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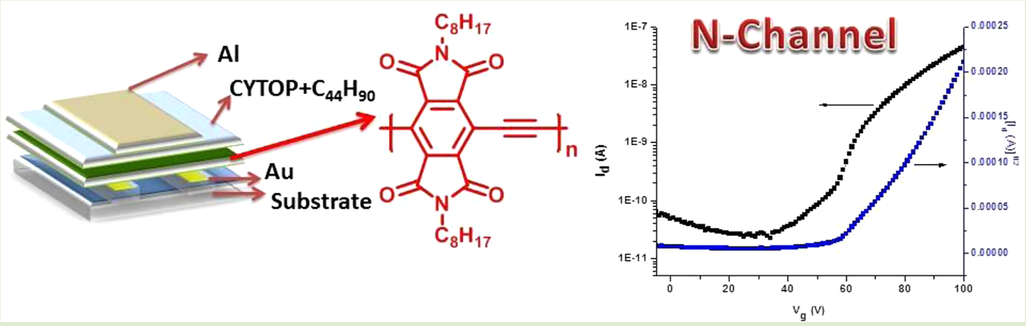
Pyromellitic Diimide−Ethynylene-Based Homopolymer Film as an N-Channel Organic Field-Effect Transistor Semiconductor

Srinivas Kola,[†] Joo Hyun Kim,[§] Robert Ireland,[†] Ming-Ling Yeh,[†] Kelly Smith,[†] Wenmin Guo,[†] and Howard E. Katz*[,†,‡]

[†]Department of Materials Science and Engineering and [‡]Department of Chemistry, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218, United States

[§]Department of Polymer Engineering, Pukyong National University, Yongdang-Dong, Nam-Gu, Busan 608-739, Korea

Supporting Information



ABSTRACT: We report the synthesis and characterization of two solution-processable pyromellitic diimide (PyDI)-acetylene-based conjugated homopolymers. Adjacent PyDI cores were connected with triple bond linkages by reacting 3,6-dibromo-*N*,*N*′-dialkyl pyromellitic diimides with bis(tributylstannyl)acetylene under Stille coupling conditions. Cyclic voltammetry revealed that these polymers have sufficient electron affinity to accept electrons. Absorption spectra revealed that one polymer, with a simple octyl chain, has greater intermolecular interaction or conjugation after forming a thin film, and that film exhibited electron transport in top-gate bottom-contact mode organic field-effect transistor (OFET) devices. X-ray diffraction (XRD) and atomic force microscopy (AFM) results show that the octyl polymer is amorphous on the bulk scale. The polymer exhibited electron mobility of about 2×10^{-4} cm^2 V^{-1} s^{-1} with on/off ratio of 10^3 and is the simplest n-channel polymer yet reported. A 4-trifluoromethylphenethyl side chain did not result in measurable electron mobility. The octyl polymer exhibited negative Seebeck coefficient on the order of −40 μV/K in thermoelectric devices, further substantiating its n-channel activity. The demonstration of electron transport from such a simple polymer has opened a new path for obtaining n-channel semiconducting activity from polymer films.

N-channel semiconducting polymers are of interest for organic field-effect transistors (OFETs), organic p−n junctions, solar cells, and complementary logic circuits.[1−3] These polymers have been enticing targets in the organic and printed electronics community. Polymeric semiconducting materials are advantageous in that they are solution processed and potentially printable, avoiding the need for conventional photolithography for patterning.[4,5] Organic semiconductors can function either as p-channel or n-channel charge carriers, depending on orbital energy levels, contact properties, dielectric interface functionalities, and the testing environment. Low-lying lowest unoccupied molecular orbital (LUMO) energies favor n-channel activity, while high-lying highest occupied molecular orbital (HOMO) energies favor p-channel behavior. Low bandgap materials with orbitals meeting both criteria are often ambipolar.[6−11] While many organic molecular solids and polymers can be used for p-channel OFETs,[12−15] and the number of n-channel molecular solids is growing,[16−21] there is only a limited number of semiconducting polymers that can be used for n-channel OFETs where the n-channel activity is strongly predominant.[22−26] This predominance is advantageous for complementary inverter switching,[27−30] in bulk heterojunction solar cells,[31−34] and for use as matrices for the n-semiconductor leg of thermoelectric composites, where the matrix should act synergistically with n-type additives.[35−38]

Several polymers with rylene diimides,[9,24,39−44] diketopyrrolopyrroles,[10,45,46] and isoindigos[47] have been reported with high electron mobilities, many of which are ambipolar. Also, the solubility of many of these polymers depends on large, branched alkyl side chains, making it necessary to explore a wide range of side chain alternatives; some of the polymers require intensive synthetic effort; and their activity is highly

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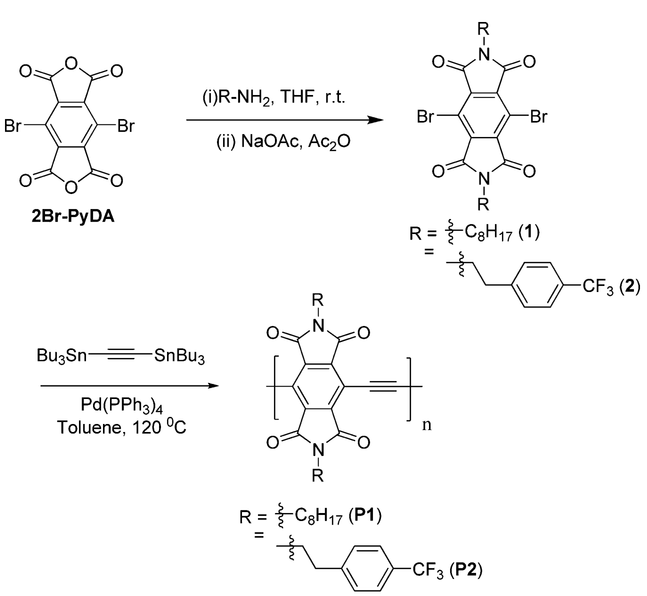
dependent on device structure and inert atmosphere processing environments. The polymers also strongly absorb light in the full visible range, limiting their use in transparent electronics. Thus, further exploration of such polymers is warranted.

Because of the high chemical stability and excellent thermal, mechanical, and electronic properties, rylene diimides have received particular attention in n-channel OFETs.[3] Pyromellitic diimides (PyDI), having the smallest rylene core, have low-lying LUMO energies, though only limited molecular areas for intermolecular π overlap. In our previous investigations, molecular solids with this core (and a trifluoromethylphenethyl side chain) showed promising electron mobility in OFETs.[48] Recently, we reported a PyDI-based polymer with C- and N-main chain links that showed limited electron transport. While this was the first proposal of a polyimide as an electron transporter, the polymer did not yield OFETs showing saturation behavior unless blended with small molecule n-semiconductors. The phenyl bridge between PyDI backbones was twisted in its most favorable conformation, limiting conjugation as well as interchain interactions.[49] Marks et al. demonstrated the importance of planarity in such polymers by studying a series of bithiophene-imide-based polymers.[50] Triple bonds, while not considered as conjugating as double bonds or double bond-containing rings,[51,52] have the minimum steric impact among conjugating subunits.[53] Small molecules and polymers with triple bonds in main chains have been considered for OFETs and organic photovoltaics.[54−57] Recently, Watson et al. reported four planar PyDI-based donor−acceptor poly(phenylethynylene)s, synthesized using Sonagashira coupling and having LUMO energy around −3.6 eV, in the range for n-channel semiconductors.[58] Building on the premise that placing an ethynyl linkage between adjacent PyDI backbones would yield better planarity and higher conjugation than with the phenyl linkage, and thus better OFET behavior, in agreement with the implication of Watson et al., we report the first demonstration of saturation OFET behavior from a simple poly(PyDI-ethynylene) synthesized using Stille coupling.

We introduced the ethynyl linkage between PyDI backbones by following the strategy illustrated in Scheme 1. 3,6-Dibromopyromellitic dianhydride (**2Br-PyDA**) was synthesized from 1,2,4,5-tetramethylbenzene by successive bromination, permanganate oxidation, and ring closure as reported[59] (>70% yield per step) and then imidized using the one-pot reaction reported by Shinmyozu et al.[60] **P1** and **P2** were prepared by adopting the Stille coupling between the corresponding monomer (**1** or **2**) and bis(tributylstannyl)acetylene in toluene using Pd(PPh$_3$)$_4$ as catalyst. The purification and detailed synthetic procedures are described in the Supporting Information. Both polymers **P1** and **P2** are highly soluble in common organic solvents. Polymer molecular weights were evaluated by gel permeation chromatography (GPC) with tetrahydrofuran as eluent, and M_n was 3.8 kDA (corresponding roughly to octamer, with weight averages of 12−18-mers) with polydispersity (PDI) of 1.76 for **P1** and 5.9 kDa/1.95 PDI for **P2** versus polystyrene standards. Soluble polymer yields were limited by coupling efficiency (**P1**) and in situ product solubility (**P2**). No phase transition was observed for these polymers as evidenced by the differential scanning calorimetry (DSC) thermogram (second cycle) (see Supporting Information, Figure S1).

Scheme 1. Syntheses of P1 and P2



The optical absorption spectra of **P1** and **P2** in chlorobenzene and as thin film are shown in Figure 1, and absorption maxima (λ_{max}) are listed in Table 1. **P1** exhibits λ_{max} at 351 nm in chlorobenzene and at 406 nm as a thin film. This large red shift of λ_{max} from solution to thin film suggests a greater degree of conjugation or a lower-lying transition associated with aggregation in the film. For **P2**, no bathochromic shift was observed from solution to thin film. The film is highly transmissive at >480 nm. While there is a yellow tint to the films because of the absorbance in the blue spectral region, the material is less absorbing than the Polyera naphthalenetetracarboxylic diimide polymer N2200, as illustrated in Figure 1.

To determine the LUMO energy level and thus the ease of electron injection from electrode to polymer, we carried out cyclic voltammetry (CV) in 0.1 M TBAPF$_6$ supporting electrolyte under nitrogen with a scan rate of 100 mV/s.[50] Pt wire was used as a counter electrode; polymer drop-cast on Pt wire was used as a working electrode; and Ag/Ag+ (0.01 M AgNO$_3$ in acetonitrile) was used as a reference electrode. **P1** and **P2** each exhibited one reversible reduction wave with onset potential of −0.96 and −0.92 V, respectively (shown in Figure 2). Within the scanning window of acetonitrile, no oxidation wave was observed, making p-channel behavior unlikely. The LUMO energy levels of **P1** and **P2** were calculated to be −3.84 and −3.88 eV, respectively, which substantiates the potentiality of these polymers to accept electrons from electrodes and serve as n-channel organic semiconductors.[61]

To observe the possible electron-transporting nature of these polymers, we chose the top-gate bottom-contact device configuration for better projected performance.[9,62,63] All of the fabrication processes, except tetratetracontane (TTC) and metal evaporation, were carried out in ambient conditions, and the devices were tested in vacuum. Semiconducting layers were spin-coated onto interdigitated S/D electrodes (50 um channel length and 8100 um channel width) and subsequently annealed at an optimized temperature of 150 °C; then a 400 nm thick CYTOP gate dielectric was deposited by spin-coating and baked at 100 °C. To avoid the device short-circuiting because of pinholes in CYTOP, we also deposited 15 nm of TTC before depositing the 100 nm-thick Al gate electrode. The capacitance of the dielectric layer was calculated by

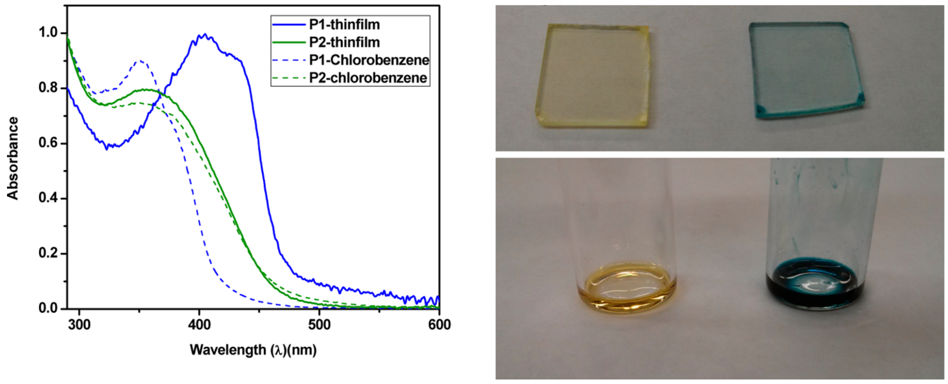


Figure 1. UV−vis absorption spectra of **P1** and **P2** in chlorobenzene solution and as thin film and photographs of thin film and bulk samples of **P1** and N2200.

Table 1. Summary of Molecular Weight and Photophysical and Electrochemical Properties of P1 and P2

			λ_{max} (nm)					
	M_n (kDa)[a]	PDI	thin film	solution[b]	E_g^{opt}[c] (eV)	E_{red} onset (V)	LUMO[d] (eV)	HOMO[e] (eV)
P1	3.8	1.76	407	352	2.57	−0.96	−3.84	−6.41
P2	5.9	1.95	362	359	2.67	−0.92	−3.88	−6.55

[a]Versus polystyrene standards. [b]Measured in chlorobenzene. [c]Calculated from the onset of thin-film absorption spectra. [d]LUMO = −4.8 eV − E_{red} onset. [e]HOMO = LUMO − E_g^{opt}.

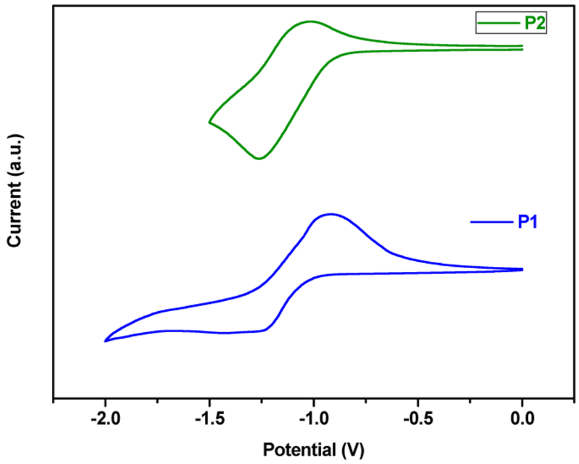


Figure 2. Cyclic voltammograms of **P1** and **P2**.

constructing a metal−insulator−metal (MIM) capacitor and found to be 4.38 nF cm^{-2}. The device geometry and the performance characteristics of **P1** are in Figure 3. Hysteresis in the on-regime was minimal. For **P2**, we did not observe any field-effect behavior. This may be due to the lack of structural organization in the thin-film state, as evidenced by the UV−vis absorption spectra, because of the more complicated and functional side chain. Very symmetrical and nonaromatic side chains may be essential to promote main-chain-based intermolecular association in this type of polymer.

P1-based OFET devices typically exhibited electron mobility (μ_e) of 0.5−2 × 10^{-4} cm^2 V^{-1} s^{-1} and threshold voltage of 55 V with I_{on}/I_{off} = 10^3. The aforementioned mobilities were obtained from five devices on four films. One outstanding device showed μ_e of 5.5 × 10^{-4} cm^2 V^{-1}s^{-1} (transfer curve shown in Supporting Information along with data from different channel lengths, Figures S2 and S3). Initially, we had fabricated simple bottom-gate top-contact devices but observed trap-limited output curves as shown in Figure S4 (see Supporting Information). We also tried baking the CYTOP−semiconductor bilayer at 150 °C, as often reported in the literature; however, lower charge-carrier mobility was then observed. Perhaps the CYTOP−semiconductor interface was degraded, as the baking temperature is well above the glass transition temperature of CYTOP (T_g = 108 °C).[64]

To examine the thermal annealing effect on thin-film morphology, we carried out X-ray diffraction studies. However, we did not see any definitive peaks in the XRD spectra (see Supporting Information, Figure S5). We also carried out AFM studies; little or no effect was observed after thermal annealing, and the film shows no obvious crystalline domains (Figure 4).

Additional evidence for the electron-only transport in this polymer comes from measurement of its Seebeck coefficient. The polymer gave Seebeck values similar in magnitude to nominal 10 nm films of vapor-deposited, hole-carrying 5,5′-bis(4-hexylphenyl)-2,2′-bithiophene (6PTTP6) or pentacene, −38 ± 4 μV/K. The negative polarity indicates electrons as the primary mobile charges, whereas the Seebeck coefficients for the p-semiconductors are positive.

In summary, we have introduced a new class of n-channel semiconducting polymers based on pyromellitic diimide by strategically placing the ethynyl linkage between them. The polymer exhibits unipolar transfer characteristics with moderate electron mobility of 2 × 10^{-4} cm^2 V^{-1} s^{-1} after ambient processing. The initial results show that a simple alkyl side chain promotes charge carrier mobility better than a phenethyl side chain. To the best of our knowledge, this is the first example of pyromellitic diimide polymer showing saturation n-channel activity and is the simplest n-channel polymer to date. While the amorphous nature of **P1** is a drawback for high mobility, this might be an advantage in electro-optical devices where light scattering must be minimized, as has been found for triaryl amine p-materials in organic light-emitting diodes.[65−68] There are many opportunities to improve ordering and reach crystallinity: side chains such as triethylene glycol (demonstrated by Patil et al.[23]), hybrid alkyl chains (demonstrated by

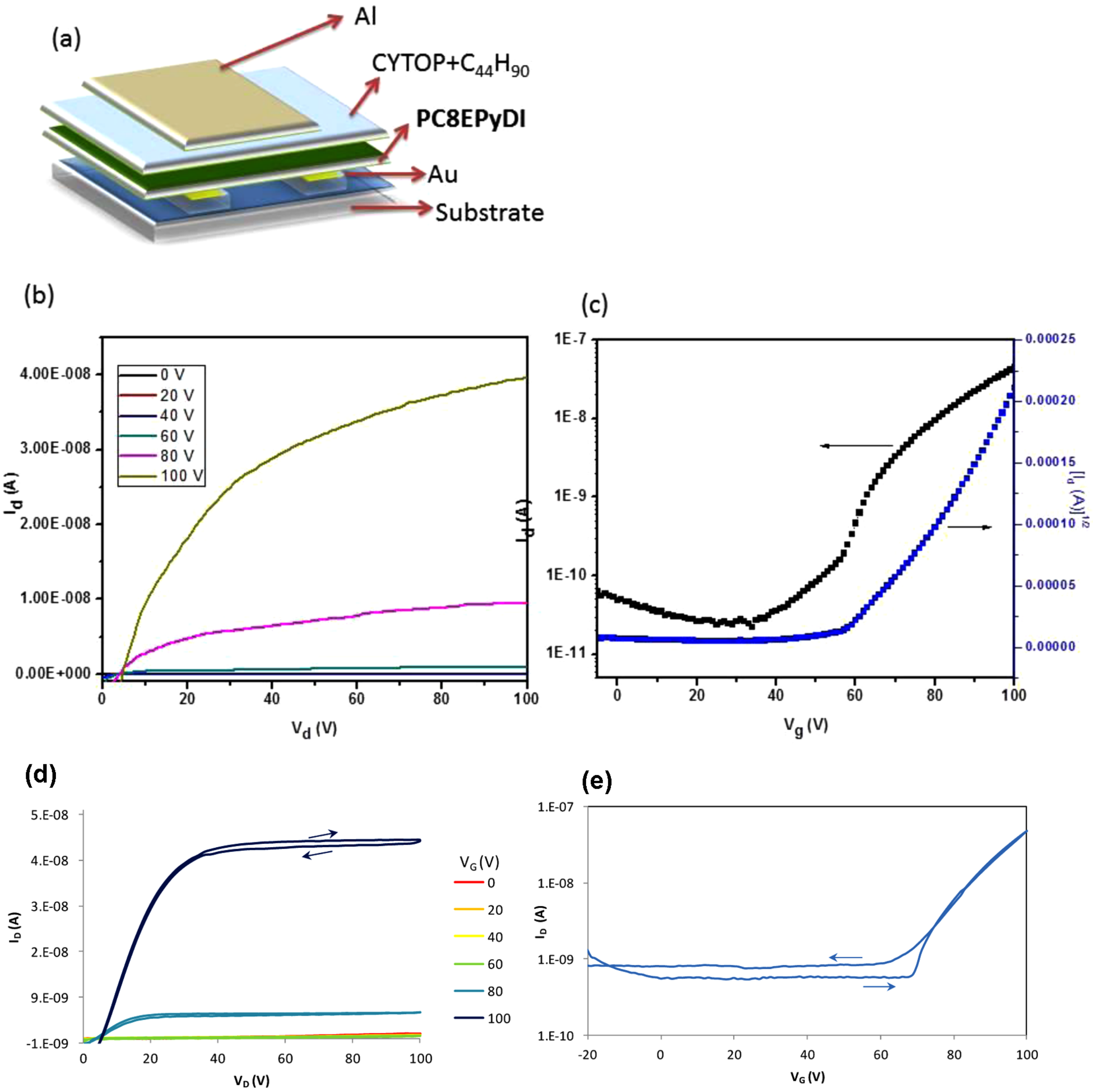


Figure 3. (a) Device structure, (b) Output curves, and (c) transfer curve of **P1**-based OFET device. (d,e) Output and transfer curves showing hysteresis.

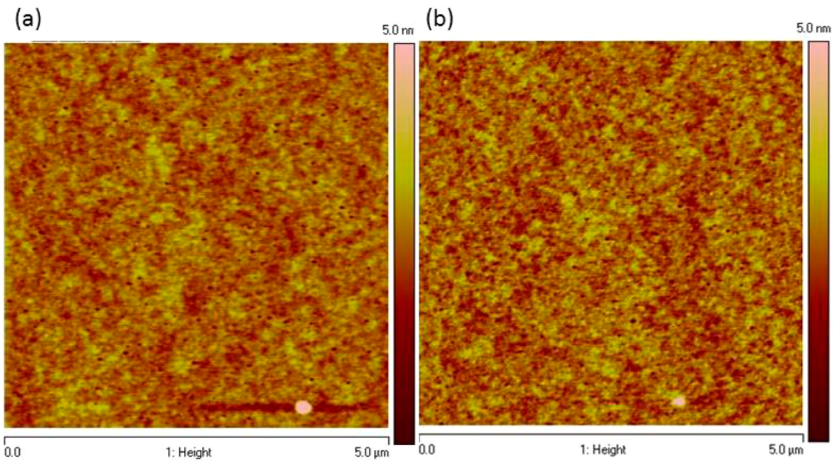


Figure 4. AFM image of the **P1** film on the Si/SiO_2 substrate at 5 μm × 5 μm scale.

Bao et al.[14]), and partially fluorinated side chains;[69] increased molecular weights;[50] copolymerization;[58] blending;[5,70,71] and chain alignment methods.[45] Further mobility improvement can arise from different spin coating solvents and electrode surface treatments. Just as the initial report of a simple monomeric subunit for p-channel polymers, hexylthiophene,[72] gave rise to an enormous family of p-polymers,[73−77] this work presents an almost equally simple n-channel monomer as a potential semiconducting polymer building block as well.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hekatz@jhu.edu.

Notes

The authors declare no competing financial interest.

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