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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/ja403624a • Publication Date (Web): 15 May 2013

Downloaded from http://pubs.acs.org on May 18, 2013

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Electron-Deficient Poly(*p*-Phenylene Vinylene) Provides Electron Mobility over 1 cm² V⁻¹ s⁻¹ under Ambient Conditions

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Supporting Information Placeholder

ABSTRACT: Poly(*p*-phenylene vinylene) derivatives (PPVs) are one of the most widely investigated *p*-type polymers in organic electronics. PPVs generally exhibit electron mobility lower than 10^{-4} cm² V⁻¹ s⁻¹, thus hindering their applications in high-performance polymer FETs and organic photovoltaics. Herein, we design and synthesize a novel electron-deficient PPV derivative, benzodifurandione-based PPV (**BDPPV**). This new PPV derivative displays high electron mobilities up to $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions (4 orders of magnitude higher than those of other PPVs), because it overcomes common defects in PPVs, such as conformational disorder, weak interchain interaction, and high LUMO level. **BDPPV** represents the first polymer that can transport electrons over 1 cm² V⁻¹ s⁻¹ under ambient conditions.

Poly(*p*-phenylene vinylene) derivatives (PPVs) are among the earliest and the most widely investigated polymers in organic electronics.¹ As typical p-type polymers,² PPVs have been used to fabricate the first polymer light-emitting diode (PLED),³ the first bulk heterojunction (BHJ) solar cell,⁴ and the first optically pumped solid-state laser.⁵ Considerable efforts have been devoted to improving their emission color, efficiency, and life time in PLED,⁶ as well as power conversion efficiency in solar cells.⁷ Nonetheless, PPVs were seldom applied in field-effect transistors (FETs) due to their low hole mobilities $(10^{-5}-10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$.⁸ Moreover, their electron mobilities are lower $(10^{-5}-10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$, even when low-work-function metal (Ca) and hydroxyl-free gate dielectric were used to fabricate the device and all operations were performed under inert atmosphere.⁹ Hence, one may ask, "can high carrier mobility be achieved in PPV-based polymers?"

Recently, the application of several electron-deficient dyes, such as diketopyrrolopyrrole (DPP),¹⁰ isoindigo (II),¹¹ naphthalene diimide (NDI),¹² and benzobisthiadiazole (BBT)¹³ in polymer FETs afforded high hole mobilities under ambient conditions and high electron mobilities in nitrogen. Nevertheless, high electron mobilities over 1 cm² V⁻¹ s⁻¹ under ambient conditions has not yet been reported, although polymers with high electron mobilities under ambient conditions are important for both fundamental understanding of carrier transport and advancing practical applications. The current scenario of new polymer design mainly focuses on thiophene-based donor-acceptor copolymers (third-generation polymer named by Heeger), and PPVs (second-generation polymer named by Heeger) are almost neglected.¹⁴



Figure 1. (a) Double bond isomerization of the PPV segment under UV irradiation. (b) Conformational isomers in PPV after single bond rotation. (c) Design strategy for the electron-deficient PPV—**BDPPV**.

Carrier mobility in conjugated polymer is determined by intrachain and interchain transport.¹⁵ Increasing the effective conjugation length and reducing torsional disorder along polymer backbone improve the intrachain transport.¹⁶ Good π - π stacking and ordered polymer packing, on the other hand, increase the interchain transport. Previously, we proved that the backbone curvature of polymers has significant influence on their carrier mobility, and polymers with linear backbones have mobilities several orders of magnitude higher than those with wave-like backbones.¹⁷ Thus, the low mobility of PPVs is presumably caused by the following:

(1) The double bonds in PPVs readily undergo *trans* to *cis* conformational transformation under UV light both in solution and in solid state (Figure 1a).¹⁸

(2) Even for all-*trans* backbones, the single bonds in PPVs rotate freely under room temperature, creating many conformational isomers (Figure 1b).

(3) PPVs generally have weak interchain interactions and are amorphous in solid state,¹⁹ thus resulting in slow interchain carrier transport.

(4) The LUMO levels of PPVs $(-2.7 \text{ to } -3.2 \text{ eV})^9$ are too high to achieve stable electron transport under ambient conditions.

The first two issues not only limit the intrachain carrier mobilities in PPVs, but also weaken the interchain π - π interactions, thus further prohibiting the interchain carrier transport. Currently, the most effective approach to obtain high electron mobility in poly-

mers, especially under ambient conditions, is to introduce electron-withdrawing groups to lower their LUMO levels.²⁰

Herein, we try to tackle these problems in traditional PPVs by synthesizing a novel PPV derivative, benzodifurandione-based PPV (BDPPV) (Figure 1c). Firstly, strong electron-withdrawing carbonyl groups are introduced on the double bonds of PPV to lower its LUMO level. Secondly, the carbonyl groups can form intramolecular hydrogen bonds to prevent the conformational transformation of the double bonds, affording a giant "locked" aromatic plane. The enlarged aromatic backbone of **BDPPV** may also contribute to the overlaps of intermolecular frontier orbitals, thus facilitating interchain transport. Thirdly, 4-octadecyldocosyl groups are used as side chains because we have demonstrated that farther branching point of side chains can enhance interchain π - π stacking and thereby improve carrier mobilities.²¹ Using BDPPV as active layer, FETs with electron mobilities up to 1.1 cm² V⁻¹ s⁻¹ are obtained under ambient conditions, 4 orders of magnitude higher than those of other PPVs! To our knowledge, this result is among the highest in *n*-type polymer FETs, and **BDPPV** represents the first polymer that can transport electron over $1 \text{ cm}^2 \text{ V}^{-1}$ s⁻¹ under ambient conditions.²²

Scheme 1. Synthetic Approach to polymer BDPPV^a



^{*a*} Reagents and conditions: (a) K_2CO_3 , THF/DMF, 50 °C, 80%; (b) Ac₂O, toluene, 100 °C, 94%; (c) LTMP, THF, -78 °C, 30 min; (d) **3**, THF, 0 °C, 2 h, two steps: 67%; (e) (*E*)-1,2-bis(tributylstannyl)ethene, $Pd_2(dba)_3$, $P(o-tol)_3$, chlorobenzene, microwave, 83%.

Scheme 1 illustrates the synthetic route to polymer BDPPV. The synthesis started from the alkylation of commercially available 6-bromoisatin (1), giving 3 in 80% yield. 2,2'-(2,5-Dihydroxy-1,4-phenylene)diacetic acid (4) was synthesized from 1,4-benzoquinone in over 10-gram scale.²³ 4 was subjected to dehydration reaction using acetic anhydride to afford dilactone 5. Lithium 2.2.6.6-tetramethylpiperidine (LTMP) was used to generate intermediate 6 and react with 3, providing the desired benzodifurandione-based oligo(p-phenylene vinylene) (BDOPV) in modorate yield. A Stille coupling polymerization between **BDOPV** and (E)-1,2-bis(tributylstannyl)ethene gave polymer BDPPV in 83% yield. The molecular weight of BDPPV was evaluated by high temperature gel permeation chromatography at 140 °C using 1,2,4-tricholorobenzene as eluent. The polymer displayed high molecular weight with M_n of 37.6 kDa and PDI of 2.38. The large PDI of BDPPV may be caused by its strong aggregation tendency. The polymer showed excellent thermal stability with decomposition temperature over 390 °C.

Figure 2 compares the ¹H NMR spectra of compounds **3**, **5**, and **BDOPV**. After the basic condensation reaction, the signal of H_a of compound **3** obviously shifted from 7.46 to 8.92 ppm (H_h in **BDOPV**). The signal of methylene (H_f) in reactant **5** disappeared, and another signal of H_e on benzene ring significantly shifted from 7.07 to 9.09 ppm (H_a in **BDOPV**). The ¹H NMR spectrum of

BDOPV displayed clearly four signals in aromatic region, agreeing well with its chemical structure and chemical environment. The optimized structure of **BDOPV** displayed almost planar backbone with small dihedral angles about 7.6° (Figure 2d). The C–H_a–O and C–H_b–O angles are approximately linear and the C– O bond distances (ca. 2.8 Å) are shorter than the combined van der Waals radii (3.3 Å).²⁴ These results indicate that four intramolecular hydrogen bonds are formed,²⁵ which may contribute to the planarity and shape-persistency of **BDOPV**.



Figure 2. ¹H NMR spectra of (a) 3, (b) 5, and (c) **BDOPV** in $CDCl_3$ (*: solvent peak). (d) The optimized molecular structure of **BDOPV** (B3LYP/6-311+G(d,p)).

Under UV light irradiation (365 nm), the double bonds in PPVs usually undergo trans to cis conformational change.¹⁸ Figure S3 displays the spectra change of a commercially available model compound 1,4-bis((E)-2-methylstyryl)benzene under UV irradiation. Clearly, the compound showed decreased long-wavelength and increased short-wavelength absorption, indicating a conformational change from trans to cis happened under UV irradiation. In contrast, BDOPV showed no spectra change under UV or visible light irradiation, which may largely due to its "locked skeleton". More importantly, both the solution and the film of polymer BDPPV showed excellent stability under UV or visible light exposure. Although one third of the double bonds in BDPPV are not locked by intramolecular hydrogen bonds, conformational change in BDPPV was not observed. This phenomenon might be attributed to largely conjugated **BDOPV** core, which has strong tendency to undergo intermolecular stacking, thus creating large steric hindrance to prevent the double bond adopting cis-conformation in **BDPPV**.

Absorption spectra of **BDOPV** in solution and polymer **BDPPV** in solution, thin film and annealed film are shown in Figure 3. **BDOPV** displays two absorption peaks with an onset at 700 nm and a bandgap of 1.80 eV. After polymerization, the new double bond in **BDPPV** further extends the conjugation length, leading to strong near-infrared absorption with a bandgap of 1.42 eV. The main absorption peak of **BDPPV** in film only showed a little red-shift compared to those in solution, and an obvious increase of the intensity of 0-0 vibrational peak was observed. Annealing the film led to a further increase of the intensity of 0-0peak. These results indicate that the polymer backbone became more planar in film and annealing was helpful for further adjust1

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ment. For conjugated polymers, intermolecular stacking and conformational change may significantly shift the absorption spectra,²⁶ which is common for most PPVs.¹⁹ However, no significant change was observed for BDPPV from solution to film. The absence of bathochromic effects indicates that the polymers probably formed some pre-aggregates in solution due to strong intermolecular interactions.²⁷ In cyclic voltammetry (CV) measurement, **BDOPV** displayed low HOMO/LUMO level of -6.21/-4.24 eV. Compared with the HOMO/LUMO level of PPV (-5.2/-2.7 eV),⁵ BDPPV exhibited significantly lowered HOMO/LUMO level (-6.12/-4.10 eV), which is also consistent with the HOMO/LUMO level (-5.83/-4.41 eV) estimated from the photoelectron spectroscopy (PES) and optical bandgap. Note that this LUMO level is also lower than those of several ambient-stable *n*-type polymers, including NDI and PDI based polymers.²⁸ Computational analysis of the oligomer of BDPPV showed that the HOMO and LUMO are well delocalized along the polymer backbone, and the HOMO and LUMO distributions of **BDPPV** are similar to those of PPV, due to their identical alternative phenylene vinylene skeletons (Figure S5).



Figure 3. (a) Normalized absorption spectra of **BDOPV** in $CHCl_3$ (10^{-5} M, dashed line) and **BDPPV** in $CHCl_3$ (10^{-5} M), in film and in annealed film. (b) Cyclic voltammograms of **BDOPV** in DCB solution (5 mg/mL) and **BDPPV** in drop-casted film.

PPVs generally form amorphous films with weak X-ray scattering, due to their weak interchain interactions and disordered packing.¹⁹ To investigate the molecular packing of **BDPPV** in thin film, grazing-incident X-ray diffraction (GIXD) and tappingmode atomic force microscopy (AFM) were used (Figure 4a and 4b). The polymer film of **BDPPV** showed a strong out-of-plane diffraction peak (100) at 2θ of 2.20 °, corresponding to a dspacing of 32.3 Å ($\lambda = 1.24$ Å). Another three diffraction peaks corresponding to (h00) were also observed, suggesting that a good lamellar edge-on packing was formed in the film. An in-plane (010) peak attributed to the interchain π - π stacking was also observed with a distance of 3.55 Å, comparable to those of other semiconducting polymers. The AFM height image of BDPPV showed crystalline fiber-like intercalating networks with a rootmean-square (RMS) deviation of 1.30 nm. Such crystalline networks are presumably caused by strong interchain interactions. Unlike other PPVs, BDPPV showed clearly much stronger aggregation tendency and more ordered packing. Thus, better interchain carrier transport is expected.



Figure 4. (a) 2D-GIXD pattern and (b) AFM height images of polymer **BDPPV** film prepared by spin-coating its DCB solution (3 mg/mL); (c) Transfer and (d) output characteristics of a **BDPPV** device under ambient conditions ($L = 10 \ \mu\text{m}$, $W = 200 \ \mu\text{m}$, $C_i = 3.7 \ \text{nF cm}^{-2}$), measured $V_T = 5 \ \text{V}$.

The low-lying LUMO of BDPPV indicates that it could be suitable for ambient-stable electron transport. Top-gate/bottomcontact (TG/BC) device configuration was used to fabricate polymer FETs, because this device configuration has better injection characteristics and encapsulation effect.29 The semiconducting layer was deposited by spin-coating a polymer solution (3 mg/mL in 1,2-dichlorobenzene) on patterned Au/SiO2/Si substrate. After thermal annealing the film for 10 min, a CYTOPTM solution was spin-coated as the dielectric layer, and an aluminum layer was thermally evaporated as the gate electrode. FET devices of **BDPPV** showed clearly *n*-type transport characteristics under ambient conditions (Figure 4c and 4d). Several annealing temperatures were tried, and annealing at 200 °C gave the best device performance. The polymer showed the highest electron mobilities up to 1.1 cm² V⁻¹ s⁻¹ with an average mobility of 0.84 cm² V⁻¹ s⁻¹. This result represents the first polymer FET that can transport electrons over 1 cm² V⁻¹ s⁻¹ under ambient conditions. Note that the transfer and output characteristics showed negligible hysteresis at high gate voltages, indicating that there are only a few traps for electrons, presumably due to the significantly lowered LUMO level. No contact resistance is observed in output curves, indicating the ohmic contact between the polymer and gold electrode. Furthermore, time-dependent decay of the BDPPV device was also performed by storing the devices under room light and ambient conditions. The device could function effectively after being stored for 30 days, affording an electron mobility of 0.31 cm² V⁻ s^{-1} (Figure S7), comparable to those of other high-performance *n*type polymer FETs.²² The slow degradation of the device was probably caused by the further diffusion of oxygen and water into the film.³⁰ However, we believe that polymers with lower LUMO levels may have better device performance and stability.

In conclusion, we have demonstrated that molecular engineering of PPV skeleton can overcome factors that limit the electron mobility in PPVs, such as conformational disorder, weak interchain interactions, and high LUMO levels. The novel designed electron-deficient PPV derivative "locked" the polymer backbone by intramolecular hydrogen bonds, endowing itself with excellent UV and visible light stability, stronger aggregation tendency, better crystallinity, lower LUMO level, and above all higher electron mobilities up to $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions. Furthermore, FET devices based on **BDPPV** also showed good ambient stability for at least 30 days. Our molecular engineering strategy effectively avoids the defects of other PPVs and increase the electron mobility of PPVs from $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to over 1 cm² V⁻¹ s⁻¹, which may trigger the renaissance of the second-generation polymer. Through further molecular modulation, the electron-deficient **BDOPV** and its derivatives could find broad applications for organic electronics requiring efficient electron transport, such as ambipolar FETs and acceptors in organic solar cells.

ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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58 59 60 The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the Major State Basic Research Development Program (Nos. 2009CB623601 and 2013CB933501) from the Ministry of Science and Technology, and National Natural Science Foundation of China. The authors thank beamline BL14B1 (Shanghai Synchrotron Radiation Facility) for providing the beam time.

REFERENCES

(1) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew. Chem. Int. Ed. **1998**, *37*, 402-428; (b) Beaujuge, P. M.; Fréchet, J. M. J. J. Am. Chem. Soc. **2011**, *133*, 20009-20029.

(2) (a) Meijer, E. J.; de Leeuw, D. M.; Setayesh, S.; van Veenendaal, E.; Huisman, B. H.; Blom, P. W. M.; Hummelen, J. C.; Scherf, U.; Klapwijk, T. M. *Nature Mater.* **2003**, *2*, 678-682; (b) Blom, P. W. M.; de Jong, M. J. M.; van Munster, M. G. *Phys. Rev. B* **1997**, *55*, R656-R659.

(3) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539-541.

(4) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Science **1995**, 270, 1789-1791.

(5) (a) Hide, F.; Díaz-García, M. A.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Science* **1996**, *273*, 1833-1836; (b) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* **1996**, *382*, 695-697.

(6) (a) Welter, S.; Brunner, K.; Hofstraat, J. W.; De Cola, L. *Nature* **2003**, *421*, 54-57; (b) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875-962.

(7) Chen, J.; Cao, Y. Acc. Chem. Res. **2009**, 42, 1709-1718; (b) Wang, L.; Liu, Y.; Jiang, X.; Qin, D.; Cao, Y. J. Phys. Chem. C **2007**, 111, 9538-9542.

(8) (a) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. *Chem. Rev.* **2011**, *112*, 2208-2267; (b) van □ Breemen, A. J. J. M.; Herwig, P. T.; Chlon, C. H. T.; Sweelssen, J.; Schoo, H. F. M.; Benito, E. M.; de □ Leeuw, D. M.; Tanase, C.; Wildeman, J.; Blom, P. W. M. *Adv. Funct. Mater.* **2005**, *15*, 872-876.

(9) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194-199.

(10) (a) Li, J.; Zhao, Y.; Tan, H. S.; Guo, Y.; Di, C.-A.; Yu, G.; Liu,
Y.; Lin, M.; Lim, S. H.; Zhou, Y.; Su, H.; Ong, B. S. *Sci. Rep.* 2012, *2*,
754; (b) Nielsen, C. B.; Turbiez, M.; McCulloch, I. *Adv. Mater.* 2013, 25,

1859-1880; (c) Chen, H.; Guo, Y.; Yu, G.; Zhao, Y.; Zhang, J.; Gao, D.; Liu, H.; Liu, Y. *Adv. Mater.* **2012**, *24*, 4618-4622.

(11) (a) Lei, T.; Cao, Y.; Fan, Y.; Liu, C.-J.; Yuan, S.-C.; Pei, J. J. Am.

Chem. Soc. **2011**, *133*, 6099-6101; (b) Mei, J.; Kim, D. H.; Ayzner, A. L.; Toney, M. F.; Bao, Z. J. Am. Chem. Soc. **2011**, *133*, 20130-20133.

(12) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Adv. Mater.* **2011**, *23*, 268-284.

(13) (a) Fan, J.; Yuen, J. D.; Cui, W.; Seifter, J.; Mohebbi, A. R.;

Wang, M.; Zhou, H.; Heeger, A.; Wudl, F. Adv. Mater. 2012, 24, 6164-6168; (b) Yuen, J. D.; Fan, J.; Seifter, J.; Lim, B.; Hufschmid, R.; Heeger,

A. J.; Wudl, F. J. Am. Chem. Soc. **2011**, 133, 20799-20807.

(14) (a) Heeger, A. J. Chem. Soc. Rev. **2010**, *39*, 2354-2371; (b) Yuen, J. D.; Wudl, F. Energy Environ. Sci. **2013**, *6*, 392-406.

(15) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926-952.

(16) Prins, P.; Grozema, F. C.; Schins, J. M.; Patil, S.; Scherf, U.; Siebbeles, L. D. A. Phys. Rev. Lett. 2006, 96, 146601.

(17) (a) Lei, T.; Cao, Y.; Zhou, X.; Peng, Y.; Bian, J.; Pei, J. *Chem. Mater.* **2012**, *24*, 1762-1770; (b) Osaka, I.; Abe, T.; Shinamura, S.; Takimiya, K. J. Am. Chem. Soc. **2011**, *133*, 6852-6860.

(18) (a) Wakioka, M.; Ikegami, M.; Ozawa, F. *Macromolecules* **2010**, *43*, 6980-6985; (b) Moslin, R. M.; Espino, C. G.; Swager, T. M. *Macromolecules* **2008**, *42*, 452-454.

(19) (a) Chen, S. H.; Su, A. C.; Huang, Y. F.; Su, C. H.; Peng, G. Y.; Chen, S. A. *Macromolecules* **2002**, *35*, 4229-4232; (b) Chen, S. H.; Su, A. C.; Han, S. R.; Chen, S. A.; Lee, Y. Z. *Macromolecules* **2003**, *37*, 181-186.

(20) (a) Lei, T.; Dou, J.-H.; Ma, Z.-J.; Yao, C.-H.; Liu, C.-J.; Wang, J.-Y.; Pei, J. J. Am. Chem. Soc. **2012**, 134, 20025-20028; (b) Lei, T.; Dou, J.-

H.; Ma, Z.-J.; Liu, C.; Wang, J.-Y.; Pei, J. *Chem. Sci.* **2013**, *4*, 2447-2452.

(21) Lei, T.; Dou, J.-H.; Pei, J. Adv. Mater. 2012, 24, 6457-6461.
(22) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dotz, F.; Kastler, M.; Facchetti, A. Nature 2009, 457, 679-686.

(23) Wood, J. H.; Cox, L. Org. Synth. **1946**, *26*, 24.

(24) Rowland, R. S.; Taylor, R. J. Phys. Chem. **1996**, 100, 7384-7391.

(25) Musah, R. A.; Jensen, G. M.; Rosenfeld, R. J.; McRee, D. E.;

Goodin, D. B.; Bunte, S. W. J. Am. Chem. Soc. 1997, 119, 9083-9084.
 (26) Kim, J.; Swager, T. M. Nature 2001, 411, 1030-1034.

(27) Zhou, N.; Guo, X.; Ortiz, R. P.; Li, S.; Zhang, S.; Chang, R. P. H.; Facchetti, A.; Marks, T. J. *Adv. Mater.* **2012**, *24*, 2242-2248.

(28) Chen, Z.; Zheng, Y.; Yan, H.; Facchetti, A. J. Am. Chem. Soc. 2009, 131, 8-9.

(29) (a) Di, C.-A.; Liu, Y.; Yu, G.; Zhu, D. *Acc. Chem. Res.* **2009**, *42*, 1573-1583; (b) Usta, H.; Newman, C.; Chen, Z.; Facchetti, A. *Adv. Mater.* **2012**, *24*, 3678-3684.

(30) Di Pietro, R.; Fazzi, D.; Kehoe, T. B.; Sirringhaus, H. J. Am. Chem. Soc. 2012, 134, 14877-14889.

