

**Rapid, facile synthesis of conjugated polymer zwitterions in ionic liquids**

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## ARTICLE

## Rapid, facile synthesis of conjugated polymer zwitterions in ionic liquids

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Ionic liquids (ILs) were utilized for the rapid air-stable Suzuki polymerization of polar zwitterionic thiophene monomers, precluding the need for volatile organic solvents, phosphine ligands and phase transfer catalysts typically required in conjugated polymer synthesis. Ten different ILs were examined, demonstrating the scope and limitations of their utility as solvents in this Suzuki polymerization. Imidazolium, pyridinium and pyrrolidinium ILs proved effective for these polymerizations, with top performance achieved using pyrrolidinium triflate, affording polymers with molecular weight values > 30 kDa. The enhanced solubility of these conjugated polymer zwitterions (CPZs) in ILs, relative to organic solvents, led to higher molecular weight polymers than obtained using previously reported methods. CPZs synthesized in ILs proved effective as cathode modification layers in solar cells, giving rise to a power conversion efficiency (PCE) of 7.57% in bulk heterojunction devices.

## Introduction.

Conjugated polymer zwitterions (CPZs) are neutral, hydrophilic, electronically active polymers. Their pendent dipoles afford solubility in polar solvents, and make them attractive in numerous applications, including as buffer layers in optoelectronics<sup>[1-5]</sup> and solar cells.<sup>[6-12]</sup> Currently, most procedures to synthesize hydrophilic conjugated polymers, such as conjugated polyelectrolytes (CPEs)<sup>[13-15]</sup> or CPZs,<sup>[1,2]</sup> involve an organometallic catalyzed polymerization (e.g., Suzuki or Stille coupling) in organic solvents, followed by post-polymerization modification to introduce the pendent charged or zwitterionic moieties. As such, pendent group density along the polymer backbone depends on the efficiency of post-polymerization modification. We recently reported an alternative approach, in which CPZs were synthesized by Suzuki coupling with the zwitterions present at the monomer stage.<sup>[5,16]</sup> This methodology gave polymer molecular weights of ~10 kDa for sulfobetaine (SB)-substituted polythiophene, **PTSB-1** (Figure 1), and 20 kDa for SB-substituted poly(thiophene-*a*-benzothiadiazole), **PTBTSB-2** (Figure S1).<sup>[16]</sup> These CPZs were incorporated as cathode modification layers in organic photovoltaics (OPVs), enhancing power conversion efficiency (PCE) from ~1 % for devices containing either bare Ag- or LiF/Ag cathodes to > 5 % for those containing a thin **PTBTSB-2** interlayer between the bulk heterojunction (BHJ) active layer and Ag-cathode.

Polymer solubility in either the aqueous or organic phase of a polymerization reaction lends towards high molecular weight, and higher molecular weight can improve film formation and charge mobility;<sup>[17]</sup> for example, higher molecular weight cathode buffer

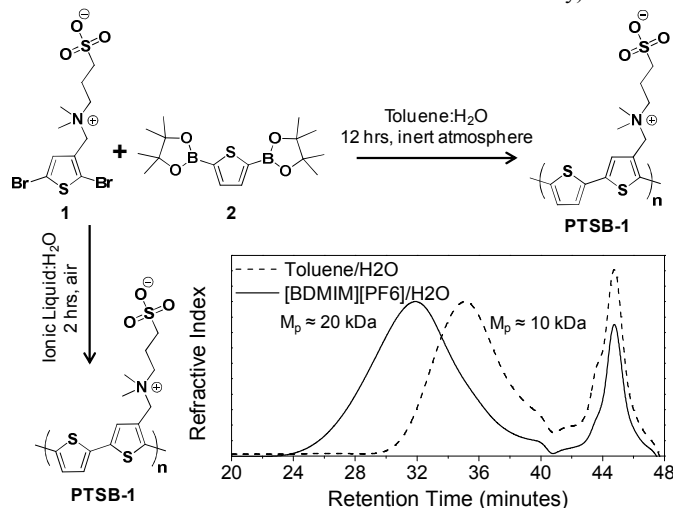
layers in OPVs afforded higher PCE values.<sup>[18]</sup> Providing a methodology for the synthesis of reasonably high molecular weight (> 10 kDa), polar conjugated polymers may prove beneficial for the production of new electronically active interlayer materials. To this end, we chose to investigate ionic liquids (ILs) as solvents for Suzuki catalyzed polymerization of zwitterion substituted aromatic dihalides, to determine whether the polarity of ILs could enhance the polymerizations and produce polymers that improve device performance.

ILs are organic salts, typically considered as room temperature liquids or having melting points < 100 °C.<sup>[19]</sup> IL properties, such as high thermal stability, negligible vapor pressure, and the ability to solvate a wide variety of small molecules and polymers, make them “green” alternatives to volatile organic liquids.<sup>[20]</sup> ILs have been utilized as solvents for numerous reactions including organometallic-catalyzed couplings (where ILs have good compatibility with transition metal catalysts),<sup>[21,22]</sup> and polymerizations, such as,<sup>[23]</sup> free radical,<sup>[24-25]</sup> ring-opening<sup>[26]</sup> and cationic and anionic mechanisms.<sup>[27,28]</sup> Palladium catalyzed carbon-carbon bond forming reactions, such as Suzuki-Miyaura coupling, have been studied in the presence of ILs, specifically taking advantage of imidazolium salts<sup>[29]</sup> that serve as ligands following *N*-heterocyclic carbene formation, which resulted in improved catalytic activity.<sup>[30-35]</sup> A report by Zhang and coworkers utilized imidazolium ILs as solvents for the phosphine-free Suzuki-coupling to give biaryls (with added water to improve reactivity).<sup>[29]</sup> Thiophene,<sup>[36,37]</sup> pyrrole<sup>[37]</sup> and aniline<sup>[38-40]</sup> have been polymerized by oxidative or electrochemical methods in ILs, typically giving insoluble films or fibrils. To our knowledge, there is no prior report on Suzuki polymerization in an IL medium. As we show, ILs impart a distinct advantage for

promoting Suzuki-type polymerizations to synthesize CPZs that markedly improved solar cell efficiency.

## Results and discussion.

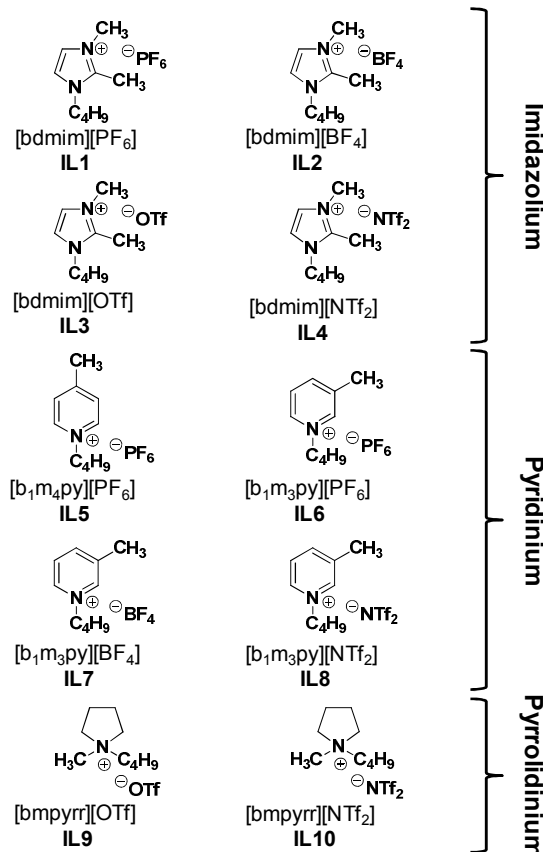
The synthesis of sulfobetaine-substituted polythiophene **PTSB-1** (Figure 1) was chosen as a test case for IL-medium polymerizations, since we were previously unable to obtain high molecular weights of this polymer.<sup>[5,16]</sup> In that work, **PTSB-1** was prepared from dibromide **1** with diboronate-ester **2** in a biphasic, toluene/water (2M NaBr, 2M K<sub>2</sub>CO<sub>3</sub>) reaction mixture, under an inert atmosphere with dichloro[bis(triphenylphosphine)] palladium(II) [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] as the catalyst and Aliquat 336 as the phase transfer catalyst (Figure 1).<sup>[5,16]</sup> The reaction terminated upon precipitation of an orange polymer product at only 5 – 10 kDa (estimated by aqueous size exclusion chromatography (SEC), and we note that regiochemistry indicated in the structures as-drawn is for convenience only).



**Figure 1.** Synthesis of **PTSB-1** using Suzuki polycondensation, and representative size exclusion chromatograms of polymers resulting from polymerization in IL1 ([BDMIM][PF<sub>6</sub>])/H<sub>2</sub>O and toluene/H<sub>2</sub>O.

Attempts to increase the molecular weight of **PTSB-1** by adjusting the oil-to-water ratio, temperature and concentration were unsuccessful. While 2,2,2-trifluoroethanol (TFE) is an excellent solvent for zwitterionic polymers, addition of TFE to any mixture containing palladium catalyst led to immediate catalyst decomposition (appearance of a black solution) and low monomer conversion. A broad-based solubility study of **PTSB-1** and selected CPZs revealed their solubility in a number of commercially available imidazolium salts.

1,2,3-Substituted imidazolium, pyridinium and pyrrolidinium ILs (Figure 2), were tested as solvents in the preparation of **PTSB-1** and **PTBTSB-2** (structure in Figure S1). Selected counterions included hexafluorophosphate [PF<sub>6</sub>], tetrafluoroborate [BF<sub>4</sub>], triflate [OTf] and bis(trifluoromethanesulfonamide) [NTf<sub>2</sub>].



**Figure 2.** Chemical structure of ILs tested as co-solvents for Suzuki polymerization.

The reaction conditions were kept constant, using a 2.5:1 weight ratio of IL to 2M NaBr (aq) and 3 mole % Pd(OAc)<sub>2</sub> loading, stirring at 100 °C for 2 hours. Conveniently, using ILs precluded the need for inert conditions typical of such metal-mediated polymerizations. All reactions in ILs were performed in air. However, some ILs proved unsuitable for polymerization of zwitterionic monomers. For example, reactions in 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF<sub>6</sub>] led to low conversion, likely due to deprotonation at the 2-position of the ring, forming an *N*-heterocyclic carbene that can coordinate to palladium.<sup>[33,41]</sup>

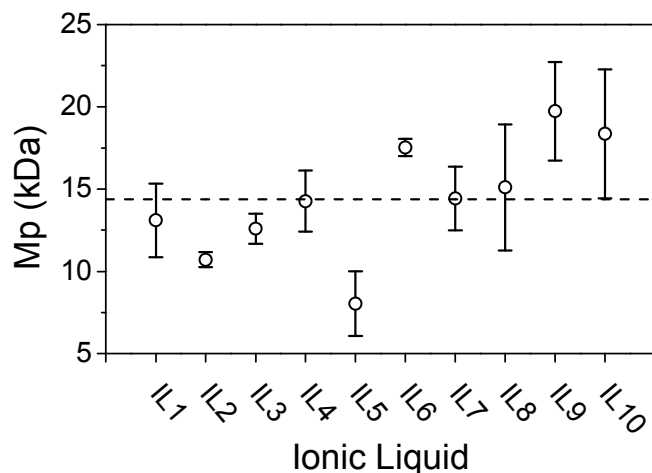
In a typical polymerization, following two hours of stirring at 100 °C in the IL, the polymers were isolated by precipitation into MeOH, and purified by centrifugation and trituration with MeOH. SEC, eluting in water (0.1 M NaNO<sub>3</sub>, 0.02 wt % NaN<sub>3</sub>) at 45 °C, provided an estimation of polymer molecular weight and dispersity. Average polymer molecular weights and molecular weight distributions resulting from the ILs tested are given in Table 1. Purification by Soxhlet extraction using MeOH led to complete removal of residual IL, confirmed by the lack of an <sup>19</sup>F NMR signal (Figure S2 in SI). The polymers were obtained as orange powders in 70-85% yield.

**Table 1.** Average polymer molecular weights and dispersities of **PTSB-1** determined with aqueous SEC relative to PEO standards for polymerizations conducted in toluene and ILs at 100 °C for two hours in air. Values represent averages from three polymerizations. \*Polymerizations in toluene were run for 12 hours in a nitrogen atmosphere.

	Toluene*	Imidazolium				Pyridinium				Pyrrolidinium	
		IL1	IL2	IL3	IL4	IL5	IL6	IL7	IL8	IL9	IL10
$M_n$	6,500	8,000	6,400	8,000	8,600	5,000	11,400	9,100	9,900	13,700	11,800
$M_p$	10,000	13,100	10,700	12,600	14,300	8,000	17,500	14,400	15,100	19,700	18,400
$\bar{D}$	1.5	1.7	1.5	1.5	1.7	1.7	1.9	1.7	1.8	1.6	1.9

CPZ formation in ILs was rapid; after only two hours, polymers were obtained with molecular weights on the order of, or higher than, those obtained using organic solvents at longer reaction times (12 hours). Allowing the reactions to proceed for a longer time (12 hours vs. 2 hours) in IL1 resulted in higher molecular weight polymers, having twice the peak apex molecular weight ( $M_p \approx 20$  kDa) relative to those typically obtained using toluene/H<sub>2</sub>O mixtures ( $M_p \approx 10$  kDa) (**Figure 1**) ( $M_p$  was chosen to remove variability associated with start and end retention times, or uneven baselines in the chromatograms). The increase in dispersity ( $\bar{D}$ ), from 1.5 to 2.0, in going from toluene as solvent to IL as solvent suggests that polymerization in the IL leads to full conversion, which agrees with the higher yields typically obtained when using ILs (75-85% in ILs; 55-70% in toluene/H<sub>2</sub>O).

$M_p$  values greater than 10,000 g/mol were obtained in all cases with the exception of IL5 (**Figure 3**). We expect that both IL polarity and viscosity influence polymerization kinetics; however other factors such as IL-catalyst interactions should be considered. We note that IL polarity typically follows the trend (most polar to least polar) OTf > BF<sub>4</sub> > PF<sub>6</sub> > NTf<sub>2</sub> for the anions used and viscosity (most viscous to least viscous) PF<sub>6</sub> > BF<sub>4</sub> > OTf > NTf<sub>2</sub>.<sup>[42-46]</sup> While a clear trend in IL properties vs. polymer molecular weight did not emerge, the solubility of CPZs increased with IL polarity, with the greatest solubility in IL3 and IL9 (OTf anions) (**Figure S3**). However, we consistently found that the highest average molecular weight was obtained with IL9, [bmpyrr][OTf] ( $M_p = 19.7$  kDa), which may be attributed to its low viscosity and high polarity relative to many of the other ILs.



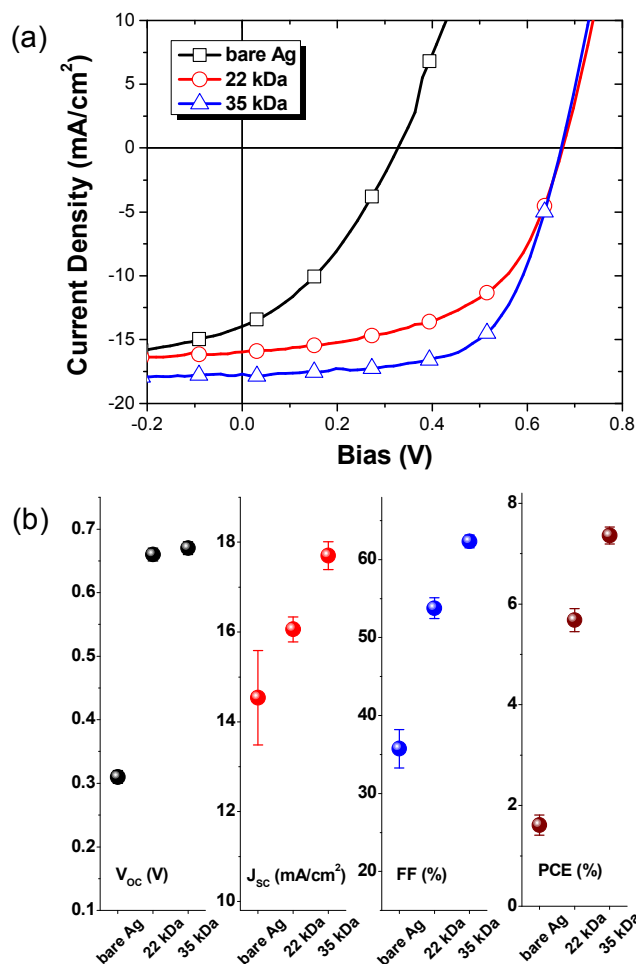
**Figure 3.** Peak-average molecular weight values of **PTSB-1** obtained from polymerizations conducted in different ILs (three reactions per IL) at 100 °C for two hours. Error bars represent  $\pm$  standard deviation.

A second CPZ, a benzothiadiazole-co-thiophene polymer, **PTBTSB-2** (**Figure S1**), was synthesized to test the versatility of this Suzuki polymerization in ILs to afford higher molecular weight, polar semiconducting polymers. The reaction mixtures were heated at 100 °C for 12 hours, where in both polymerizations containing either toluene or IL9 led to polymer precipitation. The precipitate was washed with MeOH, and size exclusion chromatography in TFE (0.02 M sodium trifluoroacetate) revealed a peak average molecular weight of greater than 40 kDa for **PTBTSB-2** synthesized using IL9, while 28 kDa was the maximum molecular weight obtainable using toluene as the organic phase. Indeed, the polymerization kinetics of **PTBTSB-2** are very rapid, yielding polymer with molecular weight > 20 kDa in minutes (**Figure S4**).

Solar cells were fabricated using **PTBTSB-2** cathode modification layers having molecular weights of 22 and 35 kDa. The solar cells contained a PTB7:PC<sub>71</sub>BM BHJ spun cast onto PEDOT:PSS covered ITO substrates. We selected Ag as the cathode, given its intrinsic stability (higher work function (WF)) relative to commonly used cathodes such as Al, and the WF modification effect of these CPZs.<sup>[5]</sup> Ultraviolet photoelectron spectroscopy (UPS) further confirmed that the 22 kDa and 35 kDa **PTBTSB-2** samples have equivalent interfacial dipole ( $\Delta$ ) values as thin layers on Ag (**Figure S5**). Previously, we reported the critical effect of CPZ interlayer thickness on device performance, where a 3 - 5 nm **PTBTSB-2** film led to the highest power conversion efficiency (PCE); this optimized thickness was utilized for the devices described here (**Figure 4**). Solar cells containing a bare Ag cathode (no CPZ interlayer), fabricated as controls, showed poor device performance (PCE 1.61%) as a result of a weak built in device potential. It was previously shown that inserting a thin layer of LiF, a common inorganic buffer layer with aluminium cathodes, does not significantly improve device performance, resulting in PCE < 2%.<sup>[5]</sup> Adding a thin layer of **PTBTSB-2** dramatically improved  $V_{OC}$ ,  $J_{SC}$  and  $FF$ , resulting in PCE > 5%. The  $\Delta$ , generated as a result of placing **PTBTSB-2** in contact with Ag led to a decrease in Ag WF at the interface. The WF modification leads to increased  $V_{OC}$ , as shown in **Figure 4**, and increased  $J_{SC}$  and  $FF$  by strengthening the built-in device potential (reducing loss to recombination).

The 22 and 35 kDa **PTBTSB-2** interlayers led to average PCE of  $5.68 \pm 0.23$  % and  $7.36 \pm 0.17$  % respectively (with the best devices having a PCE of 6.00 % and 7.57 % respectively) (**Figure 4**). The improvement in PCE correlated with higher  $J_{sc}$  and  $FF$ , with little to no change in  $V_{OC}$ . A  $V_{OC} \approx 0.7$  V suggests that **PTBTSB-2** results in an Ohmic contact with Ag, where the  $V_{OC}$  is dictated not by the anode-cathode work function offset, but rather the PTB7-HOMO/PC<sub>71</sub>BM-LUMO offset.<sup>[47]</sup> A reduction in charge build-up/recombination at the interface would lead to an increase in both  $J_{SC}$  and  $FF$ , which may occur as a result of using higher molecular weight polymer interlayers. Thus, we speculate that the higher molecular weight polymers provide better interfacial contact with the Ag electrode and/or enhanced electron mobility, relative to films

fabricated from lower molecular weight polymers. We are continuing efforts towards understanding the effects of CPZ molecular weight on polymer electronic properties and morphology as well as improved OPV device performance.



**Figure 4.** (a) Representative J-V curve of solar cells containing a ~5 nm thick layer of **PTBTSB-2**, between the active layer (PTB7:PC<sub>71</sub>BM) and Ag cathode; (b) Overall device metrics averaged over 18 devices, with error bars representing  $\pm 1$  standard deviation.

## Conclusions.

Ten different base stable ionic liquids were tested for their ability to solvate the Suzuki polycondensation of a zwitterionic sulfobetaine-thiophene monomer to form **PTSB-1**. CPZs of appreciable molecular weight (> 10 kDa) were obtained rapidly (2 hours) in the presence of air, precluding the necessity for volatile organic solvents, inert atmosphere, toxic phosphine ligands and phase transfer catalysts. The method presented was used to afford high molecular weight polymers of **PTSB-1** and **PTBTSB-2**, showing the versatility of the reaction conditions towards realizing polar conjugated polymers that have limited solubility in many solvents. This will prove useful in the design and synthesis of new conjugated polymers with orthogonal solubility to commonly used active materials in optoelectronics. **PTBTSB-2** samples of 22 and 35 kDa were cast as thin cathode modification layers in BHJ solar cells containing a stable Ag cathode, resulting in higher PCE values for the higher molecular weight CPZ interlayer.

## Experimental.

**Materials.** All ionic liquids were purchased from Io-li-tec (Ionic Liquids Technologies) and used without further purification. Sodium bromide (>99 %), silver trifluoroacetate (98%), LiF (99.99%), 1,2-dichlorobenzene (99.5%), and diiodooctane (98%) were purchased from Sigma Aldrich. Palladium(II) acetate (99+ %) was purchased from STREM Chemicals. Sodium carbonate (99 %) was purchased from Fisher Scientific. 2,5-bis-thiopheneboronic acid pinacol ester (**2**) (98 %, Combi-Blocks) was purified by column chromatography on silica with hexanes:ethyl acetate (9:1) as the eluent followed by recrystallization from hexanes. deuterium oxide (99.9%) and 2,2,2-trifluoroethanol-D<sub>3</sub> (99%) were purchased from Cambridge Isotope Laboratories. PTB7 was purchased from 1-Materials, Inc., and PCBM from American Dye Source, Inc. Hexanes, ethyl acetate and methanol were purchased from Fisher Scientific.

**Instrumentation.** <sup>1</sup>H-NMR spectra were recorded at 300 MHz and <sup>19</sup>F-NMR at 282 MHz on a Bruker-spectrospin. Molecular weights and dispersities ( $\bar{M}_w/\bar{M}_n$ ) were estimated by gel permeation chromatography (GPC) in sodium nitrate (0.1 M with 0.02 wt% of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) aqueous solution at 45 °C, calibrated against poly(ethylene oxide) standards, operating at 1.0 mL/min with an HP Series 1050 Pump, HP 1047A refractive index detector, and three Waters Ultrahydrogel linear columns (each 300 × 7.8 mm) for the PTB-1 samples and in 2,2,2-trifluoroethanol with 0.02 M sodium trifluoroacetate at 40 °C using an Agilent 1200 system equipped with an isocratic pump operated at 1 mL/min, a degasser, an Agilent 1260 infinity autosampler, one 50 mm × 8 mm PSS PFG guard column (Polymer Standards Service), three 300 mm × 7.5 mm PSS PFG analytical linear M columns with a 7 μm particle size (Polymer Standards Service), and an Agilent 1200 refractive index detector and Agilent 1200 VWD UV detector. Both systems were calibrated with poly(methyl methacrylate) standards. UPS measurements were performed on the Omicron Nanotechnology, Model ESCA+S, consisting of a helium discharge lamp (He I line, 21.2 eV) as the UV excitation source and a hemispherical SPHERA energy analyzer. All samples were negatively biased by -3V to compensate for the instrument work function difference repelling the low-kinetic energy electrons. The energy scales given in the spectra were shifted by 3 eV, removing the effect from negative bias. Polymer film thickness was determined by the surface profiler KLA Tencor, model Alpha-Step IQ.

**Device Fabrication and Testing.** The ITO-coated glass substrates (10 Ω/□, from Thin Film Devices, Inc.) were cleaned in ultrasonic bath using detergent, deionized water (twice), acetone and isopropanol for 10 minutes/step, then baked overnight and subjected to UV/Ozone for 15 minutes prior to film deposition step. PEDOT:PSS (H.C. Starck, I 4083) was spin-coated at 2000 rpm for 2 minutes and annealed at 150 °C for 15 minutes, and transferred to the glove box (N<sub>2</sub> atmosphere, < 1 ppm O<sub>2</sub>, < 1 ppm H<sub>2</sub>O) for device fabrication. A solution of PTB7 and PCBM (1:1.5 weight ratio) in 1,2-dichlorobenzene:1,8-diiodooctane (2.5 v% DIO) was stirred at 80 °C for ~1 day. The thickness of the active layer film after spin-coating was ~100-120 nm (determined by profilometry). DIO was removed under vacuum, and the devices were placed in a glove box for spin-coating of CPZs and thermal evaporation of LiF (1.5 nm) and Al (100 nm) through a shadow mask which defined the active device area of 0.06 cm<sup>2</sup>. Film thickness was measured by KLA-TENCOR Alpha-Step IQ Surface Profiler. Current-voltage (I-V) characteristics were measured using a Keithley 2400 source-meter under simulated AM1.5G irradiation using a 300 W Xe lamp solar

simulator (Newport 91160). The light intensity was adjusted with an NREL-calibrated Si reference solar cell and KG-5 filter. An aperture that exactly matched the device geometry defined the illuminated area. Device metrics are given as averages over 18 devices with error bars representing  $\pm 1$  standard deviation.

### Synthesis.

#### General Suzuki polycondensation procedure.

Palladium(II) acetate (1 mg, 0.0045 mmol), sodium carbonate (80 mg, 0.75 mmol), ionic liquid (0.75 g) and 2M NaBr (aq, 0.3 mL) were added to a 7 mL scintillation vial containing a magnetic stir-bar. The mixture was stirred at 100 °C for 5 minutes, followed by addition of monomers **1** (57.5 mg, 0.125 mmol) and **2** (42 mg, 0.125 mmol) (we note that the reaction works if all of the reagents are added prior to any heating). The reaction was stirred at 100 °C for 2 hours, then 1 mL of H<sub>2</sub>O was added and the polymer was precipitated into MeOH, giving a bright orange solid. Soxhlet extraction with MeOH was used to fully remove residual ionic liquid, suggested by a lack of fluorine signal in the <sup>19</sup>F-NMR spectra.

*Poly(thiophene-alt-thiophenemethylenesulfobetaine) (PTSB-1)* was obtained as a bright orange solid after lyophilization (35 mg, 82%). (GPC)  $M_n = 15,500$  g / mol,  $\bar{D} = 2.2$ ; <sup>1</sup>H NMR (300 MHz, 2,2,2-Trifluoroethanol-D<sub>3</sub>)  $\delta$  7.60 – 6.89 (br, 3H), 4.92 – 4.26 (br, 2H), 3.55 – 3.29 (br, 2H), 3.27 – 2.71 (br, 8H), 2.52 – 2.02 (br, 2H).

*Poly(benzothiadiazole-alt-thiophenebutylenesulfobetaine) (PTBTSB-2)* was obtained as a dark purple solid after lyophilization (50 mg, 90%). (GPC)  $M_n = 47,000$  g / mol,  $\bar{D} = 2.2$ ; <sup>1</sup>H NMR (300 MHz, 2,2,2-Trifluoroethanol-D<sub>3</sub>)  $\delta$  8.75 – 6.64 (br, 3H), 3.72 – 1.07 (br, 20H).

### Acknowledgements.

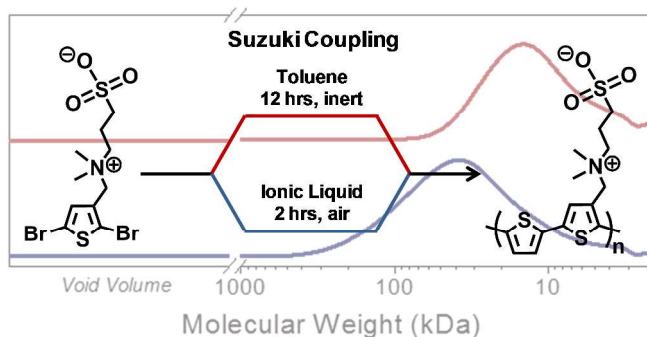
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### Notes and references

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Electronic Supplementary Information (ESI) available: [<sup>19</sup>F-NMR spectra, UPS, SEC and images of PTSB-1 in ILs]. See DOI: 10.1039/b000000x/

### Table of Contents Graphic.



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