Alternative Thieno[3,2-*b*][1]benzothiophene Isoindigo Polymers for Solar Cell Applications

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Abstract

We report the synthesis, characterization, photophysical and photovoltaic properties of five new TBTI containing low band gap donor-acceptor conjugated polymers with a series of comonomers and different side chains. When TBTI is combined with different electron-rich moieties even small structural variations can have significant impact on thin film morphology of the polymer:PCBM blends. More importantly, we used high-resolution electron energy loss spectroscopy (EELS) technique to investigate the phase separated bulk heterojunction domains, which could be accurately and precisely resolved, enabling an enhanced correlation between polymer chemical structure, photovoltaic device performance and morphology.

1. Introduction

Organic photovoltaics (OPVs) have seen a rapid increase in performance in recent years with efficiencies over 13 % being reported.¹ This resurgence in efficiency has been lead primarily through new molecular design and efficient morphological control of both donor and acceptor.²⁻¹¹ The importance of morphology for high efficiency organic photovoltaics has been highlighted many times,¹¹ an optimised interpenetrating network of the two components is needed for efficient exciton dissociation. As a result, two main strategies to control the size of the domains of each material have emerged: processing optimisation and chemical design. The former involves utilization of processing additives, thermal, solvent vapour treatments and interlayer modification,^{2,8,10} while the latter includes solubilizing group optimisation (linear or branched side chains) and polymer core modification.⁶

Isoindigo has been gaining particular interest in organic optoelectronics applications due to its simple synthesis, electron-withdrawing capability, and strong optical absorption. The easy molecular modification nature of isoindigo, through the introduction of side-groups and the interchanging of different electron-rich and electron deficient sub-units, resulted in great scientific interest over the last few years.¹²⁻²¹ Previously the π -conjugated, rigid and planar aromatic structure of isoindigo has been utilised as building blocks for high mobility polymers for OFETs.^{12,13,15,17,18} In parallel, significant progress has been achieved in OPV devices utilising donor polymers based on the isoindigo core.^{19,20,21} Recently we reported an isoindigo polymers containing an eight-rings fused new isoindigo core thieno[3,2-*b*][1]benzothiophene isoindigo (TBTI), which was solubilized with branched a 2-decyltetradecyl chain and copolymerized with thiophene. These novel low bandgap polymers allow morphological control of the bulk heterojunction through variation of molecular weight, resulting in a photovoltaic efficiency of 9.1% without the usage of any additive.¹⁴

Since the energy levels, bulk morphology and device performance were largely controlled by the alternating electron donating and electron accepting units. Therefore, regarding the

choice of the repeat unit based on TBTI framework, different electron donating comonomer units were introduced. A small optical band gap (E_g) is typically achieved in isoindigo polymers by either increased planarization along the polymer backbone or by the inclusion of electron rich units such as thiophene or preferably with selenium derivative or the more electron rich pyrrole. Difluorination of the electron rich component of the backbone however is expected to lower the lowest unoccupied molecular orbital (LUMO) whereas the highest occupied molecular orbital (HOMO) will experience a lower electron density, but increased delocalisation due to improved planarization. The vinyl bithiophene structure can lead to a more planar backbone and enhance effective conjugated length to facilitate the intramolecular and intermolecular charge transport. When the electron deficient vinylene nitrile group is attached onto the rigid vinylene backbone, the strong electron deficient effect significantly lowers both the HOMO and LUMO energy levels of the polymers to increase the V_{oc} of the solar cells.²² The nature of the side chains has an important role in the solid-state packing, aggregation and solubility of the polymers. Even the distance of branching point of the side chains to the polymer backbone can influence charge transport and OPV performance of the polymers.^{6,23,24,25,26} The variations of comonomer and size/shape of side chains affects polymer crystallinity, as well as affinity with PCBM, therefore influencing both polymer-PCBM interactions and domain sizes, which influences the photovoltaic parameters of the device. Traditional techniques such atomic force microscopy (AFM) which is sensitive just to surface interactions and roughness, or conventional transmission electron microscopy (TEM) strongly dependent on sample thickness and density variation, cannot characterize the domain structure unambiguously.

Herein, we report on five novel thieno-benzothiophene isoindigo (TBTI) donor-acceptor (D-A) polymers with different electron donating monomers of varying oxidation potential. We report how the choice of the electron rich unit influences the optical properties, molecular

energy levels and solar cell performance. Importantly, the impact of the chemical backbone modifications on the morphology of the blend has been studied using a method of scanning transmission electron microscopy (STEM) combined with high resolution electron energy loss spectroscopy (EELS).^{27,28} Using this method, the domains could be accurately and precisely resolved, enabling an enhanced correlation between polymer chemical structure, photovoltaic device performance and acquired morphology.

2. Results and Discussion

2.1 Synthesis and Characterisation

The molecular structures and synthetic route of the polymers are depicted in Scheme 1 and the Supporting Information. The synthesis of the **TBTI** monomer follows our previously reported methodology.¹⁴ Polymers **TBTISe**, **TBTIFT**, **TBTIP**, with selenophene, difluorothiophene and pyrrole as the repeat units respectively, containing branched 2-decyltetradecyl chains, have been synthesized via microwave assisted Stille polymerization in chlorobenzene, in the presence of $\text{Pd}_2(\text{dba})_3$ and $\text{P}(o\text{-Tol})_3$ as the catalyst system. In addition, a longer branched 3-octadecylheneicosyl alkyl chain was introduced to the **TBTI** to guarantee sufficient solubility of the resulting polymers, when the extended coplanar structure of the vinyl bithiophene and vinylene nitrile bithiophene were incorporated into the polymer backbone. Microwave-assisted Stille polymerization using 1,1'-[(1*E*)-1,2-ethenediyl]di-5,2-thiophenediyl]bis[1,1,1-trimethylstannane and (E)-2,3-Bis(5-(trimethylstannyl)thiophen-2-yl)acrylonitrile gave polymer **TBTITT** and **TBTITT-CN** respectively. The number average molecular weights (M_n) of the polymers were evaluated by gel permeation chromatography (GPC) in chlorobenzene at 80 °C (Figure S1, S2, S3, S4, and S5). All the polymers exhibited relatively high M_n other than **TBTIP** (Table 1), M_n and PDI are 51.5 kDa and 3.49 for **TBTISe**, 132.6 kDa and 3.0 for **TBTIFT**, 7.69 kDa and 1.89 for **TBTIP**, 152.0 kDa and 3.48 for **TBTITT**, and 291.6 kDa and

2.49 for **TBTITT-CN**. **TBTIP** has very good solubility in chloroform, chlorobenzene (CB), and dichlorobenzene (*o*-DCB) attributed to its low molecular weight. The other polymers have a reasonable solubility in warm CB and *o*-DCB. Thermogravimetric analysis (TGA) demonstrated that all polymers exhibited good thermal stability with a 5% weight-loss decomposition temperature of 445 °C for **TBTiSe**, 410°C for **TBTiTF**, 420 °C for **TBTITT**, 420 °C for **TBTITT-CN** and 405 °C for **TBTIP** (Figure S6 and S7).

Scheme 1: Polymer structures and energy levels of thieno[3,2-b][1]benzothiophene isoindigo polymers **TBTiSe**, **TBTiTF**, **TBTIP**, **TBTITT**, **TBTITT-CN** and **PC₇₀BM**.

Table 1. Molecular weights and optical properties and frontier molecular orbital energy levels of the polymers.

polymer	Mn ^a	Mw ^a	PDI ^a	E _g ^b	IP ^c	EA ^d	T _d ^e	λ _{max(soln)} ^f	λ _{max(film)} ^g
	[kDa]	[kDa]		[eV]	[eV]	[eV]	[°C]	[nm]	[nm]
TBTiSe	51.5	179.7	3.49	1.48	5.15	3.67	445	670	665
TBTiTF	132.6	397	3.00	1.59	5.39	3.80	410	642	640

TBTIP	7.7	14.6	1.89	1.52	5.10	3.58	405	627	626
TBTITT	152.0	529.1	3.48	1.57	5.18	3.61	420	671	662
TBTITT-CN	291.6	724.8	2.49	1.58	5.34	3.76	420	660	655

a) Mn, Mw, and PDI (Mw/Mn) determined by GPC using low-D (<1.10) polystyrene standards and chlorobenzene as the eluent at 80 °C; b) Estimated from the onset of UV-vis absorption spectrum ($E_g = 1240/\lambda_{onset}$); c) Measured by PESA; d) Estimated by the addition of E_g to IP ($EA = IP - E_g$). e) 5% weight loss temperature measured by thermal gravimetric analysis (TGA) under a nitrogen atmosphere. f) Measured in dilute chlorobenzene solution. g) The thin films spin-cast on glass substrate from chlorobenzene solution.

2.2 Optical Properties

The optical absorption spectra of the polymers in dilute chlorobenzene solution and as thin films spin-cast from chlorobenzene solution are shown in Figure 1 and the data is also summarised in Table 1. All the polymers exhibit typical dual absorption bands (band I : 300-500 nm and band II : 500-800 nm) both in solution and thin films. Band I ranging from 300 to 500 nm could be ascribed to the absorption of the different donor part. Absorption bands II in the low energy region was attributed to the typical charge transfer from the electron donating repeating units to the electron deficient **TBTI**. In solution, the **TBTISe** polymer exhibits the longest wavelength absorption maxima of 670 nm and **TBTIP** shows the shortest absorption maxima of 627 nm. Upon film formation, no obvious spectral shift was observed for **all** polymers compared to those in dilute solution with the absorption maxima peaks are slightly blue-shifted by 1-9 nm, suggesting some pre-aggregates in solution due to **the** strong intermolecular interactions of the large fused and rigid conjugated systems. Compared with the high Mn of **TBTIT**,¹⁴ **TBTISe** exhibits very similar thin film absorption spectra with high Mn

TBTIT, showing an absorption maximum at 665 nm along with an obvious shoulder peak, and **TBTITF** shows 25 nm blue shifted absorption spectra, as a result of the electron-withdrawing fluorine atoms on the conjugated polymer backbone. The absorption spectra of **TBTIP** is also blue shifted with maximum absorption at 626 nm due to the weak donor ability of the pyrrole groups than that of the thiophene and selenophene. In contrast with thin film of **TBTITT**, which shows absorption peak at 662 nm, the maxima of **TBTITT-CN** is blue shifted 7 nm to 655 nm due to the electron withdrawing nitrile groups in the polymer backbone. The asymmetry of the long wavelength absorption peaks has been attributed to coupling of vibrational modes with the electronic absorption bands. This is typically as a result of intermolecular aggregation, and thus the shoulders are a sensitive measure of short lengthscale interactions. **TBTITF** exhibits a pronounced absorption shoulder, suggesting that short non-covalent S-F intramolecular planarization interactions help facilitate intermolecular aggregation, whereas the rigid, planar vinyl bithiophene unit also promotes intermolecular interactions. On the other hand, the pyrrole unit seems to inhibit intermolecular interactions, and has a relatively symmetric absorption profile.

Figure 1: Normalized UV-vis absorption spectra of the polymers in dilute chlorobenzene solutions at room temperature (a) and thin films spin-cast from chlorobenzene solution (b).

The ionization potentials (IP) of polymer thin films spin cast from chlorobenzene solution were measured using photoelectron spectroscopy in air (PESA), to be 5.15 eV for **TBTiSe**, 5.39 eV for **TBTiFT**, 5.10 eV for **TBTiP**, 5.18 eV for **TBTiTt**, and 5.34 eV for **TBTiTt-CN**. The optical band gaps of **TBTiSe**, **TBTiTf**, **TBTiP**, **TBTiTt**, and **TBTiTt-CN** estimated from the thin films absorption onsets are 1.48 eV, 1.59 eV, 1.52 eV, 1.57 eV, and 1.58 eV, respectively. Interestingly, the **TBTiSe** exhibits slightly lower E_g lying 1.48 eV while the rest of the polymers show values in the range of 1.52-1.58 eV. The larger band gaps of **TBTiTf** than that of **TBTiTt** is consistent with the trend that fluorination on donor units reduce the HOMO energy level (increase the IP) more, resulting in larger band gap.¹⁸ The electron affinity (EA) estimated from the optical band gap to corresponding IP were found 3.67 eV for **TBTiSe**, 3.80 eV for **TBTiFT**, 3.58 eV for **TBTiP**, 3.61 eV for **TBTiTt**, and 3.76 eV for **TBTiTt-CN** (Table 1). Polymers that have alternating electron rich and electron poor conjugated repeat units typically have low band gaps where the HOMO energy levels resemble to HOMO of the electron rich unit, while the LUMO resembles the electron poor unit. The higher IP and EA of both the **TBTiFT** and **TBTiTt-CN** than the other four polymers can be ascribed to the strong electron withdrawing ability of the fluoro and nitrile units on the polymer backbone.

2.3 Morphological Characterisation

In an effort to correlate chemical structure with device performance and surface morphology, films were measured with: atomic force microscopy (AFM), scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). Polymer: PC₇₀BM blends were coated on top of ZnO/ITO/glass substrates at the optimum ratio and conditions used in solar cell fabrication. AFM images were obtained in tapping mode. STEM and EELS were performed on polymer: PC₇₀BM blends. The films were first coated on top of a water soluble sacrificial layer and then placed on top of lacey carbon films with 300 mesh. AFM images (Figures 2a, 2d, 2g, 2k, 2n) show that root mean square (RMS) surface roughness values for

blends of PC₇₀BM with polymers **TBTiSe**, **TBTiFT**, **TBTiTt**, and **TBTiTt-CN** was around 1.65 nm. On the other hand, **TBTiP** exhibited an RMS of around 2.7 nm. In STEM image of **TBTiP** (Figure 2h) the extensive contrast variation is distinctly observed. This, in principle, can be attributed to phase separation and isolated domains, explaining the low current density contribution in the device EQE. In figures 2b, 2e, 2h 2l and 2o some contrast variation is also observed however it cannot be reliably correlated to the domains structure since it is influenced by other factors such as films thickness or density fluctuation. To analyse phase separation systematically we combined STEM with simultaneous high-resolution EELS applied to low energy region. In low energy loss region pristine polymers and PC₇₀BM have unique EEL spectral features (or distinct signatures). In the range from 1 to 5 eV, those features result from so called inter-band transitions and have the same physical origin (related to the zone structure) as those in the UV-vis absorption spectra of polymers (Figure 1) and PC₇₀BM (Figure S8). Tracing polymer vs PC₇₀BM spectral signatures in spatially resolved EELS data from the composite films allows to obtain individual components maps. The component maps can be colorized (red for PC₇₀BM and green for polymers) and then overlaid to form a single composite image. To resolve the individual spectral features reliably, the high-resolution EELS mapping was performed with strongly monochromated electron beam achieved by method first implemented by Hillenbrand et al.²⁹ and described in details by Lopatin et al.³⁰ Thus, the phase separation (polymer vs PC₇₀BM) can be accurately mapped (Figures 2c, 2f, 2j, 2m and 2p). This is shown most strikingly in Figure 2j. The phase structure of the **TBTiP** obtained from EELS measurements is consistent with that from STEM measurements (Figure 2h), however compositional mapping shows a PC₇₀BM phase surrounded by a **TBTiP** matrix. Phase segregation of this nature has previously been suggested to be from a liquid-liquid phase segregation which occurs during the drying of the films and is detrimental to device performance.³¹ It is noted here that various solvent mixtures were tested but no significant

differences were observed. The variations between the morphologies of the samples of **TBTITF**, **TBTITT-CN**, **TBTiSe**, and **TBTITT** are smaller and less pronounced (Figure 2c, 2f, 2m, and 2p). However, it is shown that of those blends: **TBTITT-CN** has the largest PC₇₀BM aggregations (Figure 2p) and **TBTITT** (Figure 2m) has a larger amount of individual domains with a more homogeneous size distribution. **TBTiSe** and **TBTITF** (Figure 2c and 2f respectively) have similar PC₇₀BM domain sizes, with **TBTITF** having a broader distribution in sizes.

Figure 2: AFM topology (a, d, g, k, n), STEM (b, e, h, l, o) and composite EELS images (c, f, j, m, p) of **TBTiSe**, **TBTiTF**, **TBTiP**, **TBTiTT** and **TBTiTT-CN**. Green and red domains represent polymer and PC₇₀BM respectively. Scale bar is 500 nm.

2.4 Photovoltaic performance

Photovoltaic devices were fabricated with an architecture of ITO/ZnO/polymer:PC₇₀BM/MoO_x/Ag and an optimised donor: acceptor weight ratio of 1:1.5 (w/w) in chlorobenzene. Current density vs applied voltage (J/V) characteristics and photovoltaic performance parameters were obtained under air mass of 1.5 Global (AM1.5G) and irradiation of 100mW/cm² (Figure 3a and Table 2). Polymers **TBTITF**, **TBTITT** and **TBTITT-CN** show similar photogenerated current density values with selenophene based polymer (**TBTISe**) yielding the highest value of 11.6 mA/cm². One reason for this may be due to the higher degree of polarization and stronger intermolecular interactions caused by the Se atom.³² Despite the high photocurrent for **TBTISe**, champion power conversion efficiency was achieved with the bi-fluorinated-thiophene derivative, **TBTITF**, due to a higher V_{oc} of 0.91V. Moderate efficiencies of 5.1% and 5.0 % were obtained with **TBTITT-CN** and **TBTISe** respectively. Device performance seems to be unaffected by the incorporation of processing additives: 1,8-diiodoctane and 1-chloro-naphthalene and/or thermal annealing both post and pre-evaporation. External quantum efficiency measurements (Figure 3b) show the onsets of the photocurrent for **TBTISe** and **TBTITT-CN** are 800 nm +/-40 nm. For **TBTITF** the onset is slightly blue shifted, as expected from the wider E_g. In the case of **TBTIP** the polymer doesn't seem to contribute in the current generation (Figure 3b) as shown from the EQE. The lack of efficient polymer network that would allow charge carrier transportation and extraction could be the main reason, a statement clearly supported by TEM data. Metal-Insulator-Semiconductor charge extraction by linearly increasing voltage (MIS-CELIV) was employed in order to evaluate hole mobility at optimum active layer conditions and values are summarized at Table 2 and Figure S9. Blends of polymer:PC₇₀BM at optimum ratios and conditions were sandwiched between a thermally evaporated insulating layer MgF₂ (70nm) and MoO_x/Ag (6/100 nm). Charge carrier mobility value for each system was extracted from the following equation:

$$\mu = \frac{2d_s^2}{At_{tr}^2} \left(1 + \frac{\varepsilon_s d_i}{\varepsilon_i d_s}\right)$$

Where ε and d are the dielectric constant and film thickness respectively of the insulator and semiconductor.

Figure 3: a) J-V characteristics and b) EQE performance characteristics of BHJ photovoltaic devices containing **TBTiSe**, **TBTiTF**, **TBTiP**, **TBTiTT** and **TBTiTT-CN** as the donor.

Table 2: Photovoltaic performance of BHJ photovoltaic devices utilising thieno[3,2-b]benzothiophene isoindigo polymers.

Polymer	J_{sc} (mA/ cm ²)	V_{oc} (V)	FF	PCE (%)	μ_h (cm ² /Vs)
TBTiSe	11.6	0.69	0.61	5.0	7.4×10^{-5}
TBTiTF	9.9	0.91	0.62	5.6	7.9×10^{-5}
TBTiP	6.0	0.67	0.43	2.0	-
TBTiTT	9.4	0.61	0.70	4.0	4.1×10^{-4}
TBTiTT-CN	9.4	0.80	0.68	5.1	1.1×10^{-3}

It is observed that the V_{oc} of the photovoltaic devices follows the same trend as the IPs - that the larger the IP value, the higher the V_{oc} . The poor photovoltaic performance of **TBTiP** can be attributed to the unfavourable morphology as shown by the composite EELs image in Figure 2j. This undesirable segregation will result in a poor extraction of charges from the BHJ

layer under illumination and can account for the poor photovoltaic performance (Table 2). All other isoindigo polymers display fill factors of 0.61-0.70 and short circuit currents of 9.4-11.6 mA/cm². This can be correlated to the high degree of mixing observed in the EELs images in Figure 2, whereby all the blend films displayed mixed BHJ structure. It is noted that the highest fill factor obtained was with the **TBTITT** polymer. The **TBTITT** showed the largest number of domains, with a homogeneously distributed smaller domain size; suggesting this morphology is preferable to achieve high fill factors, a statement also supported by MIS-CELIV data.

3. Conclusions

A series of five different thieno-benzothiophene isoindigo D/A polymers for use in photovoltaic applications were designed and synthesised. These polymers as thin films show absorption in the 300-800 nm region with IPs ranging 5.06-5.39eV. When fabricated in photovoltaic devices, a highest device efficiency of 5.6 % was obtained for **TBTITF**. The combination of STEM and high-resolution EELS imaging technique was implemented, to identify and accurately map the individual domains of polymer and PCBM – which was not possible using stand along AFM or STEM techniques. This combination of STEM and EELS mapping was used to correlate device performance to morphology; showing the lowest performing blend of **TBTIP**: PCBM formed a **TBTIP** microstructure comprising large isolated domains of **PCBM**. All other polymers displayed similar morphologies, reflected by their similar device performance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

Appendix/Nomenclature/Abbreviations

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[1]. W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, *J. Am. Chem. Soc.* **2017**, *139*, 7148.

[2]. J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma, H. Yan, *Nat. Energy* **2016**, *1*, 15027.

[3]. C. Duan, R. E. M. Willems, J. J. van Franeker, B. J. Bruijnaers, M. M. Wienk, R. A. J. Janssen, *J. Mater. Chem. A* **2016**, *4*, 1855.

[4]. C. Duan, K. Gao, J. J. van Franeker, F. Liu, M. M. Wienk, R. A. J. Janssen, *J. Am. Chem. Soc.* **2016**, *138*, 10782.

[5]. C. Duan, K. Gao, F. J. M. Colberts, F. Liu, S. C. J. Meskers, M. M. Wienk, R. A. J. Janssen, *Adv. Energy Mater.* **2017**, *7*, 1700519.

- [6]. I. Meager, R. S. Ashraf, S. Mollinger, B. C. Schroeder, H. Bronstein, D. Beatrup, M. S. Vezie, T. Kirchartz, A. Salleo, J. Nelson, I. McCulloch, *J. Am. Chem. Soc.* **2013**, *135*, 11537.
- [7]. J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang, *Nature Commun.* **2013**, *4*, 1446.
- [8]. A. R. b. M. Yusoff, D. Kim, H. P. Kim, F. K. Shneider, W. J. d. Silva, J. Jang, *Energy Environ. Sci.* **2015**, *8*, 303.
- [9]. Y. Huang, E. J. Kramer, A. J. Heeger, G. C. Bazan, *Chem. Rev.* **2014**, *114*, 7006.
- [10]. J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan, A. J. Heeger. *J. Am. Chem. Soc.* **2008**, *130*, 3619.
- [11]. N. Gasparini, X. Jiao, T. Heumueller, D. Baran, G. J. Matt, S. Fladischer, E. Spiecker, H. Ade, C. J. Brabec, T. Ameri, *Nature Energy* **2016**, *1*, 16118.
- [12]. I. Meager, M. Nikolka, B. C. Schroeder, C. B. Nielsen, M. Planells, H. Bronstein, J. W. Rumer, D. I. James, R. S. Ashraf, A. Sadhanala, P. Hayoz, J.-C. Flores, H. Sirringhaus, I. McCulloch, *Adv. Funct. Mater.* **2014**, *24*, 7109.
- [13]. R. S. Ashraf, A. J. Kronemeijer, D. James, H. Sirringhaus, I. McCulloch, *Chem. Commun.* **2012**, *48*, 3939.
- [14]. W. Yue, R. S. Ashraf, C. B. Nielsen, E. Collado-Fregoso, M. R. Niazi, S. A. Yousaf, M. Kirkus, H-Y Chen, A. Amassian, J. R. Durrant, I. McCulloch, *Adv. Mater.* **2015**, *27*, 4702.
- [15]. W. Yue, M. Nikolka, M. Xiao, A. Sadhanala, C. B. Nielsen, A. J. P. White, H-Y. Chen, A. Onwubiko, H. Sirringhaus, I. McCulloch. *J. Mater. Chem. C.* **2016**, *4*, 9704.
- [16]. W. Yue, C. Li, X. Tian, W. Li, M. Neophytou, H. Chen, W. Du, C. Jellett, H-Y. Chen, A. Onwubiko, I. McCulloch, *J. Poly. Sci. Part A: Polym. Chem.* **2017**, *55*, 2691.

- [17]. T. Lei, J.-H. Dou, X.-Y. Cao, J.-Y. Wang, J. Pei, *J. Am. Chem. Soc.* **2013**, *135*, 12168.
- [18]. Y. Gao, Y. Deng, H. Tian, J. Zhang, D. Yan, F. Wang, *Adv. Mater.* **2017**, *29*, 1606217.
- [19]. J. Mei, K. R. Graham, R. Stalder, J. R. Reynolds, *Org. Lett.* **2010**, *12*, 660.
- [20]. E. Wang, W. Mammo, M. R. Andersson, *Adv. Mater.* **2014**, *26*, 1801.
- [21]. Y. Deng, W. Li, L. Liu, H. Tian, Z. Xie, Y. Geng, F. Wang, *Energy Environ. Sci.* **2015**, *8*, 585.
- [22]. H.-J. Yun, S.-J. Kang, Y. Xu, S. O. Kim, Y.-H. Kim, Y.-Y. Noh, S.-K. Kwon, *Adv. Mater.* **2014**, *26*, 7300.
- [23]. L. Fang, Y. Zhou, Y.-X. Yao, Y. Diao, W.-Y. Lee, A. L. Appleton, R. Allen, J. Reinspach, S. C. B. Mannsfeld, Z. Bao, *Chem. Mater.* **2013**, *25*, 4874.
- [24]. I. Kang, H.-J. Yun, D. S. Chung, S.-K. Kwon, Y.-H. Kim, *J. Am. Chem. Soc.* **2013**, *135*, 14896.
- [25]. Y. Zhou, T. Kurosawa, W. Ma, Y. Guo, L. Fang, K. Vandewal, Y. Diao, C. Wang, Q. Yan, J. Reinspach, J. Mei, A. L. Appleton, G. I. Koleilat, Y. Gao, S. C. B. Mannsfeld, A. Salleo, H. Ade, D. Zhao, Z. Bao, *Adv. Mater.* **2014**, *26*, 3767.
- [26]. J. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney, Z. Bao, *J. Am. Chem. Soc.* **2011**, *133*, 20130.
- [27]. Y. Firdaus, L. P. Maffei, F. Cruciani, M. A. Müller, S. Liu, S. Lopatin, N. Wehbe, G. O. N. Ndjawa, A. Amassian, F. Laquai, P. M. Beaujuge, *Adv. Energy Mater.* **2017**, 1700834.
- [28]. R.-Z. Liang, M. Babics, A. Seitkhan, K. Wang, P. B. Geraghty, S. Lopatin, F. Cruciani, Y. Firdaus, M. Caporuscio, D. J. Jones, P. M. Beaujuge, *Adv. Funct. Mater.* **2017**, 1705464.

[29]. A. A Govyadinov, A. Konečná, A. Chuvilin, S. Vélez, I. Dolado, A. Y Nikitin, S. Lopatin, F. Casanova, L. E Hueso, J. Aizpurua, R. Hillenbrand, *Nature Commun.* **2017**, 8, 95.

[30]. S. Lopatin, B. Cheng, W-T. Liu, M.-L. Tsai, J-H. He, A. Chuvilin, *Ultramicroscopy*, **2018**, 184, Part A, 109.

[31]. J. J. van Franeker, M. Turbiez, W. Li, M. M. Wienk, R. A. J. Janssen, *Nat. Commun*, **2015**, 6229.

[32]. R. S. Ashraf, I. Meager, M. Nikolka, M. Kirkus, M. Planells, B. C. Schroeder, S. Holliday, M. Hurhangee, C. B. Nielsen, H. Sirringhaus, and I. McCulloch, *J. Am. Chem. Soc.* **2015**, 137, 1314.

The table of contents entry should be 50–60 words long, and the first phrase should be bold.

The entry should be written in the present tense and third person. The text should be different from the abstract text.

Five alternative thieno-benzothiophene isoindigo D-A polymers have been designed, synthesized and characterized, their photo physical and photovoltaic properties have been investigated. A novel composite EELS imaging technique was used to determine the domains between polymers and PCBM, enabling an enhanced correlation between polymer chemical structure, photovoltaic device performance and acquired morphology.

M. Neophytou, D. Bryant, S. Lopatin, H. Chen, R. K. Hallani, L. Cater, I. McCulloch, W.

Yue*

Alternative Thieno[3,2-*b*][1]benzothiophene Isoindigo Polymers for Solar Cell Application