

DEVELOPMENT OF NOVEL POLYMER SEMICONDUCTORS FOR ORGANIC THIN-FILM TRANSISTORS

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Abstract

During the past two decades, design, synthesis and characterization of functional materials based on organic pi-conjugated polymers received major scientific and technological attention. Thin films prepared by these materials form favorable nanostructures, which can be used in a variety of optoelectronic applications such as organic photovoltaic cells (OPVs), thin-film transistors (OTFTs), and organic light-emitting transistors (OLETs). Compared to inorganic-based electronics, these materials enable proper ink formulations for low-cost, high-throughput printing processes on large-area, light-weight, and flexible plastic substrates. Owing to their unique features, they are envisioned as essential components of next-generation optoelectronic devices such as flexible displays, low-cost solar panels, electronic papers, printable RFID tags, and sensors. These new technologies will revolutionize the role of electronics in our daily lives and compliment current inorganic-based optoelectronic devices, which greatly impacted our society starting from the second half of the 20th century. This study demonstrates theory-aided rational design, synthesis, and characterization of a new family of functional ambipolar organic polymer semiconductors. We also report the application of these new polymers into Organic Thin-Film Transistors, which exhibit electron/hole mobilities of $\geq 0.1 \text{ cm}^2/\text{V}\cdot\text{s}$. Additionally, we found important correlations between polymer backbone structures, physicochemical properties, and device performances, providing detailed insight into charge transport characteristics. The advances we have made toward realizing truly high-performance and air-stable optoelectronic devices affirm the possibility of achieving low-cost microelectronic devices through rational materials development.^[1]

Keywords: Polymer Semiconductor, Dithienocoronenediimide, Organic Thin-Film Transistor (OTFT), Synthesis and Characterization, Ambipolar Charge Transport

1. INTRODUCTION

π -conjugated polymeric semiconductors have attracted significant scientific and technological interest as active layers in organic electronics.^[2] Favorable rheological properties of polymeric solutions allow the preparation of suitable ink formulations for high-throughput printing processes on flexible and large-area substrates.^[3] Over the past three decades, many semiconducting polymers have been designed and synthesized with a wide range of optoelectronic characteristics. These polymers have been extensively studied in various optoelectronic devices such as organic thin-film transistors (OTFTs), light-emitting transistors (OLETs) and photovoltaic cells (OPVs).^[4] However, most of these polymers are found to be unipolar – i.e., either *p*-type (hole-transporting) or *n*-type (electron-transporting) – with air-stable charge carrier mobilities of more than that of amorphous silicon ($\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[5,6] Today, there are quite few examples of low band-gap ambipolar polymers with electron/hole mobilities of $\sim 0.01 - 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under nitrogen.^[7] Although, today hole/electron mobilities of $\sim 0.3 - 1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were achieved for ambipolar polymers under nitrogen, there are still very few single-component ambipolar polymers, which are known to operate in ambient.^{[8] [9]} Ambient-stable, solution-processable ambipolar polymers are very crucial to the further development of single-component CMOS-type organic logic circuits and light emitting transistors (OLETs), as well as fundamental understanding of charge transport in polymeric thin-films.^[10]

In this study, we demonstrate the design, synthesis and characterization of three novel polymers P1 – P3 based on a new acceptor building block, dithienocoronenediimide (DTCDI), along with thiophene-based donor units (thiophene (for P1), bithiophene (for P2), and 3,3'-dialkoxybithiophene (for P3)) (**Figure 1**). Two of these polymers (P1 and P3) are found to be highly soluble in common organic solvents and top-gate bottom-contact (TG-BC) TFTs are fabricated by spin-coating these polymers solutions. Ambipolar field-effect characteristics are observed in ambient with electron and hole mobilities of up to $0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. It's noteworthy that these devices exhibit excellent ambient stability when stored in ambient for one week. To the best of our knowledge, these polymers are the very first examples of coronenediimide-based semiconductors showing respectable OTFT performances and this ambipolar performance is one of the highest reported to date in ambient for an ambipolar polymer in a top-gate/bottom-contact architecture.

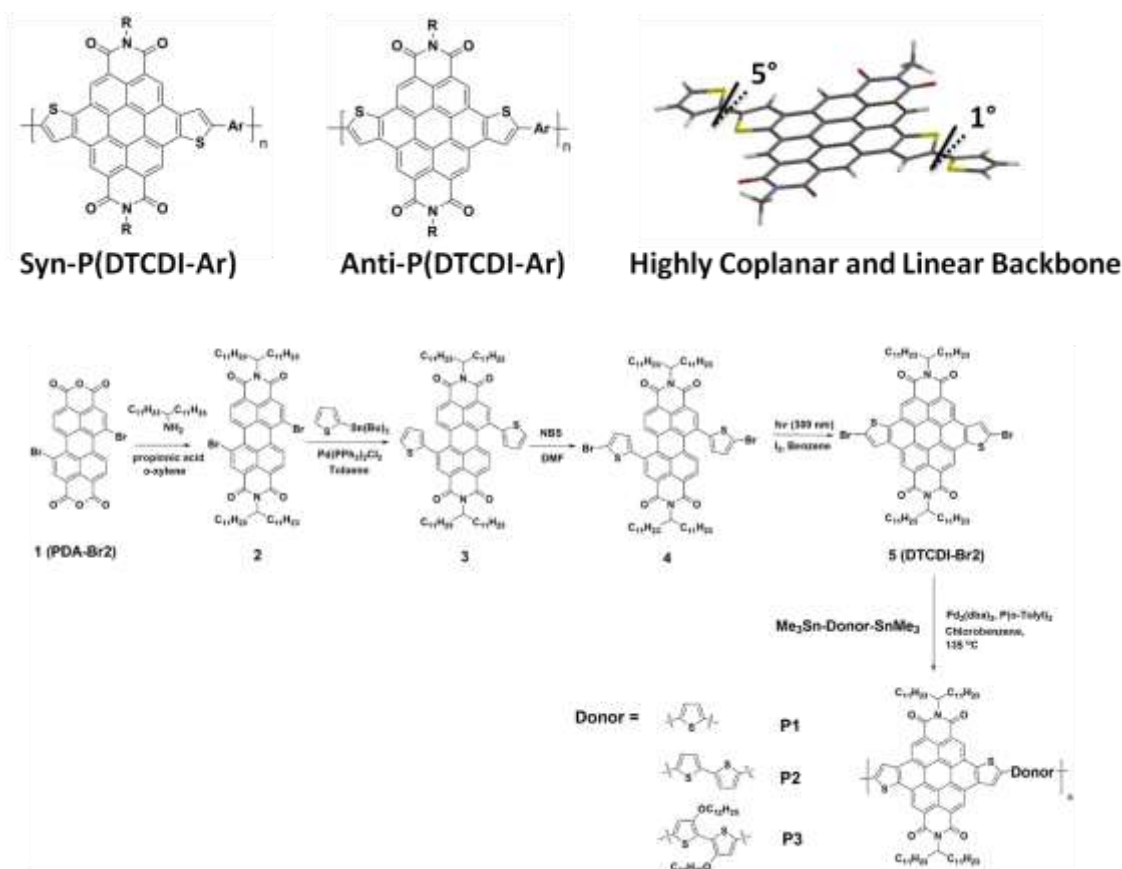


Fig. 1 Chemical structures of *syn*- and *anti*-P(DTCDI-Ar) copolymers illustrating the polymer backbone architecture. Synthetic route to monomer 5(DTCDI-Br₂) and polymers P1-P3.

2. COMPUTATIONAL MODELLING, SYNTHESIS AND CHARACTERIZATION

The pre-synthesis computational modeling on the new dithienocoronenediimide core indicates that DTCDI core adopts a highly coplanar backbone conformation with the adjacent thiophene-based comonomers and a linear monomer-linkage geometry with negligible angle difference between *syn*- and *anti*- regioisomers (**Figure 1**). It's noteworthy that this is a significant advantage over perylenediimide- (PDI-) and naphthalenediimide- (NDI)based polymeric systems, and it is very crucial to achieve a high degree of regioregularity in the semiconductor polymer backbone.^[11]

Fig. 1 shows the synthesis of dithienocoronenediimide building block DTCDI-Br₂ (5) and the corresponding copolymers P1 – P3. In the first step, 1,7(1,6)-Dibromoperylenedianhydride (1) was transformed to

compound 2 by an imidization reaction with 12-tricosanamine in glacial acetic acid/*o*-xylene in 36% yield. Then, 2 was coupled with 2-(tributylstannyl)thiophene via a Stille reaction using Pd(PPh₃)₂Cl₂/Toluene as the catalyst/solvent system to give compound 3 in 87% yield. α -Bromination of 3 with NBS in DMF gives 4 in 70% yield, which undergoes a very high-yield photocyclization reaction ($\lambda = 300$ nm) in the presence of I₂ to afford the DTCDI-Br₂ monomer in almost quantitative yields (98%). All the compounds were characterized by ¹H NMR, ¹³C NMR, Elemental Analysis, and Mass Spectroscopy (MALDI-TOF). The copolymers synthesis were done via conventional Stille polycondensation protocols in chlorobenzene using Pd₂(dba)₃/P(*o*-tolyl)₃ as the catalyst/ligand system. The copolymer P2 is found to be insoluble in common organic solvents, which prevents its further purification and characterization. The pure polymers were obtained after sequential soxhlet extraction and multiple dissolution-precipitation processes in 85 – 97% yields. Polymer molecular weights were determined by GPC, which indicates number-average molecular weights (M_n) of 11K Da (PDI = 1.6) for P1 and 51K Da (PDI = 1.7) for P3 versus polystyrene.

3. OPTOELECTRONIC PROPERTIES, THIN-FILM MORPHOLOGY AND OTFT CHARACTERIZATIONS

Solid-state optical and electrochemical characterizations of the present polymers shows that the HOMO/LUMO energies are 5.56/-3.70 eV for P1 and -5.01/-3.70 eV for P3 (**Figure 2**). The new DTCDI core has HOMO and LUMO energy levels of -6.06 eV and -3.74 eV, respectively, which are ~0.3-0.4 eV higher than those of common PDI cores. This reflects the effect of thiophene (π -electron rich) annulation to the bay region. In the present polymers, while the HOMO energy level changes dramatically with the donor unit, the LUMO levels are found to be based on the DTCDI acceptor unit. This is very similar to previously reported donor-acceptor copolymers. Due to the observed low band-gaps of P1 and P3, these polymers have well-balanced HOMO/LUMO energy levels, which should equally facilitate injection/transport of both holes and electrons.

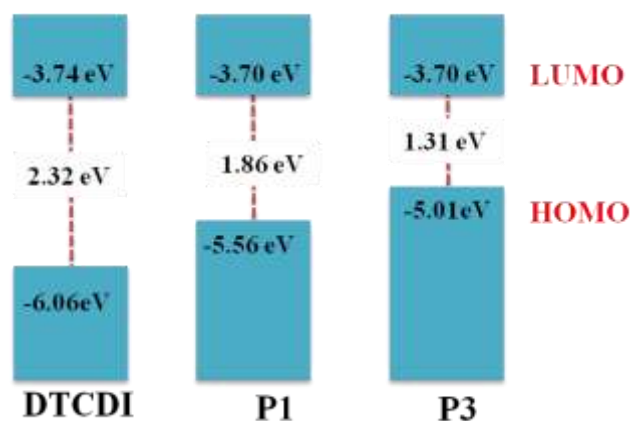


Fig. 2 The HOMO-LUMO energy diagram of the DTCDI monomer and the corresponding polymers P1 and P3

The polymer semiconductor thin-films (~40-50 nm) of P1 and P3 were deposited on untreated Au (S-D contacts)/glass substrates via spin-coating method, and OTFTs were fabricated in a top-gate bottom-contact device architecture. This device design has superior encapsulation effects and injection characteristics compared to other device architectures.^[12] All processing steps and electrical characterizations were completed in ambient except the contact electrode physical vapor deposition and thin-film drying steps. Mobilities (μ) are calculated in the saturation regime by the equation: $\mu = (2I_{sb}L)/[WC_i(V_{SG} - V_{th})^2]$. Both P1 and P3 polymer devices exhibited clear ambipolar charge transport behaviors with the average electron and hole mobilities are 0.1 – 0.2 cm² V⁻¹ s⁻¹ and 0.008 – 0.01 cm² V⁻¹ s⁻¹, respectively. The maximum mobilities are measured as 0.30 cm² V⁻¹ s⁻¹ for n-channel and 0.04 cm² V⁻¹ s⁻¹ for p-channel. The current on/off ratios

are 10^5 – 10^6 for *n*-channel operations, and 10^3 – 10^4 for *p*-channel operations. Polymer OTFT devices exhibit similar electron/hole mobilities even after 2 weeks of storage in ambient, indicating excellent device stability against ambient trapping species (O_2/H_2O). θ - 2θ X-ray diffraction (XRD) and atomic-force-microscopy (AFM) techniques were used to study the thin-film morphologies/ microstructures of the present semiconductor polymers thin-films. As shown in Figure 3, polymers form tightly packed, highly interconnected, well-defined nanofibers (width ~ 50 – 100 nm), which leads to highly uniform and smooth surface morphologies. P1 thin-films exhibit one first order Bragg reflection peak at 3.2° , corresponding to an out-of-plane *d*-spacing of 27.5 Å. This agrees well with the computed long-axis molecular length of the DTCDI acceptor unit (~ 32 Å for $\sim 45^\circ$ alkyl chain tilting), and it indicates short-range lamellar ordering.

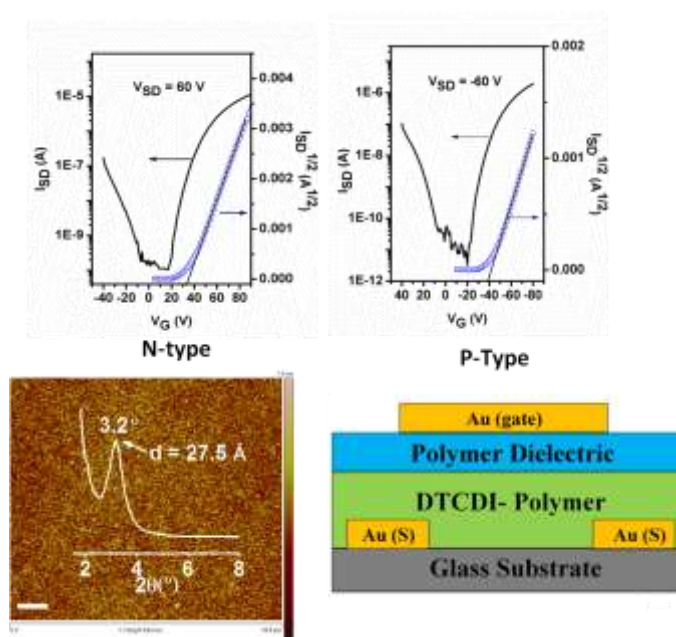


Fig. 3 Representative OTFT response plots of polymer OTFT devices. Top-gate/bottom-contact OTFT device structure, and tapping mode AFM images of spin-coated films with θ - 2θ XRD scans (inset). Scale bars denote 1 μ m.

CONCLUSION

In conclusion, we have designed, synthesized and characterized a new class of donor-acceptor conjugated polymers based on a dithienocoronenediimide core. High OTFT charge carrier mobilities of up to $0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been achieved in solution-processed ambipolar OTFTs. To the best of our knowledge, these polymers are the initial examples of coronenediimide-based semiconductors in the literature with high OTFT device performances. Our results shown here clearly demonstrates that through rational design and synthesis, dithienocoronenediimide-based acceptor building blocks are very promising for efficient electron/hole charge transport.

LITERATURE

- [1] H. Usta, C. Newman, Z. Chen, A. Facchetti *Adv. Mater.*, **2012**, *24*, 3678-3684.
 [2] a) A. Facchetti, *Mater. Today*, **2007**, *10*, 28; b) P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2011**, *133*, 20009; c) X. Zhao, X. Zhan *Chem. Soc. Rev.* **2011**, *40*, 3728; d) K. Mullen, G. Wegner, *Electronic Materials: The Material Approach*, Wiley-VCH, Weinheim **1998**; e) H. Klauk (Ed.), *Organic Electronics: Materials, Manufacturing, and*

- Applications*, Wiley-VCH, Weinheim **2006**; f) S. S. Lee, M. A. Loth, J. E. Anthony, Y.-L. Loo, *J. Am. Chem. Soc.* **2012**, *134*, 5436; g) K.-J. Baeg, J. Kim, D. Khim, M. Caironi, D.-Y. Kim, I.-K. You, J. R. Quinn, A. Facchetti, Y.-Y. Noh, *ACS Appl. Mater. Interfaces* **2011**, *3*, 3205; h) A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, A. Salleo, *Chem. Rev.* **2010**, *110*, 3.
- [3] a) A. J. Heeger, *Chem. Soc. Rev.* **2010**, *39*, 2354; b) A. Facchetti, *Chem Mater.* **2011**, *23*, 733; c) M. L. Chabiny, Y.-L. Loo, *J. Macromol. Sci. Polymer Rev.* **2006**, *46*, 1; d) Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. van Meurs, J. Tan, *J. Am. Chem. Soc.* **2011**, *133*, 2198; e) S. S. Lee, C. S. Kim, E. D. Gomez, B. Purushothaman, M. F. Toney, C. Wang, A. Hexemer, J. E. Anthony, Y.-L. Loo, *Adv. Mater.* **2009**, *35*, 3605; f) K.-J. Baeg, D. Khim, J.-H. Kim, M. Kang, I.-K. You, D.-Y. Kim, Y.-Y. Noh, *Org. Electron.* **2011**, *12*, 634; g) J. Soeda, Y. Hirose, M. Yamagishi, A. Nakao, T. Uemura, K. Nakayama, M. Uno, Y. Nakazawa, K. Takimiya, J. Takeya, *Adv. Mater.* **2011**, *23*, 3309; h) K.-J. Baeg, Y.-Y. Noh, J. Ghim, S.-J. Kang, H. Lee, D.-Y. Kim, *Adv. Mater.* **2006**, *18*, 3179; i) C. Piliago, D. Jarzab, G. Gigli, Z. Chen, A. Facchetti, M. A. Loi, *Adv. Mater.* **2009**, *21*, 1573; j) C. Kim, P.-Y. Huang, J.-W. Jhuang, M.-C. Chen, J.-C. Ho, T.-S. Hu, J.-Y. Yan, L.-H. Chen, G.-H. Lee, A. Facchetti, T. J. Marks, *Org. Electron.* **2010**, *11*, 1363; k) C. Kim, M.-C. Chen, Y.-J. Chiang, Y.-J. Guo, J. Youn, H. Huang, Y.-J. Liang, Y.-J. Lin, Y.-W. Huang, T.-S. Hu, G.-H. Lee, A. Facchetti, T. J. Marks, *Org. Electron.* **2010**, *11*, 801.
- [4] a) A. Tsumura, H. Koezuka, T. Ando, *Appl. Phys. Lett.* **1986**, *49*, 1210; b) C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* **2012**, *112*, 2208; c) M. L. Chabiny, A. Salleo, *Chem. Mater.* **2004**, *16*, 4509; d) M. Melucci, M. Zambianchi, L. Favaretto, M. Gazzano, A. Zanelli, M. Monari, R. Capelli, S. Troisi, S. Toffanin, M. Muccini, *Chem. Commun.* **2011**, *47*, 11840; e) G. Generali, F. Dinelli, R. Capelli, S. Toffanin, M. Muccini, *J. Phys. D: Appl. Phys.* **2011**, *44*, 224018; f) C. H. Peters, I. T. Sachs-Quintana, W. R. Mateker, T. Heumueller, J. Rivnay, R. Noriega, Z. M. Beiley, E. T. Hoke, A. Salleo, M. D. McGehee, *Adv. Mater.* **2012**, *24*, 663; g) J. Dacuna, A. Salleo, *Phys. Rev. B* **2011**, *84*, 195209; h) A. Salleo, R. J. Kline, D. M. DeLongchamp, M. L. Chabiny, *Adv. Mater.* **2010**, *22*, 3812; i) J. Rivnay, M. F. Toney, Y. Zheng, I. V. Kauvar, Z. Chen, V. Wagner, A. Facchetti, A. Salleo, *Adv. Mater.* **2010**, *22*, 4359.
- [5] H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastler, A. Facchetti, *Nature* **2009**, *457*, 679.
- [6] a) I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabiny, R. J. Kline, M. D. McGehee, M. F. Toney, *Nature Materials* **2006**, *5*, 328; b) I. Osaka, T. Abe, S. Shinamura, E. Miyazaki, K. Takimiya, *J. Am. Chem. Soc.* **2010**, *132*, 5000; c) J. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney, Z. Bao, *J. Am. Chem. Soc.* **2011**, *133*, 20130; d) X. Guo, F. S. Kim, S. A. Jenekhe, M. D. Watson, *J. Am. Chem. Soc.* **2009**, *131*, 7206; e) M. Zhang, H. N. Tsao, W. Pisula, C. Yang, A. K. Mishra, K. Müllen, *J. Am. Chem. Soc.* **2007**, *129*, 3472.
- [7] a) L. Bürgi, M. Turbiez, R. Pfeiffer, F. Bienewald, H.-J. Kirner, C. Winnewisser, *Adv. Mater.* **2008**, *20*, 2217; b) T. Dallos, D. Beckmann, G. Brunklaus, M. Baumgarten, *J. Am. Chem. Soc.* **2011**, *133*, 13898; c) J. D. Yuen, R. Kumar, D. Zakhidov, J. Seifert, B. Lim, A. J. Heeger, F. Wudl, *Adv. Mater.* **2011**, *23*, 3780; d) J. C. Bijleveld, A. P. Zoombelt, S. G. J. Mathijssen, M. M. Wienk, M. Turbiez, D. M. de Leeuw, R. A. J. Janssen, *J. Am. Chem. Soc.* **2009**, *131*, 16616; e) M. Shahid, T. McCarthy-Ward, J. Labram, S. Rossbauer, E. B. Domingo, S. E. Watkins, N. Stingelin, T. D. Anthopoulos, M. Heeney, *Chem. Sci.* **2012**, *3*, 181.
- [8] a) Z. Chen, M. J. Lee, R. Shahid Ashraf, Y. Gu, S. Albert-Seifried, M. M. Nielsen, B. Schroeder, T. D. Anthopoulos, M. Heeney, I. McCulloch, H. Sirringhaus, *Adv. Mater.* **2012**, *24*, 647; b) P. Sonar, S. P. Singh, Y. Li, M. S. Soh, A. Dodabalapur, *Adv. Mater.* **2010**, *22*, 5409; c) A. R. Mohebbi, J. Yuen, J. Fan, C. Munoz, M. F. Wang, R. S. Shirazi, J. Seifert, F. Wudl, *Adv. Mater.* **2011**, *23*, 4644.
- [9] a) H. Usta, C. Risko, Z. Wang, H. Huang, M. K. Delimeroglu, A. Zhukhovitskiy, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, **2009**, *131*, 5586; b) M. Irimia-Vladu, E. D. Glowacki, P. A. Troshin, G. Schwabegger, L. Leonat, D. K.

- Susarova, O. Krystal, M. Ullah, Y. Kanbur, M. A. Bodea, V. F. Razumov, H. Sitter, S. Bauer, N. S. Sariciftci, *Adv. Mater.* **2012**, *24*, 375.
- [10] a) R. P. Ortiz, H. Herrera, C. Seoane, J. L. Segura, A. Facchetti, T. J. Marks, *Chemistry- A European Journal* **2012**, *18*, 532; b) N. A. Minder, S. Ono, Z. Chen, A. Facchetti, A. F. Morpurgo, *Adv. Mater.* **2012**, *24*, 503.
- [11] a) T. Okamoto, Y. Jiang, H. A. Becerril, S. Hong, M. L. Senatore, M. L. Tang, M. F. Toney, T. Siegrist, Z. Bao, *J. Mater. Chem.* **2011**, *21*, 7078; b) I. Osaka, R. D. McCullough, *Acc. Chem. Res.* **2008**, *41*, 1202; c) C. Yang, F. P. Orfino, S. Holdcroft, *Macromolecules* **1996**, *29*, 6510; d) K. Kanai, T. Miyazaki, H. Suzuki, M. Inaba, Y. Ouchi, K. Seki, *Phys. Chem. Chem. Phys.* **2010**, *12*, 273.
- [12] D. Gamota, P. Brazis, K. Kalyanasundaram, J. Zhang, J. (eds) *Printed Organic and Molecular Electronics*, Kluwer Academic Publishers: New York **2004**.