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Siloxane-Based Hybrid Semiconducting Polymers Prepared by Fluoride-Mediated Suzuki Polymerization**

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Abstract: *Siloxane-containing materials are a large and important class of organic-inorganic hybrids. In this report, a practical variation of the Suzuki polymerization to generate semiconducting polymeric hybrids based on siloxane units, which proceeds under essentially nonbasic conditions, is presented. This method generates solution-processable poly(diketopyrrolopyrrole-alt-benzothiadiazole) (PDPPBT-Si) consisting of the hybrid siloxane substituents, which could not be made using conventional methods. PDPPBT-Si exhibits excellent ambipolar transistor performance with well-balanced hole and electron FET mobilities. The siloxane-containing DPP-thiophene polymer classes (PDPP3T-Si and PDPP4T-Si), synthesized by this method, exhibit high hole mobility of up to 1.29* $cm^2V^{-1}s^{-1}$*. This synthetic approach should provide access to a variety of novel siloxane-containing conjugated semiconductor classes by using a variety of aryldihalides and aryldiboronic acids/esters.*

Integration of organic and inorganic species, commonly referred to as hybridization, is of interest for the production of novel functional materials since the co-existence of these species in a single component is expected to induce cooperative and synergistic effects.[1] Siloxane units (-SiR_2O-, R = usually alkyl groups) composed of an inorganic silicon-oxygen backbone (Si-O-Si), with organic substituents bound to the silicon atoms, are the most widely studied frameworks for hybrid materials.[2] Because of their physicochemical properties (e.g., high thermal and weather stability), siloxane-based compounds have been used in a wide range of applications.[3] Another unique structural feature derived from the significantly longer bond length and larger bond angle of the Si-O-Si skeleton is an increased flexibility of the siloxane chains.[3a] Taking this flexibility into account, the siloxane-terminated hybrid side chains were introduced into rigid π-conjugated polymers as solubilizing groups, and showed that this approach could be used to improve charge-transport efficacy while providing good solubilizing capabilities.[4] Although the siloxane-based hybrid side chains provide a diverse combination of solubilizing ability and impact on crystal packing to create high quality semiconducting polymers, they are incompatible with the traditional Suzuki polymerization accompanied by a base, hence limiting their practical applications. Herein, we report the first synthesis of a poly(diketopyrrolopyrrole-*alt*-benzothiadiazole) (PDPPBT-Si) with hybrid siloxane-solubilizing groups by a base-free Suzuki polymerization. In this report, we discuss the structure–property relationship of PDPPBT-Si with organic field-effect transistor (OFET) properties, electronic structure, and ordering structure. Our study expands the synthetic methods available for the synthesis of various hybrid chromophoric building blocks based on siloxane units.

Based on previous reports,[4a,b,5] starting with DPP, olefinic alkyl side chains were introduced into the DPP core by a base-promoted N-alkylation, then hydrosilylation of the terminal alkene using 1,1,1,3,5,5,5-heptamethyltrisiloxane in the presence of the Karstedt catalyst, and *N*-bromosuccinimide-mediated dibromination in chloroform, thus yielding a highly soluble DPP monomer (**1**) with siloxane-terminated solubilizing chains (*CAUTION*). A series of brominations performed overnight did not provide satisfactory yields ($<30\%$), but a shorter reaction time (ca. 2 h) generated relatively high yields ($>70\%$). After collecting the desired compound **1** as the first fraction to elute from column chromatography, the second fraction was collected and analyzed by NMR spectroscopy. The integral of the resonances at $\delta = -0.02$–0.08 ppm, assigned to the methyl protons in the siloxane groups, was considerably smaller than the theoretical integration value based on ^{1}H NMR spectroscopy (see Figure S1 in Supporting Information). Based on this result, the siloxane units may not be stable under the free-radical bromination, but the reason for this remains unclear. In our initial screening experiments, the standard Suzuki polycondensation with **1** and 4,7-diboronicester-2,1,3-benzothiadiazole (**2**) was performed in the presence of either $[Pd(PPh_3)_4]$ or $[Pd_2(dba)_3]/P(o\text{-tolyl})_3$ as a catalyst system in a mixture of toluene and basic aqueous solution (K_2CO_3 or K_3PO_4), as shown in Scheme 1. However, we did not obtain a polymeric solid in which large amounts of both unreacted monomers were recovered, even when a microwave-assisted

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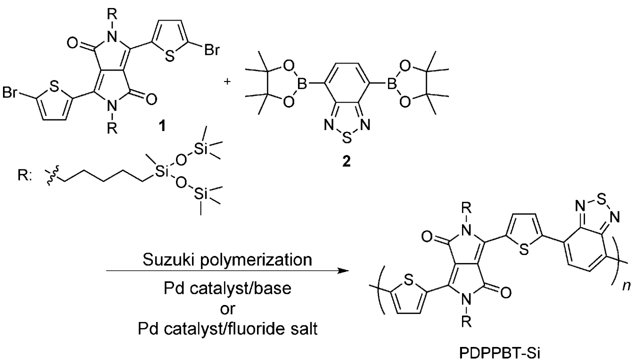

Scheme 1. PDPPBT-Si preparation by Suzuki polymerization.

heating protocol was applied (Table 1). We hypothesized that this might have been caused by an incompatibility between the siloxane functional groups and the base required for the transmetalation in the Suzuki-coupling mechanism. This hypothesis was based on our previous experience with the synthesis of various DPP-based polymers using hybrid siloxane side chains and the conventional Stille polycondensation, in which the basic reagent was not used.[4a,b,5] It was previously reported that fluoride salts [e.g., cesium fluoride (CsF) and tetrabutylammonium fluoride (TBAF)] activate palladium transmetalation during Suzuki coupling for small-molecule synthesis under essentially nonbasic conditions.[6] This method was successfully applied to Suzuki polycondensation of polyfluorene containing base-sensitive functionalities.[7]

Based on these findings, we examined the Suzuki polymerization of dibromide **1** and the diboronic ester **2** under various reaction conditions (catalyst system, solvent, temperature, reaction time, and heating protocol) with fluoride salts, as illustrated in Scheme 1 and Table 1. The first variable tested was the reaction time and solvent system under conventional and microwave irradiation heating, respectively, and four equivalents of CsF were chosen based on a previously reported optimization of fluoride-mediated polymerization.

Soluble PDPPBT-Si polymers with the hybrid siloxane substituents were successfully obtained using both microwave and thermal heating, although a shorter reaction time was required when using microwave irradiation. The molecular weights of the polymer increased with increasing reaction time. In addition, the solvent system used for the polymerization did not affect the molecular weights, but the optimal reaction time depended on the solvents and heating methods. Note that exceeding the optimal time in each case resulted in a solvent-swollen gel, thus providing only insoluble products. Further examination of the microwave-assisted Suzuki polymerization was performed under different reaction conditions, for example, different temperatures, the binary solvent mixture, and replacement of CsF with TBAF. The full set of reactions is provided in Table 1. The use of CsF/DME at 120 °C under conventional heating for 24 hours was optimal in terms of the molecular weights generated (Table 1, entry 8). Although further optimization of system-specific reactions may produce PDPPBT-Si with higher molecular weights, our screening study is the first step towards base-free Suzuki coupling for siloxane-containing semiconducting polymers, which will allow the synthesis of a wide variety of conjugated blocks with siloxane units.

The PDPPBT-Si solution in chloroform displayed strong board absorption from $\lambda = 380$ to 1000 nm. Transitioning from the solution to the solid state resulted in a bathochromic shift in the absorption onset of 32 nm, thus resulting in an optical bandgap of about 1.21 eV (Figure 1a). This data suggests that a certain degree of packing is formed in the solid state. Using the cyclic voltammetry, we predicted the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular

Table 1: Synthetic conditions and characteristics of PDPPBT-Si obtained from base-free Suzuki polymerization.

Entry[a]	Catalyst system[b]	Salt (equiv)[c]	Solvent (mL)	Heating/*T* [°C]	*t* [h]	M_n [kDa][d]	PDI[d]
1	$[Pd(PPh_3)_4]$	K_2CO_3 (10)	toluene (4)/water (2)	conventional/120 or μW/120	6 or 24	–[e]	–[e]
2[b]	$[Pd_2(dba)_3]/P(o\text{-tolyl})_3$	K_3PO_4 (5)	toluene (4)/water (2)	conventional/120 or μW/120	6 or 24	–[e]	–[e]
3	$Pd(PPh_3)_4$	CsF (4)	toluene (4)	conventional/120	6	14.9	1.53
4	$[Pd(PPh_3)_4]$	CsF (4)	toluene (4)	conventional/120	12	18.1	2.21
5	$[Pd(PPh_3)_4]$	CsF (4)	toluene (4)	conventional/120	24	–[f]	–[f]
6	$[Pd(PPh_3)_4]$	CsF (4)	DME (4)	conventional/120	6	9.43	1.69
7	$[Pd(PPh_3)_4]$	CsF (4)	DME (4)	conventional/120	12	17.2	1.77
8	$[Pd(PPh_3)_4]$	CsF (4)	DME (4)	conventional/120	24	22.7	4.02
9	$[Pd(PPh_3)_4]$	CsF (4)	toluene (2)	μW/120	2	5.3	2.30
10	$[Pd(PPh_3)_4]$	CsF (4)	toluene (4)	μW/150	3	20.4	1.86
11	$[Pd(PPh_3)_4]$	CsF (4)	toluene (4)	μW/150	6	–[f]	–[f]
12	$[Pd(PPh_3)_4]$	CsF (4)	toluene (1)/DME (1)	μW/120	2	4.7	2.29
13	$[Pd(PPh_3)_4]$	TBAF (4)	DME (2)	μW/120	2	n.d.[g]	n.d.[g]
14	$[Pd(PPh_3)_4]$	CsF (4)	DME (4)	μW/90	1	14.9	1.59
15	$[Pd(PPh_3)_4]$	CsF (4)	DME (4)	μW/90	2	–[f]	–[f]
16	$[Pd(PPh_3)_4]$	CsF (4)	DME (4)	μW/120	1	–[f]	–[f]
17	$[Pd(PPh_3)_4]$	CsF (4)	DME (4)	μW/120	2	–[f]	–[f]

[a] Unless otherwise specified, the Suzuki polymerization was carried out with 0.048 mmol of **1**, 0.048 mmol of **2**, and 5 mol% of the palladium catalyst. [b] $P(o\text{-tolyl})_3$ as the ligand (20 mol%) was added. [c] Equivalents relative to the monomer **1**. [d] Estimated value from gel-permeation chromatography (GPC) measurements using THF as the solvent and calibrated with polystyrene as standard. [e] No polymerization reaction occurred. [f] No characterization was made on these materials because of their insolubility in organic solvents. [g] Not determined because of the poor yield after precipitation and extraction. DME = 1,2-dimethoxyethane, M_n = number-average molecular weight, PDI = polydispersity index, TBAF = tetrabutylammonium fluoride.

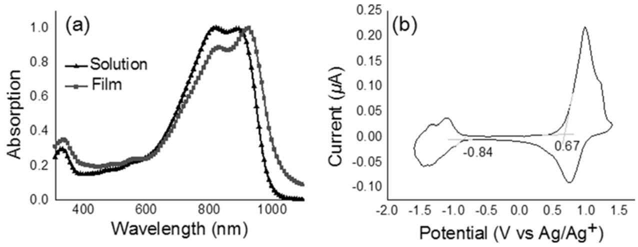

Figure 1. a) UV/Vis-NIR absorption spectra of PDPPBT-Si in chloroform solution and as thin film. b) Cyclic voltammogram of PDPPBT-Si thin film on glassy carbon electrode in 0.1 M Bu$_4$NPF$_6$/CH$_3$CN at a scan rate of 50 mV s^{-1}.

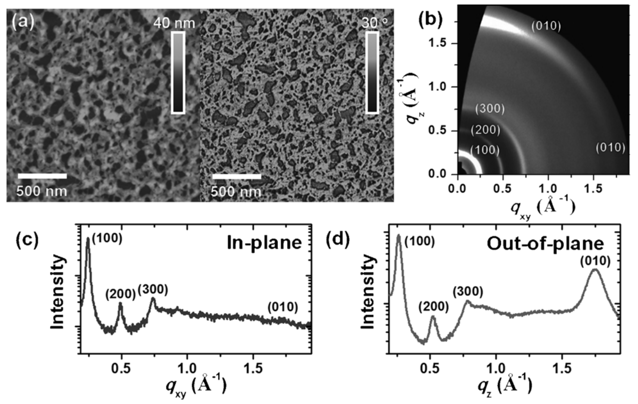

Figure 2. Microstructure analysis of drop-cast PDPPBT-Si films annealed at 220 °C. a) Tapping-mode AFM height (left) and phase (right) images. b) 2D-GIXD image and its 1D-GIXD profiles of c) in-plane and d) out-of-plane directions.

orbital (LUMO) levels of the PDPPBT-Si film to be -5.07 eV and -3.56 eV, respectively (Figure 1 b).

The morphological and microstructural features of the PDPPBT-Si films were studied using tapping-mode atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXD) analyses. PDPPBT-Si films were prepared by drop-casting from a hot chlorobenzene solution (2 mg mL^{-1}) onto *n*-octadecyltrimethoxysilane (OTS)-modified SiO$_2$/Si substrates, followed by annealing at an optimal temperature of 220 °C under a nitrogen atmosphere. As shown in Figure 2 a, the annealed film formed nanofibrillar networks with denser (about 100 nm) aggregates than the as-cast films because of the thermally induced strong intermolecular interactions (see Figure S2 in the Supporting Information). Moreover, an obvious reduction in surface roughness was observed in the annealed film (RMS roughness changed from 4.76 to 3.95 nm after annealing), which leads to better contacts with electrodes on the smooth polymer film. Figure 2 b–d show the two-dimensional (2D) GIXD image and the corresponding diffractogram profiles of the polymer film. PDPPBT-Si displayed well-defined lamellar peaks up to the third order along both the q_{xy} and q_z axes, and it is indicative of bimodal orientations of edge-on and face-on domains. The lamellar distance and coherence length of the (100) order peak were 25.5/23.9 Å and 269.3/145.5 Å for the in-plane and out-of-plane directions, respectively (see Table S1 in the Supporting Information). The comparison of the number of layers (10.6 and 6.1 layers for in-plane and out-of-plane directions, respectively) was estimated based on the ratio of $L_{c(100)}/d_{(100)}$ and revealed a relatively well-ordered edge-on lamellae. Additionally, a strong peak was observed at $q_z \approx 1.7$ Å^{-1}, thus corresponding to π–π stacking with face-on orientations (π-stack distance of ca. 3.6 Å), which resulted from the introduction of siloxane-terminated hybrid side chains.[4a–c] This arrangement suggests that the PDPPBT-Si film adopts three-dimensional (3D) conduction channels which enhance charge transport with efficient π–π planes in both the parallel and perpendicular orientations.[8] In contrast, the positive effect of the thermal annealing for the crystalline nature of the film was demonstrated based on the enhanced crystalline microstructure compared with the as-cast films (see Figure S2). To investigate the charge-transport properties of PDPPBT-Si, bottom-gate top-contact FETs were fabricated on OTS-modified SiO$_2$/Si substrates, as depicted in Figure 3 a. The experimental details of FET fabrication and measurements are included in the Supporting Information. PDPPBT-Si exhibited ambipolar field-effect behaviors, as observed in the DPPBT polymer systems. Figure 3 b–e show the representative *I–V* characteristics of the optimized FETs annealed at 220 °C (see Figure S3

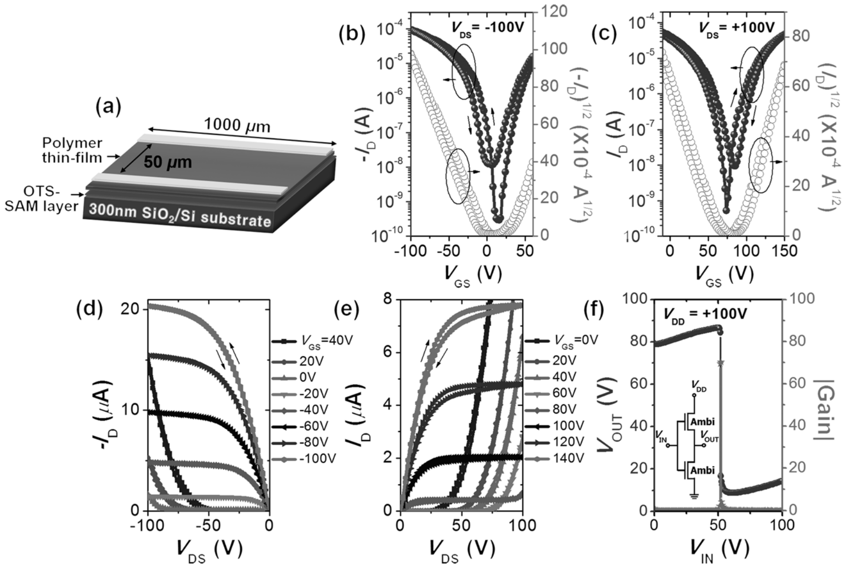

Figure 3. Schematic diagram of solution-processed PDPPBT-Si FETs and their typical electrical characteristics after annealing at 220 °C. a) Schematic illustration of the bottom-gate/top-contact OFET structure with gold electrodes ($L = 50$ μm and $W = 1000$ μm). Transfer characteristics at b) hole- and c) electron-enhancement operation with $V_{DS} = -100$ and $+100$ V, respectively. Output characteristics at d) *p*- and e) *n*-channel operation. f) CMOS-like inverter characteristics at $V_{DD} = +100$ V (Inset: schematic of the complementary inverter structure).

in the Supporting Information). The annealed films showed significantly enhanced mobilities compared with the as-cast polymer films (see Figure S4 and Table S2 in the Supporting Information). The annealed PDPPBT-Si films exhibited well-balanced ambipolar charge transport with the maximum hole and electron mobilities of 0.18 and 0.13 $cm^2V^{-1}s^{-1}$, respectively, even though the asymmetry in threshold voltages resulted from the larger injection barriers for electrons with respect to the gold contacts. The results can be comparable with those of previous highly optimized DPPBT-based OFETs.[9] Complementary metal-oxide-semiconductor (CMOS)-like inverter characteristics of PDPPBT-Si were tested by connecting two identical ambipolar transistors, which exhibited a high gain of 70.1 (Figure 3 f). To further explore the great versatility of this method, we prepared DPP-thiophene polymers with siloxane groups (PDPP3T-Si and PDPP4T-Si) in which **1** was copolymerized with the diboronic ester monomers (thiophene or dithiophene) under the optimized reaction conditions (see Scheme S1 in the Supporting Information). Furthermore, for a fair comparison correlating the base-free Suzuki and Stille polymerizations, these polymers were also prepared from conventional Stille coupling (see Table S3 in the Supporting Information). Both polymerizations produced polymers with similar molecular weights (21.7–34.2 kDa), thus suggesting that our methodology is highly complementary to the preparation of various siloxane-based hybrid polymers. All detailed polymerization procedures are presented in the Supporting Information. The polymers obtained from the base-free Suzuki coupling were used to fabricate OFETs and hole mobilities as high as 1.29 $cm^2V^{-1}s^{-1}$ were observed from PDPP3T-Si (see Figure S5 in the Supporting Information). Note that the maximum mobilities of the DPP-thiophene polymers synthesized by the base-free Suzuki-coupling method are comparable to the corresponding values obtained in each polymer prepared by Stille-type coupling (see Figure S5a-d).

In summary, we utilized base-free Suzuki polymerization by replacing a Brønsted base with fluoride salts to synthesize semiconducting polymers with hybrid siloxane-solubilizing groups, examined its scope, and optimized reaction conditions for the preparation of high molecular weights. This method allows access to a solution-processable PDPPBT-Si polymer with an acceptable molecular weight of 22.7 kDa. Not only does the PDPPBT-Si film form 3D conduction structures which can be accounted for by the strong π–π stacking in both parallel and perpendicular orientations, but its OFET also device shows well-balanced ambipolar characteristics ($\mu_{\text{hole}} = 0.18\,cm^2V^{-1}s^{-1}$ and $\mu_{\text{electron}} = 0.13\,cm^2V^{-1}s^{-1}$). To demonstrate its versatility and efficacy, we also synthesized DPP-thiophene polymers (PDPP3T-Si and PDPP4T-Si) by fluoride-mediated Suzuki coupling, thus yielding high hole mobility of up to 1.29 $cm^2V^{-1}s^{-1}$ in OFET devices based on PDPP3T-Si. Although our understanding of the synthetic mechanism is limited, the chemistry described herein provides a novel approach to the development of numerous hybrid semiconductors with siloxane functional moieties which endow highly desirable and diverse properties.

Keywords: heterocycles · polymers · materials science · microwave chemistry · silicon

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[1] a) A. B. Descalzo, R. Martínez-Máñez, F. Sancenón, K. Hoffmann, K. Rurack, *Angew. Chem. Int. Ed.* **2006**, *45*, 5924–5948; *Angew. Chem.* **2006**, *118*, 6068–6093; b) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed.* **2006**, *45*, 3216–3251; *Angew. Chem.* **2006**, *118*, 3290–3328; c) C. Sanchez, P. Belleville, M. Popall, L. Nicole, *Chem. Soc. Rev.* **2011**, *40*, 696–753; d) A. Chemtob, L. Ni, C. Croutxé-Barghorn, B. Boury, *Chem. Eur. J.* **2014**, *20*, 1790–1806; e) P. Gómez-Romero, C. Sanchez, *Functional Hybrid Materials*, Wiley-VCH, Weinheim, **2005**; f) G. Kickelbick, *Hybrid Materials: Synthesis Characterization, and Applications*, Wiley-VCH, Weinheim, **2007**; g) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **1993**, *115*, 6382–6390; h) S. Sakamoto, A. Shimojima, K. Miyasaka, J. Ruan, O. Terasaki, K. Kuroda, *J. Am. Chem. Soc.* **2009**, *131*, 9634–9635.

[2] K. Kuroda, A. Shimojima, K. Kawahara, R. Wakabayashi, Y. Tamura, Y. Asakura, M. Kitahara, *Chem. Mater.* **2014**, *26*, 211–220.

[3] a) J. E. Mark, *Acc. Chem. Res.* **2004**, *37*, 946–953; b) K. Kawahara, Y. Hagiwara, K. Kuroda, *Chem. Eur. J.* **2011**, *17*, 13188–13196; c) R. G. Jones, W. Ando, J. Chojnowski, *Silicon-Containing Polymers: The Science and Technology of Thier Synthesis and Applications*, Kluwer Academic, Dordrecht, The Netherlands, **2000**; d) J. E. Mark, H. R. Allcock, R. West, *Inorganic Polymers*, 2nd ed., Oxford University Press, New York, **2004**.

[4] a) J. Lee, A.-R. Han, J. Kim, Y. Kim, J. H. Oh, C. Yang, *J. Am. Chem. Soc.* **2012**, *134*, 20713–20721; b) J. Lee, A.-R. Han, H. Yu, T. J. Shin, C. Yang, J. H. Oh, *J. Am. Chem. Soc.* **2013**, *135*, 9540–9547; c) J. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney, Z. Bao, *J. Am. Chem. Soc.* **2011**, *133*, 20130–20133; d) S. Holliday, J. E. Donaghey, I. McCulloch, *Chem. Mater.* **2013**, *26*, 647–663.

[5] H. Li, J. Mei, A. L. Ayzner, M. F. Toney, J. B. H. Tok, Z. Bao, *Org. Electron.* **2012**, *13*, 2450–2460.

[6] a) S. W. Wright, D. L. Hageman, L. D. McClure, *J. Org. Chem.* **1994**, *59*, 6095–6097; b) R. N. Brookins, E. Berda, J. R. Reynolds, *J. Mater. Chem.* **2009**, *19*, 4197–4204; c) R. M. Walczak, R. N. Brookins, A. M. Savage, E. M. van der Aa, J. R. Reynolds, *Macromolecules* **2009**, *42*, 1445–1447.

[7] R. N. Brookins, K. S. Schanze, J. R. Reynolds, *Macromolecules* **2007**, *40*, 3524–3526.

[8] a) L. H. Jimison, M. F. Toney, I. McCulloch, M. Heeney, A. Salleo, *Adv. Mater.* **2009**, *21*, 1568–1572; b) X. Zhang, L. J. Richter, D. M. DeLongchamp, R. J. Kline, M. R. Hammond, I. McCulloch, M. Heeney, R. S. Ashraf, J. N. Smith, T. D. Anthopoulos, B. Schroeder, Y. H. Geerts, D. A. Fischer, M. F. Toney, *J. Am. Chem. Soc.* **2011**, *133*, 15073–15084; c) J. Rivnay, R. Steyrleuthner, L. H. Jimison, A. Casadei, Z. Chen, M. F. Toney, A. Facchetti, D. Neher, A. Salleo, *Macromolecules* **2011**, *44*, 5246–5255.

[9] a) S. Cho, J. Lee, M. Tong, J. H. Seo, C. Yang, *Adv. Funct. Mater.* **2011**, *21*, 1910–1916; b) A. J. Kronemeijer, E. Gili, M. Shahid, J. Rivnay, A. Salleo, M. Heeney, H. Sirringhaus, *Adv. Mater.* **2012**, *24*, 1558–1565; c) P. Sonar, S. P. Singh, Y. Li, M. S. Soh, A. Dodabalapur, *Adv. Mater.* **2010**, *22*, 5409–5413.

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