

Dependence of Crystallite Formation and Preferential Backbone Orientations on the Side Chain Pattern in PBDTTPD Polymers

Abdulrahman El Labban,[†] Julien Warnan,[†] Clément Cabanetos,[†] Olivier Ratel,[†] Christopher Tassone,[‡] Michael F. Toney,[‡] and Pierre M. Beaujuge^{*,†}

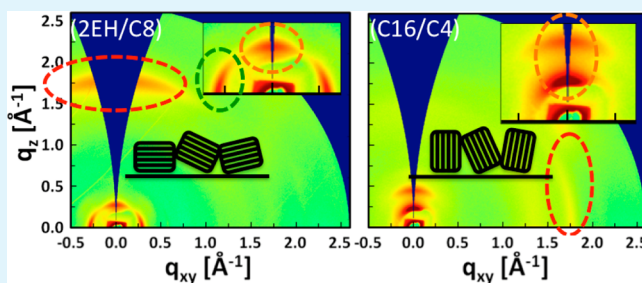
[†]King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

[‡]Stanford Synchrotron Radiation Laboratory (SSRL), Menlo Park, California 94025, United States

S Supporting Information

ABSTRACT: Alkyl substituents appended to the π -conjugated main chain account for the solution-processability and film-forming properties of most π -conjugated polymers for organic electronic device applications, including field-effect transistors (FETs) and bulk-heterojunction (BHJ) solar cells. Beyond film-forming properties, recent work has emphasized the determining role that side-chain substituents play on polymer self-assembly and thin-film nanostructural order, and, in turn, on device performance. However, the factors that determine polymer crystallite orientation in thin-films, implying preferential backbone orientation relative to the device substrate, are a matter of some debate, and these structural changes remain difficult to anticipate. In this report, we show how systematic changes in the side-chain pattern of poly(benzo[1,2-*b*:4,5-*b'*]dithiophene-*alt*-thieno[3,4-*c*]pyrrole-4,6-dione) (PBDTTPD) polymers can (i) influence the propensity of the polymer to order in the π -stacking direction, and (ii) direct the preferential orientation of the polymer crystallites in thin films (e.g., “face-on” vs “edge-on”). Oriented crystallites, specifically crystallites that are well-ordered in the π -stacking direction, are believed to be a key contributor to improved thin-film device performance in both FETs and BHJ solar cells.

KEYWORDS: side chain, benzo[1,2-*b*:4,5-*b'*]dithiophene, thieno[3,4-*c*]pyrrole-4,6-dione, π -conjugated polymers, polymer crystallite, backbone orientation



A number of recent studies have emphasized the presence of oriented crystallites in polymer thin-film devices, including field-effect transistors (FETs)^{1–4} and bulk-heterojunction (BHJ) solar cells,^{5–9} and suggested interplays between device performance, polymer self-assembly and thin-film nanostructural order. These studies have largely relied on grazing incidence X-ray scattering (GIXS), which has also been used to show how extrinsic parameters such as the material processing conditions,^{10–13} and the polymer–substrate interface,^{14,15} impact the orientation of polymer crystallites relative to the device substrate. In parallel, several π -conjugated systems have been found to yield distinct GIXS patterns, and ordering footprints in thin films,^{2,3,16} independently of processing conditions and substrate effects. However, the material design parameters that direct polymer crystallite orientation in thin films, implying preferential backbone orientation relative to the device substrate, remain a matter of some debate.⁶ Among the possible directing factors, the molecular structure of the motifs that compose the π -conjugated main chain,¹⁷ and the density of side-chain substituents appended to the backbone,^{3,7} may play a role. Several recent review reports discuss the effects of main chain substitutions in a broader context.^{18–21}

Poly(benzo[1,2-*b*:4,5-*b'*]dithiophene-*alt*-thieno[3,4-*c*]pyrrole-4,6-dione) (PBDTTPD, Figure 1) is one of the most

efficient polymer donors in BHJ solar cells with fullerene acceptors, such as phenyl-C61-butyric acid methyl ester or its C71 analog (PCBM).^{5,6,9,22–24} Conventional BHJ devices made from PBDTTPD and PCBM yield high open-circuit voltages >0.9 V,⁵ high fill-factors of ca. 70%, and power conversion efficiencies >8%.⁶ In this report, we show that incremental changes imparted to the side-chain pattern of PBDTTPD polymers direct the propensity of the π -conjugated system to crystallize in the π -stacking direction, and mediate the preferential orientation of ordered crystallites in thin films (e.g., “face-on” vs “edge-on”; see Figure S1 in the Supporting Information). Although the material design principles at the origin of preferential backbone orientation in thin films, independent of processing conditions and substrate effects, remain under debate, our results shed light on the critical role and concurrent effects of the combination of side chains appended to the polymer main chain (Figure 1, R₁ and R₂) in the development of oriented crystallites. It is worth noting that the presence of oriented crystallites in polymer FETs^{25–28} and across the active

Received: August 7, 2014

Accepted: October 27, 2014

Published: October 27, 2014



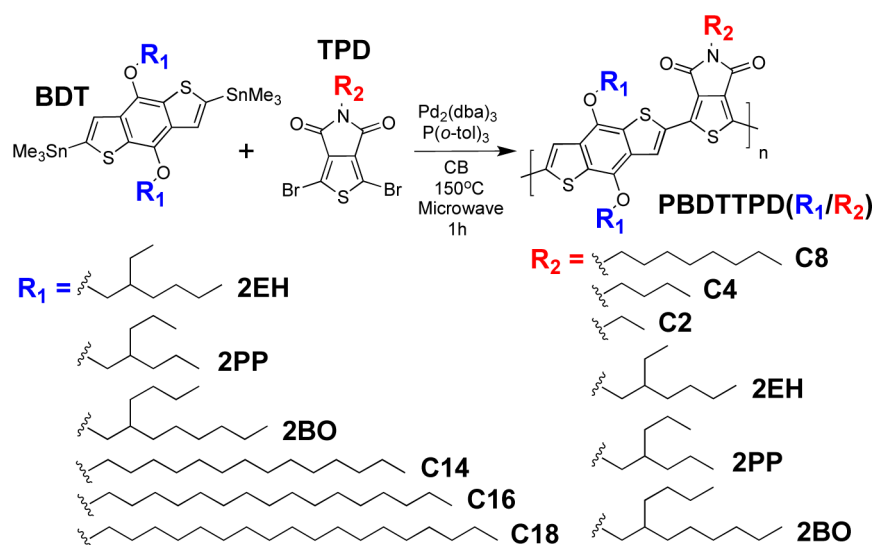


Figure 1. Synthesis of PBDTTPD(R_1/R_2) analogs bearing alkyl substituents with various lengths and side groups. Synthetic details and molecular characterizations can be found in the Supporting Information.

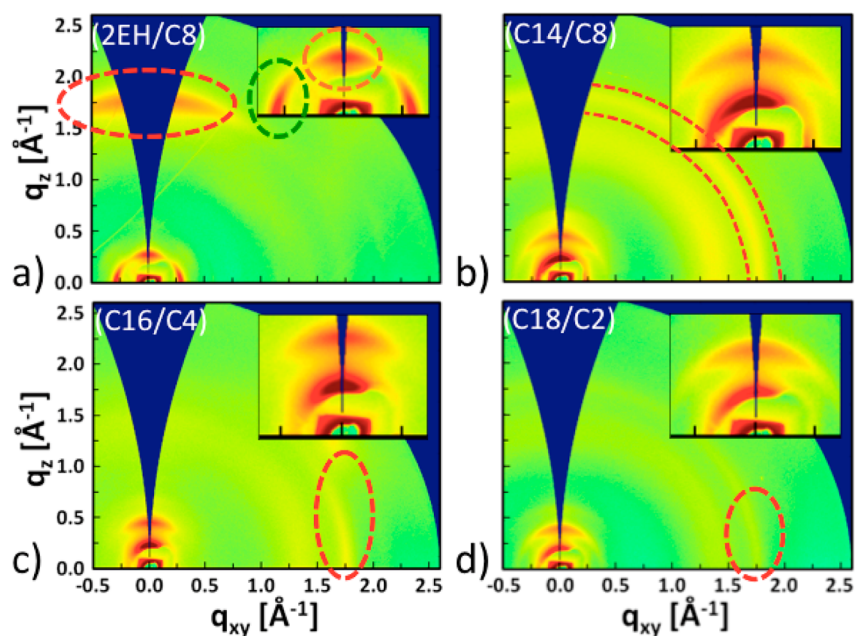


Figure 2. GIXS patterns of (a) PBDTTPD(2EH/C8), (b) PBDTTPD(C14/C8), (c) PBDTTPD(C16/C4), and (d) PBDTTPD(C18/C2) analogs (neat polymers) in thin-films cast from chlorobenzene (CB, 95%) and 1-chloronaphthalene (CN, 5%) (v/v). The use of CN with PBDTTPD is consistent with earlier reports^{6,9} that have emphasized its role on polymer self-assembly. The scattering intensity is plotted on a logarithmic scale and normalized in each GIXS pattern. The GIXS data pertaining to the films cast without CN is shown in the Supporting Information (Figure S2a–d).

layer of BHJ solar cells^{1,7,17,29,30} is often thought to contribute to improved carrier transport and device efficiency. Along these lines, the ability to mediate π - π aggregation and polymer crystallite orientation in thin films through material design can be expected to help improve material performance in both FETs and BHJ solar cells.

Throughout this study, we define polymer “crystallites” as bundles of polymer chains ordered in more than one direction of space, and for which local order is maintained over at least several repeat units.

In PBDTTPD, swapping branched 2-ethylhexyl (2EH) BDT substituents for linear tetradecyl(C14) side chains (Figure 1) results in distinct GIXS patterns. As illustrated in Figure 2a, b, PBDTTPD(2EH/C8) shows a partial arc at $q \approx 1.76 \text{ \AA}^{-1}$ that is

particularly pronounced near the out-of-plane direction ($q_{xy} \approx 0$), whereas PBDTTPD(C14/C8) shows a nearly isotropic ring of scattering intensity at $q \approx 1.77 \text{ \AA}^{-1}$ (see partial pole figures in Figure S3a in the Supporting Information). These partial arcs are characteristic of π - π stacking, and correspond to spacings of $\sim 3.6 \text{ \AA}$ and $\sim 3.5 \text{ \AA}$, respectively. In thin films of PBDTTPD-(2EH/C8), the pronounced scattering intensity near the out-of-plane direction indicates that crystallites adopt a preferential “face-on” orientation relative to the substrate (π - π stacking “out-of-plane”) (see Figure S5 in the Supporting Information), whereas the more isotropic scattering pattern of PBDTTPD-(C14/C8) indicates a distribution of isotropically oriented crystallites. Further, PBDTTPD(C14/C8) shows a strong lamellar reflection at $q \approx 0.22 \text{ \AA}^{-1}$, as well as second- and

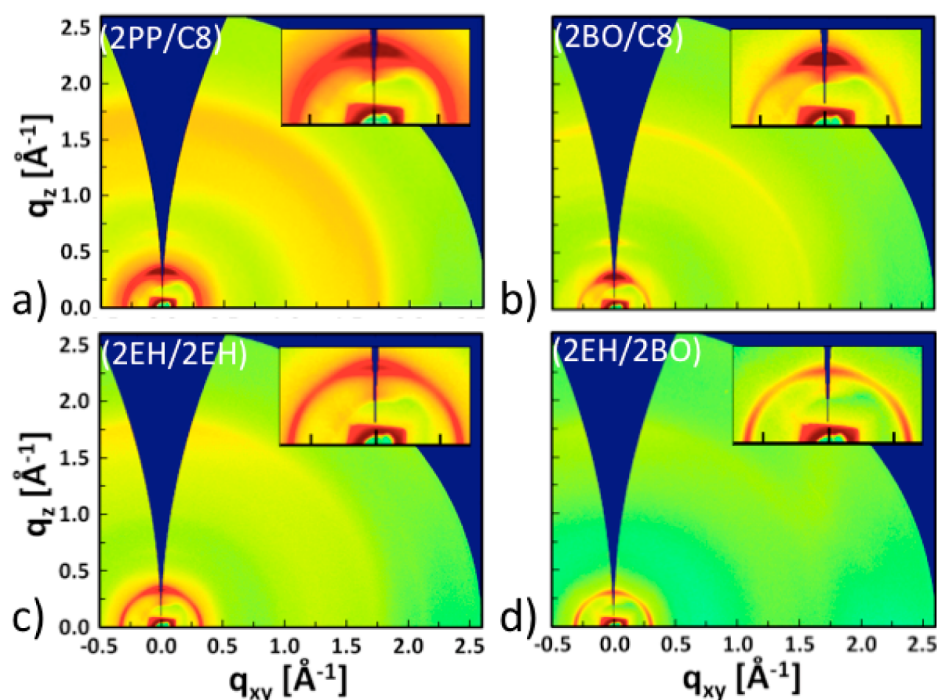


Figure 3. GIXS patterns of (a) PBDTTPD(2PP/C8), (b) (2BO/C8), (c) (2EH/2EH), and (d) (2EH/2BO) analogs (neat polymers) in thin-films cast from CB (95%) and CN (5%) (v/v). The scattering intensity is plotted on a logarithmic scale and normalized in each GIXS pattern. The GIXS data pertaining to the films cast without CN is shown in the Supporting Information (Figure S2e, h).

third-order lamellar reflections in the out-of-plane direction ($q_{xy} \approx 0$), a pattern that is consistent with the coexistence of crystallites with “edge-on” orientations relative to the substrate (π - π stacking “in-plane”).

Given the apparent directing effect of BDT substituents on the development of oriented crystallites in thin films of PBDTTPD, and the perspective to promote the formation of crystallites that adopt a preferential “edge-on” orientation, two other polymer analogs with longer linear alkyl BDT substituents were synthesized: one with hexadecyl(C16) and butyl(C4)-substituents, PBDTTPD(C16/C4), and the other with octadecyl(C18) and ethyl(C2) substituents, PBDTTPD(C18/C2) (see Figure 1). Synthetic details and molecular characterizations can be found in the Supporting Information. The GIXS patterns of PBDTTPD(C16/C4) and PBDTTPD(C18/C2), as neat polymer films, are shown in panels c and d in Figure 2, respectively. As expected for systems adopting a preferential “edge-on” orientation relative to the substrate, both patterns show partial arcs at $q \approx 1.77 \text{ \AA}^{-1}$ with the greatest peak intensity centered along the in-plane direction (see partial pole figures in Figure S3b in the Supporting Information). Here, the absence of appreciable peak intensity at $q \approx 1.77 \text{ \AA}^{-1}$ in the in-plane direction and the presence of higher-order reflections in the out-of-plane direction are also characteristic of the net predominance of crystallites with well-defined “edge-on” orientations (see Figure S5 in the Supporting Information). Predominantly “edge-on” polymer orientations may promote higher carrier mobilities in thin-film FETs.^{25–28}

Considering π -conjugated systems for thin-film device applications, it is important to build a better understanding of the material design aspects that govern the propensity of the polymers to form crystallites, specifically crystallites that are well ordered in the π -stacking direction. On this basis, we examined the effect of branching groups of different lengths appended to

the main chain of (i) BDT and (ii) TPD substituents. First, two polymer analogs with branched 2-propylpentyl(2PP) and 2-butyloctyl(2BO) BDT substituents, and linear octyl(C8)-substituted TPD motifs – PBDTTPD(2PP/C8) and PBDTTPD(2BO/C8) – (Figure 1) were synthesized following the same experimental protocol (see the Supporting Information); the GIXS patterns of the neat polymer films are shown in panels a and b in Figure 3, respectively.

Compared to the reference polymer PBDTTPD(2EH/C8) (Figure 2a), the partial arc at $q \approx 1.67 \text{ \AA}^{-1}$ characteristic of π - π stacking in the pattern of PBDTTPD(2PP/C8) is less pronounced in the out-of-plane direction and near isotropic, indicating that the crystallites adopt mixed orientations. In parallel, the ring of scattering intensity at $q \approx 0.31 \text{ \AA}^{-1}$ characteristic of the lamellar spacing is largely isotropic – consistent with the loss of preferential texture. Compared to PBDTTPD(2PP/C8) (Figure 3a), the π - π stacking reflection of the higher-branched derivative PBDTTPD(2BO/C8) (Figure 3b) is somewhat suppressed along the in-plane direction (see partial pole figures in Figure S3c in the Supporting Information), suggesting a weaker propensity to order in the π -stacking direction. Meanwhile, the rather pronounced lamellar reflection at $q \approx 0.28 \text{ \AA}^{-1}$ centered along the out-of-plane direction (see partial pole figure in Figure S4a in the Supporting Information) suggests that ordered polymer backbones in PBDTTPD(2BO/C8) are likely to adopt “edge-on” orientations. These results emphasize the requirement of a short branch on BDT substituents in promoting the development of “face-on”-oriented crystallites.

Second, two other derivatives with 2EH-substituted BDT motifs and varying branched TPD substituents. PBDTTPD-(2EH/2EH) and PBDTTPD(2EH/2BO) (Figure 1), were prepared (see the Supporting Information); the GIXS patterns of the neat polymer films are shown in panels c and d in Figure 3,

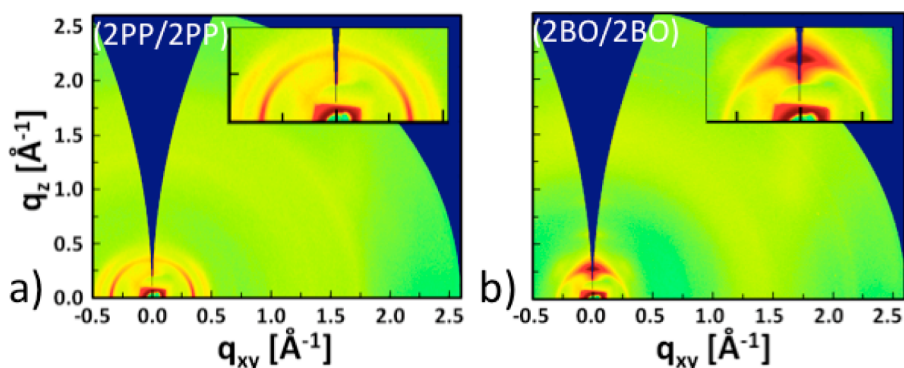


Figure 4. GIXS patterns of (a) PBDTTPD(2PP/2PP) and (b) (2BO/2BO) analogs (neat polymers) in thin-films cast from CB (95%) and CN (5%) (v/v). The scattering intensity is plotted on a logarithmic scale and normalized in each GIXS pattern. The GIXS data pertaining to the films cast without CN is shown in the Supporting Information (Figure S2i, j).

respectively. Compared to PBDTTPD(2EH/C8) (Figure 2a), neither pattern shows a net π - π stacking reflection in the out-of-plane direction (see partial pole figures in Figure S3d in the Supporting Information). In addition, considering both the overall lack of scattering intensity at $q \approx 0.31 \text{ \AA}^{-1}$ (see partial pole figures in Figure S4b in the Supporting Information), and the absence of higher-order lamellar reflections (Figure 3d), polymer backbones in PBDTTPD(2EH/2BO) show significantly less long-range order. These observations point to the detrimental role of branched TPD substituents in the development of polymer crystallites, and confirm the importance of linear TPD side chains in promoting “face-on”-oriented crystallites.

Although the solution-processability of π -conjugated polymers for thin-film device applications has commonly been induced by branched alkyl substituents appended on several motifs along the π -conjugated main chain,^{31–35} our examination of the scattering pattern of PBDTTPD(2EH/2EH) indicates that thin films of this derivative are not as textured as those cast from its counterpart PBDTTPD(2EH/C8). To confirm the direct correlation between the size of the branching groups and the extent of nanostructural order in thin films, two polymer analogs with bulkier branched BDT and TPD substituents, PBDTTPD-(2PP/2PP) and PBDTTPD(2BO/2BO) (Figure 1), were prepared (see the Supporting Information); the GIXS patterns of the neat polymer films are shown in Figure 4a and Figure 4b, respectively. Here, the gradual reduction in scattering intensity of the first-order in-plane lamellar reflection seen on going from PBDTTPD(2EH/2EH) (Figure 3c, $q \approx 0.33 \text{ \AA}^{-1}$) to PBDTTPD(2PP/2PP) (Figure 4a, $q \approx 0.35 \text{ \AA}^{-1}$), together with the absence of higher-order lamellar reflections, point to a lack of backbone correlations between polymer chains and is consistent with a deduction in long-range order. In turn, large branching groups appended on both BDT and TPD substituents can suppress interchain ordering, in addition to hindering polymer crystallization. However, the existence of a relatively pronounced first-order lamellar reflection centered along the out-of-plane direction in the pattern of PBDTTPD(2BO/2BO) (Figure 4b, $q \approx 0.30 \text{ \AA}^{-1}$) suggests that larger alkyl substituents may be able to promote interchain ordering, most likely via van der Waals interactions on short length scales. Last, although it is beyond the scope of this study, we note that the size and branching of the side-chain substituents appended to the π -conjugated main chain impact both the π - π and the lamellar spacings.

In summary, we have shown how systematic changes in the side-chain pattern of PBDTTPD can (i) influence the propensity

of the polymer to order in the π -stacking direction, and (ii) direct the preferential orientation of the polymer crystallites in thin films: from “face-on”, to “isotropic”, and to “edge-on”. While preferential “edge-on” orientations may favor in-plane carrier transport in thin-film FETs,⁸ predominantly “face-on” polymer orientations have been suggested to promote BHJ solar cell efficiency.^{1,7,17,29,30} Our results further emphasize the need to select the proper combination of side chains when several types of substituents are appended along the polymer backbone. Although branched alkyl substituents have been widely used to induce the solution-processability of π -conjugated polymers, motifs bearing linear side chains may also prove critical to the development of structural order in other systems analogous to PBDTTPD.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthetic details, monomer and polymer characterizations, device fabrication protocols, additional GIXS patterns, and pole figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pierre.beaujuge@kaust.edu.sa (P.M.B.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge financial support under Baseline Research Funding from King Abdullah University of Science and Technology (KAUST). Part of this work was supported by the Center for Advanced Molecular Photovoltaics (CAMP) (Award KUS-C1-015-21) made possible by King Abdullah University of Science and Technology. The authors thank KAUST Analytical Core Laboratories for mass spectrometry and elemental analyses. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource user facility, operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.

■ REFERENCES

- Yiu, A. T.; Beaujuge, P. M.; Lee, O. P.; Woo, C. H.; Toney, M. F.; Fréchet, J. M. J. Side-Chain Tunability of Furan-Containing Low-Band-Gap Polymers Provides Control of Structural Order in Efficient Solar Cells. *J. Am. Chem. Soc.* **2011**, *134*, 2180–2185.

- (2) Mei, J. G.; Kim, D. H.; Ayzner, A. L.; Toney, M. F.; Bao, Z. A. Siloxane-Terminated Solubilizing Side Chains: Bringing Conjugated Polymer Backbones Closer and Boosting Hole Mobilities in Thin-Film Transistors. *J. Am. Chem. Soc.* **2011**, *133*, 20130–20133.
- (3) Zhang, X. R.; Richter, L. J.; DeLongchamp, D. M.; Kline, R. J.; Hammond, M. R.; McCulloch, I.; Heeney, M.; Ashraf, R. S.; Smith, J. N.; Anthopoulos, T. D.; Schroeder, B.; Geerts, Y. H.; Fischer, D. A.; Toney, M. F. Molecular Packing of High-Mobility Diketo Pyrrolo-Pyrrole Polymer Semiconductors with Branched Alkyl Side Chains. *J. Am. Chem. Soc.* **2011**, *133*, 15073–15084.
- (4) Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P. V.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo, A. A General Relationship between Disorder, Aggregation and Charge Transport in Conjugated Polymers. *Nat. Mater.* **2013**, *12*, 1037–1043.
- (5) Piliago, C.; Holcombe, T. W.; Douglas, J. D.; Woo, C. H.; Beaujuge, P. M.; Fréchet, J. M. J. Synthetic Control of Structural Order in N-Alkylthieno[3,4-C]Pyrrole-4,6-Dione-Based Polymers for Efficient Solar Cells. *J. Am. Chem. Soc.* **2010**, *132*, 7595–7597.
- (6) Cabanetos, C.; El Labban, A.; Bartelt, J. A.; Douglas, J. D.; Mateker, W. R.; Fréchet, J. M. J.; McGehee, M. D.; Beaujuge, P. M. Linear Side Chains in Benzo[1,2-B:4,5-B']Dithiophene-Thieno[3,4-C]Pyrrole-4,6-Dione Polymers Direct Self-Assembly and Solar Cell Performance. *J. Am. Chem. Soc.* **2013**, *135*, 4656–4659.
- (7) Osaka, I.; Kakara, T.; Takemura, N.; Koganezawa, T.; Takimiya, K. Naphthodithiophene–Naphthobisthiadiazole Copolymers for Solar Cells: Alkylation Drives the Polymer Backbone Flat and Promotes Efficiency. *J. Am. Chem. Soc.* **2013**, *135*, 8834–8837.
- (8) Schmidt, K.; Tassone, C. J.; Niskala, J. R.; Yiu, A. T.; Lee, O. P.; Weiss, T. M.; Wang, C.; Fréchet, J. M. J.; Beaujuge, P. M.; Toney, M. F. A Mechanistic Understanding of Processing Additive-Induced Efficiency Enhancement in Bulk Heterojunction Organic Solar Cells. *Adv. Mater.* **2014**, *26*, 300–305.
- (9) Bartelt, J. A.; Douglas, J. D.; Mateker, W. R.; El Labban, A.; Tassone, C. J.; Toney, M. F.; Fréchet, J. M. J.; Beaujuge, P. M.; McGehee, M. D. Controlling Solution-Phase Polymer Aggregation with Molecular Weight and Solvent Additives to Optimize Polymer-Fullerene Bulk Heterojunction Solar Cells. *Adv. Energy Mater.* **2014**, DOI: 10.1002/aenm.201301733.
- (10) Rivnay, J.; Steyrleuthner, R.; Jimison, L. H.; Casadei, A.; Chen, Z. H.; Toney, M. F.; Facchetti, A.; Neher, D.; Salleo, A. Drastic Control of Texture in a High Performance N-Type Polymeric Semiconductor and Implications for Charge Transport. *Macromolecules* **2011**, *44*, 5246–5255.
- (11) DeLongchamp, D. M.; Kline, R. J.; Fischer, D. A.; Richter, L. J.; Toney, M. F. Molecular Characterization of Organic Electronic Films. *Adv. Mater.* **2011**, *23*, 319–337.
- (12) DeLongchamp, D. M.; Kline, R. J.; Jung, Y.; Germack, D. S.; Lin, E. K.; Moad, A. J.; Richter, L. J.; Toney, M. F.; Heeney, M.; McCulloch, I. Controlling the Orientation of Terraced Nanoscale “Ribbons” of a Poly(Thiophene) Semiconductor. *ACS Nano* **2009**, *3*, 780–787.
- (13) Steyrleuthner, R.; Schubert, M.; Howard, I.; Klaumunzer, B.; Schilling, K.; Chen, Z. H.; Saalfrank, P.; Laquai, F.; Facchetti, A.; Neher, D. Aggregation in a High-Mobility N-Type Low-Bandgap Copolymer with Implications on Semicrystalline Morphology. *J. Am. Chem. Soc.* **2012**, *134*, 18303–18317.
- (14) He, C.; Germack, D. S.; Kline, R. J.; DeLongchamp, D. M.; Fischer, D. A.; Snyder, C. R.; Toney, M. F.; Kushmerick, J. G.; Richter, L. J. Influence of Substrate on Crystallization in Polythiophene/Fullerene Blends. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 1375–1381.
- (15) Meredig, B.; Salleo, A.; Gee, R. Ordering of Poly(3-Hexylthiophene) Nanocrystallites on the Basis of Substrate Surface Energy. *ACS Nano* **2009**, *3*, 2881–2886.
- (16) Osaka, I.; Saito, M.; Koganezawa, T.; Takimiya, K. Thiophene-Thiazolothiazole Copolymers: Significant Impact of Side Chain Composition on Backbone Orientation and Solar Cell Performances. *Adv. Mater.* **2014**, *26*, 331–338.
- (17) Guo, J.; Liang, Y.; Szarko, J.; Lee, B.; Son, H. J.; Rolczynski, B. S.; Yu, L.; Chen, L. X. Structure, Dynamics, and Power Conversion Efficiency Correlations in a New Low Bandgap Polymer: Pcbm Solar Cell. *J. Phys. Chem. B* **2010**, *114*, 742–748.
- (18) Beaujuge, P. M.; Fréchet, J. M. J. Molecular Design and Ordering Effects in π -Functional Materials for Transistor and Solar Cell Applications. *J. Am. Chem. Soc.* **2011**, *133*, 20009–20029.
- (19) Zhou, H.; Yang, L.; You, W. Rational Design of High Performance Conjugated Polymers for Organic Solar Cells. *Macromolecules* **2012**, *45*, 607–632.
- (20) Mei, J.; Bao, Z. Side Chain Engineering in Solution-Processable Conjugated Polymers. *Chem. Mater.* **2014**, *26*, 604–615.
- (21) Lei, T.; Wang, J.-Y.; Pei, J. Roles of Flexible Chains in Organic Semiconducting Materials. *Chem. Mater.* **2014**, *26*, 594–603.
- (22) Bartelt, J. A.; Beiley, Z. M.; Hoke, E. T.; Mateker, W. R.; Douglas, J. D.; Collins, B. A.; Tumbleston, J. R.; Graham, K. R.; Amassian, A.; Ade, H.; Fréchet, J. M. J.; Toney, M. F.; McGehee, M. D. The Importance of Fullerene Percolation in the Mixed Regions of Polymer–Fullerene Bulk Heterojunction Solar Cells. *Adv. Energy Mater.* **2013**, *3*, 364–374.
- (23) Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Réda Aich, B.; Tao, Y.; Leclerc, M. A Thieno[3,4-C]Pyrrole-4,6-Dione-Based Copolymer for Efficient Solar Cells. *J. Am. Chem. Soc.* **2010**, *132*, 5330–5331.
- (24) Chu, T. Y.; Lu, J. P.; Beaupre, S.; Zhang, Y. G.; Pouliot, J. R.; Zhou, J. Y.; Najari, A.; Leclerc, M.; Tao, Y. Effects of the Molecular Weight and the Side-Chain Length on the Photovoltaic Performance of Dithienosilole/Thienopyrrolo-dione Copolymers. *Adv. Funct. Mater.* **2012**, *22*, 2345–2351.
- (25) Himmelberger, S.; Dacuna, J.; Rivnay, J.; Jimison, L. H.; McCarthy-Ward, T.; Heeney, M.; McCulloch, I.; Toney, M. F.; Salleo, A. Effects of Confinement on Microstructure and Charge Transport in High Performance Semicrystalline Polymer Semiconductors. *Adv. Funct. Mater.* **2013**, *23*, 2091–2098.
- (26) Jimison, L. H.; Himmelberger, S.; Duong, D. T.; Rivnay, J.; Toney, M. F.; Salleo, A. Vertical Confinement and Interface Effects on the Microstructure and Charge Transport of P3ht Thin Films. *J. Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 611–620.
- (27) Jimison, L. H.; Toney, M. F.; McCulloch, I.; Heeney, M.; Salleo, A. Charge-Transport Anisotropy Due to Grain Boundaries in Directionally Crystallized Thin Films of Regioregular Poly(3-Hexylthiophene). *Adv. Mater.* **2009**, *21*, 1568–1572.
- (28) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabiny, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. Liquid-Crystalline Semiconducting Polymers with High Charge-Carrier Mobility. *Nat. Mater.* **2006**, *5*, 328–333.
- (29) Guo, X.; Zhou, N.; Lou, S. J.; Smith, J.; Tice, D. B.; Hennek, J. W.; Ortiz, R. P.; Navarrete, J. T. L.; Li, S.; Strzalka, J.; Chen, L. X.; Chang, R. P. H.; Facchetti, A.; Marks, T. J. Polymer Solar Cells with Enhanced Fill Factors. *Nat. Photonics* **2013**, *7*, 825–833.
- (30) Kim, D. H.; Ayzner, A. L.; Appleton, A. L.; Schmidt, K.; Mei, J.; Toney, M. F.; Bao, Z. Comparison of the Photovoltaic Characteristics and Nanostructure of Fullerenes Blended with Conjugated Polymers with Siloxane-Terminated and Branched Aliphatic Side Chains. *Chem. Mater.* **2012**, *25*, 431–440.
- (31) Price, S. C.; Stuart, A. C.; Yang, L. Q.; Zhou, H. X.; You, W. Fluorine Substituted Conjugated Polymer of Medium Band Gap Yields 7% Efficiency in Polymer-Fullerene Solar Cells. *J. Am. Chem. Soc.* **2011**, *133*, 4625–4631.
- (32) Chen, H.-Y.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L.; Wu, Y.; Li, G. Polymer Solar Cells with Enhanced Open-Circuit Voltage and Efficiency. *Nat. Photonics* **2009**, *3*, 649–653.
- (33) Nielsen, C. B.; Turbiez, M.; McCulloch, I. Recent Advances in the Development of Semiconducting Dpp-Containing Polymers for Transistor Applications. *Adv. Mater.* **2013**, *25*, 1859–1880.