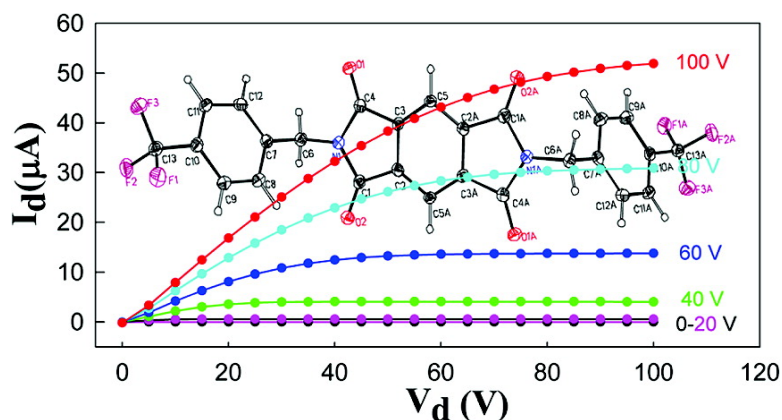


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## Pyromellitic Diimides: Minimal Cores for High Mobility n-Channel Transistor Semiconductors

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The past decade has witnessed an increasing interest in organic thin film transistors (OTFTs) due to their applications in light-emitting displays, radio frequency identification tags, and sensors.<sup>1–3</sup> Organic semiconductors can function either as a p-channel or n-channel charge carrier. While many organic materials can be used for p-channel OTFTs, there is only a limited number of organic materials that can be used for n-channel OTFTs.<sup>1,2,4</sup> Therefore, there is a need to explore more n-channel materials with high mobility and stability, to allow for combining n-channel and p-channel transistors in complementary circuits that have the advantages of low power dissipation, low noise, and greater operational stability.<sup>5</sup> Since the report of naphthalenetetracarboxylic diimides as air stable n-channel materials with mobility up to 0.1 cm<sup>2</sup>/(V.s), a large number of n-channel materials have been based on either naphthalene or perylene tetracarboxylic diimides.<sup>6,7</sup> Recently, several anthracene tetracarboxylic diimides were synthesized by Marks et al. through multistep reactions and found to be good n-channel materials with high on–off ratios.<sup>8</sup> The common structural features, the tetracarboxylic diimides, were flanked on both sides of the planar aromatic rings, which were varied from two-ring naphthalene to three-ring anthracene, and finally to five-ring perylene.

Though pyromellitic diimides are best known as segments of highly insulating polyimide dielectrics, it is nevertheless quite surprising that no attempt has been made to fabricate transistors from pyromellitic diimide derivatives, which have the simplest aromatic ring (benzene) in the center, and the tetracarboxylic diimides on both sides of the benzene ring. Pyromellitic diimide derivatives can be easily prepared by one-step reaction between pyromellitic dianhydride and various amines. Compared to naphthalene or perylene tetracarboxylic diimides, the facile synthesis of pyromellitic diimide derivatives offers an advantage in large scale synthesis due to its high conversion yield and ease of purification. Thus, it is possible to screen a large number of imide side chains and investigate the impact of side chains on the mobility and environmental stability of the pyromellitic diimide derivatives. In this Communication, we report synthesis and transistor behaviors of three pyromellitic diimide derivatives using fluorinated side chains. The fluorinated side chains are introduced to stabilize the n-channel OTFTs in air, as has been previously observed.<sup>7c,f,g</sup>

The synthesis of pyromellitic diimide derivatives involves one simple conventional reaction (Scheme 1). Amines and pyromellitic dianhydride were heated in dimethylformamide (DMF) in 110 °C. After the solution was cooled down, the crystallized product was collected by filtration, then washed with methanol, and finally sublimed under vacuum. Elemental analysis results indicate the high purity for the sublimed compounds. The synthesis and characterization details for **1–3** are described in Supporting Information.

Single crystals of **1** were obtained by slowly cooling hot saturated DMF solutions. The unit cell of the single crystal is monoclinic with  $a = 10.24 \text{ \AA}$ ,  $b = 11.53 \text{ \AA}$ ,  $c = 9.28 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 97.78^\circ$ ,

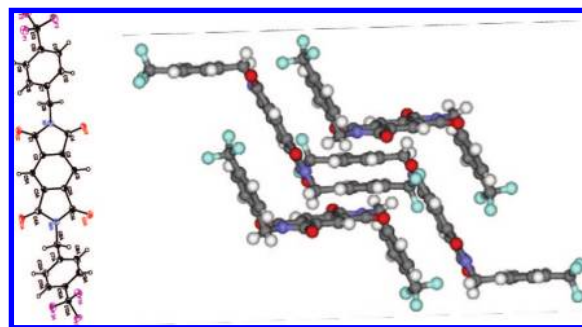
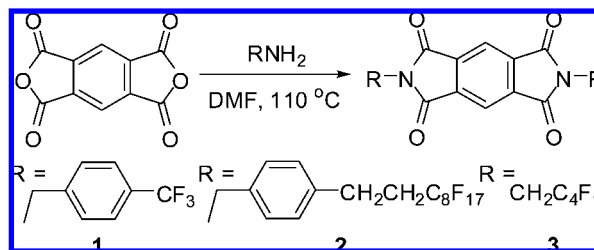


Figure 1. Crystal structure (left) and crystal packing diagram of **1** (right).

### Scheme 1. Synthetic Route to Pyromellitic Diimide Derivatives



$\gamma = 90^\circ$ . The crystal structure and crystal packing diagram of **1** are shown in Figure 1. Interestingly, the crystal structure of **1** exhibits a close  $\pi$ – $\pi$  packing between the side chain benzene ring and the pyromellitic diimide core. X-ray diffraction (XRD) spectra of the sublimed thin films for compounds **1**, **2**, and **3** showed layer spacings of 18.6, 36.8, and 22.6 Å in that order, which is consistent with their molecular lengths. Molecules are believed to orient perpendicular to the substrate, though there is a modest degree of tilting. The 18.6 Å  $d$ -spacing observed for **1** reveals that the thin-film packing of **1** is different from its single crystal packing. For **1**, several orders of the layer diffraction were observed for the samples with octadecyltrichlorosilane (OTS) surface treatment and deposited at 65 °C, indicating its high crystallinity in thin film phase (see Supporting Information).

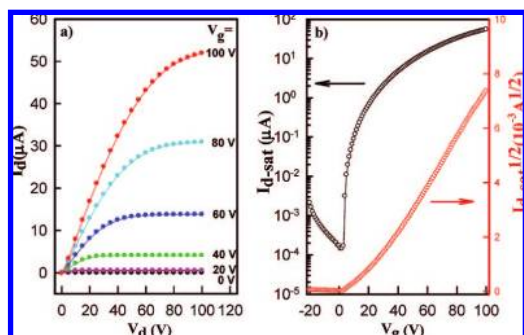
The semiconducting films of 45 nm thickness were deposited at substrate temperatures of 25–115 °C, with SiO<sub>2</sub> dielectrics, and evaporated gold top contact source and drain electrodes. The channel widths and lengths were approximately 6.5 mm, and 270 μm, respectively. Some substrates were treated with OTS to form a self-assembled monolayer. Devices on compound **1** were tested under different conditions to investigate the influence of substrate temperature and surface treatment on its mobility.

The measured current–voltage characteristics for all the devices show well-defined gate modulation. As an example, Figure 2 depicts the current–voltage characteristics of **1** prepared by sublimation

**Table 1.** Mobilities, On–Off Current Ratios and Threshold Voltages of Pyromellitic Diimides Based OTFTs Prepared by Vapor Deposition<sup>a</sup>

compounds	$T_s$ (°C)	substrate treatment	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	max $\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$V_{th}$ (V)	on/off	no. devices tested
<b>1</b>	25	OTS	0.036 ± 0.001	0.038 (0.025)	18.1 (28.5)	10 <sup>5</sup> (10 <sup>3</sup> )	12
<b>1</b>	25	N	0.004 ± 0.0004	0.0045	18.6	10 <sup>4</sup>	8
<b>1</b>	65	OTS	0.055 ± 0.001	0.056	14.9	10 <sup>6</sup>	4
<b>1</b>	65	N	0.029 ± 0.001	0.030	29.2	10 <sup>6</sup>	4
<b>1</b>	70	OTS	0.070 ± 0.003	0.074 (0.039)	22.4 (31.2)	10 <sup>6</sup> (10 <sup>5</sup> )	14
<b>2</b>	115	OTS	0.069 ± 0.004	0.079 (0.054)	14.4 (15.4)	10 <sup>6</sup> (10 <sup>4</sup> )	16
<b>3</b>	25	OTS	0.023 ± 0.004	0.030 (0.013)	13.7 (21.6)	10 <sup>5</sup> (10 <sup>5</sup> )	7

<sup>a</sup> Values in parenthesis are measured in air.  $T_s$ , substrate temperature; OTS, octadecyltrichlorosilane; N, no treatment;  $V_{th}$ , threshold voltage.



**Figure 2.** Current–voltage characteristics of **1** prepared by sublimation at substrate temperature of  $T_s = 70$  °C: (a) plot of  $I_d$  versus  $V_d$ ; (b) plot of  $I_{d-sat}$  versus  $V_g$ .

at substrate temperature of  $T_s = 70$  °C. Mobilities were calculated from the saturation regime and fitted in the regions of highest slope, and the results are listed in Table 1. Table 1 also lists a summary of device performance of **1** deposited under some other conditions, and of **2** and **3** deposited at 115 and 25 °C, respectively. The results show that the charge carrier mobility for **1** increases when there is a self-assembled OTS thin layer between the gate dielectrics and organics. At the same time, mobility increases with increased substrate temperature due to increased crystallinity and enlarged grain sizes, which are confirmed by XRD spectroscopy and AFM images, respectively (Supporting Information). The highest mobility for **1** is 0.074 cm<sup>2</sup>/(V.s) obtained from a device deposited at 70 °C, and with OTS surface treatment. For **2** we also achieved a high mobility of 0.079 cm<sup>2</sup>/(V.s) and a on/off ratio of 10<sup>6</sup>, when it was deposited on the OTS-treated surface at 115 °C (Supporting Information). All obtained film effect transistors can be operated under ambient conditions in air, although their mobilities in air are not as high as those in vacuum. For example, the mobility and on/off ratio for **2** dropped to 0.054 cm<sup>2</sup>/(V.s) and 10<sup>4</sup>, respectively, due to the presence of water and oxygen.

Values in vacuum and in air were obtained from devices which had been previously exposed to air for at least 15 and 30 min, respectively. We did generally observe a decrease in mobilities when the devices were operated in air and an increase in mobilities when the devices resumed being operated in vacuum. Attempts to improve mobilities, solubilities, and air stabilities are currently underway through synthesis of further derivatives.

The electrochemical properties of **1** and **3** were investigated by cyclic voltammetry. The voltammograms are shown in Supporting Information, Figures S12–S13, and their reduction potentials and lowest unoccupied molecular orbital (LUMO) levels (ca. 3.9 eV) are given in Table S1 (Supporting Information). Both **1** and **3** exhibit

two reversible one-electron reductions, which are in agreement with reported observations for pyromellitic diimide derivatives.<sup>9</sup>

In summary, a novel family of n-channel materials based on pyromellitic diimide derivatives have been synthesized and fabricated for organic field effect transistors. The field effect electron mobility of these materials is found to be as high as 0.079 cm<sup>2</sup>/(V.s). In addition, the on/off ratios of pyromellitic diimide based transistors can reach a high value of 1 000 000. With its shorter  $\pi$ -conjugation length, the pyromellitic diimides are relatively transparent to visible light compared to naphthalene or perylene tetracarboxylic diimides with the same side chain, which makes them promising candidates for transparent electronics.

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**Supporting Information Available:** Details of synthesis, experiment procedures, DSC traces, UV–vis/electrochemical data for compound **1** and **3**, X-ray diffraction graphs, AFM images, current–voltage characteristics of **2** and crystallographic data of **1** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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