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Thieno[2,3-*b*]indole-Based Small Push−Pull Chromophores: Synthesis, Structure, and Electronic Properties

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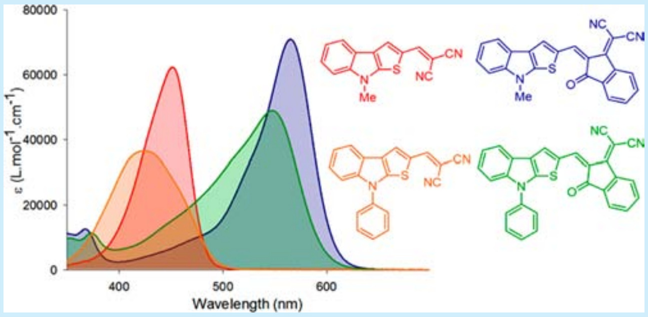
Supporting Information

ABSTRACT: Small push−pull molecules were synthesized in high yields by connecting a *N*-methyl or *N*-phenyl substituted thieno[2,3-*b*]indole electron-donating block directly to a 2,2-dicyanovinyl or (1-(dicyanomethylene)-3-oxo-1-inden-2-ylidene)methyl electron-withdrawing group. The effects of the N-substitution on thieno[2,3-*b*]indole and the nature of the electron-accepting group on the electrochemical, optical, and charge-transport properties were investigated by cyclic voltammetry, UV−vis spectroscopy, and the space-charge-limited current method, respectively. These results, together with the 1% power conversion efficiency of a bilayer solar cell prepared with the smallest compound of the series, show the potential of thieno[2,3-*b*]indole for organic electronics.



While arylamine derivatives have been used as hole-transporting materials for organic-light emitting diodes (OLEDs),[1,2] organic (OSCs),[3] dye-sensitized (DSSCs),[4] and perovskite-sensitized solar cells,[5] their strong electron-donating properties make them ideal donor building-blocks (D) for the synthesis of D-π-A push−pull molecules, which are efficient electron-donor materials in OSCs[3,6] or metal-free sensitizers for DSSCs.[7]

Triarylamine units have been widely used in linear[6g,8−10] or star-shaped[6g,11−13] push−pull molecules for OSCs, whereas alkyldiarylamine[14] and dialkylarylamine[15] have also led to D-π−A systems with interesting photovoltaic performance. To restrict the well-known propeller shape associated with triarylamine derivatives and thus favoring $\pi-\pi$ intermolecular interactions, covalent bridging by methylene groups or heteroatoms has been pursued leading to planarized triphenylamine,[16] indoline,[17] and phenoxa(thia)zine[18] derivatives. Similarly, merocyanine dyes with constrained arylamino electron-donating groups have been successfully reported for OSCs.[19] On the other hand, fused aromatic *N*-heterocycles, such as carbazole and its derivatives, represent also a well-known class of planarized D building-blocks for the synthesis of push−pull molecules for photovoltaic applications.[3,6,7,10c,20]

In this context, thieno[2,3-*b*]indole (TI) which constitutes one isoelectronic structure of carbazole, could be of interest in the field of organic electronics. While TI itself or derivatives constitute important targets due to their biological activities leading to potential applications in treating diseases or plant-growth regulation,[21] their use as functional material in organic electronics is scarce. Thus, the structure and the electronic properties of fused thieno[2,3-*b*]indole benzothiadiazole derivatives have been recently described.[22] Few organic electroluminescent compounds derived from *N*-arylthieno-[2,3-*b*]indole[23] and condensed *N*-aroylthieno[2,3-*b*]indole[24] have been reported in recent patents. Two dyes derived from thieno[2,3-*b*]indole have been recently evaluated in DSSCs.[25]

We present herein the synthesis and the electronic properties of small push−pull D-π−A molecules where *N*-methyl or *N*-phenyl substituted thieno[2,3-*b*]indole **3a** (MTI) or **3b** (PTI) as D building-block is directly connected to 2,2-dicyanovinyl (DCV) or (1-(dicyanomethylene)-3-oxo-1-inden-2-ylidene)-methyl (DCI) as electron-accepting group (A) (Scheme 1). Preliminary results on the hole-transporting properties of these compounds and their potential in OSCs are also reported.

The synthetic strategy is depicted in Scheme 1. Phenyl-substituted thieno[2,3-*b*]indole **3a** was prepared in one step via a pallado catalyzed domino N−H/C−H bond activation reaction involving diphenylamine and 2,3-dibromothiophene.[26] Interestingly, the use of the *N*-methylaniline instead of the diarylamine does not afford the methyl analogue **3b** despite multiple attempts and conditions changes. Consequently, the latter was prepared according to a three-step procedure starting with a microwave assisted Suzuki-Miyaura cross-coupling reaction between 1-iodo-2-nitrobenzene and 3-thienylboronic acid under atmospheric pressure. The resulting 3-(2-nitrophenyl)thiophene **1** was subsequently involved in a Cadogan reductive cyclization yielding 8H-thieno[2,3-*b*]indole

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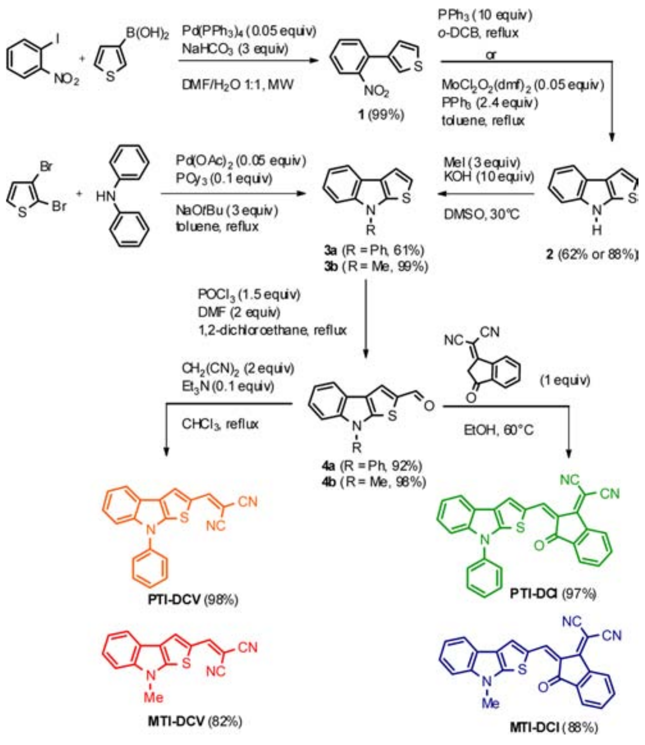
Scheme 1. Synthesis of Thieno[2,3-*b*]indole-Based Push−Pull Molecules



2, as already reported.[27] For scale-up purpose, the microwave irradiation was replaced by a conventional oil bath and $P(OEt)_3$ by a mixture of 10 equiv of PPh_3 in 1,2-dichlorobenzene since $P(OEt)_3$, used as a solvent and reactant, systematically afforded undesired byproducts. In these optimized conditions, several grams of compound **2** were prepared in 62% yield (Scheme 1). Since dioxomolybdenum(VI) complexes are efficient catalysts for oxo-transfer reactions, the Cadogan reaction was finally performed in the presence of a catalytic amount of $MoCl_2O_2(dmf)_2$.[28] While improving the yield to 88%, it allowed us to reduce the quantities of PPh_3 and to switch over toluene (Scheme 1). Thieno[2,3-*b*]indole **2**, thus prepared in good yields and grams scale quantity, was then easily alkylated with methyl iodide affording compound **3b**. Note that an alternative route to compound **2** starting from **1** has been recently described.[29] Finally, an aldehyde group was introduced at the 2-position of both *N*-aryl and *N*-alkyl thienoindoles **3a** and **3b** via a regioselective Vilsmeier−Haack formylation. The resulting formyl derivatives **4a** and **4b** were subjected to a Knœvenagel condensation with either malononitrile or 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile leading to the four target push−pull molecules in high overall yields.

Figure 1 presents the cyclic voltammograms (CVs) of the push−pull molecules recorded in CH_2Cl_2 in the presence of Bu_4NPF_6 as supporting electrolyte. Each CV shows an irreversible reduction wave with a cathodic peak potential value E_{pc} which depends on both the nature of the electron-accepting group and the N-substitution of the thienoindole moiety. The E_{pc} values of the DCI derivatives **PTI-DCI** (E_{pc} = −1.16 V) and **MTI-DCI** (E_{pc} = −1.29 V) are significantly shifted toward positive potentials compared to DCV compounds **PTI-DCV** (E_{pc} = −1.55 V) and **MTI-DCV** (E_{pc} = −1.72 V) due to the stronger electron-accepting ability of DCI group. Similarly, albeit to a lesser extent, the replacement of the methyl by a phenyl substituent on the thienoindole unit leads to a ca. 0.2 V positive shift of E_{pc} resulting from the concomitant suppression of the +*I* inductive effect of the alkyl chain and occurrence of the −*M* mesomeric effect of the phenyl ring.

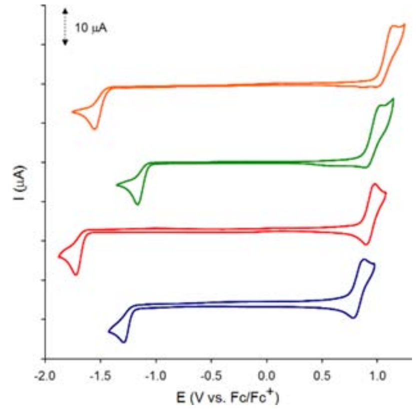


Figure 1. Cyclic voltammograms of **PTI-DCV** (orange), **PTI-DCI** (green), **MTI-DCV** (red), and **MTI-DCI** (dark blue): 1 mM in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrode, scan rate 100 mV s^{-1}.

On the other hand, one oxidation wave with an anodic peak potential E_{pa} associated with the formation of a radical cation is also observed on each CV. While this oxidation process is irreversible for **PTI-DCV** (E_{pa} = +1.15 V) and **PTI-DCI** (E_{pa} = +1.04 V), the *N*-methyl substituted thienoindole derivatives **MTI-DCV** (E_{pa} = +0.97 V) and **MTI-DCI** (E_{pa} = +0.87 V) exhibit more reversible oxidation waves at more negative E_{pa} values (ca. − 0.2 V shift) owing to the +*I* effect of methyl groups. It is worth noting that the use of the stronger electron accepting group DCI leads to ca. −0.1 V shifts of E_{pa} which is counterintuitive but may be related to the extension of the π-conjugated system and hence to a better stabilization of the radical-cation.

The UV−vis absorption spectrum of titled compounds in CH_2Cl_2 shows a main band in the visible region attributed to an intramolecular charge transfer (Figure 2). Comparison of the λ_{max} of DCV (424 and 452 nm, respectively, for **PTI-DCV** and **MTI-DCV**) and DCI derivatives (548 and 566 nm, respectively, for **PTI-DCI** and **MTI-DCI**) shows that the

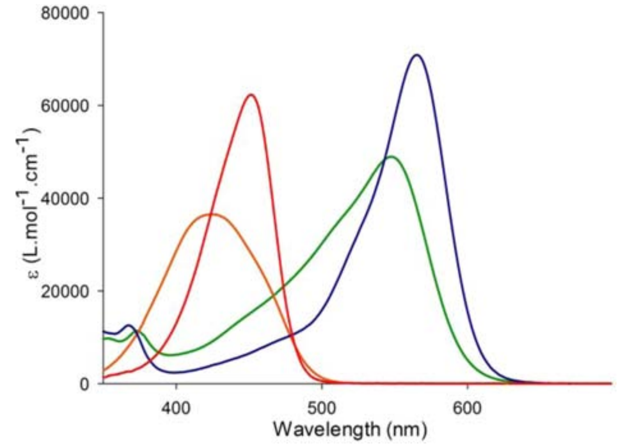


Figure 2. Absorption spectra of 10^{-5} M solutions of **PTI-DCV** (orange), **PTI-DCI** (green), **MTI-DCV** (red), and **MTI-DCI** (dark blue) in CH_2Cl_2.

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stronger electron-withdrawing DCI group leads to a significant bathochromic shift of ca. 120 nm. Absorption maxima of MTI derivatives are subject to 20−30 nm bathochromic shifts compared to the corresponding PTI derivatives. In addition, it is interesting to note that MTI derivatives present higher extinction molar coefficients ε than those of PTI ones with high values for **MTI-DCV** (ε = 62 000 $M^{-1}\cdot cm^{-1}$) and **MTI-DCI** (ε = 71 000 $M^{-1}\cdot cm^{-1}$).

The thermal properties of titled compounds have been analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Except for **MTI-DCV** that decomposes at 298 °C before melting, the first DSC traces show a sharp endothermic peak with an onset corresponding to the melting point (Table S1, Figure S20). TGA indicates decomposition temperatures T_d, defined at 5% weight loss, of ca. 230 and 310 °C for DCV and DCI derivatives, respectively.

Thermal evaporation of these compounds under vacuum readily affords homogeneous thin-films without any sign of decomposition as confirmed by MALDI-TOF and UV−vis analysis of redissolved films. The absorption spectrum of films of 15 nm thickness of these compounds evaporated on PEDOT−PSS coated ITO on glass shows a red shift of λ_{max} and a broadening of the absorption band compared to the solution spectrum together with the apparition of well-defined shoulders attributed to intermolecular π-interactions in the solid state (Figure S22). The thin-films absorption onsets at low energy give optical band gaps E_g of 2.39 eV (**PTI-DCV**), 1.93 eV (**PTI-DCI**), 2.38 eV (**MTI-DCV**), and 1.86 eV (**MTI-DCI**). Note that the absorption coefficient of the film derived from **MTI-DCV** exhibits the highest value of 2.22 × 10^5 cm^{-1} (Supporting Information (SI)).

The hole mobility (μ_h) of titled compounds has been estimated on hole only devices using the space-charge-limited current (SCLC) method (SI). The devices consist of a 115 nm thick layer of each push−pull molecule vacuum-deposited on a PEDOT−PSS/ITO/glass substrate on which a gold cathode (100 nm) is thermally evaporated. X-ray diffraction analysis of these organic thin films did not show any diffraction peak suggesting their amorphous character. Figure 3 displays the current density vs voltage plots of hole-only diodes based on the different compounds and clearly shows higher current density for DCV derivatives. The hole-mobility extracted from these curves for **PTI-DCV** (μ_h = 2.68 × 10^{-5} $cm^2\ V^{-1}\ s^{-1}$), **PTI-DCI** (μ_h = 2.3 × 10^{-7} $cm^2\ V^{-1}\ s^{-1}$), **MTI-DCV** (μ_h = 2.27 × 10^{-5} $cm^2\ V^{-1}\ s^{-1}$), and **MTI-DCI** (μ_h = 1.3 × 10^{-6} $cm^2\ V^{-1}\ s^{-1}$) show close values for the DCV derivatives at least 1 to 2 orders of magnitude higher than those of DCI derivatives.

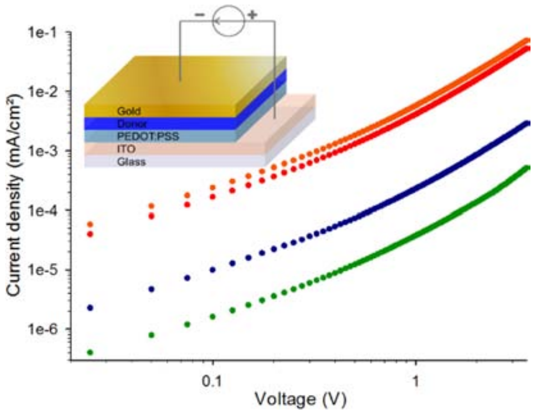

Figure 3. Current density−voltage characteristics of hole-only diodes based on **PTI-DCV** (orange), **PTI-DCI** (green), **MTI-DCV** (red), and **MTI-DCI** (dark blue).

Single crystals of **MTI-DCV** grown by slow evaporation of a solution of DMF were analyzed by X-ray diffraction (SI). Two independent molecules are present per asymmetric unit. With the exception of methyl groups, the molecules adopt a quasi-planar conformation. As expected, the thieno[2,3-*b*]indole core is fully planar, whereas a slight deviation from planarity results from small dihedral angles of 4° or 6.8° between the thiophene and DCV units, the latter adopting a cis conformation relative to the sulfur atom. Figure 4 shows that molecules are stacked along the *b* axis with a parallel orientation and significant overlaps (SI). The short mean intermolecular distances inside the column d_1 (3.402 Å) and d_2 (3.414 Å) are consistent with a compact packing associated with $\pi-\pi$ stacking interactions of high interest for charge transport.

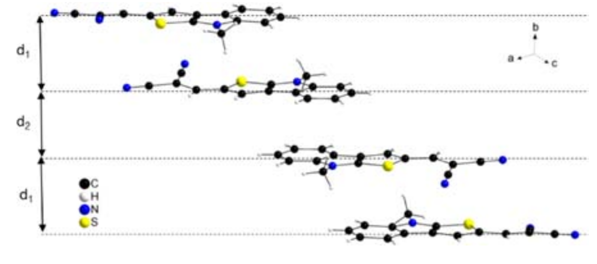

Figure 4. Molecular packing of **MTI-DCV** along the *b* axis.

The relatively good hole transport properties of thin-films of **MTI-DCV** combined with their high absorption coefficient and thermal stability incite us to evaluate the photovoltaic performance of this small push−pull molecule as donor material. As a preliminary test, simple bilayer planar heterojunction solar cells of 27 mm^2 active area were fabricated by successive thermal evaporations of 15 nm of **MTI-DCV**, 20 nm of C_{60}, as acceptor material, and 150 nm of aluminum on ITO substrates precoated with a 40 nm layer of spin-cast PEDOT−PSS. After a thermal treatment of 15 min at 100 °C, 8 devices under AM 1.5 simulated solar illumination (80 mW·cm^{-2}) led to average values of short-circuit current density J_{sc} of 2.92 mA·cm^{-2}, open-circuit voltage V_{oc} of 0.69 V, fill-factor FF of 0.40, and power conversion efficiency PCE of 1.00% with a maximum of 1.06% for the best device (SI).

In conclusion, we have developed a straightforward, scalable, and high yield synthetic strategy to *N*-alkyl and *N*-aryl thieno[2,3-*b*]indole heterocycles and used them as electron-donating blocks for the preparation of new push−pull chromophores. The latter combine good absorption properties in the visible spectrum and hole transport properties; as such, the photovoltaic performance of one of these reduced-size molecules has been evaluated showing interesting potential. To the best of our knowledge, **MTI-DCV** represents the smallest push−pull molecule ever reported with a PCE higher than 1%.[6f] Further investigations of the photovoltaic properties of the other thieno[2,3-*b*]indole derivatives and the synthesis of more extended push−pull systems are underway. More generally, these results show that thieno[2,3-*b*]indole can be a useful electron-donating building block for various applications in organic electronics or in nonlinear optics, for example.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00438.

Synthetic procedures and characterization of compounds; electrochemical, optical, thermal and charge transport data; devices fabrication and characterization; crystalline structure of **MTI-DCV** (PDF)
Crystallographic data for **MTI-DCV** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953.

(2) Moonsin, P.; Prachumrak, N.; Rattanawan, R.; Keawin, T.; Jungsuttiwong, S.; Sudyoadsuk, T.; Promarak, V. *Chem. Commun.* **2012**, *48*, 3382.

(3) Mishra, A.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2012**, *51*, 2020.

(4) Hsu, C.-Y.; Chen, Y.-C.; Lin, R. Y.-Y.; Ho, K.-C.; Lin, J. T. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14099.

(5) (a) Cabau, L.; Garcia-Benito, I.; Molina-Ontoria, A.; Montcada, N. F.; Martin, N.; Vidal-Ferran, A.; Palomares, E. *Chem. Commun.* **2015**, *51*, 13980. (b) Ameen, S.; Rub Abdul, M.; Kosa, S. A.; Alamry, K. A.; Akhtar, M. S.; Shin, H.-S.; Seo, H.-K.; Asiri, A. M.; Nazeerudin, M. K. *ChemSusChem* **2016**, *9*, 10.

(6) (a) Roncali, J. *Acc. Chem. Res.* **2009**, *42*, 1719. (b) Würthner, F.; Meerholz, K. *Chem. - Eur. J.* **2010**, *16*, 9366. (c) Li, Y.; Guo, Q.; Li, Z.; Pei, J.; Tian, W. *Energy Environ. Sci.* **2010**, *3*, 1427. (d) Walker, B.; Kim, C.; Nguyen, T.-Q. *Chem. Mater.* **2011**, *23*, 470. (e) Lin, Y.; Li, Y.; Zhan, X. *Chem. Soc. Rev.* **2012**, *41*, 4245. (f) Roncali, J.; Leriche, P.; Blanchard, P. *Adv. Mater.* **2014**, *26*, 3821. (g) Malytskyi, V.; Simon, J.-J.; Patrone, L.; Raimundo, J.-M. *RSC Adv.* **2015**, *5*, 354.

(7) (a) Yen, Y.-S.; Chou, H.-H.; Chen, Y.-C.; Hsu, C.-Y.; Lin, J. T. *J. Mater. Chem.* **2012**, *22*, 8734. (b) Liang, M.; Chen, J. *Chem. Soc. Rev.* **2013**, *42*, 3453. (c) Wu, Y.; Zhu, W. *Chem. Soc. Rev.* **2013**, *42*, 2039.

(8) Xia, P. F.; Feng, X. J.; Lu, J.; Tsang, S.-W.; Movileanu, R.; Tao, Y.; Wong, M. S. *Adv. Mater.* **2008**, *20*, 4810.

(9) (a) Chiu, S.-W.; Lin, L.-Y.; Lin, H.-W.; Chen, Y.-H.; Huang, Z.-Y.; Lin, Y.-T.; Lin, F.; Liu, Y.-H.; Wong, K.-T. *Chem. Commun.* **2012**, *48*, 1857. (b) Chen, Y.-H.; Lin, L.-Y.; Lu, C.-W.; Lin, F.; Huang, Z.-Y.; Lin, H.-W.; Wang, P.-H.; Liu, Y.-H.; Wong, K.-T.; Wen, J.; Miller, D. J.; Darling, S. B. *J. Am. Chem. Soc.* **2012**, *134*, 13616.

(10) (a) Leliège, A.; Le Régent, C. H.; Allain, M.; Blanchard, P.; Roncali, J. *Chem. Commun.* **2012**, *48*, 8907. (b) Leliège, A.; Grolleau, J.; Allain, M.; Blanchard, P.; Rousseau, T.; Demeter, D.; Roncali, J. *Chem. - Eur. J.* **2013**, *19*, 9948. (c) Jeux, V.; Demeter, D.; Leriche, P.; Roncali, J. *RSC Adv.* **2013**, *3*, 5811. (d) Diac, A.; Demeter, D.; Allain, M.; Grosu, I.; Roncali, J. *Chem. - Eur. J.* **2015**, *21*, 1598. (e) Mohamed, S.; Demeter, D.; Laffitte, J.-A.; Blanchard, P.; Roncali, J. *Sci. Rep.* **2015**, *5*, 09031.

(11) (a) Roquet, S.; Cravino, A.; Leriche, P.; Alévêque, O.; Frère, P.; Roncali, J. *J. Am. Chem. Soc.* **2006**, *128*, 3459. (b) Ripaud, E.; Rousseau, T.; Leriche, P.; Roncali, J. *Adv. Energy Mater.* **2011**, *1*, 540.

(12) Zhang, J.; Deng, D.; He, C.; He, Y.; Zhang, M.; Zhang, Z.-G.; Zhang, Z.; Li, Y. *Chem. Mater.* **2011**, *23*, 817.

(13) Min, J.; Luponosov, Y. N.; Ameri, T.; Elschner, A.; Peregudova, S. M.; Baran, D.; Heumüller, T.; Li, N.; Machui, F.; Ponomarenko, S.; Brabec, C. J. *Org. Electron.* **2013**, *14*, 219.

(14) Jiang, Y.; Cabanetos, C.; Allain, M.; Liu, P.; Roncali, J. *J. Mater. Chem. C* **2015**, *3*, 5145.

(15) (a) Bürckstümmer, H.; Kronenberg, N. M.; Gsänger, M.; Stolte, M.; Meerholz, K.; Würthner, F. *J. Mater. Chem.* **2010**, *20*, 240. (b) Bürckstümmer, H.; Tulyakova, E. V.; Deppisch, M.; Lenze, M. R.; Kronenberg, N. M.; Gsänger, M.; Stolte, M.; Meerholz, K.; Würthner, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 11628.

(16) Do, K.; Kim, C.; Song, K.; Yun, S.; Lee, J. K.; Ko, J. *Sol. Energy Mater. Sol. Cells* **2013**, *115*, 52.

(17) Montcada, N. F.; Cabau, L.; Kumar, C. V.; Cambarau, W.; Palomares, E. *Org. Electron.* **2015**, *20*, 15.

(18) (a) Cheng, M.; Yang, X.; Chen, C.; Tan, Q.; Sun, L. *J. Mater. Chem. A* **2014**, *2*, 10465. (b) Tan, Q.; Yang, X.; Cheng, M.; Wang, H.; Wang, X.; Sun, L. *J. Phys. Chem. C* **2014**, *118*, 16851.

(19) Steinmann, V.; Kronenberg, N. M.; Lenze, M. R.; Graf, S. M.; Hertel, D.; Meerholz, K.; Bürckstümmer, H.; Tulyakova, E. V.; Würthner, F. *Adv. Energy Mater.* **2011**, *1*, 888.

(20) Vybornyi, O.; Jiang, Y.; Baert, F.; Demeter, D.; Roncali, J.; Blanchard, P.; Cabanetos, C. *Dyes Pigm.* **2015**, *115*, 17.

(21) (a) Kanbe, K.; Okamura, M.; Hattori, S.; Naganawa, H.; Hamada, M.; Okami, Y.; Takeuchi, T. *Biosci., Biotechnol., Biochem.* **1993**, *57*, 632. (b) Olesen, P. H.; Hansen, J. B.; Engelstoft, M. *J. Heterocycl. Chem.* **1995**, *32*, 1641. (c) Pedras, M. S. C.; Suchy, M. *Bioorg. Med. Chem.* **2006**, *14*, 714.

(22) Kato, S.-i; Furuya, T.; Kobayashi, A.; Nitani, M.; Ie, Y.; Aso, Y.; Yoshihara, T.; Tobita, S.; Nakamura, Y. *J. Org. Chem.* **2012**, *77*, 7595.

(23) (a) Martynova, I.; Franz, A. W.; Pflumm, C.; Parham, A. H.; Buesing, A.; Anémian, R. M.; Gerhard, A., U.S. Patent 20130126792, 2013. (b) Sawada, Y.; Hotta M.; Matsumoto, M. EP2628743, 2013. (c) Ahn, H. C.; Kim, N. K.; Cho, Y. J.; Kwon, H. J.; Kim, B. O.; Kim, S. M. PCT Int. Appl. WO 2011099718 A1 20110818, 2011.

(24) Parham, A. H.; Pflumm, C.; Stoessel, P.; Buesing, A.; Joosten, D. PCT Int. Appl., WO 2011137951 A1 20111110, 2011; Ger. Offen., DE 102010019306 A1 20111110, 2011.

(25) Irgashev, R. A.; Karmatsky, A. A.; Kozyukhin, S. A.; Ivanov, V. K.; Sadovnikov, A.; Kozik, V. V.; Grinberg, V. A.; Emets, V. V.; Rusinov, G. L.; Charushin, V. N. *Synth. Met.* **2015**, *199*, 152.

(26) Mentioned in ref 18 in Ackermann, L.; Althammer, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 1627.

(27) Appukkuttan, P.; Van de Eycken, E.; Dehaen, W. *Synlett* **2005**, 127.

(28) (a) Sanz, R.; Escribano, J.; Aguado, R.; Pedrosa, M. R.; Arnáiz, F. J. *Synthesis* **2004**, *2004*, 1629. (b) Sanz, R.; Escribano, J.; Pedrosa, M. R.; Aguado, R.; Arnáiz, F. J. *Adv. Synth. Catal.* **2007**, *349*, 713.

(29) Gao, H.; Xu, Q.-L.; Yousufuddin, M.; Ess, D. H.; Kürti, L. *Angew. Chem., Int. Ed.* **2014**, *53*, 2701.