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COMMUNICATION

Facile synthesis of unsymmetrical and π -extended furan-diketopyrrolopyrrole derivatives through C-H direct (hetero)arylation using a heterogeneous catalyst system

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A mono functionalization of bis-furandiketopyrrolopyrrole (DPPFu₂) via direct (hetero)arylation has been developed. This method allows for rapid access to a new family of narrow band-gap, π -extended DPP derivatives via consecutive C-H bond activation between mono-arylated DPP and aryl bromides with heterogeneous catalysts in a simple fashion.

In the past decade, direct (hetero)arylation (DHA) methods have been widely utilized for the synthesis of solution-processable small molecule and polymer organic π -conjugated materials due to their superior atom economy, less toxic reagents, fewer synthetic steps, and cost effective approach compared to classical carbon-carbon bond coupling Stille or Suzuki reactions.¹⁻⁴ Traditionally, these carbon-hydrogen (C-H) DHA methods are catalyzed by soluble homogeneous palladium catalyst systems, which has the drawbacks of lower selectivity, sensitivity to air, need for high temperature, and high-levels of residual palladium contamination in the resultant material.⁵⁻⁶

In our group, we have recently reported on the synthesis of symmetrical small molecule-based semiconductors through a heterogeneous palladium (Pd) catalyzed DHA procedure.⁷ The benefit of this heterogeneous catalyst is that it is stable in air, works under mild conditions, is easily isolated from reaction mixtures, and results in less Pd contamination of the final product. The use of heterogeneous catalysts in the organic electronics community is still in its infancy, with only few organic semiconductors synthesized in this manner reported to date.⁷⁻⁹

Diketopyrrolopyrrole (DPP) is a well-known chromophore, extensively utilized to construct organic semiconductors for use in organic solar cells and field effect transistors.¹⁰⁻¹³ Recently, Chen and co-workers have presented the DHA cross coupling between

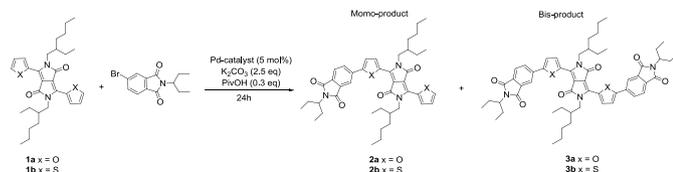
thiophene functionalized DPPs and aryl bromides under a nitrogen atmosphere in the presence of homogeneous palladium catalyst, Pd(OAc)₂ yielding various symmetrical thiophene-DPP derivatives.¹⁴ Other related practical organic materials have also been synthesized by DHA.¹⁵

In this paper we extend the scope of previous studies and synthesize a new series of π -extended DPP based materials using the heterogeneous palladium catalyst system, SiliaCat® DPP-Pd. Emphasis is placed on the mono-arylation of furan-DPPs (**1a**), which allows for the construction of a diverse range of symmetrical and unsymmetrical materials. Furan-DPPs have been used to construct high performance conjugated polymers; however, there are only a few reports investigating small molecule semiconductors based upon the furan-DPP core building block.¹⁶⁻¹⁷ Thus, we have sought to develop a simple, low-cost approach towards the synthesis of non-symmetrical push-pull DPPs; excellent for low band-gap materials, and π -extended multi-chromophoric DPPs that are suggested to improve optoelectronic device performance.^{12, 18-19}

We have chosen 3,6-(bis-furan-2-yl)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dione (**1a**) as the C-H activation partner. **1a** was prepared according to a modified literature procedure,²⁰ and 5-bromo-*N*-(2-ethylpropyl)-phthalimide as the aryl bromide moiety.⁷ Phthalimide has recently emerged as a promising end-capping unit for organic small molecule semiconductors owing to its ease of synthesis, ability to fine tune electronic energy levels, and affect materials solubility and solution processability through incorporation of pendant alkyl chains on the N-atom.²¹⁻²³ Optimization of the reaction to yield mono-substituted DPP was performed using 1.0 eq of 5-bromo-*N*-(2-ethylpropyl)-phthalimide in the presence of 2.5 eq K₂CO₃, 0.3 eq. pivalic acid

and 5 mol% of palladium catalyst in 24 h reaction time. Complete reaction optimization procedures are summarized in Table 1.

Table 1. Optimization for direct heteroarylation of DPP (**1a-1b**) with 5-bromo-*N*-(2-ethylpropyl)-phthalimide (1 eq), 24 h reaction time



Entry	Compound	Catalyst ^a	Solvent	T	2^b	3^b
1	1a	Het	DMF	85	38	26
2	1a	Het	DMF	70	41	21
3	1a	Het	DMF	55	43	20
5	1a	Het	Toluene	85	18	2
6	1a	$Pd(OAc)_2$	DMF	55	25	34
7	1b	Het	DMF	85	38	23
8	1b	Het	DMF	70	35	21
9	1b	Het	DMF	55	42	22

a) Het = SiliaCat® DPP-Pd. b) All yields are isolated.

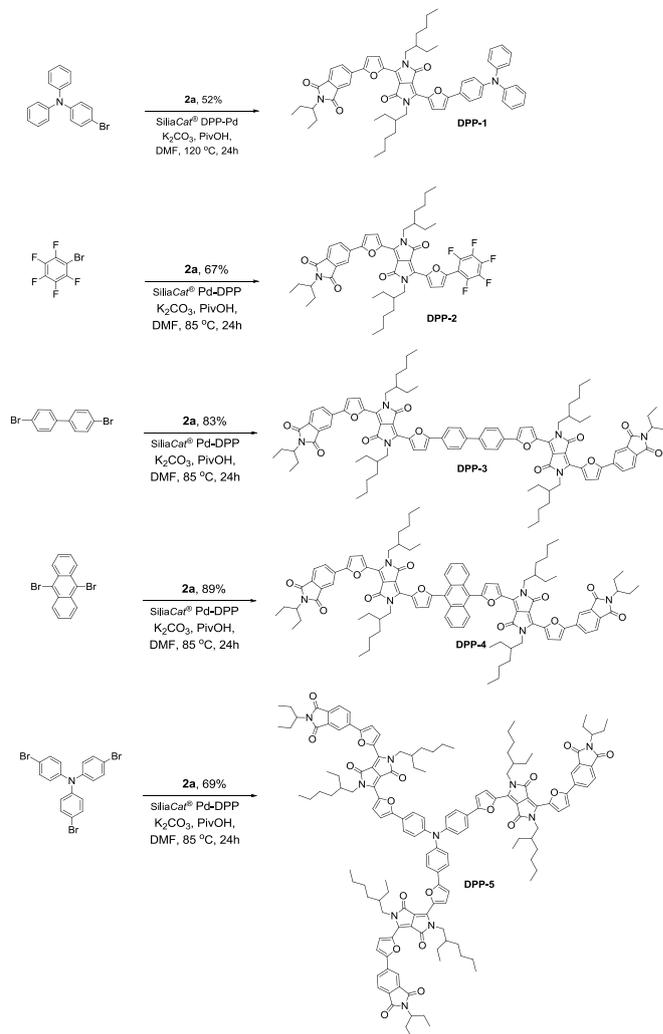
Using DMF as the reaction solvent and the heterogeneous system SiliaCat® DPP-Pd we found that reactions proceeded smoothly at temperatures as low as 55 °C to yield a respectable amount of mono-adduct **2a** (~40%, Entry 1-3 in Table 1). The reactions can be carried out in air and with benchtop solvents without reduction of product yield. As a direct comparison we also investigated the homogeneous catalyst $Pd(OAc)_2$ at 55 °C in DMF, only 25% of mono-substituted product was obtained, highlighting the potential of the SiliaCat® DPP-Pd system for the synthesis of conjugated organic materials. Use of the polar solvent DMF proved to be critical as attempts to use the non-polar solvent toluene resulted in a considerable decreased yield of mono-adduct (18%). The proton at the 2-position of furan is more acidic than that of thiophene and should be more prone to undergo C-H activation. Considering thiophene functionalized DPP (**1b**) is an extremely popular building block used to construct high performance materials, we also investigated the synthesis of thiophene based mono-adduct **2b** under the present conditions. Similar results were obtained to furan-DPP (**1a**) with approximately 40% conversion to mono-adduct **2b** at all temperatures (Entry 7-9, Table 1) highlighting the generality of the reaction procedure.

While **2a** is mono end-capped with the phthalimide moiety; the other reactive furan site can react with other electron donor or electron acceptor aryl bromides to generate new non-symmetric DPP based materials, including multi-DPP chromophores made by reacting **2a** with multi-bromo arenes. Therefore, we explored the DHA reactivity of mono-adduct **2a** with a series of aryl bromide building blocks. First we probed the reaction of **2a** with the electron rich building block 1-bromo-triphenylamine using our standard conditions at 85 °C; unfortunately only 26% of the desired product (**DPP-1**) was obtained. By increasing the reaction temperature up to 120 °C, product yield was maximized at 52%. Reaction of the electron deficient building block bromo-

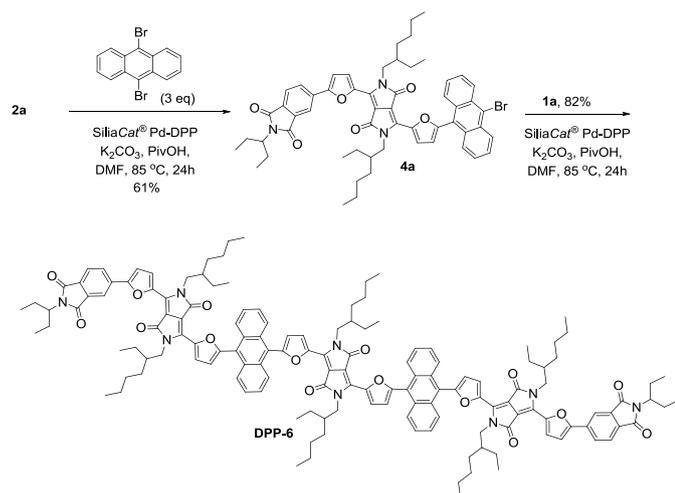
pentafluorobenzene using our standard conditions at 85 °C, **DPP-2** was obtained in 67% yield.

Next we explored the synthesis of π -extended (macro) DPP molecules **DPP-3** to **DPP-5** via the heterogeneous catalyzed DHA coupling reaction of **2a** with 4,4'-dibromobenzene (twisted core), 9,10-dibromoanthracene (planar core), and tris-tribromophenylamine (pin-wheel core). Good to excellent yields were obtained for all products as shown in scheme 1.

Scheme 1. Synthesis of π -extended DPP via direct arylation **DPP-1** to **DPP-5**



As a further extension of our synthetic method we synthesized the large DPP-based oligomer **DPP-6**. The designed **DPP-6** was made by coupling **2a** in the excess amount of 9,10-dibromoanthracene (3 eq) to obtain non-symmetric DPP **4a**. The remaining bromide on the anthracene moiety of **4a** can undergo further DHA reactivity with DPP **1a** to yield bis-adduct **DPP-6** in excellent yield as shown in Scheme 2. Thus we have shown a simple and facile method to synthesize a complicated structure, **DPP-6**, without the use of organoboron or toxic organotin directing groups, both of which require extra synthetic steps. It is important to note that reaction conditions are relatively mild and amenable to scale up, both advantageous for industrial applications of conjugated organic materials.

Scheme 2. Synthesis of π -extended DPP oligomer **DPP-6**

All materials presented are novel and thus have been fully characterized by ^1H , ^{13}C NMR, mass spectrometry, elemental analysis (see Supporting Information). Owing to the potential applications of each new compound as active materials in electronic devices, we determined the optical, electrochemical, and thermal properties of each. Figure 1 (top) shows the UV-Vis absorption profiles of the seven DPP small molecules in CHCl_3 solution. All DPP compounds exhibit strong absorption bands in the visible region of the solar spectrum. The symmetrical compound **3a** was used as a model compound for comparison. In CHCl_3 solution **3a** shows a maximum absorption at 620 nm with molar absorptivity of $69,000 \text{ M}^{-1}\text{cm}^{-1}$. The absorption peaks of **DPP-1** to **DPP-6** in solution state are 635 nm ($\epsilon = 58,700 \text{ M}^{-1}\text{cm}^{-1}$), 605 nm ($\epsilon = 84,100 \text{ M}^{-1}\text{cm}^{-1}$), 630 nm ($\epsilon = 166,000 \text{ M}^{-1}\text{cm}^{-1}$), 605 nm ($\epsilon = 107,000 \text{ M}^{-1}\text{cm}^{-1}$), 645 nm ($\epsilon = 214,000 \text{ M}^{-1}\text{cm}^{-1}$) and 600 nm ($\epsilon = 245,000 \text{ M}^{-1}\text{cm}^{-1}$), respectively. The molar absorptivities of **DPP-3** and **DPP-4** are approximately two times that of model compound **3a** due to the presence of two DPP units on the biphenyl and anthracene cores. **DPP-5** shows three times higher molar absorptivity than **DPP-1**, which is corresponding to the presence of three DPP units on the triphenylamine core. Notably, the oligomer **DPP-6** exhibit significantly higher molar absorptivity compared to those of the corresponding monomeric dyes due to the increased π -conjugation length. Model compound **3a**, **DPP-2** and biphenyl-core **DPP-3** exhibit strong fluorescent emission at 640, 624 and 652 nm, respectively, while fluorescent emission intensity of **DPP-1** and **DPP-5** is decreased owing to the intramolecular charge transfer of triphenylamine electron donor to DPP electron acceptor.²⁴ Interestingly, DPP substituted planar anthracene core **4a**, **DPP-4** and oligomer **DPP-6** show fluorescence quenching upon excitation at 600 nm.

In the solid-state, the thin film absorption maxima of **3a** and **DPP-1** to **DPP-6** shift to longer wavelengths with strong vibronic shoulder peaks (Figures S8-S14, see Supporting Information). Upon thermally annealing the film to 100°C for 5 min, small molecules **3a** and **DPP-1** exhibit dramatic hypsochromic shifts of absorption maxima. Similar observations have been made for related DPP based small molecules upon solvent vapor annealing and have been attributed to the formation of H-aggregates.²⁵ **DPP-2** shows small increases in optical density upon thermal annealing.

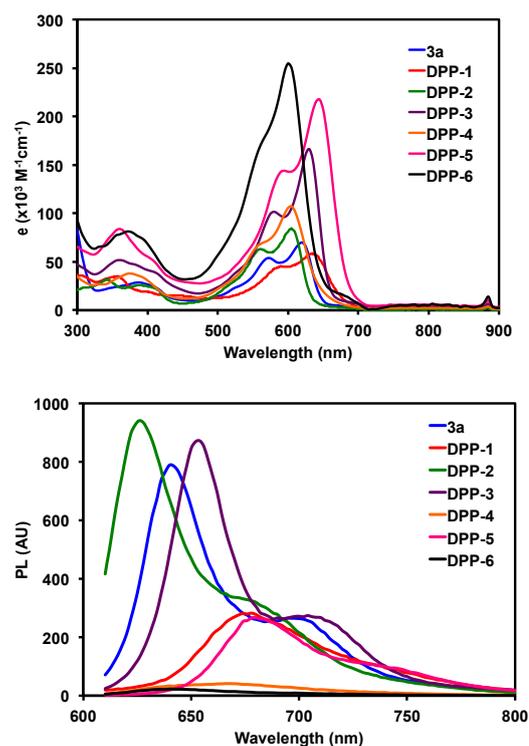
Macromolecules **DPP-3** to **DPP-6**; however, form thermally stable films and minimal changes in the absorption profiles are observed after annealing at 100°C for 5 min, this is characteristic of larger oligomers.²⁶

Table 2. Optical, electrochemical and melting point data of compound **3a** and **DPP-1** to **DPP-6**

Entry	λ_{max} (nm) ^s (ϵ)	λ_{max} (nm) ^f	Pl_{max} (nm)	IE (eV)	EA (eV)	M.P. ($^\circ\text{C}$)
3a	620 (69.7)	634	640	-5.24	-3.58	265-266
DPP-1	635 (58.7)	652	676	-4.98	-3.42	213-214
DPP-2	605 (84.1)	624	626	-5.14	-3.60	219-220
DPP-3	630 (166.0)	645	662	-5.12	-3.49	324-325
DPP-4	605 (107.0)	609	668	-5.16	-3.56	174-176
DPP-5	645 (214.0)	655	680	-4.99	-3.43	255-256
DPP-6	600 (254.3)	609	640	-5.26	-3.60	186-188

S= solution, $\epsilon = \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$, f= film, IE and EA calculated from onset oxidation and reduction potential vs $E_{(\text{Fc}/\text{Fc}^+)} = 0$

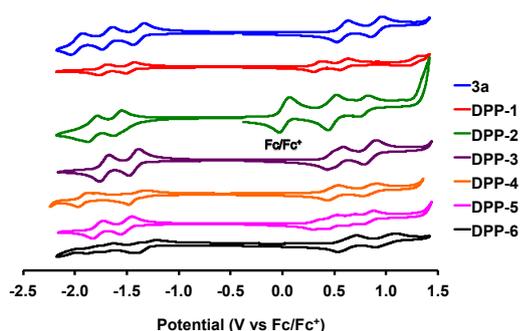
Figure 1. Top) UV-Vis absorption and below) Photoluminescence emission spectra of **3a** and **DPP-1** to **DPP-6** in ($6 \times 10^{-6} \text{ M}$ CHCl_3), excited at 600 nm.



The electronic properties of the π -extended DPPs and the model compound were studied by cyclic voltammetry as shown in Figure 2. The ionization energy and electron affinity of these DPP derivatives were calculated from the oxidation and reduction onset potential as summarized in Table 2. Model compound **3a** exhibited a HOMO level at -5.24 eV and LUMO level at -3.58 eV . Introducing electron donor, triphenylamine moiety, the energy of

HOMO level is significantly increased to -4.9 eV, while the presence of electron withdrawing, pentafluorobenzene moiety, gives a deeper LUMO level. In addition, the HOMO levels of **DPP-3** to **DPP-6** are slightly increased to -5.1 eV. LUMO levels of new DPP derivatives are ca. -3.4 to -3.5 eV with the band-gap energies around 1.6 eV. The energy levels of these new DPP are similar to related DPP compounds reported in the literature.^{15, 19} Melting points are listed in Table 2 and follow expected trends. It is interesting to point out that **DPP 1-6** all exhibit similar HOMO/LUMO energy levels and optical band gaps, but very different thermal properties owing to the dramatically different molecular shapes and sizes. Thus, this series of compounds offers an opportunity to study the impact of morphology on optoelectronic device performance without the interference of vastly different electronic properties.

Figure 2. Cyclic voltammetry plots of compound **3a** and **DPP-1** to **DPP-6** in 0.1 M TBAPF₆/CH₂Cl₂ at scan rate 100 mV/s.



In summary, we have demonstrated an atom economical and facile synthesis of mono-arylated furan DPP derivatives via direct heteroarylation reactions using a heterogeneous catalyst under mild reaction conditions. This has allowed us to prepare, in a simple fashion, non-symmetrical materials (**DPP-1** and **DPP-2**) and large multi-substituted materials (**DPP-3** to **DPP-6**) via consecutive direct heteroarylation reactions. This approach proved to be effective for the construction of a variety of simple and complex chemical structures that allow for the fine tuning of HOMO-LUMO energy levels, optical properties, and thermal behavior. Materials evaluation in electronic devices and extension of this synthetic methodology to other organic building blocks is of current interest in our research laboratory.

NOTES AND REFERENCES

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Electronic Supplementary Information (ESI) available: Complete synthetic details, NMR spectra, UV-vis spectra and CV traces.

- 1) K. Okamoto, J. Zhang, J. B. Housekeeper, S. R. Marder, C. K. Luscombe, *Macromolecules*, **2013**, *46*, 8059-8078.
- 2) L. G. Mercier, M. Leclerc, *Acc. Chem. Res.* **2013**, *46*, 1597-1605
- 3) D. J. Schipper, K. Fagnou, *Chem. Mater.* **2011**, *23*, 1594-1600

- 4) S. Fuse, K. Matsumura, A. Wakaiya, H. Masui, H. Tanaka, S. Yoshikawa, T. Takahashi *ACS Comb. Sci.* **2014**, *16*, 494-499
- 5) F. C. Krebs, R. B. Nyberg, M. Jørgensen, *Chem. Mater.* **2004**, *16*, 1313-1318
- 6) M. Parisien, D. Valette, K. Fagnou, *J. Org. Chem.* **2005**, *70*, 7578-7584
- 7) (a) S. M. McAfee, J. M. Topple, A. -J. Payne, J. -P. Sun, I. G. Hill, G. C. Welch, *ChemPhysChem* **2015**, *16*, 1190-1202 (b) S.M. McAfee, J. S. J. McCahill, C. Macaulay A. D. Hendsbee, G. C. Welch, *RSC Advances*, **2015**, *5*, 26097-26106
- 8) S. Alesi, F. D. Maria, M. Melucci, D. J. Macquarrie, R. Luque, G. Barbarella, *Green Chem.* **2008**, *10*, 517-523
- 9) S. -Y. Liu, H. -Y. Li, M. -M. Shi, H. Jiang, X. -L. Hu, W. -Q. Li, L. Fu, H. -Z. Chen, *Macromolecules* **2012**, *45*, 9004-9009
- 10) S. Qu, H. Tian, *Chem. Commun.* **2012**, *48*, 3039-3051
- 11) C. B. Nielsen, M. Turbiez, I. McCulloch, *Adv. Mater.* **2013**, *25*, 1859-1880
- 12) A. B. Tamayo, M. Tantiwiwat, B. Walker, T. -Q. Nguyen, *J. Phys. Chem. C*, **2008**, *112*, 15543-15552
- 13) A. B. Tamayo, B. Walker, T. -Q. Nguyen, *J. Phys. Chem. C*, **2008**, *112*, 11545-11551
- 14) (a) S. -Y. Liu, M. -M. Shi, J. -C. Huang, Z. -N. Jin, X. -L. Hu, J. -Y. Pan, H. -Y. Li, A. K. -Y. Jen, H. -Z. Chen, *J. Mater. Chem. A*, **2013**, *1*, 2795-2805; (b) S. -Y. Liu, W. -Q. Liu, J. -Q. Xu, C. -C. Fan, W. -F. Fu, J. Ling, J. -Y. Wu, M. -M. Shi, A. K. -Y. Jen, H. -Z. Chen, *ACS Appl. Mater. Interfaces* **2014**, *6*, 6765-6775
- 15) (a) J. Zhang, W. Chen, A. J. Rojas, E. V. Jucov, T. V. Timofeeva, T. C. Parker, S. Barlow, S. R. Marder, *J. Am. Chem. Soc.* **2013**, *135*, 16376-16379; (b) J. Kudrjasova, R. Herckens, H. Penxten, P. Adriaensens, L. Lutsen, D. Vanderzande, W. Maes, *Org. Biomol. Chem.* **2014**, *12*, 4663-4672; (c) R. Matsidik, J. Martin, S. Schmidt, J. Obermayer, F. Lombeck, F. Nübling, H. Komber, D. Fazzi, M. Sommer, *J. Org. Chem.* **2015**, *80*, 980-987
- 16) M. S. Chen, O. P. Lee, J. R. Niskala, A. T. Yiu, C. J. Tassone, K. Schmidt, P. M. Beaujuge, S. S. Onishi, M. F. Toney, A. Zettl, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2013**, *135*, 19229-19236
- 17) E. Ripaud, D. Demeter, T. Rousseau, E. Boucard-Cétol, M. Allain, R. Po, P. Leriche, J. Roncali, *Dyes Pigments*, **2012**, *95*, 126-133
- 18) W. Shin, T. Yasuda, Y. Hidaka, G. Watanabe, R. Arai, K. Nasu, T. Yamaguchi, W. Murakami, K. Makita, C. Adachi, *Adv. Energy. Mater.* **2014**, *4*, DOI: 10.1002/aenm.201400879
- 19) J. Liu, Y. Sun, P. Moonsin, M. Kuik, C. M. Proctor, J. Lin, B. B. Hsu, V. Promarak, A. J. Heeger, T. -Q. Nguyen, *Adv. Mater.* **2013**, *25*, 5898-5903
- 20) P. Sonar, S. P. Singh, E. L. Williams, Y. Li, M. S. Soha, A. Dodabalapur, *J. Mater. Chem.* **2012**, *22*, 4425-4435
- 21) J. -P. Sun, A. D. Hendsbee, A. F. Eftaiha, C. Macaulay, L. R. Rutledge, G. C. Welch, I. G. Hill, *J. Mater. Chem. C* **2014**, *2*, 2612-2621
- 22) A. D. Hendsbee, J. -P. Sun, L. R. Rutledge, I. G. Hill, G. C. Welch, *J. Mater. Chem. A*, **2014**, *2*, 4198-4207
- 23) J. T. Bloking, X. Han, A. T. Higgs, J. P. Kastrop, L. Pandey, J. E. Norton, C. Risko, C. E. Chen, J. -L. Brédas, M. D. McGehee, A. Sellinger, *Chem. Mater.* **2011**, *23*, 5484-5490
- 24) S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère, J. Roncali, *J. Am. Chem. Soc.* **2006**, *128*, 3459-3466
- 25) (a) A. Viterisi, F. G. Guirado, J. W. Ryan, E. Palomares, *J. Mater. Chem.*, **2012**, *22*, 15175-15182 (b) K. Sun, Z. Xiao, E. Hanssen, M. F. Klein, H. H. Dam, M. Pfaff, D. Gerthsen, W. W. H. Wong, D. J. Jones, *J. Mater. Chem. A* **2014**, *2*, 9048
- 26) X. Liu, B. B. Y. Hsu, Y. Sun, C. -K. Mai, A. J. Heeger, G. C. Bazan, *J. Am. Chem. Soc.* **2014**, *136*, 16144-16147