Macromolecules

Volume 42, Number 7 April 14, 2009

Communications to the Editor

Low-Bandgap Pyrazine Polymers: Ladder-Type Connectivity by Intramolecular S···N(sp^2) Interactions and Hydrogen Bonds

Yong-Hui Tian and Miklos Kertesz*

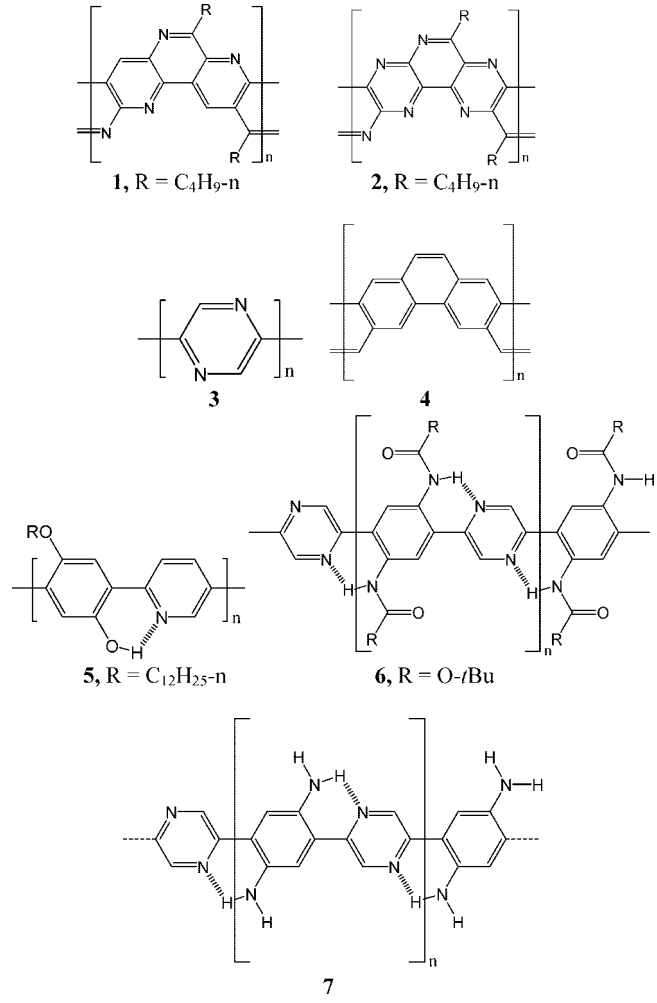
Department of Chemistry, Georgetown University, 37th & O Street, Washington, D.C. 20057-1227

Received January 14, 2009
Revised Manuscript Received February 20, 2009

Bandgap control of π-conjugated polymers is one of the important aspects of materials science.[1] For π-conjugated polymers, the molecular orbital levels of the monomers disperse into broad π-bands narrowing the energy gap between the highest occupied (HO) and the lowest unoccupied (LU) energy level.[2] Therefore, the bandgap is strongly affected by π-band dispersion, where larger π-band dispersion and π-electron delocalization usually go hand in hand with higher mobility and smaller bandgaps. The good overlap of the highest occupied orbitals (HOMO) and/or lowest unoccupied orbitals (LUMO) between the neighboring unit cells generally favors larger π-bandwidth (BW). Building ladder-type π-conjugated polymers can be an effective way to enhance this overlap of either or both orbitals. Following this line of argument, a number of ladder-type semiconducting polymers have been designed such as thienoacene,[3] polyacene,[4] and acetylenic coupled ladder polymers.[5] Poly(*p*-phenylene) (PPP) and corresponding nitrogen heterocyclic polymers are a class of semiconducting polymers that have attracted interest.[6] Efforts have been made to reduce the bandgaps of these polymers by planarization. One of the approaches is to build ladder polymers by bridging the repeat units through chemical bonds as shown for **1**[7] and **2**[8] in Chart 1. In another scheme, the polymers are planarized by forming ladderlike structures through intramolecular hydrogen bonding between the neighboring unit cells as shown for **5**[9] and **6**[10] in Chart 1.

In this paper, we show that these nitrogen-rich PPPs synthesized following the two strategies have large bandgaps in their undoped states. Furthermore, we propose alternative strategies to lower the bandgap by forming ladderlike polymers

Chart 1. Chemical Structures of (a) 1 (Ref 7) and 2 (Ref 8), Previously Synthesized Ladder Pyridine and Pyrazine Polymers; (b) 3 (Ref 11), Nonladder Poly(pyrazine-2,5-diyl) (PPyrz); (c) 4, All-Carbon Ladder Polymer Corresponding to 1 and 2; (d) 5 (Ref 9), and 6 (Ref 10), Pyridine and Pyrazine Polymers with Ladder Connectivity by Hydrogen Bonds; (e) 7 Is a Model Polymer



* Corresponding author.

10.1021/ma900082w CCC: $40.75
Published on Web 03/09/2009

Table 1. Calculated and Experimental Bandgaps (in eV) of the Fused Pyridine Polymers and the Fused Pyrazine Polymers[a]

	1	2	3	4
theory	3.24	3.13	3.00	3.16
expt	1.50 (ref 7)	N/A	2.82 (ref 11)	N/A

[a] The theory level is B3LYP/6-31G(d) under PBC. The $C_{12}H_{25}$-*n* in **1** and C_4H_9-*n* in **2** are replaced with methyl groups in the calculations to save computer time.

Table 2. Experimental and Calculated Bandgaps (eV) and the Calculated Dihedral Angle (ϕ, deg)[a]

		5	6	7a[b]	7b[c]
theory	E_g	3.04	2.55	2.30	2.01
	ϕ	26.37	13.78	24.54	0.00
expt	E_g	2.92 (ref 9)	2.78 (ref 10)	N/A	N/A

[a] The theory level is B3LYP/6-31G(d,p) under PBC conditions. $C_{12}H_{25}$-*n* in **5** and O-*t*Bu in **6** are replaced with methyl groups for the computations. [b] The bandgap calculated based on the fully optimized geometry. [c] The bandgap calculated based on the optimized geometry with ϕ constrained at 0°.

through intramolecular secondary interactions already known to exist. We focus on S···N(sp^2) interactions and hydrogen bonds to establish planarized low-gap polymers based on pyrazine derivatives.

First, we comment on the electronic structures of the class of previously synthesized ladder polymers **1** and **2**. The calculated and experimental bandgaps of ladder polymers **1** and **2** are listed in Table 1. The bandgap of poly(pyrazine-2,5-diyl) (PPyrz(**3**)) is also presented for comparison. We applied hybrid density functional theory (DFT) at the B3LYP/6-21G(d) level using periodic boundary conditions (PBC) for the polymers and molecular orbital theory for the oligomers and monomers.

Our PBC calculations indicate that PPyrz (**3**) takes a planar configuration as reported before,[11] and the predicted bandgap is in good agreement with the optical bandgap. Surprisingly, our calculated bandgap for **1** is significantly larger than the low experimental bandgaps claimed by the authors.[7a] On the basis of the good performance of the employed theory level for PPyrz (**3**) and other reported polymers,[12] our predictions appear reliable. The likely reason for the small experimental optical gap for **1** is that it was measured in acidic media, leading to doping and thus reducing the optical bandgaps. The reason for the large calculated bandgaps of **1** and **2** is that they adopt a topology similar to polybenzanthracene (**4**), which has been theoretically studied to have a large bandgap.[13] Therefore, we conclude that building ladder polymers like **1** and **2** is not effective to lower bandgaps as claimed earlier.[7,8]

We now turn to the class of synthesized polymers **5** and **6** and the corresponding model polymer **7** (see Chart 1), where the ladderlike connectivity is acted by a hydrogen bond between neighboring units. As shown in Table 2, our calculated bandgaps for **5** and **6** are in good agreement with the optical bandgaps. According to our PBC calculations as shown in Table 2, the two polymers are nonplanar and show large bandgaps. To evaluate the effect of the nonplanarity on the bandgaps, we calculate the bandgaps of model polymer **7**. The bandgap of **7a** is based on the fully optimized geometry of **7**, while that of **7b** is based on the geometry of **7** optimized with the dihedral angle constrained to zero degrees. Our calculations on the model polymer **7** indicate that even at the planar structure, this class of materials would still exhibit large gaps above 2.0 eV.

Meijer et al. suggested that the difference in donor−acceptor strength of the different units in polymers **6** and **7** might reduce the bandgaps,[10] where the functionalized phenylene units acts as electron donors and the electron-deficient pyrazine units act as acceptors. However, polymers based on donor−acceptor units usually have narrow bands due to the weak interactions between the frontier orbitals of the donor and acceptor units. For the model polymer **7**, our calculated width of the HO band is only around 0.3−0.4 eV, and that for LU band is about 1.00 eV. As shown by the band plots in Figure 1, the HO band of the model polymer **7** is very narrow which is due to the small inter-unit-cell overlap as reflected by the crystal orbitals (CO) shown in Figure 2. The HOCO is close to the HOMO of the isolated donor unit. The weak interactions originate from the large energy difference of the HOMO of the donor and acceptor units, which generally lead to low bandwidth.[14] The calculated energy difference between the HOMOs of the donor and the acceptor units is as large as 4.38 eV, leading to weak coupling and a small BW.[2,15]

Polymers with bandgaps smaller than 1.00−1.50 eV are usually considered as low-gap polymers.[1] In order to realize low-bandgap polymers, we propose a set of ladderlike polymers

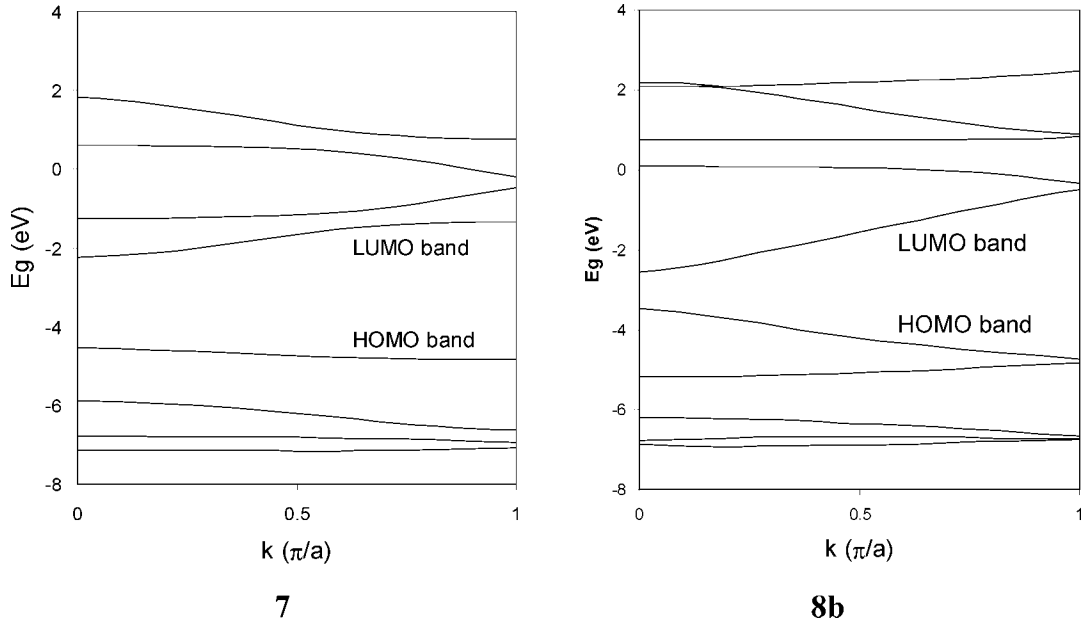


Figure 1. Band structures of **7** and **8b**. The unit of *k* is defined as π/a, where *a* is the length of the translation vector along the polymer chains.

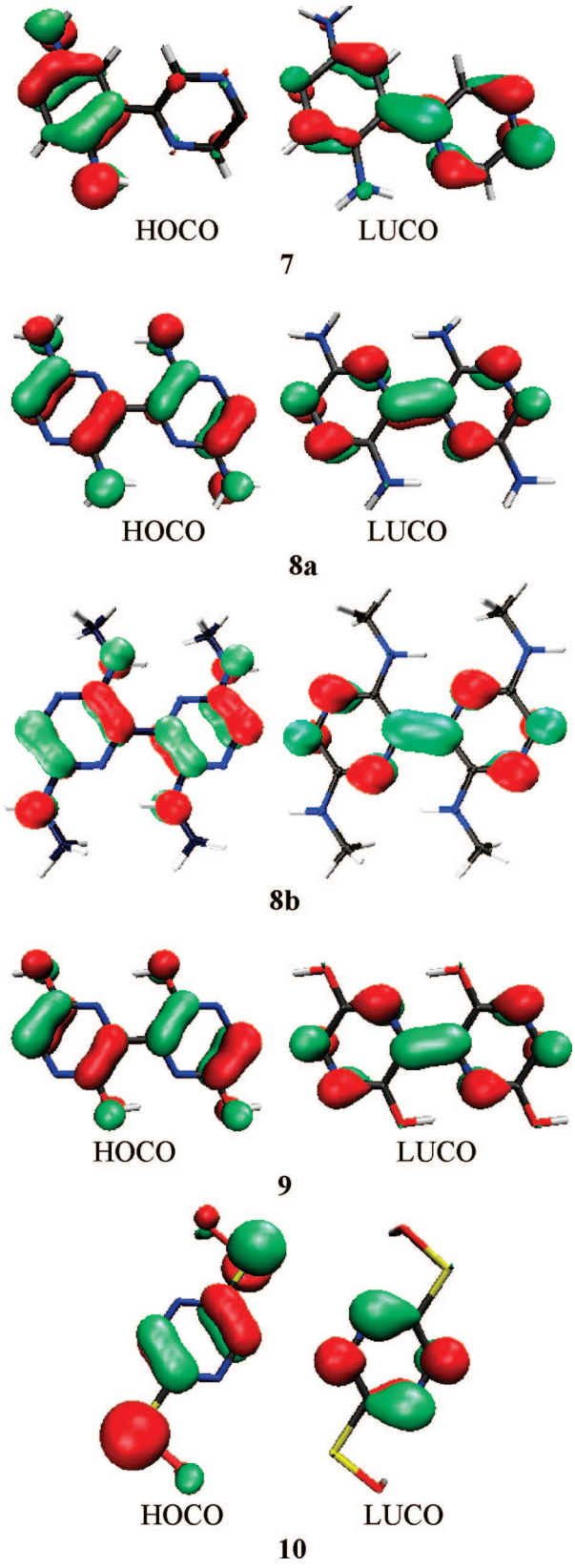


Figure 2. Orbital diagram of HOCO (at $k = 0$) and LUCO (at $k = 0$) of the repeat units from PBC calculations.

based on pyrazine as presented in Chart 2, which are likely feasible for synthesis. The common features of these polymers are the electron-donating substituents on the pyrazine backbone and the secondary linkages between unit cells through weak interactions instead of chemical bonds. In polymers **8** and **9**, the secondary linkages between neighboring units are two N···H and O···H hydrogen bonds, respectively. The synthesis of the monomer of **8** has been described by Tour et al.[8] The R groups in **8b** provide an opportunity to functionalize the polymers improving solubility. Our PBC calculations at the B3LYP/6-31G(d,p) level indicate that both of the two polymers prefer planar structures. The performance of our theory level has been validated by finding a good agreement between the optimized geometries and the crystal structures of the dimers of **8** and **9** (see Figure S1). Both the calculated and X-ray structures of the two dimers indicate planar geometries, which are consistent with the planar structure of these polymers.

Chart 2. Illustration of the Chemical Structures of the Proposed Ladderlike Polymers

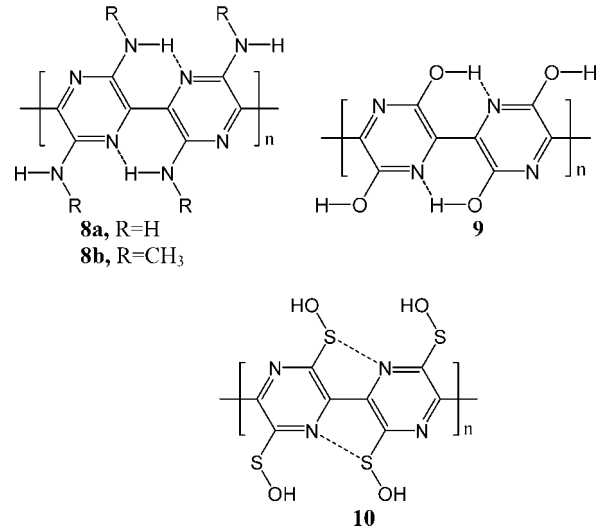


Table 3. Calculated Bandgaps (in eV) of the Proposed Ladderlike Polymers[a]

	8a	8b	9	10
E_g	1.37	0.88	1.55	1.65

[a] The theory levels are B3LYP/6-31G(d,p) for **8a**, **8b**, and **9**, and B3LYP/6-31G(2d,p) for **10** under PBC conditions.

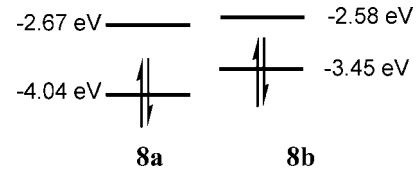


Figure 3. Relative positions of the HOCO (at $k = 0$) and LUCO (at $k = 0$) levels of **8a** and **8b**.

The calculated bandgaps are listed in Table 3. The proposed polymers show bandgaps significantly smaller than those of the previously reported polymers **1**, **2**, **3** **4**, **5**, and **6**. The low bandgaps of **8** and **9** can be attributed to three factors.

Planarity of course improves conjugation and BW and generally reduces the bandgap. However, as discussed before for model polymer **7**, planar geometry alone is not sufficient to reduce the gap below 2.0 eV. As shown in Figure 2, the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) of **8** and **9** show interesting features. For the HOCO, there are nodes at the nitrogen in the rings, and for the LUCO, there is significant electron density on nitrogen. Therefore, the relatively large electronegativity value of nitrogen only lowers the LUCO but does not affect the HOCO, overall reducing the gaps. Moreover, the π-electron-donating ability of the amino or hydroxyl groups increases the HOCO levels as

manifested by the nodes between NH_2 (or OH) and the rings, further decreasing the bandgaps. Beside their small bandgaps, the proposed polymers **8** and **9** show significantly larger BW (around 1.20 and 1.90 eV for the HOMO and LUMO bands, respectively) than the ladderlike polymers **5** and **6**, which is reflected by the HOCO and LUCO diagrams as depicted in Figure 2 and by the large band dispersions shown in Figure 1 for **8b**.

In addition, we also notice that the bandgap of 0.88 eV for **8b** is much smaller than that for **8a**. Time-dependent DFT (TDDFT) is often considered as a more accurate approximation for excitation energies. Our time-dependent B3LYP calculations for **8b** show that the small HOCO−LUCO gap agrees well with the lowest allowed singlet excitation energy (see Figure S2). It has been suggested that the electron-donating abilities of alkyl substituents on polythiophene chains affect the energy levels of HOCO and LUCO.[16] In this case, the overall gap reduction, as shown in Figure 3, is significant and amounts to 0.5 eV.

Planarity can also be realized through the donor−acceptor C−S···N interactions, where the σ lone pair of the sp^2-hybridized N interacts with the unoccupied σ^* orbital of the S−OH bonds. Such nonbonded interactions widely occur in compounds containing divalent sulfurs and have been analyzed by X-ray structures and theoretical calculations.[17] The structure of the proposed polymer based on such interactions is illustrated by **10** in Chart 2. The geometry optimized at B3LYP/6-31G(d) level under PBC conditions indicates a planar structure for **10**. The calculated nonbonded S···N distance is 2.554 Å, much smaller than the sum of van der Waals distance of sulfur and nitrogen, indicating strong intramolecular S···N(sp^2) interactions. It is interesting to note that the HOCO and LUCO orbital patterns (see Figure 2) of polymer **10** are very similar to those of polymers **8** and **9**. Therefore, the relatively low bandgap of 1.65 eV obtained for **10** can also be attributed to the planar structure and the specific HOCO and LUCO patterns. The basis set convergency for the bandgap is appended in Table S1.

In summary, we propose a set of ladderlike pyrazine polymers which show significantly lower bandgaps than PPP and the corresponding nitrogen heterocyclic polymers previously reported. The ladderlike connectivity between unit cells are the intramolecular hydrogen bonds or nonbonded S···N intercalations. The low bandgaps of the proposed polymers are attributed to the planarization of the polymer chains, the specific HOCO and LUCO patterns, and the electron-releasing substitutes of amino groups and hydroxyl groups. The proposed polymers **8b** shows a bandgap smaller than 1.00 eV due to the strong electron-donating property of methyl groups.

Acknowledgment. Support from the National Science Foundation (Grant DMR-0331710) is gratefully acknowledged. GridChem is acknowledged for providing generous computational resources. Some computations were done by Materials Studio of Accelrys, Inc.

Supporting Information Available: Description of computational details, optimized and X-ray geometries of the dimers of **8** and **9** (Figure S1), calculated excitation energies and oscillator strengths for select oligomers (Figures S2 and S3), basis set convergency data (Table S1), and details of the optimized polymer calculations (Tables S2 and S3). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Rasmussen, M.; Pomerantz, M. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC: Boca Raton, FL, 2007; Vol. 1,Chapter 12.
(2) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH: New York, 1997.
(3) (a) Zhang, X.; Côté, A. P.; Matzger, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 10502. (b) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Chem.—Eur. J.* **2007**, *13*, 548. (c) Oyaizu, K.; Iwasaki, T.; Tsukahara, Y.; Tsuchida, E. *Macromolecules* **2004**, *37*, 1257. (d) Tian, Y.-H.; Park, G.; Kertesz, M. *Chem. Mater.* **2008**, *20*, 3266.
(4) (a) Coulson, C. A. *Proc. Phys. Soc. A* **1948**, *60*, 257. (b) Salem, L.; Longuet-Higgins, H. C. *Proc. R. Soc. London A* **1960**, *255*, 435. (c) Kertesz, M.; Lee, Y. S.; Stewart, J. J. P. *Int. J. Quantum. Chem.* **1989**, *35*, 305. (d) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891.
(5) Yang, S.; Kertesz, M. *Macromolecules* **2007**, *40*, 6740.
(6) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267.
(7) (a) , 000Yao, Y.; Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 2805.
(8) Zhang, C. Y.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 8783.
(9) Vetrichelvan, M.; Valiyaveettil, S. *Chem.—Eur. J.* **2005**, *11*, 5889.
(10) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 8717.
(11) Yamamoto, T.; Fujiwara, Y.; Fukumoto, H.; Nakamura, Y.; Koshihara, S.; Ishikawa, T. *Polymer* **2003**, *44*, 4487.
(12) Kertesz, M.; Choi, H. C.; Yang, S. *Chem. Rev.* **2005**, *105*, 3448.
(13) Toussaint, J. M.; Bredas, J. L. *Synth. Met.* **1992**, *46*, 325.
(14) Salzner, U.; Karalti, O.; Durdagi, S. *J. Mol. Modeling* **2006**, *12*, 687.
(15) Burdett, J. K. *Chemical Bonding in Solids*; Oxford University Press: New York, 1995.
(16) (a) Medina, B. M.; Van Vooren, A.; Brocorens, P.; Gierschner, J.; Shkunov, M.; Heeney, M.; McCulloch, I.; Lazzaroni, R.; Cornil, J. *Chem. Mater.* **2007**, *19*, 4949. (b) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328.
(17) Minkin, V. I.; Minyaev, R. M. *Chem. Rev.* **2001**, *101*, 1247.

MA900082W