

## Supporting Information

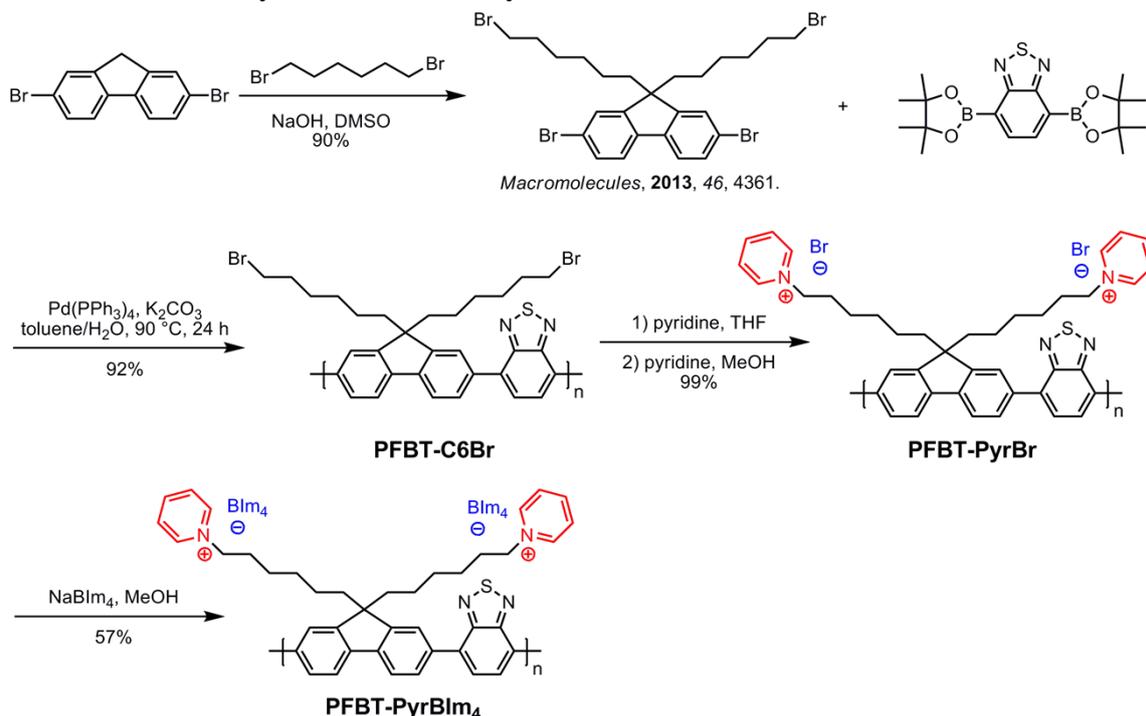
### **Varying the ionic functionalities of conjugated polyelectrolytes leads to both *p*- and *n*-type carbon nanotube composites for flexible thermoelectrics**

*Cheng-Kang Mai, Boris Russ, Stephanie L. Fronk, Nan Hu, Mary B. Chan-Park, Jeffrey J. Urban, Rachel A. Segalman, Michael L. Chabinyc, Guillermo C. Bazan\**

#### **General Information for Chemical Synthesis**

All glassware was oven-dried or flame-dried. Unless specifically mentioned, all chemicals are commercially available and were used as received. Thin layer chromatography (TLC) was performed using EM Science Silica Gel 60 F254 glass plates. Flash chromatography was performed using 60 Å silica gel (37-75 µm). The dialysis membrane (MWCO: 3500–5000 Da) was purchased from Spectrum® Laboratories Inc. <sup>1</sup>H NMR spectra were recorded at either 500 MHz or 600 MHz in CD<sub>2</sub>Cl<sub>2</sub> or CD<sub>3</sub>OD. Chemical shifts are reported in ppm referenced to residual solvent peaks as follows: CD<sub>2</sub>Cl<sub>2</sub>, 5.32 ppm; and CD<sub>3</sub>OD, 3.31 ppm. Gel Permeation Chromatography (GPC) was measured in Waters® system using CHCl<sub>3</sub> as the solvent and calibrated versus polystyrene standards.

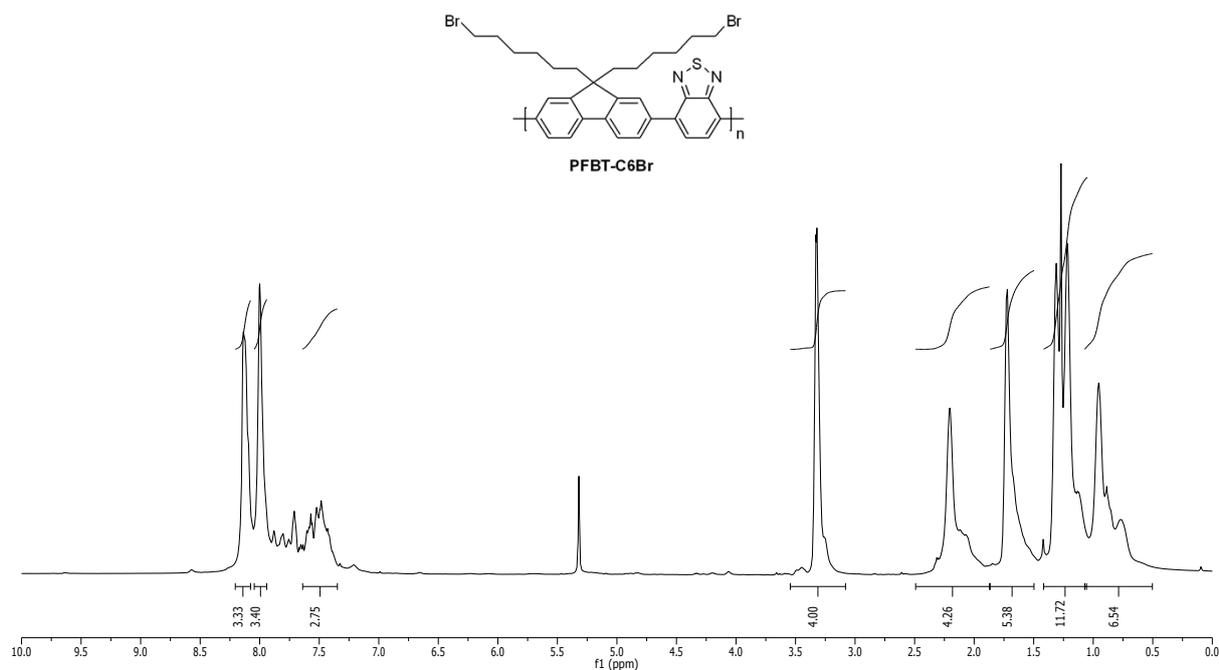
## Synthesis of PFBT-PyrBr and PFBT-PyrBlm<sub>4</sub>



**Scheme S1** Chemical synthesis of PFBT-PyrBr and PFBT-PyrBlm<sub>4</sub>

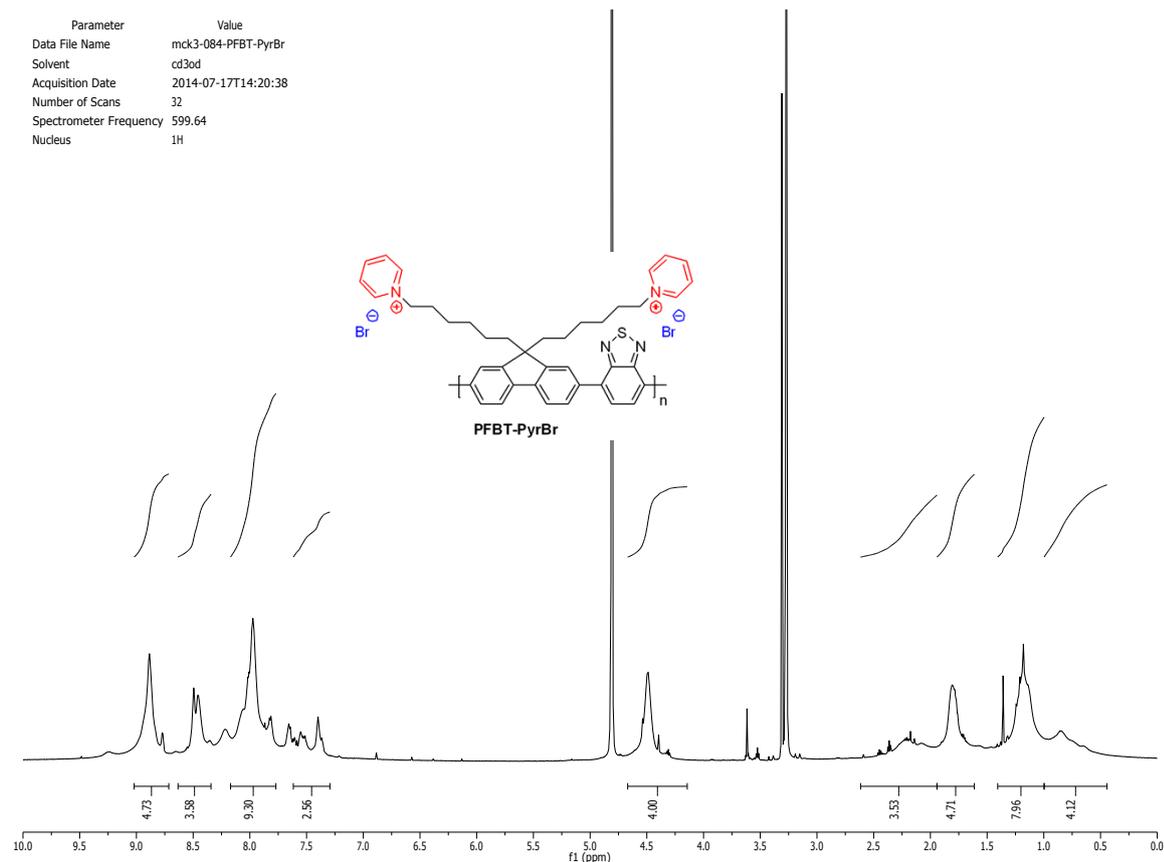
2,7-Dibromo-9,9-di(6-bromohexyl)fluorene (460 mg, 0.708 mmol, 1.0 equiv, synthesized according to the literature from commercially available 2,7-dibromofluorene),<sup>[1]</sup> 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (275 mg, 0.708 mmol, 1.0 equiv), K<sub>2</sub>CO<sub>3</sub> (138 mg, 3.54 mmol, 5.0 equiv), and Pd(PPh<sub>3</sub>)<sub>4</sub> (82 mg, 10 mol%) were combined in a microwave tube with a stir bar in a glove box. The tube was sealed with a septum, and taken out of the glove box. A mixture of toluene (21 mL) and H<sub>2</sub>O (2.1 mL) was degassed by sparging with Ar for 5 min, and cannulated into the above microwave tube. The septum on the tube was removed quickly under positive pressure of Ar, and the tube was resealed with a special cap for the microwave tubes. The yellow suspension was placed into an oil bath, and heated to 90 °C. The reaction was allowed to stir at 90 °C for 24 hrs, and poured into MeOH (100 mL). The orange precipitate was collected in a cellulose thimble, and washed by Soxhlet extraction with MeOH, acetone, and hexanes. The product was collected by extraction with CHCl<sub>3</sub>, and concentrated to provide PFBT-C6Br as an orange solid (408 mg, 92%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.20 – 7.95 (6H), 7.80 – 7.30 (2H), 3.32 (4H), 2.20 (4H), 1.72 (4H), 1.42 – 1.15 (8H), 0.95 (4H). GPC (CHCl<sub>3</sub>). M<sub>n</sub> = 12.8k, M<sub>w</sub> = 29.7k, PDI = 2.32.

| Parameter              | Value                |
|------------------------|----------------------|
| Data File Name         | mck3-084-PFBT-C6Br-H |
| Solvent                | cd2cl2               |
| Acquisition Date       | 2014-07-17T14:08:16  |
| Number of Scans        | 40                   |
| Spectrometer Frequency | 599.64               |
| Nucleus                | <sup>1</sup> H       |



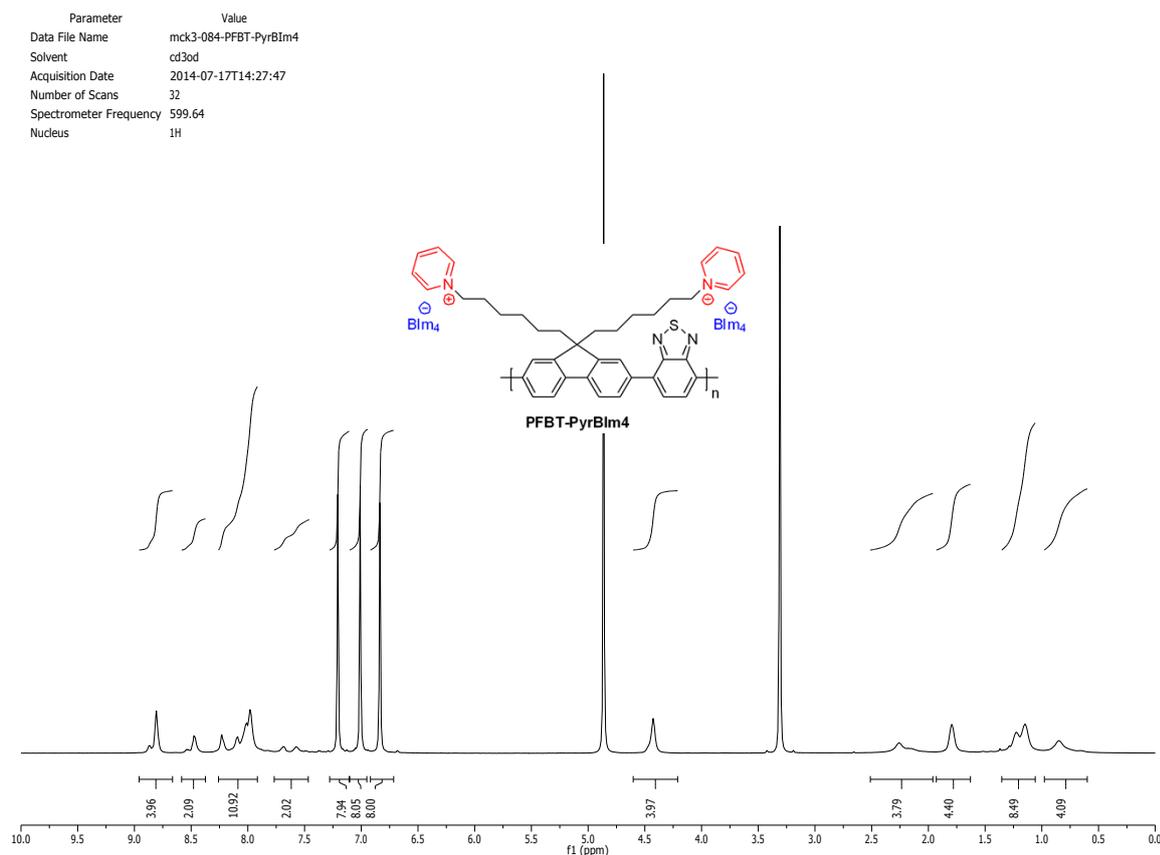
**Fig. S1** <sup>1</sup>H NMR of PFBT-C6Br in CD<sub>2</sub>Cl<sub>2</sub>

PFBT-C6Br was dissolved in THF:pyridine (1:1) in a microwave sealed tube, and the mixture was heated to 65 °C in an oil bath overnight. After removing the solvents, MeOH:pyridine (1:1) was added, and the solutions were also heated to 65 °C in an oil bath overnight. After the mixture was cooled down to room temperature, the solvents were removed under vacuum to yield a yellow solid. The solid was dissolved in MeOH, precipitated into acetone, centrifuged, decanted. This washing process was repeated twice, and the obtained yellow solid PFBT-PyrBr was dried under vacuum (99% yield). PFBT-PyrBr: <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD) δ 9.02 – 8.70 (4H), 8.60 – 8.30 (4H), 8.17 – 7.16 (8H), 7.60 – 7.30 (2H), 4.65 – 4.10 (4H), 2.60 – 1.95 (4H), 1.95 – 1.60 (4H), 1.40 – 1.00 (4H), 1.00 – 0.45 (4H).



**Fig. S2** <sup>1</sup>H NMR of PFBT-PyrBr in CD<sub>3</sub>OD

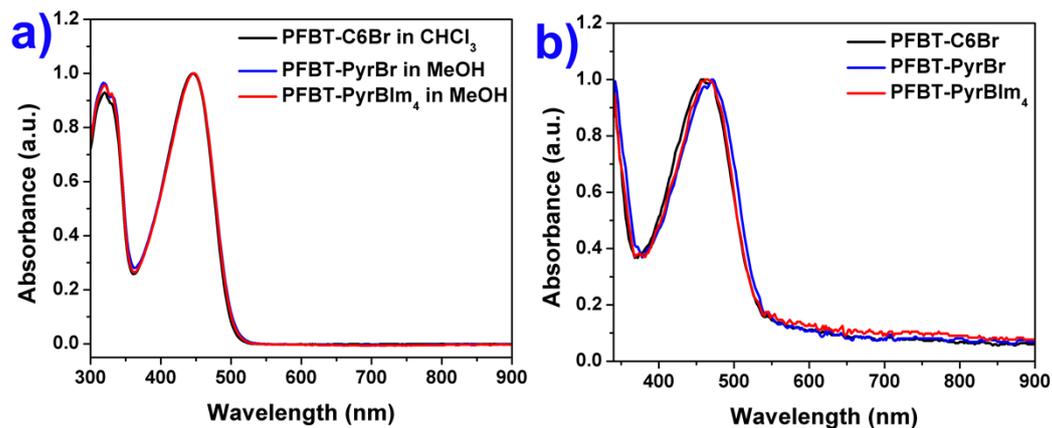
PFBT-PyrBr was dissolved in MeOH, 10 equiv of NaBIm<sub>4</sub> was added, and the mixture was stirred overnight before the solvent was removed under vacuum. The resulting yellow solid was washed with water, centrifuged, decanted. This washing process was repeated twice, before the yellow solid (PFBT-PyrBIm<sub>4</sub>) was rinsed with acetone, dried under vacuum overnight (95%). PFBT-PyrBIm<sub>4</sub>: <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD) δ 8.95 – 8.65 (4H), 8.60 – 8.35 (2H), 8.26 – 7.95 (10H), 7.78 – 7.50 (2H), 7.21 (8H), 7.01 (8H), 6.84 (8H), 4.43 (4H), 2.50 – 2.00 (4H), 1.80 (4H), 1.34 – 1.08 (8H), 0.98 – 0.60 (4H).



**Fig. S3** <sup>1</sup>H NMR of PFBT-PyrBIm<sub>4</sub> in CD<sub>3</sub>OD

### Optical Measurements

All the measurements were performed using a Perkin Elmer Lambda 750 spectrophotometer at room temperature. Thin film samples were prepared on glass substrates by spin-coating.

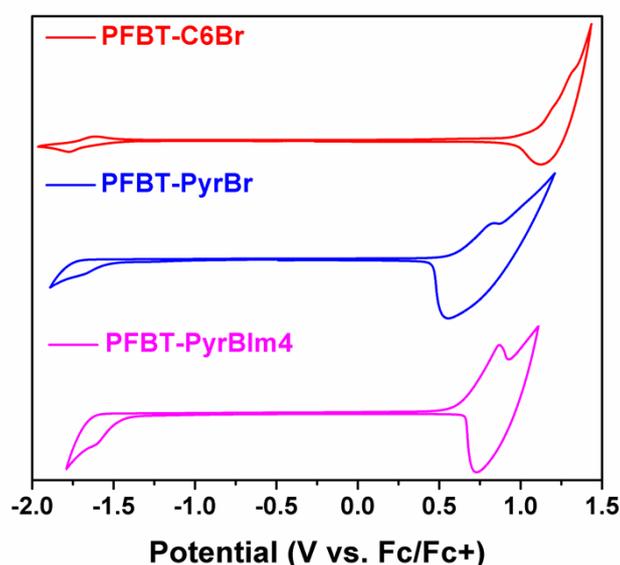


**Fig. S4** Normalized absorptions of PFBT-C6Br (black), PFBT-PyrBr (blue), and PFBT-PyrBIm<sub>4</sub> (red) in a) solutions, and b) thin films.

### Electrochemical Measurements:

All electrochemical measurements were performed using CHI instrument model 730B in a standard three-electrode, one compartment configuration equipped with a Ag wire quasi reference electrode, Pt wire counter electrode, and glassy carbon (dia. 3 mm) working

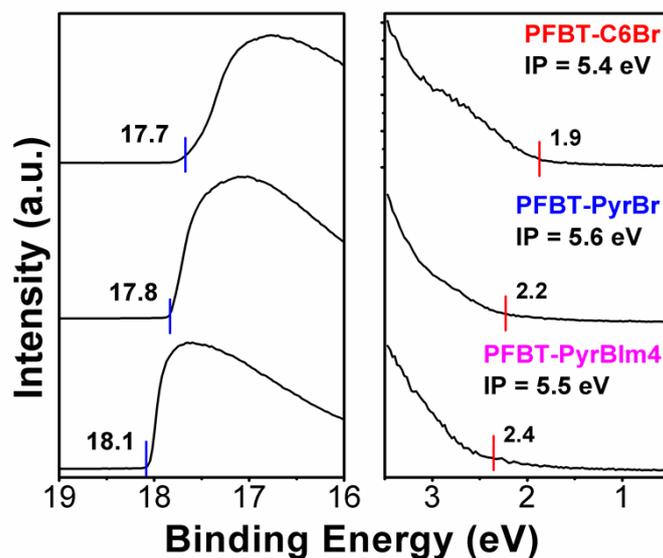
electrode. Glassy carbon electrodes were polished with alumina. The cyclic voltammetry (CV) experiments were performed in anhydrous acetonitrile (PFBT-C6Br) or dichloromethane (PFBT-PyrBr and PFBT-PyrBIm<sub>4</sub>) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte at scan rate 100 mV/s. All electrochemical solutions were purged with dry Argon for 15 minutes at least to deoxygenate the system. Ferrocene was used as the internal standard. The HOMO and LUMO levels were obtained by correlating the onsets ( $E_{\text{ox}}^{\text{Fc/Fc}^+}$ ,  $E_{\text{red}}^{\text{Fc/Fc}^+}$ ) to the normal hydrogen electrode (NHE), assuming HOMO of Fc/Fc<sup>+</sup> to be 4.88 eV. All the polymer films were formed by casting about 5  $\mu\text{L}$  of 5 mg/mL solution (PFBT-C6Br in CHCl<sub>3</sub>; PFBT-PyrBr and PFBT-PyrBIm<sub>4</sub> in 1:1 H<sub>2</sub>O:MeOH) on the glassy carbon working electrode, and dried under vacuum (1 h) before measurements.



**Fig. S5** CV plots of PFBT-C6Br (red), PFBT-PyrBr (blue), and PFBT-PyrBIm<sub>4</sub> (pink).

#### **Ultraviolet photoelectron spectroscopy (UPS) measurements:**

The UPS measurements were performed in a Kratos Ultra spectrometer (base pressure of  $1 \times 10^{-9}$  Torr) using monochromatized Al K $\alpha$  X-ray photons and a HeI ( $h\nu = 21.2$  eV for UPS) discharge lamp. The polymer solutions were spun cast on top of pre-cleaned ITO substrates. Films were fabricated inside a N<sub>2</sub> atmosphere glove box and were transferred via an airtight sample holder to the UPS/XPS analysis chamber. Samples were also kept in a high vacuum chamber overnight to remove solvent residues.



**Fig. S6** UPS spectra of PFBT-C6Br, PFBT-PyrBr, and PFBT-PyrBIIm<sub>4</sub>.

**Table S1** Summary of molecular energy levels (in eV) obtained via UPS, UV-Vis absorption, and CV

| Polymer                   | IE <sup>a</sup> | EA  <sup>b</sup> | E <sub>g</sub> <sup>c</sup> | HOMO <sup>d</sup> | LUMO <sup>d</sup> | E <sub>g</sub> <sup>d</sup> |
|---------------------------|-----------------|------------------|-----------------------------|-------------------|-------------------|-----------------------------|
| PFBT-C6Br                 | 5.4             | 3.1              | 2.3                         | -6.0              | -3.4              | 2.6                         |
| PFBT-PryBr                | 5.6             | 3.2              | 2.4                         | -5.5              | -3.3              | 2.2                         |
| PFBT-PyrBIIm <sub>4</sub> | 5.5             | 3.2              | 2.3                         | -5.5              | -3.5              | 2.0                         |

<sup>a</sup> Obtained from UPS measurements. <sup>b</sup> Estimated by using the IE value and the optical E<sub>g</sub>. <sup>c</sup> Estimated from the onset of film absorption. <sup>d</sup> Obtained from CV measurements.

### Preparations of CPE/SWNT dispersions and SWNT mats:

Purified arc discharge SWNTs (P2-SWNT) were purchased from Carbon Solutions, Inc. (Riverside, CA, USA) and used without any further purification. Different amounts of SWNT powder were added into the CPE solutions (2 mg mL<sup>-1</sup> in 1:1 H<sub>2</sub>O:MeOH) to provide CPE:SWNT at different weight ratios. SWNTs were dispersed using probe sonication (SONICS, VCX-130) at 85 W in a water–ice bath for 1 h.

SWNT mats were prepared by filtration of SWNT (1 mg mL<sup>-1</sup> in 1:1 H<sub>2</sub>O:MeOH) with or without NaBIIm<sub>4</sub>, which was homogenized via probe sonication for 1 h, on top of filter paper (cellulose acetate, diameter = 13 mm, pore size = 0.45 μm). The SWNT mats were heated on a hot plate (80 °C) for 1 h, and attached to the same glass substrate as CPE/SWNT composites via double-side conductive nickel tape. Good thermal contact was made with thermal paste. The rest of the procedure is the same as CPE/SWNT composites.

### Thermoelectric Measurements:

The low-ion borosilicate glass substrates (D263) were purchased from University Wafer. Prior to use, the substrates were cleaned by sonication in soapy water, de-ionized water, acetone, and isopropyl alcohol for 30 min each, dried with compressed air, treated with

oxygen plasma for 2 min. CPE/SWNT composite thin films were spun-cast from the respective dispersions (CPE concentration is 2 mg mL<sup>-1</sup> in 1:1 H<sub>2</sub>O:MeOH) onto glass substrates, and heated at 80 °C for 1 h on a hot plate in air. The thin films were transferred into a thermal evaporator in a nitrogen-filled glove box to deposit gold electrodes (100 nm thick) on the top through a shadow mask.

Current-sourced four-point conductivity measurements were conducted in an N<sub>2</sub> glovebox. All devices measured with four-point probe conductivity had a channel length ( $L$ ) of 200 μm and a channel width ( $w$ ) of 1 mm. The electrical conductivity was determined by  $\sigma = \frac{I}{V} \times \frac{L}{A}$ , where  $A$  is the cross-sectional area of the sample between the electrodes.  $A$  was calculated as the film thickness ( $t$ , measured by profilometer) times the channel width ( $w$ ).<sup>[2]</sup> At least three different samples were measured and averaged.

Seebeck coefficients ( $S$ ) were determined on the same samples as electrical conductivity, by linear fitting of a data series taken by imposing temperature differences across the sample and measuring the corresponding thermovoltage ( $S = -\Delta V/\Delta T$ ) from two thermocouples contacting the sample in parallel to the two voltage probes. Thermocouples are attached to the sample via a spring force from the probe arm and good thermal contact is made with thermal paste. The system was calibrated by measuring samples of bismuth telluride, silicon, and indium tin oxide, and the uncertainty was determined to be ±15%.<sup>3</sup> At least three different samples were measured and averaged.

**Table S2** Thermoelectric properties of CPE/SWNT composites.

| Materials                      | weight ratio (CPE/SWNT) | $\sigma$ (S cm <sup>-1</sup> ) | $S$ (μV K <sup>-1</sup> ) | $\sigma S^2$ (μW m <sup>-1</sup> K <sup>-2</sup> ) |
|--------------------------------|-------------------------|--------------------------------|---------------------------|--|
| <b>CPE-Na</b>                  | 2:1                     | 9.48 ± 0.58                    | 79 ± 12                   | 6 ± 2.2  |
|                                | 1:1                     | 167 ± 10                       | 64 ± 9                    | 68 ± 24  |
|                                | 2:3                     | 514 ± 55                       | 65 ± 9                    | 218 ± 89   |
| <b>CPE-PyrBlm<sub>4</sub></b>  | 2:1                     | 1.92 ± 0.05                    | -55 ± 8                   | 0.58 ± 0.18  |
|                                | 1:1                     | 106 ± 3                        | -41 ± 6                   | 17.8 ± 5.8   |
|                                | 2:3                     | 19 ± 1                         | 52 ± 8                    | 5.22 ± 1.84  |
| <b>PFBT-Na</b>                 | 2:1                     | 0.039 ± 0.002                  | 72 ± 10                   | 0.02 ± 0.007                                       |
|                                | 1:1                     | 0.19 ± 0.01                    | 75 ± 11                   | 0.11 ± 0.04  |
|                                | 2:3                     | 0.59 ± 0.03                    | 75 ± 11                   | 0.33 ± 0.12  |
| <b>PFBT-PyrBlm<sub>4</sub></b> | 2:1                     | 0.62 ± 0.03                    | -21 ± 3                   | 0.028 ± 0.010                                      |
|                                | 1:1                     | 8.7 ± 0.8                      | 22 ± 3                    | 0.42 ± 0.16  |
|                                | 2:3                     | 13.6 ± 0.3                     | 31 ± 5                    | 1.33 ± 0.43  |

**Table S3** Thermoelectric properties of CPE-PyrBIm<sub>4</sub>/SWNT composites as a function of [CPE-PyrBIm<sub>4</sub>] ([SWNT] = 2 mg mL<sup>-1</sup> is constant).

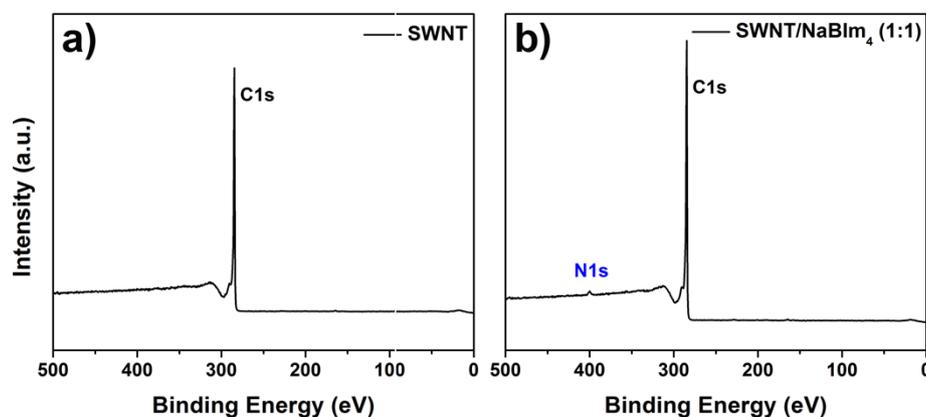
| [CPE-PyrBIm <sub>4</sub> ] (mg mL <sup>-1</sup> ) | $\sigma$ (S cm <sup>-1</sup> ) | $S$ ( $\mu$ V K <sup>-1</sup> ) | $\sigma S^2$ ( $\mu$ W m <sup>-1</sup> K <sup>-2</sup> ) |
|---|--------------------------------|---------------------------------|--|
| 0.75  | 92 $\pm$ 6                     | 41 $\pm$ 6                      | 15.5 $\pm$ 5.6   |
| 1   | 53 $\pm$ 4                     | -26 $\pm$ 4                     | 3.6 $\pm$ 1.4  |
| 1.5   | 21 $\pm$ 1.5                   | -8 $\pm$ 1                      | 0.13 $\pm$ 0.05  |
| 2   | 106 $\pm$ 3                    | -41 $\pm$ 6                     | 17.8 $\pm$ 5.8   |
| 3.5   | 32 $\pm$ 2                     | -48 $\pm$ 6                     | 7.4 $\pm$ 2.7  |
| 5   | 4.0 $\pm$ 0.2                  | -72 $\pm$ 11                    | 2.1 $\pm$ 0.7  |
| 7.5   | 0.32 $\pm$ 0.02                | -72 $\pm$ 11                    | 0.17 $\pm$ 0.11  |

### Scanning electron microscopy (SEM)

Scanning electron microscopy spectra were obtained using FEI XL30 Sirion FEG digital electron scanning microscope. Samples were prepared by spin-coating (same parameters as thermoelectric measurements) CPE/SWNT dispersion on silicon substrates, baked on a hot plate at 80 °C for 1 h. The cross sections were fresh-broken by hands, sputtered with 5 nm Au/Pd on top prior to measurements.

### XPS Spectra of SWNT mats

XPS spectra were recorded on a Kratos Axis Ultra XPS system with a base pressure of  $1 \times 10^{-10}$  mbar (UHV), using a monochromated Al K $\alpha$  X-ray source at  $h\nu = 1486$  eV.

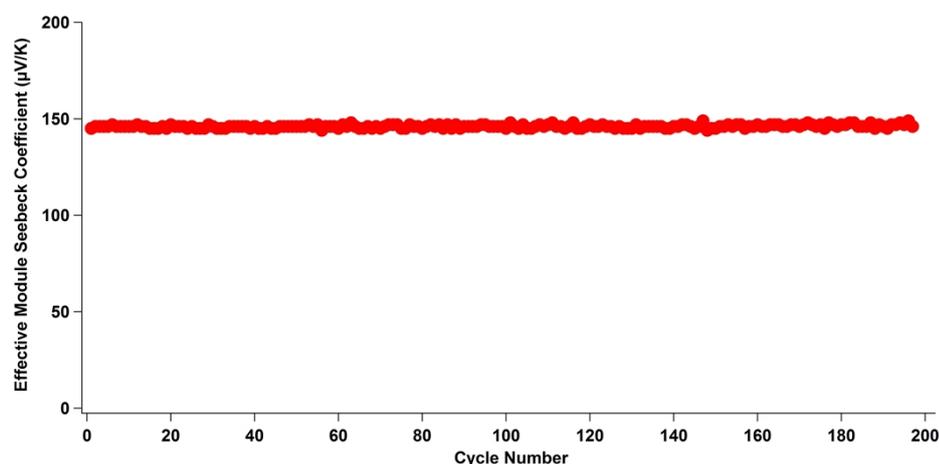


**Fig. S7** XPS spectra of SWNT and SWNT/NaBIm<sub>4</sub> (1:1) mat. The new peak in spectra b) at ~400 eV (N1s) confirms the presence of NaBIm<sub>4</sub>.

### Fabrication of Thermoelectric (TE) Module

CPE/SWNT dispersions were sonicated for 30 minutes prior to deposition. Individual *p*-type (CPE-Na/SWNT = 1:1) and *n*-type (CPE-PyrBIm<sub>4</sub>/SWNT = 1:1) legs (~ 1 μm in thickness) were drop-cast on a Kapton substrate and dried at 80 °C. Electrical contacts were made using silver paint (PELCO, Ted Pella). To establish a temperature gradient across the device, one side of the TE module legs was placed in contact with a hot plate/heating block, while the other side of the legs in the TE module was exposed to the ambient. The temperature gradient was quantified using an infra-red imaging camera (FLIR OSXL-E50). To establish module performance, electrical contact with the appropriate number of *p/n* legs in series was made using thin tip movable probes; the  $V_{oc}$  generated by the module under a temperature difference was measured using an Agilent voltmeter. The associated thermally driven current for a given temperature difference was calculated from the  $V_{oc}$  and the measured resistance ( $R$ ) at that temperature as  $I = V_{oc} / R$ . The power was calculated as  $P = I^2R = (V_{oc})^2 / R$ . All measurements were performed in air.

Cycling tests were performed on module configurations combining two *p*-type and two *n*-type legs on a Kapton substrate. The stability of the *Seebeck* coefficient (the reproducibility of generating open circuit voltage) was evaluated by fluctuating the temperature difference between +10 °C to -10 °C around room temperature in each cycle. Ten data points were collected at each temperature variation after thermal equilibration. As seen in Fig. S8, the module was highly stable during the cycling with no deviation in the effective *Seebeck* coefficient of the device observed over the 200 cycling steps.



**Fig. S8** Evolution of *Seebeck* coefficient of the thermoelectric module as a function of cycle number.

## Comparison of Recent Developments on *n*-Type Flexible Thermoelectric Materials

**Table S4** Examples of *n*-type organic thermoelectric materials in current literature.

|   | Materials                           | $\sigma$ (S cm <sup>-1</sup> ) | $S$ ( $\mu$ V K <sup>-1</sup> ) | $\sigma S^2$ ( $\mu$ W m <sup>-1</sup> K <sup>-2</sup> ) | method     | references  |
|---|-------------------------------------|--------------------------------|---------------------------------|--|------------|-------------|
| 1 | CPE-PyrBIm <sub>4</sub> /SWNT (1:1) | 106                            | -41                             | 18   | drop-cast  | this work   |
| 2 | CoCp <sub>2</sub> @SWNTs            | 430                            | -40                             | 71   | filtration | 2015, ref 4 |
| 3 | SWNT/dppp                           | 124                            | -52                             | 25   | filtration | 2013, ref 5 |
| 4 | SWNT/PEI/NaBH <sub>4</sub>          | 60                             | -80                             | not reported   | filtration | 2012, ref 6 |
| 5 | PDI derivatives                     | 0.5                            | -170                            | 1.4  | drop-cast  | 2014, ref 7 |

## References

- [1] D. Stay, M. C. Lonergan, *Macromolecules* **2013**, *46*, 4361–4369.
- [2] G.-H. Kim, L. Shao, K. Zhang, K. P. Pipe, *Nat. Mater.* **2013**, *12*, 719–723.
- [3] A. Burkov, in *Thermoelectric Handbook* (Ed: D. Rowe), CRC Press, Boca Raton, FL **2005**.
- [4] T. Fukumaru, T. Fujigaya and N. Nakashima, *Sci. Rep.* 2015, **5**, 7951.
- [5] Y. Nonoguchi, K. Ohashi, R. Kanazawa, K. Ashiba, K. Hata, T. Nakagawa, C. Adachi, T. Tanase and T. Kawai, *Sci. Rep.* 2013, **3**, 3344.
- [6] C. Yu, A. Murali, K. Choi and Y. Ryu, *Energy Environ. Sci.* 2012, **5**, 9481.
- [7] B. Russ, M. J. Robb, F. G. Brunetti, P. L. Miller, E. E. Perry, S. N. Patel, V. Ho, W. B. Chang, J. J. Urban, M. L. Chabynyc, C. J. Hawker and R. A. Segalman, *Adv. Mater.* 2014, **26**, 3473.