Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

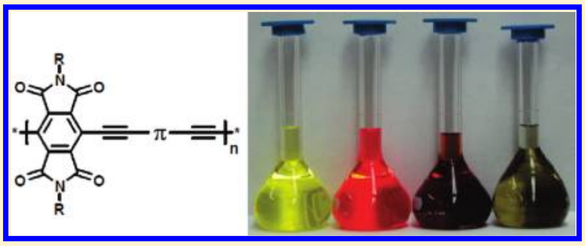
Pyromellitic Diimide-Based Donor−Acceptor Poly(phenylene ethynylene)s

Xugang Guo and Mark D. Watson*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, United States

Supporting Information

ABSTRACT: A series of donor−acceptor poly(phenylene ethynylene)s (PPEs) with *N,N*′-dialkylpyromellitic diimide (PMDI) as electron acceptor and various donor units are reported. Optoelectronic properties were investigated by UV/vis absorption and electrochemical measurements, revealing constant LUMO energies (∼−3.6 eV) across the series with HOMO energy levels governed by the donor monomers and optical band gaps from 2.30 to 1.50 eV. With a high volume fraction of solubilizing side chains, the polymers are soluble in common organic solvents, but solution NMR measurements and thermochromism in solution indicate aggregation due to additive intermolecular interactions between donor and acceptor units.



INTRODUCTION

Strongly electron-accepting imide-functionalized arylenes have been widely studied as small-molecule n-type organic semiconductors.[1−4] The rylenes naphthalene diimide (NDI)[5−7] and perylene diimide (PDI)[8−10] in particular have been extensively studied. They are also attractive electron-accepting building blocks for donor−acceptor (D−A) conjugated polymers[11−17] for two reasons (among others): (1) Optical energy gaps (E_g^{opt}) can be widely varied via electron-donating substituents attached to the rylene core,[18] translatable to D−A polymers with constant lowest unoccupied molecular orbital (LUMO) energies but varied E_g^{opt} via variable donor units.[12] (2) The imide nitrogens allow attachment of side chains distal from the polymer backbone to manipulate solubility, morphology, and solid-state packing without disrupting backbone electronic conjugation. However, with the exception of polymers based on thiophene imide (thieno[3,4-*c*]pyrrole-4,6-dione, TPD),[19,20] D−A polymers with arylene imides electronically conjugated along the backbone have only recently begun to appear in the literature.[11,12,21−23] A PDI D−A copolymer yielded moderately good organic field-effect transistor (OFET) and all-polymer organic photovoltaic (OPV) device performance.[11] We reported[12] a series of D−A polymers with NDI acceptor units with absorption profiles spanning the UV/vis/near-IR. These and other NDI D−A copolymers have since been shown to yield good to excellent device performance.[13,14,21,24,25] Copolymers based on phthalimide[22,26,27] and imide-functionalized thiophenes[23,28−35] have also very recently provided good to near state-of-the-art device performance.

Pyromellitic diimide (PMDI) has been all but overlooked as a building block for organic electronic materials. Recently, Katz demonstrated small molecule PMDI-based OFETs with electron mobility of 0.079 $cm^2\ V^{-1}\ s^{-1}$ (Figure 1).[36] Although PMDI has been widely used as a building block for insulating aromatic polyimides for advanced applications ranging from communications to aerospace,[37−39] to the best of our knowledge, the only published example of a polymer with the benzene ring of PMDI serving as part of the electronically "conjugated" polymer backbone is a poly(*p*-phenylene) with limited backbone conjugation due to steric hindrance (Figure 1).[40]

Variably colored dyes resulting from core functionalization of PMDI units with electron donors have been reported.[42−46] In hopes of translating this to variable band gap polymers, we prepared D−A copolymers with thiophene derivatives as donor and PMDI as acceptor (not shown). Perhaps due to intramolecular steric/electronic repulsion, conjugation seemed relatively limited in those preliminary examples. Insertion of alkyne linkages between successive rings along the backbone would lead to donor−acceptor poly(phenylene ethynylene)s (PPE)[47,48] with more planarized backbones. PPEs have been extensively studied in sensor applications.[49−53] Their applications in OFET and OPV devices have achieved much less success, which may be partially due to their large band gaps and suboptimal frontier molecular orbital (FMO) energy levels. Published PPEs usually have relatively broad band gaps of ∼2.5 eV and low lying highest occupied molecular orbital (HOMO) energy levels of −5.9 to −6.3 eV.[54] To advance their potential applications in OFETs and OPVs, a primary concern is to engineer the band gaps and FMO energy levels. Roy reported an end-functionalized oligo(phenylene ethynylene), which demonstrated promising OFET performance with hole mobility of 0.3 $cm^2\ V^{-1}\ s^{-1}$.[55] Recently, solution-processable oligo(phenylene ethynylene)s reported by Marks showed hole mobility up to 0.07 $cm^2\ V^{-1}\ s^{-1}$ in OFETs and power conversion

Received: April 19, 2011
Revised: July 11, 2011
Published: August 03, 2011

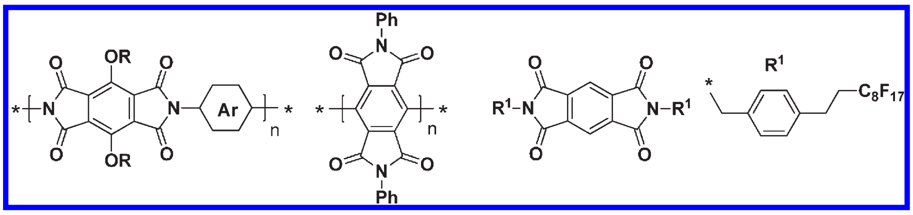
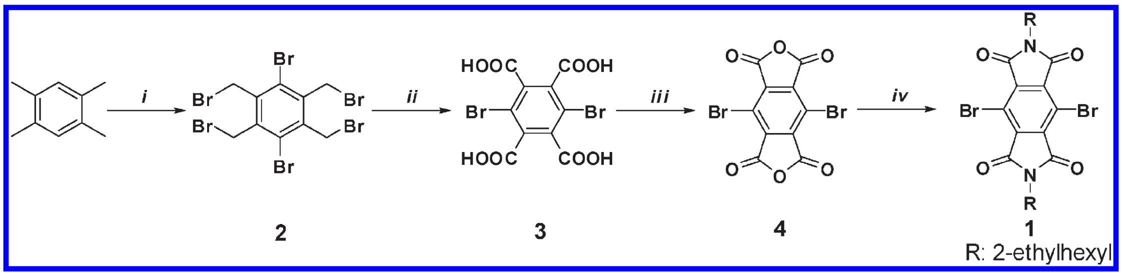


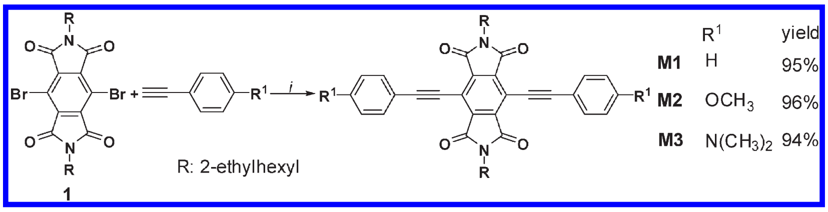
Figure 1. PMDI-based materials: polyimide (left),[41] PMDI-based poly(*p*-phenylene) (middle),[40] and PMDI-based n-type organic semiconductor (right).[36]

Scheme 1. Synthetic Route to PMDI Monomer 1[a]



[a] Reagents and conditions: (i): (a) Br_2, CCl_4, 54 °C, dark; (b) Br_2, CCl_4, *hv*, reflux; (ii) 65% HNO_3, $NaVO_3$, reflux; (iii) 205 °C sublimation, vacuum; (iv) HOAc, 2-ethylhexylamine, reflux.

Scheme 2. Synthesis of PMDI-Based Model Compounds M1−M3[a]



	R^1	yield
M1	H	95%
M2	OCH_3	96%
M3	$N(CH_3)_2$	94%

[a] Reagents and conditions: (i) $Pd_2(dba)_3$, PPh_3, CuI, DIPA, toluene 80 °C.

efficiency greater than 1% in OPVs.[56] We report here a series of D−A PPE's with PMDI as acceptor to impart essentially constant LUMO energies and different donor units to vary HOMO energy and therefore E_g^{opt}. The polymers are all soluble but appear to aggregate extensively in solution due to additive intermolecular attraction between the strongly electron accepting PMDI units and the donor units.

RESULTS AND DISCUSSION

Synthesis of PMDI monomer. The published procedure[57] to synthesize the key building block, **1**, was simplified by combining steps and minimizing purification (Scheme 1, see Supporting Information for details). Durene was consecutively brominated in near quantitative yield in one pot to 1,4-dibromo-2,3,5,6-tetrakis(bromomethyl)benzene **2**, which was oxidized to the tetracarboxylic acid **3**, and then directly dehydrated/sublimed to afford dianhydride **4**. Finally, **4** was reacted with 2-ethylhexylamine in glacial acetic acid[18] to afford key monomer **1** in 58% isolated yield.

Model Study for Related Polymerizations and Engineering of E_g^{opt}. PMDI-based monomer **1** was functionalized, via Sonagashira coupling, with phenylacetylene derivatives having different electron-donating abilities (Scheme 2). Two purposes for these studies are (a) demonstrate control over optical properties when donor groups are electronically conjugated to the PMDI core through phenyl acetylene bridges and (b) demonstrate that Sonogashira coupling with **1** proceeds cleanly with conversions sufficiently high for analogous polymerizations. This second point is particularly relevant given that some of the polymers reported here, though soluble in organic solvents, seem to aggregate so extensively as to prevent structure proof via NMR.

All three model compounds were obtained in near quantitative isolated yield (≥94%) under standard Sonagashira coupling conditions (Scheme 2). Highly electron-deficient **1** facilitates oxidative addition, and the electron-rich aryl acetylenes favor transmetalation. The model compounds are colored yellow (**M1**), orange (**M2**), and red (**M3**) in the solid state. The absorption maxima were bathochromatically shifted from **M1** (377 nm) to **M2** (407 nm) to **M3** (477 nm) in chloroform. Each absorption spectrum (Figure 2) contains a low-intensity shoulder or tail on the low-energy side of the absorption profile. The absorption onsets shift bathochromically from **M1** (472 nm) to **M2** (512 nm) to **M3** (606 nm); therefore, the HOMO−LUMO gaps were decreased with the increasing electron-donating ability of donor counits, following the same trend observed for NDI[18] and PDI[58] based chromophores.

Shinmyozu[59] reported a compound similar to **M1**, differing only in the alkyl chains attached to the imide nitrogens. Their

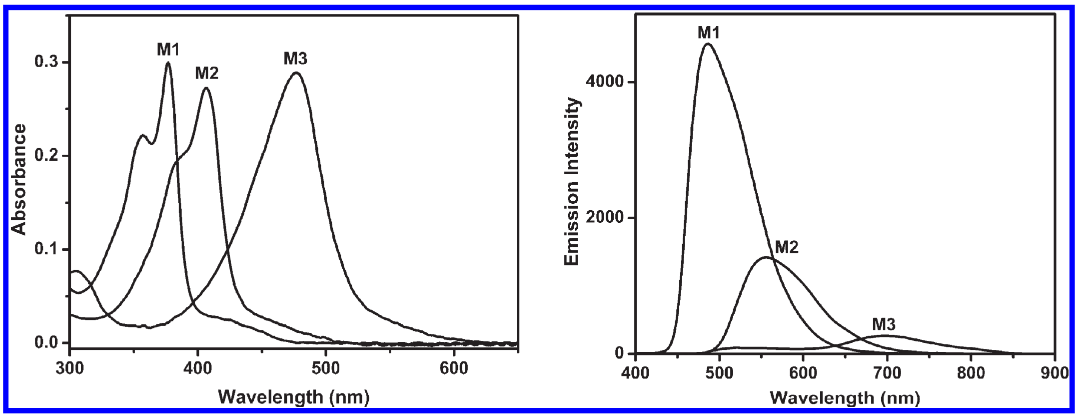
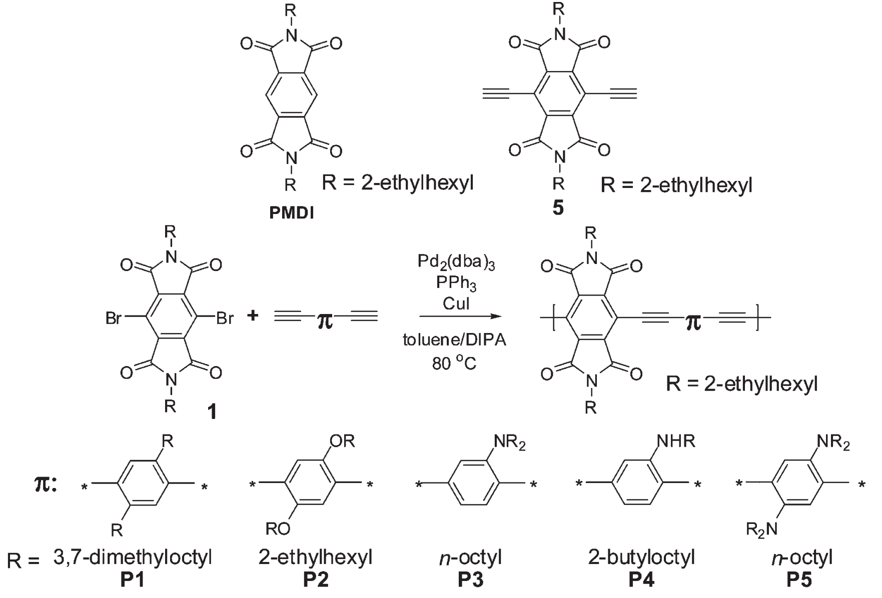


Figure 2. UV–vis absorption (left, 7 × 10^{-6} M in $CHCl_3$) and photoluminescence spectra (right, 7 × 10^{-8} M in $CHCl_3$) of **M1**–**M3**.

Scheme 3. Synthesis and Properties of PMDI-Based Polymers P1–P5; Properties of PMDI and Compound 5 Are Included for Comparison



	Yield (%)	M_n[a] (kDa) [PDI]	λ_{max}[b] (soln) (nm)	λ_{max}[c] (film) (nm)	λ_{onset}[c] (film) (nm)	E_g^{opt}[d] (eV)	$E_{1/2}{}^{1}{}_{red}$[e] (V)	$E_{1/2}{}^{2}{}_{red}$[e] (V)	E_{LUMO}[f] (eV)	E_{HOMO}[g] (eV)
PMDI	-	-	-	-	-	-	-1.18	-1.82	-3.62	N/A
5	-	-	-	-	-	-	-1.12	-1.76	-3.68	N/A
P1	92	5.4 [1.49]	490	493	536	2.31	-1.23	-1.79	-3.57	-5.88
P2	99	70.5 [3.6]	555	555	586	2.12	-1.25	-1.82	-3.55	-5.67
P3	98	21.3 [3.9]	566	583	651	1.90	-1.22	-1.76	-3.58	-5.48
P4	96	24.5 [3.8]	597	598	664	1.87	-1.23	-1.77	-3.57	-5.44
P5	92	15.7 [2.2]	591	607	812	1.53	-1.25	-1.86	-3.55	-5.08

[a] GPC vs polystyrene standards; THF as eluent. [b] 7 × 10^{-6} M in $CHCl_3$. [c] spin-cast from toluene solution (1 mg/mL). [d] $E_g^{opt} = 1240/\lambda_{onset}$ of thin films. [e] $(E_{pa}+E_{pc})/2$ vs Fc/Fc^+ (Fc/Fc^+: -4.8 eV vs vacuum); All solution-cast thin films, except PMDI and **5** from dichloromethane solution. [f] $E_{LUMO} = -4.8 - E_{1/2}{}^{1}{}_{red.}$ [g] $E_{HOMO} = E_{LUMO} - E_g^{opt}$.

calculations indicated HOMO and LUMO+1 were delocalized over the phenylene ethynylene scaffold, while LUMO was mainly localized on the PMDI unit along the perpendicular axis. The oscillator strength of the HOMO → LUMO transition should be significantly lower than the HOMO → LUMO+1 (λ_{max}), giving rise to the low-intensity absorption tails seen here. Quantum yields were not measured, but photoluminescence visible to the naked eye dramatically decreases from **M1** to **M2** to **M3**. This might be attributed to enhanced charge transfer (CT) character when a stronger donor is coupled with the PMDI core, leading to photoluminescence quenching.[60] The starting materials for **M3**, 4-ethynyl-*N*,*N*′-dimethylaniline, and **1** produce a deep purple

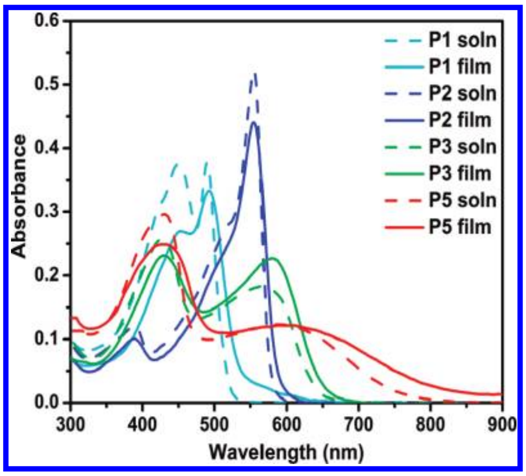


Figure 3. Solution (dashed line, 7 × 10^{-6} M in $CHCl_3$, based on polymer repeat unit) and film (solid line) absorption spectra of PPEs.

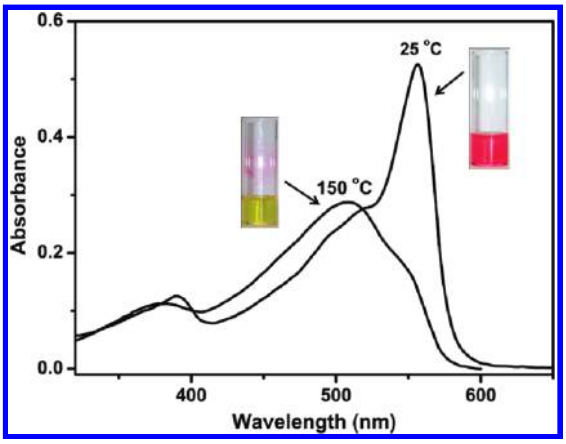


Figure 4. Thermochromism of **P2** solution (7 × 10^{-6} M in *o*-DCB, based on polymer repeat unit) at room temperature and 150 °C.

solution, suggesting intermolecular charge transfer,[61] similar to studies of the parent PMDI with various donor small molecules.[62] The high isolated yields and optical properties of **M1**−**M3** establish respectively that well-defined PMDI-based PPEs can be prepared cleanly and with broadly variable optical energy gaps.

Synthesis of PMDI-Based Poly(phenylene ethynylene)s (PPEs). PPEs **P1**−**P5** were synthesized via Sonagashira coupling (Scheme 3, see Supporting Information for details) with number-average molecular weights (M_n) ranging from 5.4 to 70.5 kDa (GPC vs polystyrene standards; eluent: THF). All of the polymers, except **P1**, are readily soluble in common organic solvents. The relative solubility of **P1**−**P5** depends on the side-chain volume fraction, the relative placement of side chains along the polymer backbone, and the symmetry of the side-chain placement around the monomer units. An analogue built with unsubstituted donor units (**P1**, with R = H) was completely insoluble and therefore not included in this study. Polymer **P5**, with a high side-chain volume fraction and great steric bulk in the vicinity of the backbone, is understandably the most soluble. This allowed collection of the only reasonably well-resolved ^{1}H and ^{13}C NMR spectra at relatively low temperature (60 °C, Supporting Information). The signals within the ^{1}H NMR spectra of **P1**−**P4** were very broad even at high temperature (up to 130 °C), likely due to extensive aggregation. A low-molecular weight version of **P2** (**P2a**: M_n = 9.3 kDa; PDI: 3.9) was prepared via monomer stoichiometric imbalance and postpolymerization end-capping with phenyl acetylene (Supporting Information). The ^{1}H NMR spectrum collected from **P2a** at 160 °C (Figure S19) is consistent with the expected structure.

Polymer Optical Properties. Polymers **P1**−**P5** all share PMDI as the electron-accepting unit; therefore, the absorption and emission profiles should vary with donor monomers. The longest-wavelength absorption maxima shift to lower energies in the order **P1** → **P2** → **P3** → **P5** (**P4** discussed below) as follows —490 nm (**P1**), 555 nm (**P2**), 566 nm (**P3**), and 591 nm (**P5**)— with a similar trend in thin film spectra.

Increasing electron-donating ability of donor monomers from dialkylarylene (**P1**) to dialkoxyarylene (**P2**) and monoaminoarylene (**P3**) to diaminoarylene (**P5**) destabilizes HOMO, decreasing the HOMO−LUMO gap. There is also some similarity between the absorption profiles of model compounds and polymers: **P1** containing dialkylbenzene displays some fine structure, while dialkoxybenzene-containing **P2** shows just a weakly discernible shoulder, and finally aminobenzene-containing **P3** and **P5** have broad and featureless absorption profiles. Polymer thin film E_g^{opt} values are decreased as the electron density on the donor monomers is increased: 2.31 eV (**P1**), 2.12 eV (**P2**), 1.90 eV (**P3**), and 1.53 eV (**P5**). In comparison to the relatively large E_g^{opt} reported for most PPEs in the literature,[47] these PMDI-based polymers demonstrated rather narrow E_g^{opt} and that of **P5** seems to be the lowest reported for a PPE.

The absorption profiles change little on going from solution to solid state, indicating little difference in electronic states. In other words, the polymers are likely extensively aggregated in solution. The small red shifts on going to the solid state might be attributed to slightly increased intermolecular interaction and rigidification in the film state. As seen in Figure 4, the "solution" absorption profile of **P2** (7 × 10^{-6} M in *o*-DCB) is relatively sharp at room temperature but significantly broadened at 150 °C with λ_{max} blue-shifted by ~50 nm, corresponding to a color change from red to yellow. At higher temperature, the shift closer to a molecularly dissolved solution should lead to broadened and featureless absorption profile as a consequence of diminished aggregation and/or more randomized thermal population of states.[63] The changes in color and absorption profile are completely reversible upon cooling to RT.

From photoluminescence (PL) measurements, the trend in PL λ_{max} versus donor strength followed the same trend as observed for absorption (Supporting Information). PL could not be measured at all from **P5**, and PL from any of the polymers in solution or film state was barely visible to the naked eye. This can be attributed to aggregation-induced[64] and/or charge-transfer induced quenching.[60,65]

The solution absorption λ_{max} for **P4** is red-shifted (31 nm) relative to **P3** (Figure 5), and even slightly red-shifted relative to **P5**, which contains the more strongly electron-donating diaminobenzene units. In addition to obvious differences in side-chain steric demands, this could be attributed to the ability of **P4** to form intramolecular H-bonds between neighboring secondary amino and carbonyl substituents, thus increasing backbone coplanarity and rigidity. Zhao[66] proposed similar intramolecular hydrogen bonding between pendant amide and ester groups in monodisperse oligo(*p*-phenylene ethynylene)s.

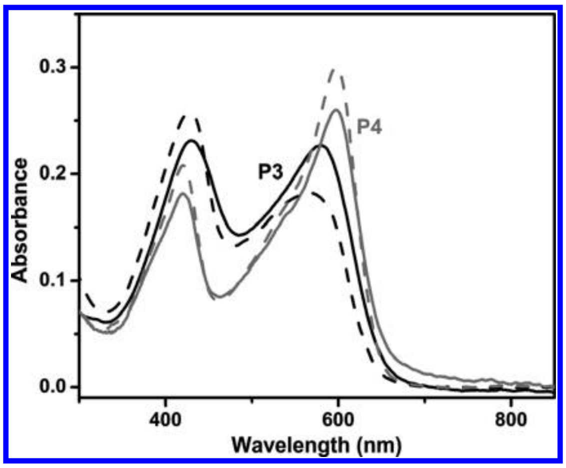


Figure 5. UV−vis absorption spectra of **P3** and **P4** in solution (dashed line, 7×10^{-6} M in $CHCl_3$, based on polymer repeat unit) and film (solid line).

Electrochemical Characterization. LUMO energy levels of the PMDI-based PPEs were estimated via cyclic voltammetry (CV) scans of polymer films, and relevant data are tabulated at the bottom of Scheme 3. Similar to the parent PMDI, all the new PMDI-based polymers show two reversible or quasireversible reduction waves with first half-wave potentials near −1.20 V vs Fc/Fc^+. Taking the energy of the redox couple for Fc/Fc+ to be −4.8 eV vs vacuum,[67] E_{LUMO} of all of the polymers are estimated to be between −3.5 and −3.6 eV, comparable to two PMDI small molecules evaluated here and in good agreement with reported data for other PMDI derivatives.[36,68] The variation of donor monomers has essentially no effect on E_{LUMO} of the polymers because all polymers share PMDI as the acceptor unit and the LUMO likely localizes on the PMDI along the axis perpendicular to the polymer backbone, similar to the case of the analogue to **M1** reported by Shinmyozu.[59] For **P1**, no features attributable to oxidation were seen at potentials up to 2.0 V. Weak features are seen for the other polymers, appearing at progressively more positive potentials in the order **P5** → **P4** → **P3** → **P2** (Figure S23). HOMO energy levels were estimated from polymer optical energy gaps and LUMO levels based on the following equation: $E_{HOMO} = E_{LUMO} - E_g^{opt}$. As expected, the HOMO energy levels of **P1**−**P5** rise from −5.88 to −5.08 eV as the electron-donating ability of donor counits is increased.

■ CONCLUSION

Pyromellitic diimide (PMDI) units impart near constant LUMO energies to PPEs, allowing facile tuning of optical energy gap via variation of donor comonomers. The polymers reported here are soluble in common organic solvents, but extensive aggregation prevents full characterization of all the polymers. NMR data for two polymers along with small-molecule model studies indicate that the polymers can be prepared cleanly by Sonogashira coupling. One of the polymers (**P5**) demonstrated E_g^{opt} as low as ∼1.50 eV, which seems to represent the lowest value reported for any PPE. Broad absorption profiles and moderately deep HOMO energies suggest that a couple of these polymers could be good candidates for photovoltaic applications and the low-lying LUMO levels of all these PMDI-based polymers suggest some promise as n-type polymer semiconductors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis and characterization details, ^1H and ^{13}C NMR spectra, photoluminescence spectra, and cyclic voltammograms of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mdwatson@uky.edu.

■ ACKNOWLEDGMENT

We thank NSF (CHE-0616759) for financial support and Dr. Manfred Wagner (Max-Planck Institut fuer Polymerforschung) for high-temperature NMR measurements of polymer **P2a**.

■ REFERENCES

(1) Jung, B. J.; Tremblay, N. J.; Yeh, M.-L.; Katz, H. E. *Chem. Mater.* **2011**, *23*, 568.

(2) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2011**, *22*, 3876.

(3) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Adv. Mater.* **2011**, *23*, 268.

(4) Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, *76*, 2386.

(5) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478.

(6) Jones, B. A.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Chem. Mater.* **2007**, *19*, 2703.

(7) Gao, X.; Di, C.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *J. Am. Chem. Soc.* **2010**, *132*, 3697.

(8) Schmidt, R.; Oh, J. H.; Sun, Y.-S.; Deppisch, M.; Krause, A.-M.; Radacki, K.; Braunschweig, H.; Künemann, M.; Erk, P.; Bao, Z.; Würthner, F. *J. Am. Chem. Soc.* **2009**, *131*, 6215.

(9) Piliego, C.; Jarzab, D.; Gigli, G.; Chen, Z.; Facchetti, A.; Loi, M. A. *Adv. Mater.* **2009**, *21*, 1573.

(10) Ortiz, R. P.; Herrera, H.; Blanco, R.; Huang, H.; Facchetti, A.; Marks, T. J.; Zheng, Y.; Segura, J. L. *J. Am. Chem. Soc.* **2010**, *132*, 8440.

(11) Zhan, X.; Tan, Z.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 7246.

(12) Guo, X.; Watson, M. D. *Org. Lett.* **2008**, *10*, 5333.

(13) Chen, Z.; Zheng, Y.; Yan, H.; Facchetti, A. *J. Am. Chem. Soc.* **2009**, *131*, 8.

(14) Durban, M. M.; Kazarinoff, P. D.; Luscombe, C. K. *Macromolecules* **2010**, *43*, 6348.

(15) Kudla, C. J.; Dolfen, D.; Schottler, K. J.; Koenen, J.-M.; Breusov, D.; Allard, S.; Scherf, U. *Macromolecules* **2010**, *43*, 7864.

(16) Zhan, X.; Tan, Z.; Zhou, E.; Li, Y.; Misra, R.; Grant, A.; Domercq, B.; Zhang, X.; An, Z.; Zhang, X.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem.* **2009**, *19*, 5794.

(17) Zhou, E.; Cong, J.; Wei, Q.; Tajima, K.; Yang, C.; Hashimoto, K. *Angew. Chem., Int. Ed.* **2010**, *50*, 2799.

(18) Würthner, F.; Ahmed, S.; Thalacker, C.; Debaerdemaeker, T. *Chem.—Eur. J.* **2002**, *8*, 4742.

(19) Zhang, Q.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5355.

(20) Nielsen, C. B.; Bjørnholm, T. *Org. Lett.* **2004**, *6*, 3381.

(21) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457*, 679.

(22) Guo, X.; Kim, F. S.; Jenekhe, S. A.; Watson, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 7206.

(23) Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Aïch, B. R.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2010**, *132*, 5330.

(24) Rivnay, J.; Toney, M. F.; Zheng, Y.; Kauvar, I. V.; Chen, Z.; Wagner, V.; Facchetti, A.; Salleo, A. *Adv. Mater.* **2010**, *22*, 4359.

(25) Kim, F. S.; Guo, X.; Watson, M. D.; Jenekhe, S. A. *Adv. Mater.* **2010**, *22*, 478.

(26) Xin, H.; Guo, X.; Kim, F. S.; Ren, G.; Watson, M. D.; Jenekhe, S. A. *J. Mater. Chem.* **2009**, *19*, 5303.

(27) Zhang, G.; Fu, Y.; Zhang, Q.; Xie, Z. *Macromol. Chem. Phys.* **2010**, *211*, 2596.

(28) Piliego, C.; Holcombe, T. W.; Douglas, J. D.; Woo, C. H.; Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2010**, *132*, 7595.

(29) Guo, X.; Xin, H.; Kim, F. S.; Liyanage, A. D. T.; Jenekhe, S. A.; Watson, M. D. *Macromolecules* **2011**, *44*, 269.

(30) Zhang, Y.; Hau, S. K.; Yip, H. L.; Sun, Y.; Acton, O.; Jen, A. K. Y. *Chem. Mater.* **2010**, *22*, 2696.

(31) Zhang, G.; Fu, Y.; Zhang, Q.; Xie, Z. *Chem. Commun.* **2010**, *46*, 4997.

(32) Yuan, M.-C.; Chiu, M.-Y.; Liu, S.-P.; Chen, C.-M.; Wei, K.-H. *Macromolecules* **2010**, *43*, 6936.

(33) Letizia, J. A.; Salata, M. R.; Tribout, C. M.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 9679.

(34) Guo, X.; Ortiz, R. P.; Zheng, Y.; Hu, Y.; Noh, Y.-Y.; Baeg, K.-J.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 1405.

(35) Najari, A.; Beaupré, S.; Berrouard, P.; Zou, Y.; Pouliot, J.-R.; Lepage-Pérusse, C.; Leclerc, M. *Adv. Funct. Mater.* **2011**, *21*, 718.

(36) Zheng, Q.; Huang, J.; Sarjeant, A.; Katz, H. E. *J. Am. Chem. Soc.* **2008**, *130*, 14410.

(37) Hergenrother, P. M. *High Perform. Polym.* **2003**, *15*, 3.

(38) Ghosh, M. K., Mittal, K. L., Eds. *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, 1996.

(39) Kricheldorf, H. R., Ed. *Progress in Polyimide Chemistry I*; Advances in Polymer Science 140; Springer-Verlag: Berlin, Germany, 1999.

(40) Rhee, T. H.; Choi, T.; Chung, E. Y.; Suh, D. H. *Macromol. Chem. Phys.* **2001**, *202*, 906.

(41) Lee, S. J.; Jung, J. C.; Lee, S. W.; Ree, M. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3130.

(42) Hopff, H.; Manukian, B. K. *Helv. Chim. Acta* **1960**, *43*, 1645.

(43) Hopff, H.; Manukian, B. K. *Helv. Chim. Acta* **1961**, *44*, 700.

(44) Manukian, B. K. *Helv. Chim. Acta* **1961**, *44*, 1922.

(45) Hopff, H.; Manukian, B. K. *Helv. Chim. Acta* **1962**, *45*, 1287.

(46) Manukian, B. K. *Helv. Chim. Acta* **1963**, *46*, 2747.

(47) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605.

(48) Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998.

(49) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339.

(50) VanVeller, B.; Miki, K.; Swager, T. M. *Org. Lett.* **2010**, *12*, 1292.

(51) Esser, B.; Swager, T. M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8872.

(52) Bajaj, A.; Miranda, O. R.; Phillips, R.; Kim, I.-B.; Jerry, D. J.; Bunz, U. H. F.; Rotello, V. M. *J. Am. Chem. Soc.* **2009**, *132*, 1018.

(53) Bajaj, A.; Miranda, O. R.; Kim, I. B.; Phillips, R. L.; Jerry, D. J.; Bunz, U. H. F.; Rotello, V. M. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 10912.

(54) Voskerician, G.; Weder, C. *Adv. Polym. Sci.* **2005**, *177*, 209.

(55) Roy, V. A. L.; Zhi, Y.; Xu, Z.; Yu, S.; Chan, P. W. H.; Che, C. M. *Adv. Mater.* **2005**, *17*, 1258.

(56) Silvestri, F.; Marrocchi, A.; Seri, M.; Kim, C.; Marks, T. J.; Facchetti, A.; Taticchi, A. *J. Am. Chem. Soc.* **2010**, *132*, 6108.

(57) Hopff, H.; Manukian, B. K.; Doswald, P. *Helv. Chim. Acta* **1961**, *44*, 1231.

(58) Dubey, R. K.; Efimov, A.; Lemmetyinen, H. *Chem. Mater.* **2011**, *23*, 778.

(59) Kato, S. I.; Nonaka, Y.; Shimasaki, T.; Goto, K.; Shinmyozu, T. *J. Org. Chem.* **2008**, *73*, 4063.

(60) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765.

(61) Reczek, J. J.; Villazor, K. R.; Lynch, V.; Swager, T. M.; Iverson, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 7995.

(62) Rasberry, R. D.; Smith, M. D.; Shimizu, K. D. *Org. Lett.* **2008**, *10*, 2889.

(63) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655.

(64) Li, J.; Kendig, C. E.; Nesterov, E. E. *J. Am. Chem. Soc.* **2007**, *129*, 15911.

(65) Zhao, X.; Pinto, M. R.; Hardison, L. M.; Mwaura, J.; Muller, J.; Jiang, H.; Witker, D.; Kleiman, V. D.; Reynolds, J. R.; Schanze, K. S. *Macromolecules* **2006**, *39*, 6355.

(66) Hu, W.; Zhu, N.; Tang, W.; Zhao, D. *Org. Lett.* **2008**, *10*, 2669.

(67) Pavlishchuk, V. V.; Addison, A. W. *Inorg. Chim. Acta* **2000**, *298*, 97.

(68) Carroll, J. B.; Gray, M.; McMenimen, K. A.; Hamilton, D. G.; Rotello, V. M. *Org. Lett.* **2003**, *5*, 3177.