Supporting information

Alcohol-Soluble Conjugated Polymers as Cathode Interlayers for All-Polymer Solar Cells

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1. Synthesis of Materials

Monomer Synthesis



Figure S1. Synthesis of monomer M1.

Synthesis of Monomer 1 (M1)

Compound **1** (5.0 g, 15.4 mmol) and KOH (4.3 g, 76.8 mmol) were added to a round bottom flask under nitrogen atmosphere. A solution of 1,3-dibromopropane (4.7 g, 23.1 mmol) in anhydrous DMSO (50 mL) was degassed and added in one portion. The mixture was stirred at 80 °C overnight. The reaction was quenched with water. The organic phase was extracted with diethyl ether (3×50 mL), washed with water (3×100 mL) and dried over anhydrous MgSO₄. After drying the crude product in a vacuum oven, it was precipitated from methanol and recrystallized once from methanol to yield **M1** as light yellow crystals (3.06 g, 35.1%). ¹H NMR (400 MHz, Chloroform-d) δ 7.52 (m, 6H), 3.13 (t, 4H), 2.12 (t, 4H), 1.11 (m, 4H). ¹³C NMR (101 MHz, Chloroform-d) δ 150.65, 138.93, 130.94, 126.14, 121.94, 121.44, 54.46, 38.49, 33.60, 26.93. (MALDI-TOF, m/z): [M+] calc: 565.81, found: 565.48.

Polymer Synthesis



Synthesis of PFBr. Monomer M1 (1.1319 g, 2.00 mmol), monomer M2 (1.2850 g, 2.00 mmol), tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (36.5 mg, 40 μ mol) and tri(o-tolyl)phosphine (P(*o*-Tol)₃) (48.6 mg, 160 μ mol) were dissolved in anhydrous toluene (20 mL) under nitrogen. 1 M K₃PO₄ (5 mL) and 5 drops of Aliquat 336 were added and the reaction mixture was heated to 80 °C with vigorous stirring for 72 h. After cooling to room temperature, the copolymer was precipitated by dropwise addition of the solution into methanol and was collected by filtration through a 0.45 μ m Teflon filter. The polymer was then extracted in a Soxhlet apparatus with petroleum ether, diethyl ether, acetone and chloroform. The chloroform fraction was purified by passing it though a short silica plug and precipitated from methanol. Finally, the copolymer was obtained by filtration through a 0.45 μ m Teflon filter and dried under vacuum at 40 °C overnight to afford a light yellow polymer (1.21 g, 76%).

Synthesis of PBzFN. Monomer M3 (59.0 mg, 0.25 mmol), monomer M4 (147.2 mg, 0.25 mmol), $Pd_2(dba)_3$ (4.5 mg, 5 µmol) and $P(o\text{-Tol})_3$ (6.0 mg, 20 µmol) were dissolved in anhydrous toluene (5 mL) under nitrogen. 1 M K₃PO₄ (1 mL) and 3 drops of Aliquat 336 were added and the reaction mixture was heated to 80 °C with vigorous stirring for 72 h. After cooling to room temperature, the copolymer was precipitated by dropwise addition of the solution into methanol and was collected by filtration through a 0.45 µm Teflon filter. The polymer was then extracted in a Soxhlet apparatus with petroleum ether, diethyl ether, acetone and chloroform. The chloroform fraction was purified by passing it though a short silica plug and precipitated from methanol. Finally, the copolymer was obtained by filtration through a 0.45 µm Teflon filter and dried under vacuum at 40 °C overnight to afford a light yellow polymer (39 mg, 38%).

Polymer Functionalization

Three of the CIM polymers were synthesized by post polymer functionalization from the precursor PFBr with pendant bromines (Figure 1) following previously reported literature procedures, with altered reactant ratios and reaction times.^[28,31] In the case of PFIm, no potassium iodide was used and tetra-n-butylammonium bromide (TBAB) was added instead.

Synthesis of PFN

PFBr (100 mg) was dissolved in chloroform (10 mL) and degassed for 30 min. A 2 M solution of Me₂NH (4 mL) was added and the mixture was refluxed overnight. The solution was diluted with 10 mL of chloroform and passed through a plug of neutral alumina. The solvent was removed *in vacuo*, and the polymer was dissolved in chloroform (2 mL) and precipitated from hexane. The brownish yellow polymer was dried in a vacuum oven at 40 °C overnight. (83.2 mg, 75.7%)

Synthesis of PFN(EtOH)₂

PFBr (100 mg) was dissolved in THF (20 mL) and degassed for 30 min. (EtOH)₂NH (5 mL) was added and the solution was refluxed overnight. The solution was diluted with THF (10 mL) and passed through a plug of neutral alumina. Most of the solvent was removed *in vacuo*, and the polymer was precipitated from hexane. The bright yellow polymer was dried in a vacuum oven at 40 °C overnight. (69.0 mg, 64%)

Synthesis of PFIm

PFBr (100 mg) was dissolved in THF (20 mL) and degassed for 30 min. 1*H*-imidazole (120 mg, 1.76 mmol), KOH (0.117 mg, 2.09 mmol) and TBAB (17 mg, 0.05 mmol) were dispersed in THF (2 mL) and stirred vigorously for 30 min. This mixture was added to the polymer solution in one portion and the reaction was refluxed overnight. Most of the solvent was removed *in vacuo*, and the polymer was precipitated from hexanes. The bright yellow polymer was dried in a vacuum oven at 40 °C overnight. (45.3 mg, 42.1%)

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2. Absorption spectra of the interfacial polymers



Figure S3. Normalized absorbance of the four interfacial polymers and the precursor polymer in a) chloroform solution b) as thin film.

3. Absorption spectra of the polymers in the active layer



Figure S4. Absorption of the active layer polymers in a) solution, and b) as thin film



4. Electrochemical properties

Figure S5. Square wave voltammograms for the four interfacial polymers and the precursor polymer.



Figure S6. Comparison of oxidation potential of the polymers with N(EtOH)₃.



5. Thermogravimetric analysis measurements

Figure S7. Thermal degradation of the four interlayer polymers and the precursor PFBr.