7864 *Macromolecules* **2010**, *43*, 7864–7867
DOI: 10.1021/ma1014885

Macromolecules
NOTE

Cyclopentadithiazole-Based Monomers and Alternating Copolymers

Christof J. Kudla, Daniel Dolfen, Kristina J. Schottler, Jan-Moritz Koenen, Dietrich Breusov, Sybille Allard, and Ullrich Scherf*

Macromolecular Chemistry Group and Institute for Polymer Technology, Bergische Universität Wuppertal, Gauss-Strasse 20, D-42097 Wuppertal, Germany

Received July 7, 2010; Revised Manuscript Received August 17, 2010

Introduction

Conjugated, alternating copolymers composed of electron-rich (so-called "*donor*") and electron-poor (so-called "*acceptor*") building blocks are in the focus of very intense research activities both on the academic and industrial scale. Main driving force for this research is their application as hole-generation/hole-transport material (donor material) in bulk heterojunction-type organic solar cells (BHJ-OSCs). [There is some confusion in the use of the term "*donor*". "*Donor*" is both used for the electron-rich building blocks of the alternating copolymers and the copolymer material itself in its function as hole-generating/hole-transport component of the active polymer/fullerene blend in bulk heterojunction-type organic solar cells (BHJ-OSCs).] The number of published copolymer structures is currently rapidly increasing. A couple of examples allow, in combination with soluble fullerene acceptors ($PC_{61}BM$, $PC_{71}BM$), for power conversion efficiencies (PCEs) of > 5.5%.[1−6] Unfortunately, reliable design rules in the selection of the electron-rich and electron-poor building blocks of the alternating copolymers are not available until now.

Nevertheless, a few donor and acceptor building blocks have proved to be effective toward maximum PCEs including *N*-alkylcarbazole-2,7-diyl[7] and 4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6-diyl[8] (**CPDT**) as "*donor*" and benzo-2,1,3-thiadiazole-4,7-diyl, 4,7-dithienyl-2,1,3-benzothiadiazole-5′,5″-diyl,[9,10] and thiophene-3,4-dicarbimide-2,5-diyl[4] as "*acceptor*" units. The combination of 4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6-diyl and benzo-2,1,3-thiadiazole-4,7-diyl building blocks leads to the well-known poly(4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6-diyl-*co*-benzo-2,1,3-thiadiazole-4,7-diyl) **PCPDTBT** copolymer (introduced by Konarka) for which a PCE of 5.5% in alternating copolymer/fullerene BHJ-OSCs has been reported after a careful optimization of blend composition and processing conditions by Peet et al.[6] One shortcoming in the application of **PCPDTBT** and related copolymers in donor−acceptor couples with soluble fullerene acceptors ($PC_{61}BM$, $PC_{71}BM$) is the relatively low open circuit voltage of the resulting BHJ-OSCs with a V_{oc} of ca. 0.6−0.7 V.[11]

An increase of the V_{oc} value in related alternating copolymers can be expected for a decreased HOMO energy level of the alternating copolymer. Hereby, the energetic position of the copolymer HOMO level is mainly determined by the structure of the electron-rich ("*donor*") building block of the alternating copolymer. The favorable downshift of the HOMO energy level can be accomplished by a successive replacement of aromatic (sp^2) carbons of the thiophene unit by sp^2 nitrogens. Following this idea we have focused our synthetic efforts on 7,7-dialkyl-cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-type monomers as target for further condensation with suitable electron-poor "*acceptor*" moieties.

Results and Discussion

Monomer Synthesis. Our synthetic targets (7,7-dialkylated cyclopenta[1,2-*d*:4,3-*d*′]dithiazole **CPDTz** monomers) are produced in a multistep sequence. The first couple of steps generates the tricyclic ketone 2,5-bis(triisopropylsilyl)cyclopenta[1,2-d:4,3-*d*′]dithiazole-7-one **1** and follows a recently published synthetic procedure.[12] The final four steps of monomer synthesis have been developed in our group and involve (i) a Wittig-type carbonyl olefination of the keto function yielding the exocyclic olefin **2**, (ii) the regioselective alkylation of the olefinic double bound in 7-position with LAH/alkyl bromide to the corresponding 7,7-dialkylated cyclopentadithiazole intermediate **3**, (iii) the cleavage of the triisopropylsilyl protecting groups (TIPS) with tetrabutylammonium fluoride (TBAF) to **CPDTz 4**, and (iv) its distannylation to the desired target monomer, 2,5-bis(tributylstannyl)-7,7-dialkyl-cyclopenta[1,2-*d*:4,3-*d*′]dithiazole **5** (Scheme 1). Alternatively, 7,7-dialkyl-cyclopenta[1,2-*d*:4,3-*d*′]dithiazole **4** can be dibrominated (v) to 2,5-dibromo-7,7-dialkyl-cyclopenta[1,2-*d*:4,3-*d*′]dithiazole **6**.

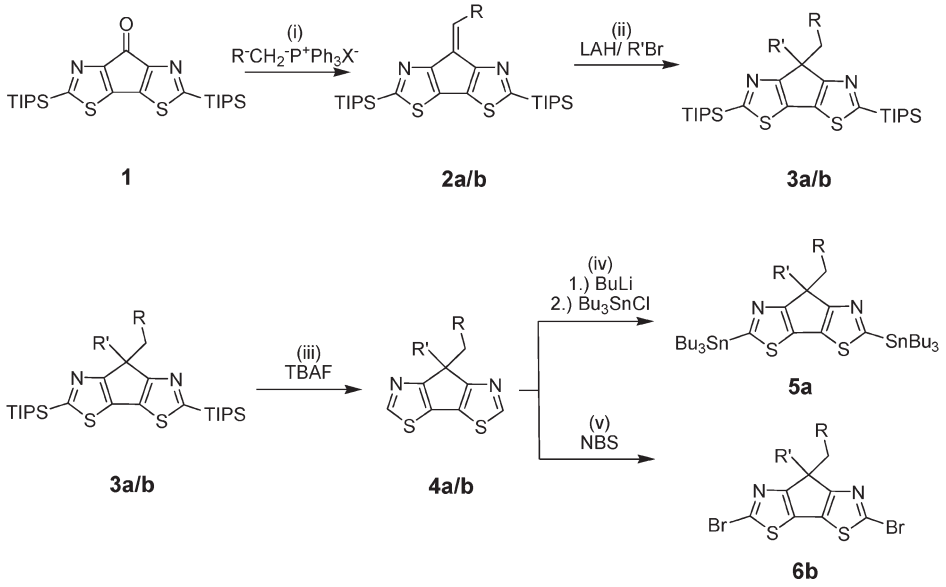
Polymer Synthesis and Characterization. The 2,5-distannylated 7,7-bis(2-etylhexyl)-cyclopentadithiazole monomer **5a** was subsequently reacted with suitable acceptor monomers as 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide **8**, and 2,6-bis(2-bromothien-5-yl)naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide **9** into the alternating copolymers poly[7,7-bis(2-ethylhexyl)-cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-naphthalene-1,4,5,8-tetracarboxylic-*N,N*′-bis(2-octyldodecyl) diimide-2,6-diyl], **PCPDTzN**, and poly[7,7-bis(2-ethylhexyl)-cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-2,6-[bis(2-thienyl)naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-5,5′-diyl], **PCPDTzNT**, in aryl−aryl cross couplings of the Stille-type (Scheme 2). The corresponding 2,5-dibromo-substituted 7,7-didodecyl-**CPDTz** monomer **6b** was condensed with 4,8-bis(octyloxy)-2,6-bis(trimethylstannyl)benzo[1,2-*b*:3,4-*b*′]dithiophene **7** to the alternating copolymer poly[7,7-didodecyl-cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-(4,8-bis(octyloxy)benzo-[1,2-*b*:3,4-*b*′]dithiophene)-2,6-diyl] **PCPDTzBDT**, also in an aryl−aryl cross coupling according to Stille.

The resulting, dark colored alternating copolymers exhibit mean average molecular weights M_n of > 8000 g/mol and weight-average molecular weights M_w of > 10 000 g/mol (see Table 1). The copolymers show long wavelength absorption maxima $\lambda_{max,abs}$ in dilute chloroform solution at 550 nm (**PCPDTzBDT**) for the benzo[1,2-*b*:3,4-*b*′]dithiophene (**BDT**)-based copolymer, and 641 (**PCPDTzN**) or 651 nm (**PCPDTzNT**), respectively, for the two naphthalene diimide-based copolymers (Figure 1). The corresponding photoluminescence maxima $\lambda_{max,em}$ are observed at 634 (**PCPDTzBDT**), and

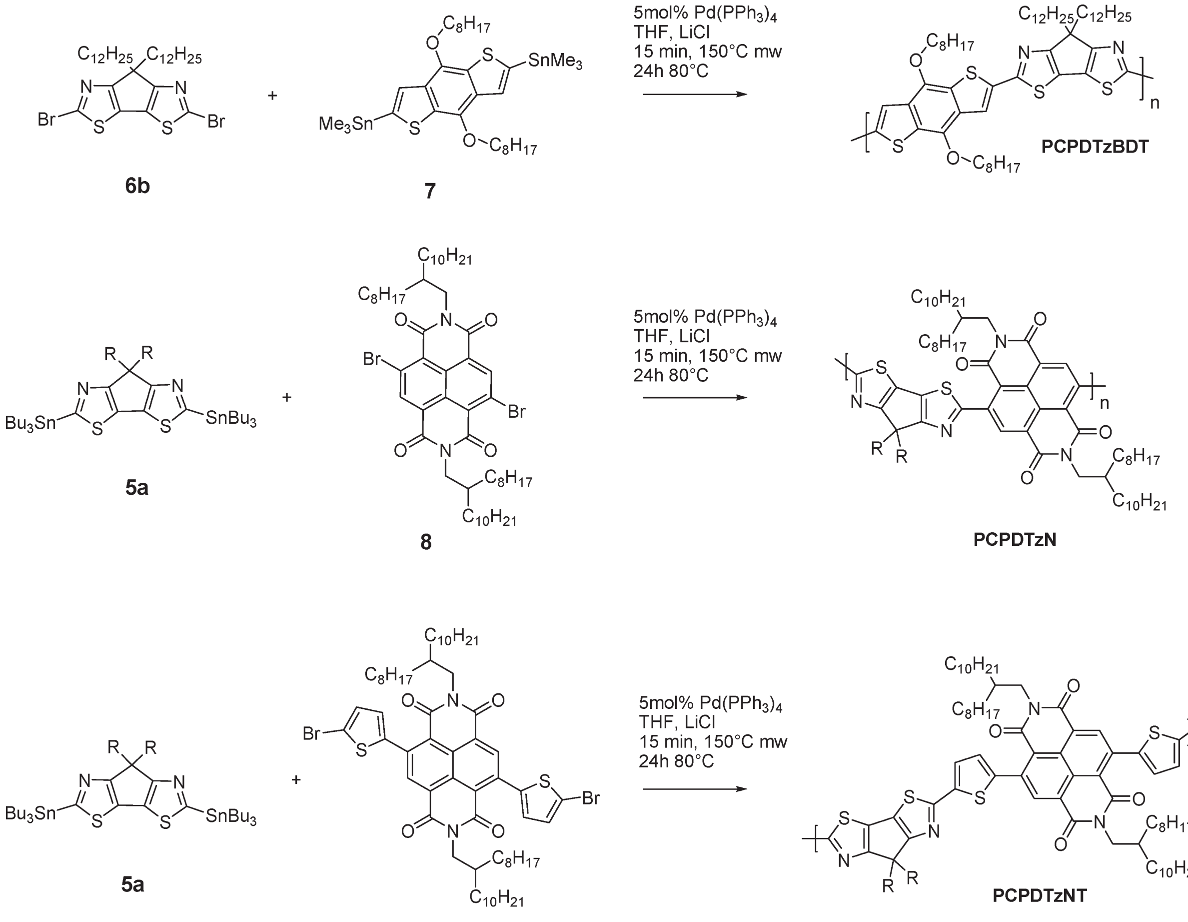
---

*Corresponding author. E-mail: scherf@uni-wuppertal.de.

Scheme 1. Synthesis of the CPDTz Monomers 2,5-Bis(tributylstannyl)-7,7-didodecylcyclopenta[1,2-*d*:4,3-*d*′]dithiazole, 5a, and 2,5-Dibromo-7,7-bis(2-ethylhexyl)cyclopenta[1,2-*d*:4,3-*d*′]dithiazole, 6b (a, *R* = 3-heptyl, R′ = 2-ethylhexyl; b, *R* = 1-undecyl, R′ = 1-dodecyl)



Scheme 2. Synthesis of the Alternating Copolymers Poly[7,7-didodecylcyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-(4,8-bis(octyloxy)benzo[1,2-*b*:3,4-*b*′]dithiophene)-2,6-diyl], PCPDTzBDT, Poly[7,7-bis(2-ethylhexyl)cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-2,6-diyl], PCPDTzN, and Poly[7,7-bis(2-ethylhexyl)cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-2,6-[bis-(2-thienyl)naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-5,5′-diyl], PCPDTzNT, in Aryl−Aryl Cross Couplings According to Stille (*R* = 2-Ethylhexyl) with Coupling Conditions 5 mol % $Pd(PPh_3)_4$, LiCl in THF, 15 min at 150 °C under Microwave Heating, and Then 24 h at 80 °C



771 (**PCPDTzN**) or 820 nm (**PCPDTzNT**), respectively. Hereby, the photoluminescence of the two naphthalene diimide-based copolymers is relatively weak, especially for **PCPDTzN** (Figure 1).

Table 1. Alternating Copolymers Containing the 7,7-Dialkylcyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl, CPDTz, Building Block

alternating copolymer	yield [%]	M_n [g/mol]	M_w [g/mol]	PDI	absorption maxima λ_{max} [nm]
PCPDTzBDT	84	12 000	28 800	2.4	550
PCPDTzN	28	15 900	26 300	1.65	641, 385
PCPDTzNT	51	8000	10 800	1.35	651, 446, 389

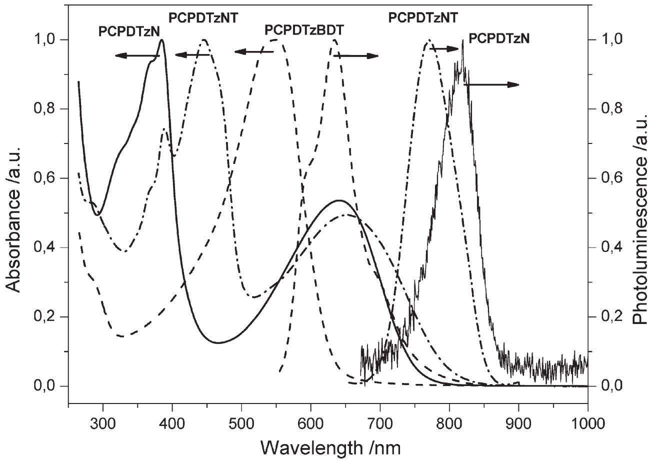


Figure 1. Solution UV−vis and photoluminescence spectra of the alternating copolymers poly[7,7-didodecylcyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-(4,8-bis(octyloxy)benzo[1,2-*b*:3,4-*b*′]dithiophene)-2,6-diyl], **PCPDTzBDT** (dashed lines, λ_{ext}: 550 nm), poly[7,7-bis(2-ethylhexyl)-cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-2,6-diyl], **PCPDTzN** (solid lines, λ_{ext}: 641 nm), and poly[7,7-bis(2-ethylhexyl)cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-2,6-[bis(2-thienyl)naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-5,5′-diyl], **PCPDTzNT** (dash−dotted lines, λ_{ext}: 651 nm) (solvent: chloroform).

A comparison of our novel copolymers **PCPDTzN** (or **PCPDTzNT**) with the corresponding 4,4-dialkyl-cyclopenta-[2,1-*b*:3.4-*b*′]dithiophene-2,6-diyl (**CPDT**)-based alternating copolymers that contain the same on-chain naphthalene-1,4,-5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-2,6-diyl (**PCPDTN**) (or bis(2-thienyl)naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-5,5′-diyl **PCPDTNT**) building blocks illustrates the result of the thiazole−thiophene replacement. Exemplarily, the solution UV−Vis spectra of **PCPDTzN** and **PCPDTN** (M_n, 23 000; M_w, 32 200 g/mol) are depicted in Figure 2 (for the copolymer structures see Scheme 3) and show a high energy (hypsochromic) shift of the long wavelength absorption band by replacing the **CPDT** by **CPDTz** units, thus reflecting the weaker donor character of the **CPDTz** unit (long wavelength absorption band, λ_{max} = 641 nm/1.93 eV for **PCPDTzN** and 764 nm/1.62 eV for **PCPDTN**; ΔE_{abs} = 0.31 eV). Please note that both **CPDT** and **CPDTz** act as electron-rich ("*donor*") component in combination with the electron-poor naphthalene diimide-based acceptor units. The incorporated electron-rich ("*donor*") moiety should particularly influence the position of the HOMO energy level (HOMO downshift for a replacement of thiophene in **CPDT** by thiazole in **CPDTz**). This expected trend was documented in measurements of the HOMO energy level position (ionization potential IP) by photoemission spectroscopy (AC-2, Riken Keiki) yielding HOMO energy values of 5.95 eV for **PCPDTzN** and 5.68 eV for **PCPDTN** (ΔE_{IP}: 0.27 eV) thus impressively illustrating that the increase of the HOMO/LUMO gap for the **CPDTz**-based copolymer mainly results from a downshift of the HOMO energy level (ionization potential IP). Similar trends have been observed for the second couple of copolymers (**PCPDTzNT** and **PCPDTNT**).

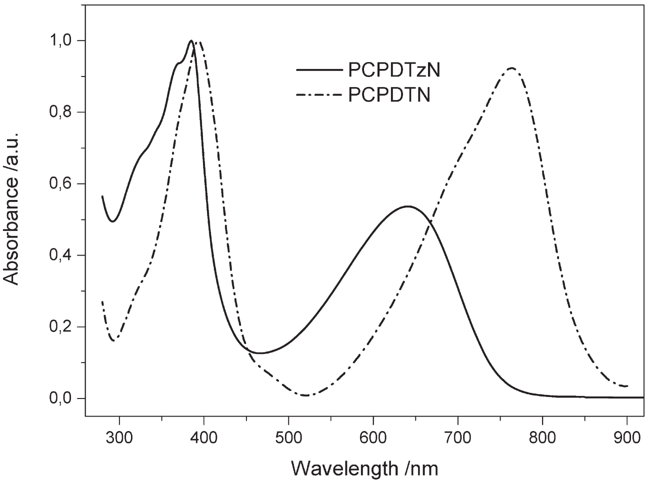
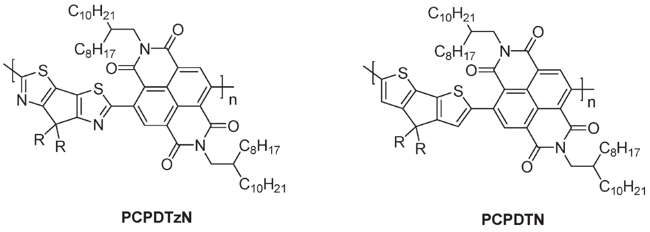


Figure 2. Solution UV−vis spectra of the alternating copolymers poly-[7,7-bis(2-ethylhexyl)cyclopenta[1,2-*d*:4,3-*d*′]dithiazole-2,5-diyl-*co*-naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-2,6-diyl] **PCPDTzN** and poly[4,4-bis(2-ethylhexyl)cyclopenta[2,1-*b*:3.4-*b*′]dithiophene-2,6-diyl-*co*-naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl) diimide-2,6-diyl] **PCPDTzN** (solvent: chloroform).

Scheme 3. Chemical Structures of the Alternating Copolymers PCPDTzN and PCPDTN (R = 2-ethylhexyl)



Conclusions

In summary, we have introduced a novel cyclopentadithiazole (**CPDTz**) building block for subsequent incorporation into alternating donor−acceptor copolymers. First examples of such conjugated, alternating copolymers are reported. Alternating copolymers with electron-poor naphthalene diimide "*acceptor*" moieties exhibit long wavelength absorption bands up to 800 nm. A comparison of corresponding cyclopenta[1,2-*d*:4,3-*d*′]dithiazole (**CPDTz**) and cyclopenta[2,1-*b*:3.4-*b*′]dithiophene (**CPDT**) based alternating copolymers shows the expected HOMO energy downshift for the replacement of the thiophene by the "less" electron-rich thiazole unit.

Acknowledgment. The research leading to these results has received partially funding from the BMBF through the MaDriX project and from the European Community's Seventh Framework Programme (FP7/2007-2013) under Grant Agreement No. 212311 of the ONE-P project. The authors would also like to thank Evonik Industries (Science to Business S2B Center Nanotronics, Marl, Germany) for the AC-2 measurements.

Supporting Information Available: Text giving detailed experimental procedures of monomer and polymer synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For a review see: Zhan, X.; Zhu, D. *Polym. Chem.* **2010**, *1*, 409–419.

(2) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. *Adv. Mater.* **2010**, *22*, E135–E138.

(3) Huo, L.; Hou, J.; Zhang, S.; Chen, H.-Y.; Yang, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 1500–1503.

(4) Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Aich, B. R.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2010**, *132*, 5330–5331.

(5) Chan, S.-H.; Hsiao, Y.-S.; Hung, L.-I.; Hwang, G.-W.; Chen, H.-L.; Ting, C.; Chen, C.-P. *Macromolecules* **2010**, *43*, 3399–3405.

(6) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497–500.

(7) Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295–2300.

(8) Mühlbacher, D.; Scharber, M.; Morana, M.; Zhu, Z.; Waller, D.; Gaudiana, R.; Brabec, C. *Adv. Mater.* **2006**, *18*, 2884–2889.

(9) Slooff, L. H.; Veenstra, S. C.; Kroon, J. M.; Moet, D. J. D.; Sweelssen, J.; Koetse, M. M. *Appl. Phys. Lett.* **2007**, *90*, 143506.

(10) Moulé, A. J.; Tsami, A.; Bünnagel, T. W.; Forster, M.; Kronenberg, N. M.; Scharber, M.; Koppe, M.; Morana, M.; Brabec, C. J.; Meerholz, K.; Scherf, U. *Chem. Mater.* **2008**, *20*, 4045–4050.

(11) Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323–1338.

(12) Ie, Y.; Nitani, M.; Karakawa, M.; Tada, H.; Aso, Y. *Adv. Funct. Mater.* **2010**, *20*, 907–913.