices, symmetric molecules with identical sidechains represent the majority of active element. In contrast, very few asymmetric molecules have been employed in the fabrication of high electron mobility organic transistors although asymmetric molecules may provide more options and adaptability for achieving high performance devices [34–39].

In this paper, a new asymmetric perylene diimide (*a*-PDI) compound (Scheme 1) with a fluorinated side chain at one imide nitrogen and a branched alkyl side chain at other imide position is reported and synthesized. Furthermore, we have demonstrated *a*-PDI single-crystal OFETs on polystyrene (PS)/SiO<sub>2</sub> bilayer gate dielectric. The well aligned single-crystals are in-situ grown on substrate by adopting simple solvent evaporation method, thus may be suitable for large area electronics applications. The PS modified gate dielectric could minimize surface polarity and charge trapping by the hydroxyl groups of the SiO<sub>2</sub> surface, resulting in high performance devices. The solution processed single crystal transistors are characterized in ambient air, and exhibited

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**Scheme 1.** Synthetic routes, reagents and conditions.

maximum electron mobility of ca.  $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is among the highest yet reported for an n-channel OFET based on a solution-processed PDI small molecule.

## 2. Experimental

### 2.1. Synthesis details

The target compound (**4**, *a*-PDI) was synthesized based on the methodology outlined in **Scheme 1**. The imidization reaction of perylene-3,4,9,10-tetracarboxylic dianhydride (**1**) with 2-ethylhexylamine in the presence of imidazole gave diimide **2**. Imide **3** was then obtained after diimide **2** was treated with potassium hydroxide in tert-butyl alcohol at 90 °C for 40 min. Finally, the reaction of compound **3** with 2,2,3,3,4,4,4-heptafluorobutylamine provided diimide **4** in 95% yield.

#### 2.1.1. Synthesis of compound **2**

A mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (compound **1**, 2.0 g, 5.10 mmol), imidazole (10.0 g, 146.90 mmol), 2-ethylhexyl amine (3.8 mL, 20.40 mmol) in toluene (5 mL) was heated at 140 °C under nitrogen for 24 h, then cooled to room temperature. Then hydrochloric acid (2 N, 25 mL) was added to the reaction mixture. The mixture was then stirred for overnight and filtered. The solid was collected, washed with water and purified with flash column chromatography ( $\text{CH}_2\text{Cl}_2$ ) to give N,N'-di(2-ethylhexyl)-perylene-3,4:9,10-tetracarboxylic diimide (compound **2**) as a red solid (2.4 g, 76%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.72–8.63 (m, 8H), 4.20–4.14 (m, 4H), 1.99–1.97 (m, 2H), 1.43–1.25 (m, 16H), 0.98–0.87 (m, 12H) (see [Supplementary data](#)).

MS-MALDI ( $m/z$ ):  $[M]^+$  calc. for  $\text{C}_{40}\text{H}_{42}\text{N}_2\text{O}_4$ : 614.315; found: 614.878.

#### 2.1.2. Synthesis of compound **3**

A mixture of N,N'-di(2-ethylhexyl)-perylene-3,4:9,10-tetracarboxylic diimide (compound **2**, 500.0 mg, 0.81 mmol) and potassium hydroxide (228.0 mg, 406 mmol) in tert-butyl alcohol (13.8 mL) was heated at 90 °C under nitrogen for 40 min, then cooled to room temperature. Then acetic acid (8 mL) was added to the reaction mixture. After the mixture was stirred for 2 h, hydrochloric acid (2 N, 25 mL) was added. Then, the system was stirred for another 30 min and filtered to give a solid, which was collected and washed with water. The solid was then purified with flash column chromatography ( $\text{CH}_2\text{Cl}_2$ , then  $\text{CH}_2\text{Cl}_2$ :AcOH = 8:1) to give N-(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-imide (compound **3**) as a red solid (225.3 mg, 55%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$  + TFA):  $\delta$  8.87–8.85 (m, 8H), 4.30–4.18(m, 2H), 2.05–1.95 (m, 1H), 1.44–1.32 (m, 8H), 0.98–0.86 (m, 6H) (see [Supplementary data](#)).

MS-MALDI ( $m/z$ ):  $[M]^+$  calc. for  $\text{C}_{32}\text{H}_{25}\text{NO}_5$ : 503.173; found: 503.917.

#### 2.1.3. Synthesis of compound **4** (*a*-PDI)

A mixture of N-(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-imide (compound **3**, 110.0 mg, 0.22 mmol), imidazole (1.05 g, 15.52 mmol) and 2,2,3,3,4,4,4-heptafluorobutylamine (87.01 mg, 0.44 mmol) in toluene (5 mL) was heated at 140 °C under nitrogen for 24 h, then cooled to room temperature. Then hydrochloric acid (2 N, 25 mL) was added to the reaction mixture. The mixture was then stirred for overnight and filtered. The solid was collected, washed with water and purified with flash column chromatography ( $\text{CH}_2\text{Cl}_2$ ) to give N-(2-ethylhexyl)-N'-(2,2,3,3,4,4,4-heptafluorobutyl)-perylene-3,4,9,10-tetracarboxylic diimide (compound **4**) as a red solid (142 mg, 95%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.72–8.59 (m, 8H), 5.04 (t,  $J_{\text{F-H}} = 15.5 \text{ Hz}$ ,  $\text{CH}_2\text{-CF}_2$ ), 4.21–4.08 (m, 2H), 1.98–1.94 (m, 1H), 1.47–1.25 (m, 8H), 0.98–0.87 (m, 6H) (see [Supplementary data](#)).

$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  –81.98, –117.50, –129.28.

EI-HRMS ( $m/z$ ): calc. for  $\text{C}_{36}\text{H}_{27}\text{N}_2\text{O}_4\text{F}_7$ : 684.1859; found: 684.1855.

### 2.2. Single crystal growth and device fabrication

The *a*-PDI single crystals were grown on highly doped p-type Si wafer with a thermally grown 300 nm thick  $\text{SiO}_2$  layer. Single-crystal OFET devices were assembled in bottom gate top contact configuration, whereas the oxide layer served as gate dielectric and the wafer acted as gate electrode. Prior to the surface treatment of the  $\text{SiO}_2$ , the wafer was cleaned in piranha solution and then washed in deionized water. The dielectric was treated with a thin layer of polystyrene (PS) film and thermally cross-linked at 100 °C for 12 h [40]. For surface treatment, 10 mg of PS ( $M_w = 127 \text{ k}$ ) was dissolved in 1 mL of NMP solvent and stir overnight. Divinylbenzene (DVB) of 10 vol% was added to the PS solution and stir for at least 4 h and mixed solution was spin coated on the cleaned  $\text{SiO}_2$  substrate for 1 min at 3000 rpm. Finally, the substrate was annealed at 100 °C for 12 h to complete the cross-linking process. For single crystal growth, 1 mg of *a*-PDI was dissolved in 1 mL of chlorobenzene solution. A small piece of Si wafer as solution pinner was placed on the PS/ $\text{SiO}_2$  bilayer gate dielectric and then the *a*-PDI solution was dropped onto the substrate. The substrate was placed in a sealed Petri dish and the temperature of the system was maintained at 30 °C. After the solvent

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