**Electronic Supplementary Information** 

# Systematic Control of Heteroatoms in Donor-Acceptor Copolymers and Its Effects on Molecular Conformation and Photovoltaic Performance

Sebastian Wood, Ji-Hoon Kim, Jessica Wade, Jong Baek Park, Do-Hoon Hwang, \* Ji-Seon Kim\*

Department of Physics and Centre for Plastic Electronics, Imperial College London, London, SW7 2AZ, United Kingdom

Department of Chemistry, and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea

### 1. Material Synthesis and Analysis

2,5-Bis(trimethylstannyl)thiophene was purchased from Aldrich. All organic starting materials were purchased from Aldrich, Alfa Aesar, or TCI Korea and were used without further purification. Tetrakis(triphenylphosphine)palladium(0) was purchased from Strem. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled under a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, Kieselgel 60 63-200 MYM SC). 4,7-Dibromo-5,6-bis(octyloxy)-2,1,3-benzothiadiazole (BT),<sup>[1]</sup> 4,7-dibromo-5,6-bis(octyloxy)-2,1,3-benzoselenadiazole (BSe),<sup>[2]</sup> and 2,5-bis(trimethylstannyl)selenophene (Se),<sup>[3]</sup> were synthesised according to methods described in previous reports.



Figure S1. Synthetic routes and chemical structures of polymers.

All polymers were synthesised by Stille polymerisation as shown in Figure S1. The bis(arylstannyl)s and bis(arylbromide)s monomers were synthesised as described previously. The reaction mixture of the tetrakis(triphenylphosphine)palladium in a mixed solvent containing 5 mL of anhydrous toluene and 1 mL of anhydrous DMF was stirred at 120 °C with N<sub>2</sub> for 16h, and then the excess amount of 2-bromothiophene and tripropyl(thiophen-2-yl)stannane, the end-capper, dissolved in 1 mL of anhydrous toluene was added and the reaction was continued for 12 h. After completion of polymerisation, the reaction mixture was cooled to approximately 50 °C and 200 mL of methanol was added slowly with vigorous stirring of the reaction mixture. The precipitated polymers were collected by filtration. They were re-dissolved in chloroform solvent and re-precipitated in methanol and one more time in acetone. The polymers were then purified further by washing for 2 days in a Soxhlet apparatus, with acetone used to remove oligomers and catalyst residues. The re-precipitation procedure in chloroform/methanol was then repeated several times. The resulting polymers were soluble in common organic solvents.

#### Poly{5,6-bis(octyloxy)-4-(thiophen-2-yl)benzo[c]-1,2,5-thiadiazole} (PSBS)

2,5-Bis(trimethylstannyl)thiophene (200 mg, 0.04 mmol) was mixed with 4,7-dibromo-5,6bis(octyloxy)-2,1,3-benzothiadiazole (BT) (268 mg, 1.0 equiv), tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6  $\mu$ mol) and toluene (5 mL) and DMF (1 mL) for this polymerisation. The polymer yield was 68%. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.808.58 (m, 2H), 4.45-4.12 (m, 4H), 2.25-1.98 (m, 4H), 1.72-1.18 (m, 20H), 0.98-0.85 (m, 6H). Element Anal. Found : C, 66.06; H, 7.68; N, 5.93; S, 13.57.

#### Poly{5,6-bis(octyloxy)-4-(thiophen-2-yl)benzo[c]-1,2,5-selenadiazole} (PSBSe)

2,5-Bis(trimethylstannyl)thiophene (200 mg, 0.04 mmol) was mixed with 4,7-dibromo-5,6bis(octyloxy)-2,1,3-benzoselenadiazole (BSe) (291 mg, 1.0 equiv), tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6  $\mu$ mol) and toluene (5 mL) and DMF (1 mL) for this polymerisation. The polymer yield was 59%. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.86-8.61 (m, 2H), 4.52-4.23 (m, 4H), 2.38-2.05 (m, 4H), 1.81-1.25 (m, 20H), 0.97-0.88 (m, 6H). Element Anal. Found : C, 60.10; H, 6.98; N, 5.39; S, 6.17.

### Poly{5,6-bis(octyloxy)-4-(selenophen-2-yl) benzo[c]-1,2,5-thiadiazole} (PSeBS)

2,5-Bis(trimethylstannyl)selenophene (200 mg, 0.04 mmol) was mixed with 4,7-dibromo-5,6bis(octyloxy)-2,1,3-benzothiadiazole (BT) (241 mg, 1.0 equiv), tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6  $\mu$ mol) and toluene (5 mL) and DMF (1 mL) for this polymerisation. The polymer yield was 49%. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.90-8.71 (m, 2H), 4.43-4.16 (m, 4H), 2.31-1.92 (m, 4H), 1.69-1.20 (m, 20H), 1.01-0.85 (m, 6H). Element Anal. Found : C, 60.10; H, 6.98; N, 5.39; S, 6.17.

#### Poly{5,6-bis(octyloxy)-4-(selenophen-2-yl) benzo[c]-1,2,5-selenadiazole} (PSeBSe)

2,5-Bis(trimethylstannyl)selenophene (200 mg, 0.04 mmol) was mixed with 4,7-dibromo-5,6bis(octyloxy)-2,1,3-benzoselenadiazole (BSe) (261 mg, 1.0 equiv), tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6  $\mu$ mol) and toluene (5 mL) and DMF (1 mL) for this polymerisation. The polymer yield was 28%. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, ppm):  $\delta$  9.05-8.81 (m, 2H), 4.50-4.15 (m, 4H), 2.38-1.95 (m, 4H), 1.71-1.22 (m, 20H), 0.97-0.88 (m, 6H). Element Anal. Found : C, 55.12; H, 6.41; N, 4.95.

#### **Gel Permeation Chromatography (GPC)**

The relatively low molecular weights attained by this synthesis arise from poor solubility, and in particular, the lower solubility of the selenium-containing polymers results in the four materials having different molecular weights – in particular, PSeBSe has a lower value. The chromatograms are shown below:

**PSBS** 



Figure S2. GPC data for PSBS.

### **PSBSe**

90%

1.5039e5

g/mol



Figure S3. GPC data for PSBSe.





Figure S4. GPC data for PSeBS.

#### **PSeBSe**



Figure S5. GPC data for PSeBSe.

### Cyclic Voltammetry (CV)

HOMO energy levels were measured from the oxidation onsets measured by cyclic voltammetry as described in the manuscript. The measured data are given in Figure S6.



**Figure S6.** Cyclic voltammograms measured for PSBS, PSBSe, PSeBS, and PSeBSe. Note the arbitrary current scale with offsets between curves for clarity.

LUMO energy levels were calculated as the sum of the optical energy gap (measured from the optical absorption onset) and the HOMO energy level (measured with CV) – see Table 1 in the manuscript.

## 2. Density Functional Theory Calculations



### Geometry Optimisation and Molecular Orbitals

**Figure S7.** Geometry optimised segments of the copolymer backbone showing HOMO and LUMO distributions (isovalue is 0.02 in all cases; green and red are the positive and negative isosurfaces).



**Figure S8.** Mulliken population analysis showing charges on each atom for the different copolymers (atomic units), based on the DFT geometry optimisation.

#### Vibrational Raman Activity Analysis



Figure S9. Comparison of simulated Raman spectrum with experimental measurement showing a

good match for the four main modes.

### 3. Resonant Raman Spectroscopy



Figure S10. Resonant Raman spectra for the four copolymers comparing Raman spectra for thin films measured under different excitation wavelengths.



**Figure S11.** (left) Ratio of Raman peak intensities  $(I_{1494}/I_{1430})$  for the main donor (1430 cm<sup>-1</sup>) and acceptor (1494 cm<sup>-1</sup>) ring stretching modes, and (right) FWHM of donor (1430 cm<sup>-1</sup>) peak plotted as a function of excitation wavelength for each material.

The ratio of Raman peak intensities increases with shorter excitation wavelength for each material. An increase in the value of this ratio indicates a stronger coupling between the absorption transition at that wavelength and the vibrational mode localised on the acceptor unit. Since these excitation wavelengths all lie within the low energy absorption bands of the polymers this shows that the higher energy absorptions in this band couple more strongly to the acceptor unit.<sup>[4]</sup> The widths of the donor unit peak (1430 cm<sup>-1</sup>) also increase with decreasing excitation wavelength. A similar trend has been observed for polythiophenes, where a large peak width was associated with increased conformational disorder.<sup>[5]</sup> It is not necessarily clear that the same relationship should apply to copolymers but the wavelength dependence suggests a similar effect, where shorter wavelengths selectively excite more disordered polymer.

One important observation is that the spectra for all the polymers show similar trends, indicating that the natures of their electronic transitions are similar. It is also significant that the 785 nm spectra (off-resonance) are similar to those measured in resonance near the absorption onset

(633 nm). This demonstrates that resonance effects around the low energy absorption edge are not significant and so spectra measured at 785 nm for all four copolymers can be reasonably compared (*i.e.* Figure 3 in the manuscript).

#### C-Se N-Se S-N S-O 1.0 Raman Intensity (norm.) 0.8 PSBS 0.6 PSBSe 0.4 PSeBS 0.2 PSeBSe 0.0 700 500 600 800 900 1000 Raman Shift (cm<sup>-1</sup>)

### 4. Sulfur/Selenium Bond Raman Peaks

**Figure S12.** Comparison of Raman peaks for the four copolymers measured in the 500-1000 cm<sup>-1</sup> range showing the C-Se/C-S and N-Se/N-S bond stretching modes.

These Raman spectra measured using 514 nm excitation to exploit the resonant enhancement of Raman scattering show peaks corresponding to the C-S and N-S bond stretching modes in PSBS. The selenium substitutions result in shifts of these peaks to lower frequencies since the C-Se and N-Se bonds have lower force constants. This is consistent with the increases in bond length predicted by DFT (manuscript Table 2).

## 5. X-Ray Diffraction



Figure S13. GIXRD scattering line-cuts taken from manuscript Figure 6 along the a)  $q_z$ , and b)

q<sub>xy</sub> directions for each copolymer.

## 6. Transistor Transfer Characteristics



**Figure S14.** Transfer characteristics measured for thin film transistors with copolymer active layers, corresponding with the hole mobilities quoted in the manuscript (Table 3).

### 7. Polymer:PC<sub>71</sub>BM Blend Film Raman Spectroscopy



**Figure S15.** Raman spectra comparing pristine polymer:PC<sub>71</sub>BM (1:2 weight ratio) blend films (pristine films and films processed using the DIO additive and thermal annealing) with the neat polymer and PC<sub>71</sub>BM films, measured using 785 nm excitation, for a) PSBS:PC<sub>71</sub>BM, b)

PSBSe:PC<sub>71</sub>BM, c) PSeBS:PC<sub>71</sub>BM, and d) PSeBSe:PC<sub>71</sub>BM.

In addition to the use of absorption spectroscopy to compare the morphologies of the polymer: $PC_{71}BM$  blend films with the neat materials, Raman spectroscopy provides a highly sensitive probe for detecting differences in molecular conformation. Figure S15 compares the Raman spectra (using 785 nm excitation for non-/pre-resonant excitation) of blend films with their neat component films. Under this excitation condition, the spectra are dominated by the

polymer Raman scattering and the peak assignments are discussed in the manuscript.

Significantly, the blend film Raman spectra overlap closely with the neat polymer spectra (showing additional small peaks from the  $PC_{71}BM$ ), though there are some significant differences – in particular we note that the relative intensity of the ~1290 cm<sup>-1</sup> peak is increased in the blend with respect to the neat polymer for the PSBS and PSBSe cases and the ~1490 cm<sup>-1</sup> peak shows some intensity variations too. Both of these modes are identified in the manuscript as vibrational modes localised on the benzothiadiazole/benzoselenadiazole (acceptor) unit and so suggest that the morphological impact on the polymer identified using UV-visible absorption spectroscopy in the manuscript relates specifically to the conformation of this part of the molecule.

### References

- [1] W. Lee, H. Choi, S. Hwang, J. Y. Kim, H. Y. Woo, *Chem. Eur. J.* 2012, 18, 2551.
- [2] S. A. Shin, J. B. Park, J.-H. Kim, D.-H. Hwang, Synth. Met. 2013, 172, 54.
- [3] T. Earmme, Y.-J. Hwang, N. M. Murari, S. Subramaniyan, S. A. Jenekhe, *J. Am. Chem. Soc.* **2013**, *135*, 14960.
- [4] M. E. Reish, S. Nam, W. Lee, H. Y. Woo, K. C. Gordon, J. Phys. Chem. C 2012, 116, 21255.
- [5] W. C. Tsoi, D. T. James, J. S. Kim, P. G. Nicholson, C. E. Murphy, D. D. C. Bradley, J. Nelson, J.-S. Kim, J. Am. Chem. Soc. 2011, 133, 9834.
- [6] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, J. V Manca, Nat. Mater. 2009, 8, 904.
- [7] L. Pandey, C. Risko, J. E. Norton, J.-L. Brédas, *Macromolecules* 2012, 45, 6405.
- [8] G. L. Gibson, T. M. McCormick, D. S. Seferos, J. Am. Chem. Soc. 2012, 134, 539.
- [9] A. A. B. Alghamdi, D. C. Watters, H. Yi, S. Al-Faifi, M. S. Almeataq, D. Coles, J. Kingsley, D. G. Lidzey, A. Iraqi, *J. Mater. Chem. A* **2013**, *1*, 5165.