

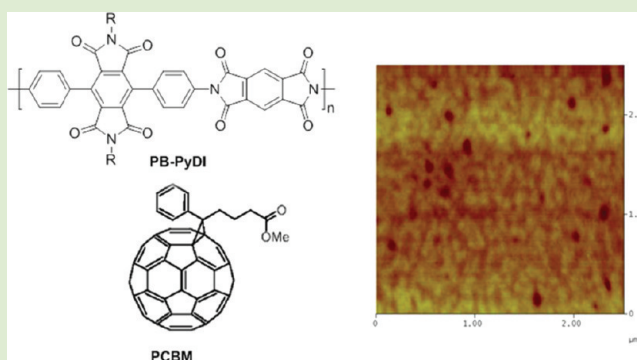
Synthesis and Characterization of a Pyromellitic Diimide-Based Polymer with C- and N-Main Chain Links: Matrix for Solution-Processable n-Channel Field-Effect Transistors

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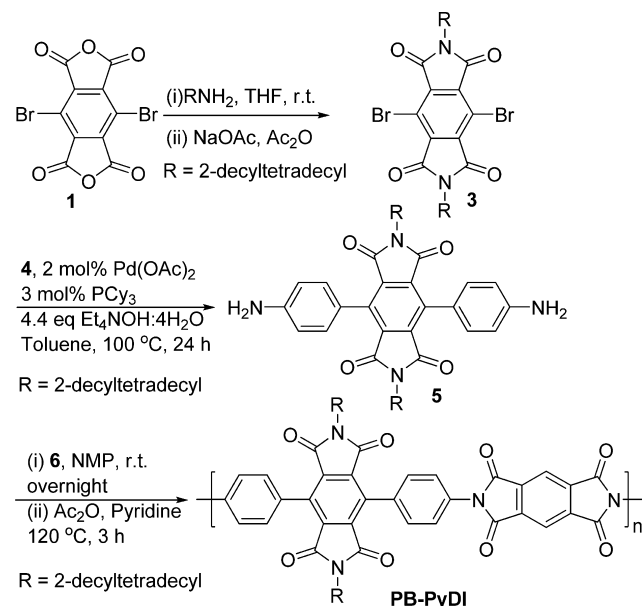
S Supporting Information

ABSTRACT: A highly soluble pyromellitic diimide-based polymer was obtained through imidization polymerization. The novel architecture features diimide subunits linked alternately at 3,6 and *N,N'* positions. The polymer is highly transparent in the near-ultraviolet–visible regions. Smooth and uniform thin-films were obtained through spin-coating even after blending the polymer with PCBM in 1:9 polymer/PCBM weight ratio. While the polymer itself has modest electron mobility in typical bottom-gate top-contact OFETs, an electron mobility of $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved for the blend, which increased to $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ on exposure to propylamine. Thus, polyimides are demonstrated as promising binder materials for solution-processable n-channel semiconductor blends, of which very few examples are known.



Organic field-effect transistors (OFETs) are receiving increasing attention due to their potential applications in display technologies, smart cards, and radio frequency identification (RFID) tags.^{1–3} Improving the performance characteristics of

Scheme 1. Synthesis of PB-PyDI



n-channel (electron transporting) OFETs has become a major goal toward implementation of organic complementary circuits. Several vapor-deposited and solution-processable small molecules and polymers based on aromatic diimides,^{4–13} acenes/condensed/heterocyclic rings,^{14–19} and fullerenes^{20–23} have been reported with relatively high electron mobilities. Furthermore, organic semiconducting polymers have several advantages such as printability and smooth coating from solution to fabricate flexible transistors.

Aromatic diimides such as naphthalenetetracarboxylic diimide (NTCDI), perylenetetracarboxylic diimide (PTCDI), and pyromellitic diimide (PyDI) have high dimensional stability, good chemical resistance, and excellent thermal, mechanical, and electronic properties.⁴ Among these, PyDI is the smallest moiety with sufficient electron affinity for electron injection and transport. In our previous investigations, n-channel materials with this core showed promising electron mobility in OFETs.²⁴ By varying side-chain length, degree of fluorination, and incorporation of phenyl or oxygenated groups, we were able to tune the solubility or volatility of the molecules and packing and morphology of the deposited film. The performance characteristics such as mobility and stability in air were optimized. Much of the work until now has been devoted to

Received: August 7, 2011

Accepted: December 1, 2011

Published: December 5, 2011

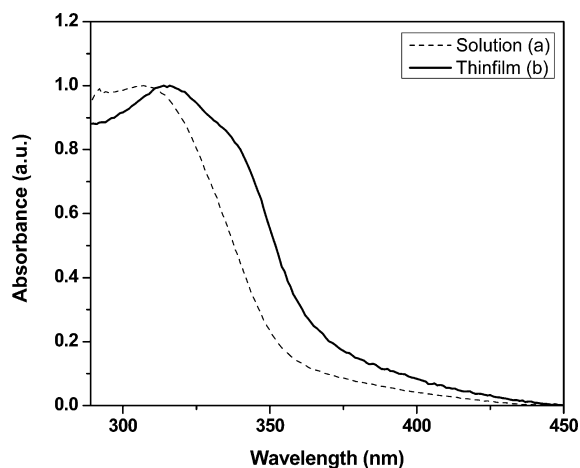


Figure 1. (a) Solution and (b) thin-film UV/vis absorption spectra of PB-PyDI.

Table 1. Optical and Electrochemical Data of PB-PyDI

	solution ^a λ_{\max} (nm)	film λ_{\max} (nm)	$E_g^{\text{opt}b}$ (eV)	E_{red} onset (V)	LUMO ^c (eV)	HOMO ^d (eV)
PB-PyDI	307	315	3.21	-1.00	-3.80	-7.01

^aMeasured in chlorobenzene solution. ^bCalculated from the onset of thin-film absorption spectrum. ^cLUMO = -4.8 eV - E_{red} onset. ^dHOMO = LUMO - E_g^{opt} .

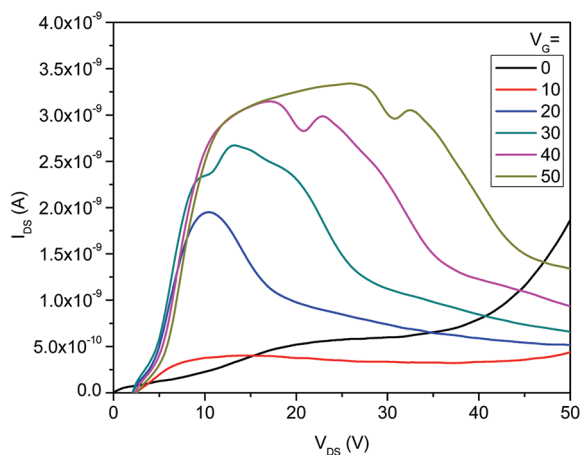


Figure 2. Gate voltage dependent transistor behavior of PB-PyDI-based device.

ascertaining the effect of substitution at the imide linkage. Although the 3,6-carbon-functionalized PyDIs would be important compounds in terms of their optoelectronic and electrochemical properties, they have not been considered as organic semiconductors.

On the basis of the above considerations, we have synthesized a new PyDI-based polymer (PB-PyDI; shown in Scheme 1) and fabricated a solution-processed OFET. Modest electron mobility was observed using the polymer as the sole semiconductor. The excellent film-forming ability of PB-PyDI extended to a blend with a 1:9 weight ratio of the polymer and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), which also formed a smooth and uniform film with electron mobility of $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off ratio of 1000 in an OFET.

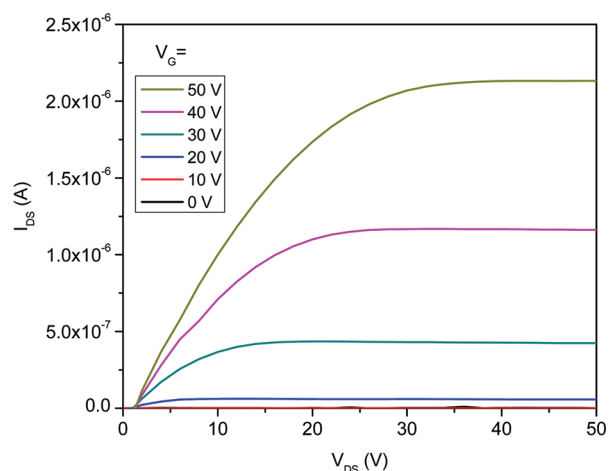


Figure 3. Output curves of semiconducting blend (9:1 PCBM + polymer)-based device.

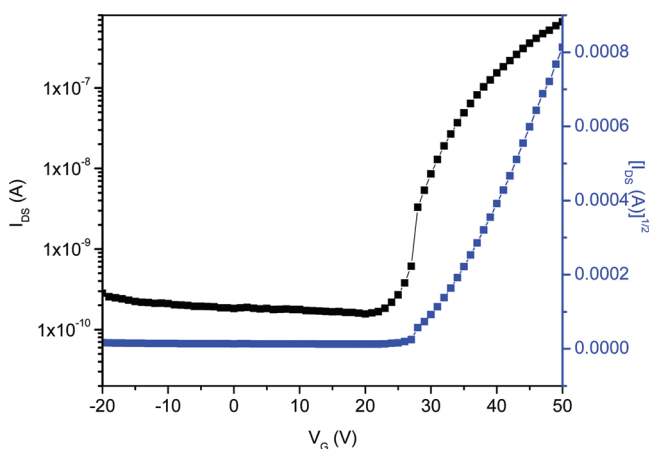


Figure 4. Transfer curves of semiconducting blend (9:1 PCBM + polymer)-based device.

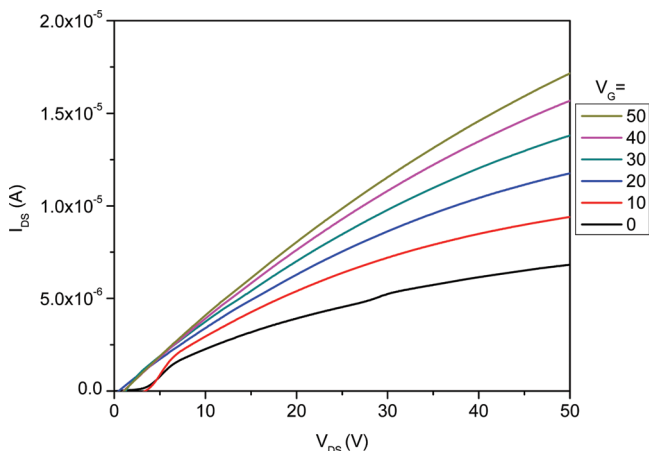


Figure 5. Output curves for the "normally on" OFET after exposure to propylamine.

The synthetic strategy illustrated in Scheme 1 was used to prepare the polymer. The starting materials 3,6-dibromopyromellitic dianhydride²⁵ (**1**) and 2-decyl-1-tetradecyl amine²⁶ (**2**) were prepared according to the reported procedures. Compounds **1** and **2** were reacted at room temperature in dry THF solution to form the amic acid and consequently treated

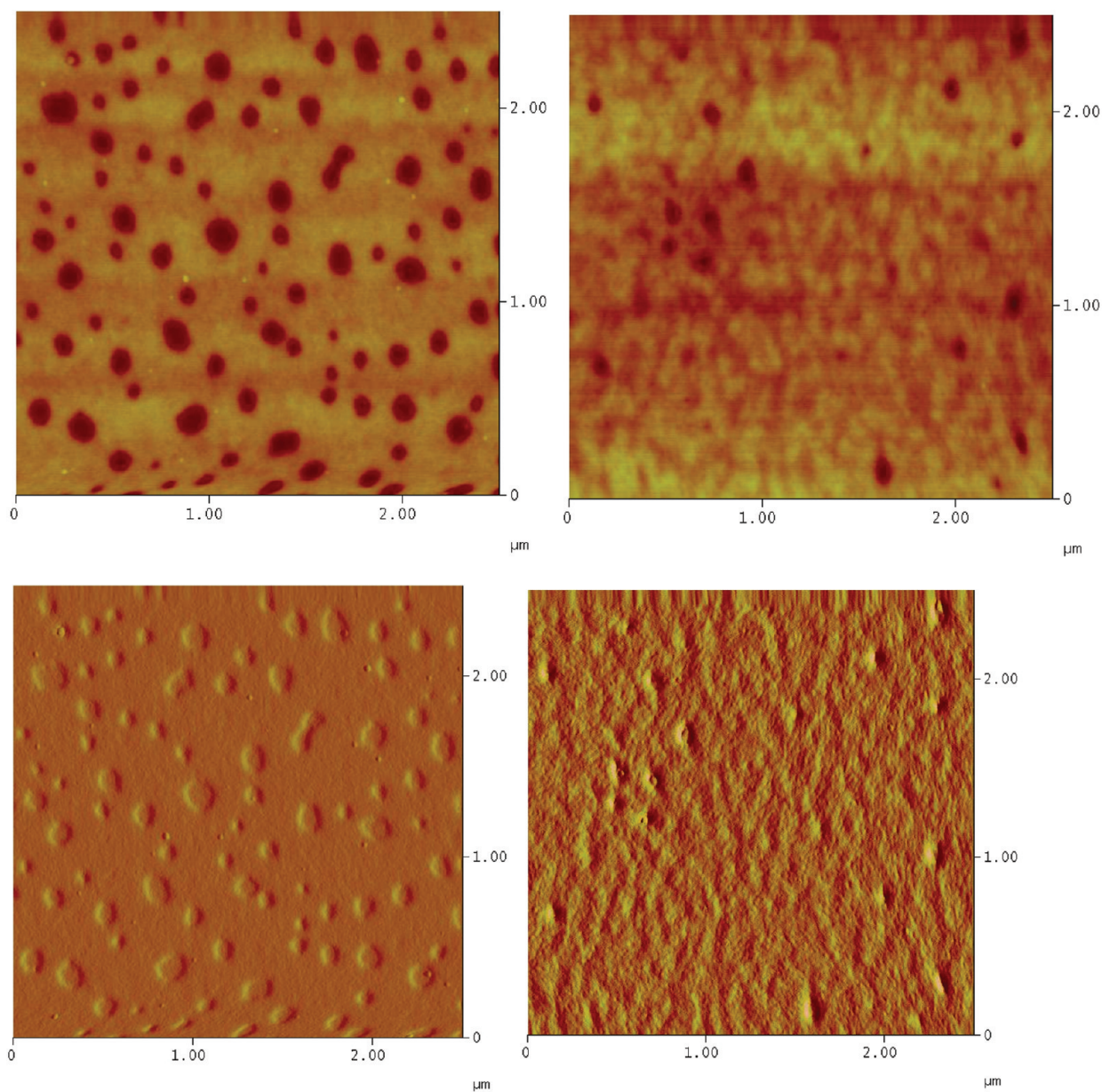


Figure 6. AFM images of films of 90% PCBM-10% polymer spin-coated from 1% solutions in chlorobenzene: left, polystyrene binder; right, **PB-PyDI**. Height scale for the top images is 0–25 nm. The bottom images are scans of voltage needed to restore the cantilever. Though heights are not defined, domain shapes are clearly visible.

with NaOAc and Ac₂O to give *N,N'*-bis(2-decyltetradecyl)-3,6-dibromopyromellitic diimide (**3**).²⁷ *N,N'*-Di-2-decyltetradecyl-3,6-bis(4-aminophenyl)pyromellitic diimide (**5**) was prepared by adopting the Suzuki–Miyaura reaction between **3** and 4-aminophenylboronic acid pinacol ester (**4**). Compound **5** was purified by column chromatography and then by precipitating in chloroform/methanol. Its red color is typical of other 3,6-diamino-substituted PyDIs that we have made and disappears on amidization/imidization. **PB-PyDI** was prepared by polycondensation of diamine **5** and pyromellitic dianhydride (**6**) via a conventional two-step process, that is, the formation of a poly(amic acid) by stirring **5** and **6** in 2 mL of 1-methyl-2-pyrrolidone and subsequent chemical imidization by using a dehydrating agent, a mixture of acetic anhydride and pyridine. Among the thermal and chemical imidizations, we have chosen the chemical imidization method to obtain highly soluble polymer, as observed by the Hsiao and co-workers.²⁸ As

expected, the title polymer showed very good solubility in chloroform, toluene, and chlorobenzene, which enables spin coating from solution.

FTIR spectra of the polymer (see Supporting Information, Figure S1) show two carbonyl stretching bands at 1714 and 1768 cm⁻¹ that can be assigned to symmetric and asymmetric imide stretching bands. For this polymer, number-average molecular weight (*M_n*) of 16.63 kDa and polydispersity (PDI) of 1.9 were determined by gel permeation chromatography (GPC) in chloroform versus polystyrene standards. Differential scanning calorimetry (DSC) did not provide evidence of a glass transition temperature in the second heating curve (see Supporting Information, Figure S2). We have observed small artifacts in the first heating curve, which can be assigned to the release of captured solvent molecules activated by the thermal motion of the polymer chains. The UV–visible absorption spectra of the polymer exhibited λ_{max} of 307 nm in solution and

315 nm in thin film, demonstrating the transparent nature of PB-PyDI in the thin film state (Figure 1 and Table 1).

The electrochemical measurements of the polymer were carried out on a thin film (drop cast onto a platinum electrode) in 0.1 M solution of Bu_4NPF_6 in anhydrous acetonitrile under N_2 at a scan rate of 100 mV/s. The ferrocene/ferrocenium redox couple (Fc/Fc^+) was used as an internal reference. It is assumed that the redox potential of Fc/Fc^+ has an absolute energy level of -4.80 eV to vacuum.²⁹ The LUMO energy level was calculated from the onset of the reduction curve obtained from cyclic voltammetry (CV) and found to be -3.80 eV (Table 1), which reflects the strong electron affinity of the PyDI core, similar to the NTCDI core and to PCBM. This value is about 0.3 eV farther from vacuum than our measurement for a monomeric dialkyl PyDI. The optical band gap of 3.2 eV is estimated from the absorption onset of the thin film.

To study the electrical performance of PB-PyDI, OFETs were fabricated using the typical top-contact, bottom-gate geometry on hexamethyldisilazane (HMDS)-treated n-doped Si wafers as gate electrodes with 300 nm of thermally grown SiO_2 as a dielectric layer. The gate dielectric capacitance is calculated to be 11.5 nF cm^{-2} assuming a dielectric constant of 3.9 for SiO_2 . Aluminum source and drain electrodes were deposited with the channel width (W) of $8000 \mu\text{m}$ and length (L) of $100 \mu\text{m}$. The active layer was spin-coated onto the substrate at 2500 rpm from a 10 wt % chlorobenzene solution and annealed at 56°C in vacuum.

PB-PyDI showed n-channel transistor characteristics as shown in Figure 2. We were unable to calculate a precise charge carrier mobility for this device because of not attaining the saturation region, but the increased current at gate voltage of 20 V versus gate voltage of 10 V indicates a $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ mobility magnitude. Improved electron injection mechanisms, shorter device lengths, main chain conjugation, and shorter and fluorinated alkyl side chains are all expected to improve this mobility. More importantly, we observed a smooth and continuous film quality for PB-PyDI, and combined with its electron affinity, reasoned that it could serve as an effective binder matrix for polycrystalline n-channel molecular solids. Hence, we blended the polymer with PCBM in a 1:9 weight ratio to combine the advantages of excellent film forming ability of the former and semiconducting behavior of the latter to fabricate an organic semiconducting blend-based OFET. After annealing at 56°C , this device exhibited an electron mobility (μ_e) of $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and threshold voltage (V_T) of about 20 V with $I_{\text{on}}/I_{\text{off}}$ 10^3 . Output and transfer curves in vacuum are shown in Figures 3 and 4, respectively. The mobility is likely trap-limited. Support for the influence of traps comes from exposure of the device to propylamine, an n-dopant that led to increased mobility^{30,31} to $1.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, though the device also became “normally on” (significant current even at zero gate voltage, generally because of doping or interface dipoles), as shown in Figure 5. This mobility is comparable to published values for PCBM itself spincoated onto oxide dielectric.^{32–35}

A significant advantage of PB-PyDI as a binder polymer is the smoothness it confers on solution-deposited films of PCBM. Spin-coated films of PCBM are often so rough as to be discontinuous. The use of a conventional polymer, polystyrene, as binder, gives a film with separated domains of PCBM and the polymer, as shown by atomic force microscopy (AFM) in Figure 6. The PB-PyDI blend, however, has many fewer

separated domains and instead shows most of the PCBM continuously blended. Preliminary results indicate that electron-transporting PB-PyDI blends can also be made with small molecule NTCDIs; further investigations of these compositions are in progress.

In summary, we have reported the synthesis and characterization of a novel 3,6 and N,N' -linked pyromellitic diimide-based polymer. The polymer has excellent film-forming ability and is transparent in nature, which makes it a potentially valuable material for flexible and transparent electronics. The polymer blended with PCBM in 1:9 weight ratio was used in an OFET that showed charge carrier mobility of 10^{-3} – $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. We thus verified that polyimides, with their rarely recognized electron transporting ability,^{36,37} can serve as binder materials to form organic semiconducting blends and composites,^{38–43} with potential capability of bridging closely spaced but disconnected domains of small molecules with diminished barriers to electron transport. When used in OFETs, the blends produce n-channel characteristics, in addition to their well-known roles as dielectrics.

■ ASSOCIATED CONTENT

📄 Supporting Information

Detailed synthetic procedures and characterization of starting compounds and polymer, device fabrication, FT-IR, DSC, CV and current–voltage characteristics. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was primarily supported by the Air Force Office of Scientific Research, Grant #FA9550-09-01-0259. Support for monomer synthesis and fullerene chemistry is from National Science Foundation, Division of Materials Research, Grant No. 0905176 and Division of Electronic, Communications, and Cyber Systems, Grant No. 0823947, respectively. N.J.T. thanks the National Institute of Environmental Health Sciences Training Program [ES 07141] for a fellowship.

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