Insights into the Influence of Fluorination Positions on Polymer Donor Materials on Photovoltaic Performance

Xue Gong,^a Guangwu Li,^a Jianya Chen,^b Shiyu Feng,^a Danyang Ma,^c Ran Hou,^a
Cuihong Li,^{*a} Wei Ma,^b Zhishan Bo^{*a}

^a Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China

^{**}(C.L.) Email: licuihong@bnu.edu.cn. (Z.B.) Email: zsbo@bnu.edu.cn.

^b State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

^c State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Abstract

To explore the influence of fluoro substitution position and number on optical, electrochemical and photovoltaic properties, three novel donor-acceptor (D-A) alternative copolymers (**PHF**, **PFH** and **PFF**) were synthesized by Stille polycondensation of 2,3-diphenyl-5,8-di(thiophen-2-yl)quinoxaline (DTQx) acceptor unit and indacenodithiophene (IDT) donor unit. As films, **PHF** and **PFF** comprising two fluoro substituents on the lateral phenyl groups displayed a broad absorption ranging from 350 to 700 nm; whereas **PFH** containing two fluorine atoms on the polymer main chain exhibited a slightly narrower absorption ranging from 350 to 650 nm. In addition, fluoro substitution on the polymer main chain can lower the HOMO level of the resulted polymers. As expected, **PFH** and **PFF** possess deeper HOMO energy level than **PHF**. Polymer solar cells (PSCs) were fabricated with these three polymers as donor materials and PC₇₁BM as acceptor material. **PHF** based PSCs gave a power conversion efficiency (PCE) of 7.2% with a V_{oc} of 0.84 V, a J_{sc} of 12.46 mA/cm² and an FF of 0.69. And **PFH** based PSCs showed a PCE of 6.19% with a V_{oc} of 0.93 V, a J_{sc} of 9.57 mA/cm² and an FF 0.70. However, a PCE of only 2.9% with a V_{oc} of 0.92 V, a J_{sc} of 4.61 mA/cm² and an FF of 0.68 was obtained for **PFF** based PSCs. Transmission electron microscopy (TEM) and resonant soft X-ray scattering (R-SoXS) studies indicated that the introduction of four fluorine atoms at each repeating unit can spoil the morphology of active layer. These results highlight the importance of fluorination position and number to the performance of PSCs.

Keywords:

Polymer solar cells, fluorination position and number, morphology

Introduction

Polymer solar cells (PSCs) with a bulk heterojunction (BHJ) structure by blending a *p*-type donor material and an *n*-type acceptor material as the active layer have attracted particular attention in the past decades.¹⁻⁴ Power conversion efficiency (PCE) of single junction BHJ PSCs has reached 11%.⁵⁻⁷ Different strategies including device engineering (thermal annealing, solvent annealing, adding additives etc.)^{8, 9} and developing new donor and acceptor materials have been used to improve the photovoltaic performance.¹⁰⁻¹⁸ Tremendous effort was put forward to developing new donor materials to achieve high efficiency PSCs.¹⁹⁻²³ The absorption, energy level and charge mobility of polymers and even the morphology of blend films can be modulated by polymer structure engineering.²⁴⁻²⁹ The design of polymers with a donor (D)-acceptor (A) alternating structure is an effective way to broaden their absorption.³⁰⁻³³ The introduction of fluorine atoms onto either donor unit or acceptor unit of the polymers can enhance the crystallization of polymers and decrease their energy levels,³⁴⁻³⁹ due to its strong electron-withdrawing nature and the ability of forming noncovalent bond between fluorine and hydrogen or sulfur atom (F...H or F...S). However, the change of surface energy caused by fluorine substitution may spoil the blend film morphology and lead to serious phase separation.^{33, 40-42} Therefore, it is highly demanded to investigate the effect of fluorination on the energy level, charge mobility, film morphology and device performance.

Although the introduction of fluorine atoms on the D or A unit has been widely used in the synthesis of conjugated donor materials, the systematic investigation of the influence of fluoro substitution position and number on the optical, electrochemical and photovoltaic properties of conjugated polymers was seldom reported.⁴³ Here we designed and synthesized a series of fluorinated D-A alternating conjugated polymers (**PHF**, **PFH** and **PFF**) to explore their structure property relationship. The chemical structures of these polymers are shown in Chart 1. **PHF** contains two fluoro substituents on the two lateral phenyl groups; **PFH** comprises two fluoro substituents on the polymer main chain; and **PFF** contains two fluoro substituents on the lateral

phenyl groups and two fluoro atoms on the polymer backbone. The influence of fluoro substitution (number and position) on the energy level, charge mobility, morphology and photovoltaic performance was systematically investigated. **PFF** based PSCs displayed a PCE of 6.19% with a V_{oc} of 0.93 V, a J_{sc} of 9.57 mA/cm² and an FF of 0.70; **PHF** based PSCs displayed a PCE of 7.2% with a V_{oc} of 0.84 V, a J_{sc} of 12.46 mA/cm² and an FF of 0.69; and **PFF** based PSCs only afforded a PCE of 2.9% with a V_{oc} of 0.92 V, a J_{sc} of 4.61 mA/cm² and an FF of 0.68. Morphology investigations revealed that **PFF**:PC₇₁BM blend films formed large aggregates due to the introduction of four fluorine atoms at each repeating unit, which decreased the surface energy of polymers.

Chart 1. Chemical structures of **PFF**, **PHF** and **PFH**

Results and discussion

Material Synthesis and Characterization

Scheme 1. Synthetic routes of **M1**, **M2** and **PFF**, **PHF** and **PFH**.

thermal stability with the 5% decomposition temperature up to 448 °C for **PHF** and **PFH**, 440 °C for **PFF** and the data are summarized in Table 1.

Table 1. Molecular Weights and Thermal Properties of Copolymers

Polymer	T _d (°C)	M _n (Kg/mol)	M _w (Kg/mol)	PDI
PHF	448	52.7	137.7	2.61
PFH	448	54.9	87.4	1.59
PFF	440	63.2	139.8	2.21

Optical and electrochemical properties

To investigate the optical properties of these copolymers, the ultraviolet-visible (UV) absorption spectra were measured. As shown in Figure 1, in dilute solutions these polymers displayed a broad absorption ranging from 400-700 nm with two distinct peaks located at 457 and 603 nm for **PHF**, 442 and 589 nm for **PFH**, and 452 and 607 nm for **PFF**. For all polymers, the side chains, which perpendicular to the polymer main chain (Figure S2), could effectively prevent the polymer main chains from forming close packing in the solid state. Therefore, these polymers exhibited a good solubility in most commonly used organic solvents as mentioned before. The unique structure of these polymers could well elucidate that there is almost no red-shift for absorption spectra of **PHF** and **PFH** in going from solution to film. As for **PFF**, there is only an 11 nm red-shift in going from solution to film, indicating it may form closer packing than those two polymers. These results demonstrated that these polymers probably form amorphous films. The optical band gaps ($E_{g,opt}$) of **PHF**, **PFH** and **PFF** were calculated to be 1.74, 1.82 and 1.74 eV, respectively, by equation of $E_{g,opt} = 1240/\lambda_{edge}$. The optical band gap is related to the electron withdrawing ability of acceptor unit and the electron donating ability of donor unit. Due to the strong electron withdrawing ability, the introduction of fluorine atom on different positions of the acceptor unit has different influence on the electron withdrawing ability of acceptor unit. The introduction of fluorine atom on the meta position of lateral phenyl group may have more significant influence to the electron withdrawing ability of acceptor unit than that on the polymer main chain.⁴⁴⁻⁴⁸

Figure 1. a) UV-visible absorption spectra of **PHF** (**PFH** or **PFF**) in dilute DCB solutions at room temperature; b) UV-visible absorption spectra of **PHF** (**PFH** or **PFF**) as film; c) Cyclic voltammograms of **PHF** (**PFH** or **PFF**) as film on the platinum electrode in 0.1 M Bu₄NPF₆ acetonitrile solution at a scan rate of 50 mV/s.

Cyclic voltammograms of **PHF** (**PFH** or **PFF**) as film was measured on the platinum electrode in a standard three-electrode electrochemical cell. As shown in Figure 1c, the onset oxidation potentials of **PHF**, **PFH** and **PFF** were determined to be 0.65, 0.72 and 0.72 V, respectively. According to the equation: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.71)$ eV, the HOMO energy levels of **PHF**, **PFH** and **PFF** were calculated to be -5.36, -5.43 and -5.43 eV, respectively. It can be seen that fluoro substitution at the lateral phenyl groups of DTQx has little effect on the onset oxidation potential of polymers; whereas, the introduction of fluorine atoms onto the polymer backbone could markedly lower the HOMO energy levels of polymers **PFH** and **PFF**. LUMO energy levels of polymers were calculated by equation: $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g,opt}}$ to be -3.62, -3.61 and -3.69 eV for **PHF**, **PFH** and **PFF**, respectively. The results are listed in Table 2.

Table 2. Optical and electrochemical properties of **PFF** (**PFH** or **PFF**)

Polymer	$\lambda_{\max}$ (nm) ^a	$\lambda_{\max}$ (nm) ^b	λ_{edge} (nm) ^b	$E_{g, \text{opt}}$ (eV) ^c	HOMO (eV)	LUMO (eV) ^d
PHF	457,603	455,603	714	1.74	-5.36	-3.62
PFH	442,589	442,589	680	1.82	-5.43	-3.61
PFF	452,607	450,618	714	1.74	-5.43	-3.69

^a In solutions at room temperature; ^b As films; ^c Calculated from the absorption band edge of copolymer films, $E_{g, \text{opt}} = 1240/\lambda_{\text{edge}}$; ^d Calculated by the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g, \text{opt}}$

Photovoltaic properties

To evaluate the photovoltaic properties of polymer **PHF** (**PFH** or **PFF**), devices with a structure of ITO/PEDOT:PSS/Polymer:PC₇₁BM/LiF/Al were fabricated. The optimized devices were fabricated in a polymer:PC₇₁BM weight ratio of 1:4 in a solvent mixture of DCB and 1-chloronaphthalene (98:2, by volume). The best PCE of 7.2% was achieved with a V_{oc} of 0.84 V, a J_{sc} of 12.46 mA/cm² and an FF of 0.69 for **PHF** based solar cells. For **PFH** and **PFF** based solar cells, higher V_{oc} can be expected due to their deeper HOMO energy levels since the V_{oc} is related with the difference between HOMO energy level of donor materials and LUMO energy level of acceptor materials. A PCE of 6.19% with a high V_{oc} of 0.93 V, a J_{sc} of 9.57 mA/cm² and an FF of 0.70 was obtained for **PFH** based solar cells. Compared with **PHF**, narrower absorption of **PFH** might result in decreased J_{sc} . A very low PCE of 2.90% with a V_{oc} of 0.92 V, a low J_{sc} of 4.61 mA/cm² and an FF of 0.68 for **PFF** based solar cells was acquired under the optimized conditions. Both the hole mobility and morphology of **PFF** based blend layer could illuminate its low photovoltaic performance. The data are summarized in Table 3 and the related J - V curves of devices fabricated under optimized conditions are shown in Figure 2a. The EQE curves of optimized devices are shown in Figure 2b. The J_{sc} values obtained from J - V measurements are close to the current densities calculated by the integration of EQE curves, which verified the accuracy of the J - V measurement.

Table 3. Optical performance of **PHF** (**PFH** or **PFF**) based solar cells under optimized conditions.

Polymer	PCE (Average) (%)	J_{sc} [mA/cm ²]	V_{oc} [V]	FF	Hole	Thickness (nm)
					Mobility	
					SCLC	
					(cm ² V ⁻¹ s ⁻¹)	
PHF	7.20 (6.95)	12.46	0.84	0.69	3.5×10^{-5}	215
PFH	6.19 (5.96)	9.57	0.93	0.70	1.2×10^{-5}	98
PFF	2.90 (2.79)	4.61	0.92	0.68	1.1×10^{-6}	105

Figure 2. a) J - V and b) EQE curves of **PHF** (**PFH** or **PFF**) based solar cells under optimized conditions.

Hole mobilities of **PHF** (**PFH** or **PFF**) based devices were determined by SCLC method with a device structure of ITO/PEDOT:PSS/Polymer:PC₇₁BM/Au to provide insight into charge mobility performance of polymers. The active layer thicknesses of devices and the results are listed in Table 3. Hole mobilities of 3.5×10^{-5} , 1.2×10^{-5} , and 1.1×10^{-6} cm² V⁻¹ s⁻¹ were obtained for **PHF**:PC₇₁BM, **PFH**:PC₇₁BM and **PFF**:PC₇₁BM blend films, respectively. It is reasonable that **PHF** and **PFH** gave high hole mobility as well as high photovoltaic performance. The low hole mobility of **PFF**:PC₇₁BM based devices is probably originated from its poor morphology (vide infra) and increased effect of bimolecular recombination.³³

Morphology

To profoundly reveal what caused the photovoltaic performance difference of these

three polymers, the nanoscale phase separation of the blend films was investigated by Resonant soft X-ray scattering (R-SoXS). A photon energy of 284.2 eV is selected to provide highly enhanced contrast between components. As shown in Figure 3, the blend films based on **PHF**:PC₇₁BM and **PFH**:PC₇₁BM exhibited adjacent peaks located at $q \approx 0.069 \text{ nm}^{-1}$ and $q \approx 0.064 \text{ nm}^{-1}$, corresponding to characteristic phase separation length scale of about 91 nm and 98 nm by the calculated mold of $2\pi/q$, respectively. As for **PFF**:PC₇₁BM based blend films, two noteworthy peaks located at $q \approx 0.024 \text{ nm}^{-1}$ and $q \approx 0.044 \text{ nm}^{-1}$ were observed, indicating that two phase regions existed in the blend film with very large phase separation scale of about 260 and 140 nm, respectively. The formation of large phase separation, which is not beneficial for charge separation, is consistent with the low PCE and J_{sc} for **PFF** based solar cells.

Figure 3. R-SoXS profiles in log scale for **PHF** (**PFH** or **PFF**)based active layers spin-coated under optimized conditions

The morphology of polymer:PC₇₁BM blend films was also investigated by transmission electron microscopy (TEM) and the TEM images are shown in Figure 4. The **PHF**:PC₇₁BM and **PFH**:PC₇₁BM exhibited a homogenous morphology without large scale phase separation; whereas for the **PFF**:PC₇₁BM blend films, spherical domains in a diameter of about 200 nm were observed. It is worthy to note that TEM and R-SoXS results are fully consistent. Since the introduction of fluorine atoms onto polymers can decrease the surface energy of the resulted polymers and change the intermolecular interactions between polymers and PC₇₁BM, therefore it is reasonable that fluoro substitution on the polymers can alter the morphology of blend films.

Usually, fluorinated polymers showed a very low energy surface.

Figure 4. TEM images of a) **PHF**, b) **PFH** and c) **PFF** based blend layers. The scale bar is 200 nm.

Conclusion

Three novel D-A alternating fluorinated polymers **PHF**, **PFH** and **PFF** were synthesized by Stille reaction of 2,3-diphenyl-5,8-di(thiophen-2-yl)quinoxaline (DTQx) based dibromo monomers (**M1**, **M2** and **M3**) and indacenodithiophene (IDT) based bis(trimethylstannyl) monomer (**M4**). The number and position of fluorine atoms on the polymers have a significant influence on the optical, electrochemical and photovoltaic properties of polymers. As films, all these polymers exhibited a broad absorption ranging from 350 to 750 nm. **PFH** and **PFF** with the fluoro substitution on the polymer main chain showed deeper HOMO and LUMO energy level than **PHF** with the fluoro substitution only at the side chain. **PHF** based devices achieved a high PCE of 7.2% with a V_{oc} of 0.84 V, a J_{sc} of 12.46 mA/cm² and an FF of 0.69, and **PFH** based devices afforded a PCE of 6.19% with a high V_{oc} of 0.93 V, J_{sc} of 9.57 mA/cm² and FF of 0.70. However, **PFF** based devices only gave a PCE of 2.9% with V_{oc} of 0.92 V, a low J_{sc} of 4.61 mA/cm² and an FF of 0.68. The introduction of four fluorine atoms at each repeat unit could markedly influence the morphology of polymer:PC₇₁BM blend films and resulted in large spherical domains.

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References

- 1 S. Gunes, H. Neugebauer and N. S. Sariciftci, Conjugated polymer-based organic solar cells. *Chem. Rev.*, 2007, **107**, 1324-1338.
- 2 Y. Cheng, S. Yang and C. Hsu, Synthesis of Conjugated Polymers for Organic Solar Cell Applications. *Chem. Rev.*, 2009, **109**, 5868-5923.
- 3 Y. Huang, E. J. Kramer, A. J. Heeger and G. C. Bazan, Bulk Heterojunction Solar Cells: Morphology and Performance Relationships. *Chem. Rev.*, 2014, **114**, 7006-7043.
- 4 J. Roncali, Molecular Bulk Heterojunctions: An Emerging Approach to Organic Solar Cells. *Acc. Chem. Res.*, 2009, **42**, 1719-1730.
- 5 J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma and H. Yan, Efficient organic solar cells processed from hydrocarbon solvents. *Nature Energy*, 2016, **1**, 15027.
- 6 L. Nian, K. Gao, F. Liu, Y. Kan, X. Jiang, L. Liu, Z. Xie, X. Peng, T. P. Russell and Y. Ma, 11% Efficient Ternary Organic Solar Cells with High Composition Tolerance via Integrated Near-IR Sensitization and Interface Engineering. *Adv. Mater.*, 2016, **28**, 8184-8190.
- 7 Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell and Y. Cao, Single-junction polymer solar cells with high efficiency and photovoltage. *Nat. Photonics*, 2015, **9**, 174-179.
- 8 Q. Mei, C. H. Li, X. Gong, H. Lu, E. Jin, C. Du, Z. Lu, L. Jiang, X. Meng, C. Wang and Z. Bo, Enhancing the Performance of Polymer Photovoltaic Cells by

- Using an Alcohol Soluble Fullerene Derivative as the Interfacial Layer. *Acs App. Mater. Interfaces*, 2013, **5**, 8076-8080.
- 9 H. Ma, H. Yip, F. Huang and A. K. Y. Jen, Interface Engineering for Organic Electronics. *Adv. Funct. Mater.*, 2010, **20**, 1371-1388.
 - 10 H. Zhang, L. Ye and J. Hou, Molecular design strategies for voltage modulation in highly efficient polymer solar cells. *Polym. Int.*, 2015, **64**, 957-962.
 - 11 M. Zhang, X. Guo, W. Ma, S. Zhang, L. Huo, H. Ade and J. Hou, An Easy and Effective Method to Modulate Molecular Energy Level of the Polymer Based on Benzodithiophene for the Application in Polymer Solar Cells. *Adv. Mater.*, 2014, **26**, 2089-2095.
 - 12 N. Wang, Z. Chen, W. Wei and Z. Jiang, Fluorinated Benzothiadiazole-Based Conjugated Polymers for High-Performance Polymer Solar Cells without Any Processing Additives or Post-treatments. *J. Am. Chem. Soc.*, 2013, **135**, 17060-17068.
 - 13 H. Wei, Y. Chao, C. Kang, C. Li, H. Lu, X. Gong, H. Dong, W. Hu, C. Hsu and Z. Bo, High-Efficiency Large-Bandgap Material for Polymer Solar Cells. *Macromol. Rapid Commun.*, 2015, **36**, 84-89.
 - 14 C. Cui, W. Wong and Y. Li, Improvement of open-circuit voltage and photovoltaic properties of 2D-conjugated polymers by alkylthio substitution. *Energy & Environ. Sci.*, 2014, **7**, 2276-2284.
 - 15 C. Cui, Z. He, Y. Wu, Cheng, H. Wu, Y. Li, Y. Cao and W. Wong, High-performance polymer solar cells based on a 2D-conjugated polymer with an alkylthio side-chain. *Energy & Environ. Sci.*, 2016, **9**, 885-891.
 - 16 Z. Lu, C. Li, C. Du, X. Gong and Z. Bo, 6,7-dialkoxy-2,3-diphenylquinoxaline based conjugated polymers for solar cells with high open-circuit voltage. *Chin. J. Polym. Sci.*, 2013, **31**, 901-911.
 - 17 H. Wei, H. Lu, T. Fang and Z. Bo, Evaluating the photovoltaic properties of two conjugated polymers synthesized by Suzuki polycondensation and direct C-H activation. *Sci. China-Chem.*, 2015, **58**, 286-293.

- 18 Y. Chen, S. Zhang, Y. Wu and J. Hou, Molecular Design and Morphology Control Towards Efficient Polymer Solar Cells Processed using Non-aromatic and Non-chlorinated Solvents. *Adv. Mater.*, 2014, **26**, 2744-2749.
- 19 L. Bian, E. Zhu, J. Tang, W. Tang and F. Zhang, Recent progress in the design of narrow bandgap conjugated polymers for high-efficiency organic solar cells. *Prog. Polym. Sci.*, 2012, **37**, 1292-1331.
- 20 J. Hou, N. Ye, S. Liao, Y. Li, Y. Cheng and S. Chen, Review on the Recent Progress in Low Band Gap Conjugated Polymers for Bulk Hetero-junction Polymer Solar Cells. *J. Chin. Chem. Soc.*, 2014, **61**, 115-126.
- 21 M. Zhang, X. Guo, S. Zhang and J. Hou, Synergistic Effect of Fluorination on Molecular Energy Level Modulation in Highly Efficient Photovoltaic Polymers. *Adv. Mater.*, 2014, **26**, 1118-1123.
- 22 H. Yao; L. Ye; H. Zhang; S. Li; S. Zhang; J. Hou, Molecular Design of Benzodithiophene-Based Organic Photovoltaic Materials. *Chem. Rev.* 2016, **116**, 7397-7457.
- 23 H. Yao; J. Hou, Design and Application of Highly Efficient Polymers for Polymer Solar Cells. *Acta Polymerica Sinica* 2016, 1468-1481.
- 24 X. Zhan, Z. a. Tan, B. Domercq, Z. An, X. Zhang, S. Barlow, Y. Li, D. Zhu, B. Kippelen and S. R. Marder, A high-mobility electron-transport polymer with broad absorption and its use in field-effect transistors and all-polymer solar cells. *J. Am. Chem. Soc.*, 2007, **129**, 7246-7247.
- 25 J. W. Jo, J. W. Jung, E. H. Jung, H. Ahn, T. J. Shin and W. H. Jo, Fluorination on both D and A units in D-A type conjugated copolymers based on difluorobithiophene and benzothiadiazole for highly efficient polymer solar cells. *Energy & Environ. Sci.*, 2015, **8**, 2427-2434.
- 26 D. Lee, E. Hubijar, G. J. D. Kalaw and J. P. Ferraris, Enhanced and Tunable Open-Circuit Voltage using Dialkylthio Benzo 1,2-b:4,5-b ' dithiophene in Polymer Solar Cells. *Chem. Mater.*, 2012, **24**, 2534-2540.
- 27 G. Li, C. Kang, X. Gong, J. Zhang, C. Li, Y. Chen, H. Dong, W. Hu, F. Li and Z. Bo, 5-Alkyloxy-6-fluorobenzo[c][1,2,5]thiadiazole- and Silafluorene-Based

- D–A Alternating Conjugated Polymers: Synthesis and Application in Polymer Photovoltaic Cells. *Macromolecules*, 2014, **47**, 4645-4652.
- 28 W. Li, W. S. C. Roelofs, M. M. Wienk and R. A. J. Janssen, Enhancing the Photocurrent in Diketopyrrolopyrrole-Based Polymer Solar Cells via Energy Level Control. *J. Am. Chem. Soc.*, 2012, **134**, 13787-13795.
- 29 Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells. *Nat. Commun.*, 2014, **5**.
- 30 H. A. M. van Mullekom, J. Vekemans, E. E. Havinga and E. W. Meijer, Developments in the chemistry and band gap engineering of donor-acceptor substituted conjugated polymers. *Mater. Sci. Engin. R-Rep.*, 2001, **32**, 1-40.
- 31 E. Bundgaard and F. C. Krebs, Low band gap polymers for organic photovoltaics. *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 954-985.
- 32 C. Duan, F. Huang and Y. Cao, Recent development of push-pull conjugated polymers for bulk-heterojunction photovoltaics: rational design and fine tailoring of molecular structures. *J. Mater. Chem.*, 2012, **22**, 10416-10434.
- 33 Y. Li, Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption. *Acc. Chem. Res.*, 2012, **45**, 723-733.
- 34 S. C. Price, A. C. Stuart, L. Yang, H. Zhou and W. You, Fluorine Substituted Conjugated Polymer of Medium Band Gap Yields 7% Efficiency in Polymer-Fullerene Solar Cells. *J. Am. Chem. Soc.*, 2011, **133**, 4625-4631.
- 35 A. C. Stuart, J. R. Tumbleston, H. Zhou, W. Li, S. Liu, H. Ade and W. You, Fluorine Substituents Reduce Charge Recombination and Drive Structure and Morphology Development in Polymer Solar Cells. *J. Am. Chem. Soc.*, 2013, **135**, 1806-1815.
- 36 H. J. Son, W. Wang, T. Xu, Y. Liang, Y. Wu, G. Li and L. Yu, Synthesis of Fluorinated Polythienothiophene-co-benzodithiophenes and Effect of Fluorination on the Photovoltaic Properties. *J. Am. Chem. Soc.*, 2011, **133**, 1885-1894.

- 37 K. Wang, B. Guo, Z. Xu, X. Guo, M. Zhang and Y. Li, Solution-Processable Organic Molecule for High-Performance Organic Solar Cells with Low Acceptor Content. *Acs App. Mater. Interfaces*, 2015, **7**, 24686-24693.
- 38 C. Huang, J. Chang, S. Huang, K. Wu, J. Jheng, W. Chuang, C. Hsu and C. Wang, Polymorphisms and morphological studies of a difluorobenzothiadiazole conjugated copolymer with 7.8% polymer solar cell efficiency. *J. Mater. Chem. A*, 2015, **3**, 3968-3974.
- 39 Y. Zheng, Z. Wang, J. Dou, S. Zhang, X. Luo, Z. Yao, J. Wang and J. Pei, Effect of Halogenation in Isoindigo-Based Polymers on the Phase Separation and Molecular Orientation of Bulk Heterojunction Solar Cells. *Macromolecules*, 2015, **48**, 5570-5577.
- 40 D. Patwardhan, H. Zimmer and J. Mark, Synthesis of some fluorinated phenylmethylsiloxane polymers and characterization of their surface properties. *J. Inorg. Organomet. Polym. Mater.*, 1997, **7**, 93-109.
- 41 K. Kawashima; T. Fukuhara; Y. Suda; Y. Suzuki; T. Koganezawa; H. Yoshida; H. Ohkita; I. Osaka; K. Takimiya, Implication of Fluorine Atom on Electronic Properties, Ordering Structures, and Photovoltaic Performance in Naphthobisthiadiazole Based Semiconducting Polymers. *J. Am. Chem. Soc.* **2016**, *138*, 10265-10275.
- 42 B. C. Schroeder; Z. Huang; R. S. Ashraf; J. Smith; P. D'Angelo; S. E. Watkins; T. D. Anthopoulos; J. R. Durrant; I. McCulloch, Silaindacenodithiophene-Based Low Band Gap Polymers - The Effect of Fluorine Substitution on Device Performances and Film Morphologies. *Adv. Funct. Mater.* **2012**, *22*, 1663-1670.
- 43 D. Liu, W. Zhao, S. Zhang, L. Ye, Z. Zheng, Y. Cui, Y. Chen and J. Hou, Highly Efficient Photovoltaic Polymers Based on Benzodithiophene and Quinoxaline with Deeper HOMO Levels. *Macromolecules*, 2015, **48**, 5172-5178.

- 44 J. W. Jo, J. H. Kim, J. W. Jung, Isoindigo-based fluorinated low band gap polymers for environmentally stable field effect transistor. *Dyes and Pigments* **2016**, *133*, 333-338.
- 45 H. Yao, Y. Cui, R. Yu, B. Gao, H. Zhang, J. Hou, Design, Synthesis, and Photovoltaic Characterization of a Small Molecular Acceptor with an Ultra-Narrow Band Gap. *Angew. Chem.* **2017**, DOI: 10.1002/ange.201610944.
- 46 S. Dai, F. Zhao, Q. Zhang, T.-K. Lau, T. Li, K. Liu, Q. Ling, C. Wang, X. Lu, W. You, X. Zhan, Fused Nonacyclic Electron Acceptors for Efficient Polymer Solar Cells. *J. Am. Chem. Soc.* **2017**, *139*, 1336-1343.
- 47 Zhang, Y.; Zou, J.; Cheuh, C.-C.; Yip, H.-L.; Jen, A. K. Y., Significant Improved Performance of Photovoltaic Cells Made from a Partially Fluorinated Cyclopentadithiophene/Benzothiadiazole Conjugated Polymer. *Macromolecules* **2012**, *45*, 5427-5435.
- 48 Wang, Z.; Xu, X.; Li, Z.; Feng, K.; Li, K.; Li, Y.; Peng, Q., Solution-Processed Organic Solar Cells with 9.8% Efficiency Based on a New Small Molecule Containing a 2D Fluorinated Benzodithiophene Central Unit. *Adv. Electron. Mater.* **2016**, 2.1600061.

Graphic abstract:

Three novel donor-acceptor (D-A) alternative copolymers **PHF**, **PFH** and **PFF** were synthesized and applied for polymer solar cells (PSCs) to explore the influence of fluoro substitution position and number on optical, electrochemical and photovoltaic properties. **PHF**, **PFH** and **PFF** based PSCs gave power conversion efficiencies of 7.2% , 6.19% and 2.9% , respectively. TEM and R-SoXS studies indicated that the introduction of four fluorine atoms at each repeating unit can spoil the morphology of active layer.

Keywords:

Polymer solar cells, fluorination position and number, morphology