

ELECTRONIC SUPPLEMENTARY INFORMATION

Solution-processed bi-layer polythiophene-fullerene organic solar cells

Toon Ghoois,^a Olga Malinkiewicz,^b Bert Conings,^c Laurence Lutsen,^{a,d} Dirk J. Vanderzande,^{a,d} Henk J. Bolink^{*b} and Wouter Maes^{*a,d}

^a Institute for Materials Research (IMO-IMOMECE), Design & Synthesis of Organic Semiconductors (DSOS), Hasselt University, Agoralaan 1 - Building D, B-3590 Diepenbeek, Belgium. Fax: +32-11-268299; Tel: +32-11-268312; E-mail: wouter.maes@uhasselt.be

^b Instituto de Ciencia Molecular, Universidad de Valencia, C/Catedrático J. Beltrán 2, ES-46980 Paterna (Valencia), Spain. Fax: +34963543273; Tel: +34963544416; E-mail: henk.bolink@uv.es

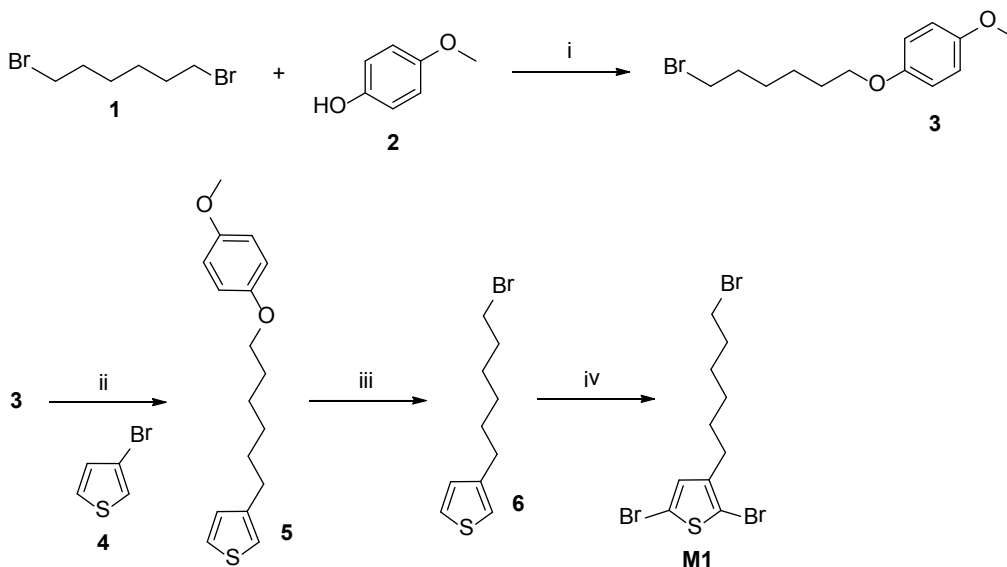
^c Institute for Materials Research (IMO-IMOMECE), Nanostructure Physics (NSP), Hasselt University, Universitaire Campus - Wetenschapspark 1, B-3590 Diepenbeek, Belgium.

^d IMOMECE Assoc. Lab., IMEC, Universitaire Campus - Wetenschapspark 1, B-3590 Diepenbeek, Belgium.

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1. Details on the monomer synthesis



Scheme S1 Synthesis of 2,5-dibromo-3-(6-bromohexyl)thiophene (**M1**): i. KO t Bu, MeOH/acetone, reflux; ii. a) Mg, Et $_2$ O, b) **4**, Ni(dppp)Cl $_2$, Et $_2$ O; iii. HBr, Ac $_2$ O; iv. NBS, THF.

1-(6-Bromohexyloxy)-4-methoxybenzene (3).¹ 4-Methoxyphenol (**2**) (20.0 g, 161 mmol) and potassium *tert*-butoxide (21.7 g, 193 mmol, 1.2 equiv) were dissolved in a mixture of MeOH (80 mL) and acetone (80 mL) and stirred for 30 min at rt. The reaction mixture was then added dropwise to a solution of 1,6-dibromohexane (**1**) (77.9 g, 322 mmol, 2 equiv.) in acetone (80 mL) at reflux temperature, and the reaction was further heated at reflux temperature until completion (as analyzed by TLC). The mixture was cooled down to rt and water was added. The product was extracted with diethyl ether and the organic layer was washed with brine. The organic layer was dried with MgSO $_4$, filtered and evaporated to dryness under reduced pressure. The unreacted 1,6-dibromohexane was removed by vacuum distillation. The pure product was recrystallized from MeOH and the resulting white crystals were dried under vacuum (32.6 g,

¹ R. Toyoshima, M. Narita, K. Akagi and H. Shirakawa, *Synth. Met.*, 1995, **69**, 289.

71%). ^1H NMR (300 MHz, CDCl_3): δ = 6.83 (s, 4H), 3.91 (t, J = 6.4 Hz, 2H), 3.77 (s, 3H), 3.43 (t, J = 6.7 Hz, 2H), 1.89 (q, J = 7.0 Hz, 2H), 1.77 (q, J = 6.7 Hz, 2H), 1.54–1.46 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ = 154.4, 153.9, 116.1 (CH), 115.3 (CH), 69.0 (CH_2), 56.4 (CH_3), 34.6 (CH_2), 33.4 (CH_2), 29.9 (CH_2), 28.6 (CH_2), 26.0 (CH_2); MS (EI): m/z = 286/288 (M^+).

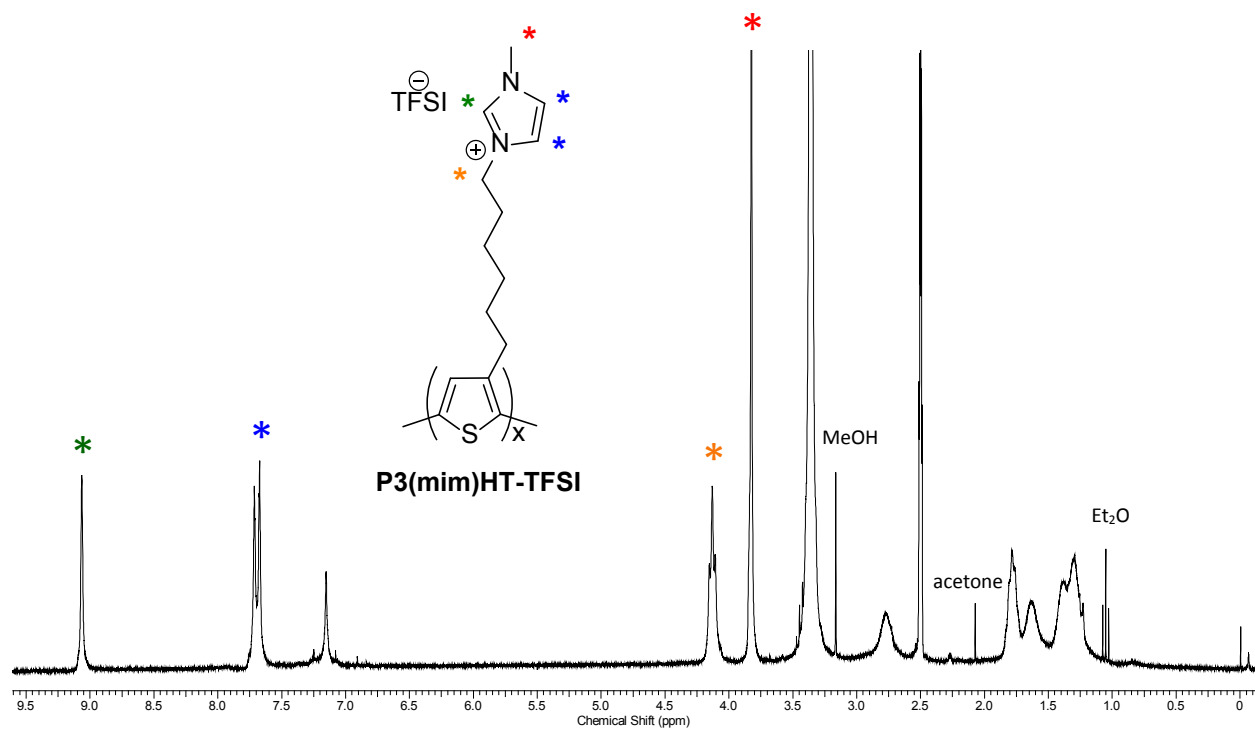
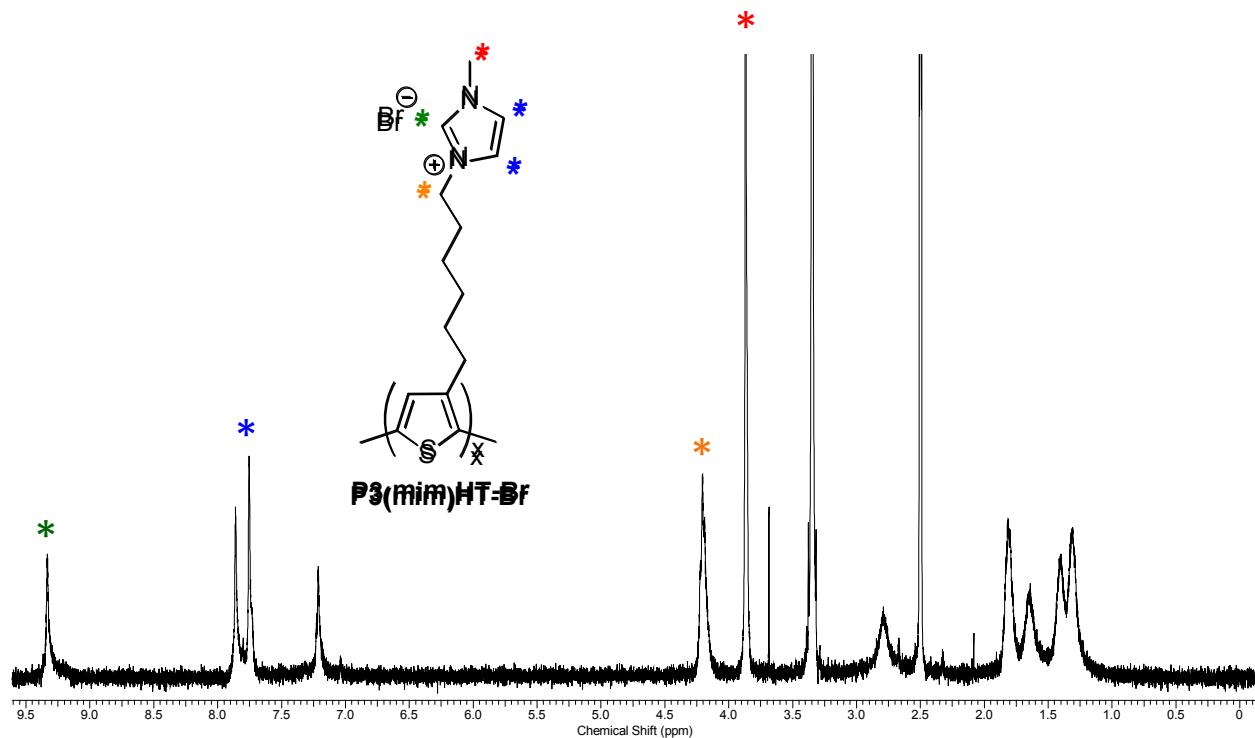
3-[6-(4-Methoxyphenoxy)hexyl]thiophene (5). 1-(6-Bromohexyloxy)-4-methoxybenzene (**3**) (10.57 g, 36.8 mmol, 1 equiv), dissolved in a minimum amount of anhydrous diethyl ether (50 mL), was added under inert atmosphere to a suspension of Mg turnings (0.97 g, 40 mmol, 1.3 eq.) in anhydrous diethyl ether (10 mL) at reflux temperature. The reaction mixture was further refluxed for 1 h. The Grignard solution was cooled down to rt and then transferred dropwise via a cannula to an ice-cooled mixture of $\text{Ni}(\text{dppp})\text{Cl}_2$ (4 mol%) and 3-bromothiophene (5.0 g, 30.7 mmol) in dry diethyl ether (15 mL). The reaction mixture was refluxed for 12–15 h and afterwards hydrolyzed with a mixture of HCl (10 mL of a 1 N solution) and ice-water (20 mL), followed by extraction with several portions of Et_2O . Drying of the combined organic phases with MgSO_4 , filtration and removal of the solvent under reduced pressure afforded an orange oil which solidified upon standing. The product was purified by crystallization from hexane to provide an off-white solid. The filtrate was evaporated and additionally purified via column chromatography (silica) with a 50/50 hexanes/ CH_2Cl_2 eluent mixture. Removal of the solvent gave the product as an off-white solid (overall yield 6.14 g, 69%). ^1H NMR (300 MHz, CDCl_3): δ = 7.23 (dd, J = 4.9 Hz and 3.0 Hz, 1H), 6.93–6.89 (m, 2H), 6.82 (s, 4H), 3.89 (t, J = 6.5 Hz, 2H), 3.75 (s, 3H), 2.63 (t, J = 7.6 Hz, 2H), 1.82–1.30 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3): δ = 154.3, 153.9, 143.7, 128.9 (CH), 125.8 (CH), 120.5 (CH), 116.1 (CH), 115.2 (CH), 69.2 (CH_2), 56.4 (CH_3), 31.1 (CH_2), 30.8 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 26.5 (CH_2); MS (EI): m/z = 290 (M^+).

3-(6-Bromohexyl)thiophene (6). Procedure as reported by Bäuerle et al.² ¹H NMR (300 MHz, CDCl₃): δ = 7.22 (dd, J = 4.8 and 2.9 Hz, 1H), 6.93–6.88 (m, 2H), 3.39 (t, J = 6.7 Hz, 2H), 2.62 (t, J = 7.7 Hz, 2H), 1.84 (q, J = 7.0 Hz, 2H), 1.62 (q, J = 7.6 Hz, 2H), 1.52–1.21 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 143.5, 128.9 (CH), 125.8 (CH), 120.6 (CH), 34.7 (CH₂), 33.4 (CH₂), 31.0 (CH₂), 30.8 (CH₂), 29.0 (CH₂), 28.6 (CH₂); MS (EI): m/z = 246/248 (M⁺).

2,5-Dibromo-3-(6-bromohexyl)thiophene (M1). 3-(6-Bromohexyl)thiophene (**6**) (2.62 g, 10.6 mmol) was dissolved in THF (100 mL), cooled to 0 °C and protected from light. NBS (4.34 g, 24.4 mmol, 2.3 equiv) was added portion wise and the mixture was stirred further at rt for 8 h in the absence of light. The reaction mixture was quenched by pouring it into an ice-cold solution of 1 M NaOH and the product was extracted with Et₂O. The organic layer was dried with MgSO₄, filtered and the solvent was evaporated under reduced pressure. The residue was purified on a silica plug with 50/50 hexanes/CH₂Cl₂ as the eluent. The pure fractions were collected and the solvent was removed under reduced pressure affording a colourless oil (3.9 g, 91%). ¹H NMR (300 MHz, CDCl₃): δ = 6.75 (s, 1H), 3.38 (t, J = 6.9 Hz, 2H), 2.49 (t, J = 7.7 Hz, 2H), 1.84 (q, J = 7.2 Hz, 2H), 1.54 (q, J = 7.7 Hz, 2H), 1.48–1.38 (m, 2H), 1.38–1.25 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ = 143.2, 131.4 (CH), 111.0, 108.6, 34.4 (CH₂), 33.1 (CH₂), 29.9 (CH₂), 29.8 (CH₂), 28.7 (CH₂), 28.4 (CH₂); MS (EI): m/z = 402/404/406/408 (M⁺).

² P. Bäuerle, F. Würthner and S. Heid, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 419.

2. ^1H NMR spectra of the ionic polythiophenes and the precursor polymer



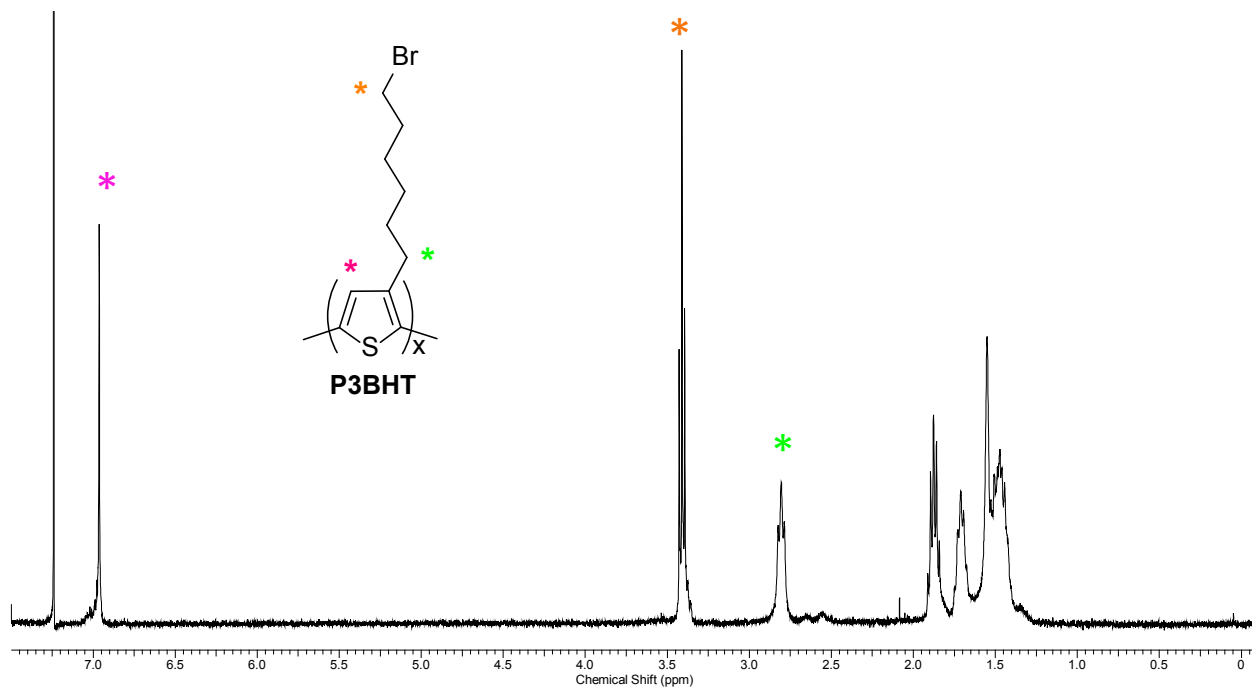


Fig. S1 ^1H NMR spectra of the ionic polythiophenes and the precursor polymer.

3. UV-Vis spectra of the ionic polythiophenes

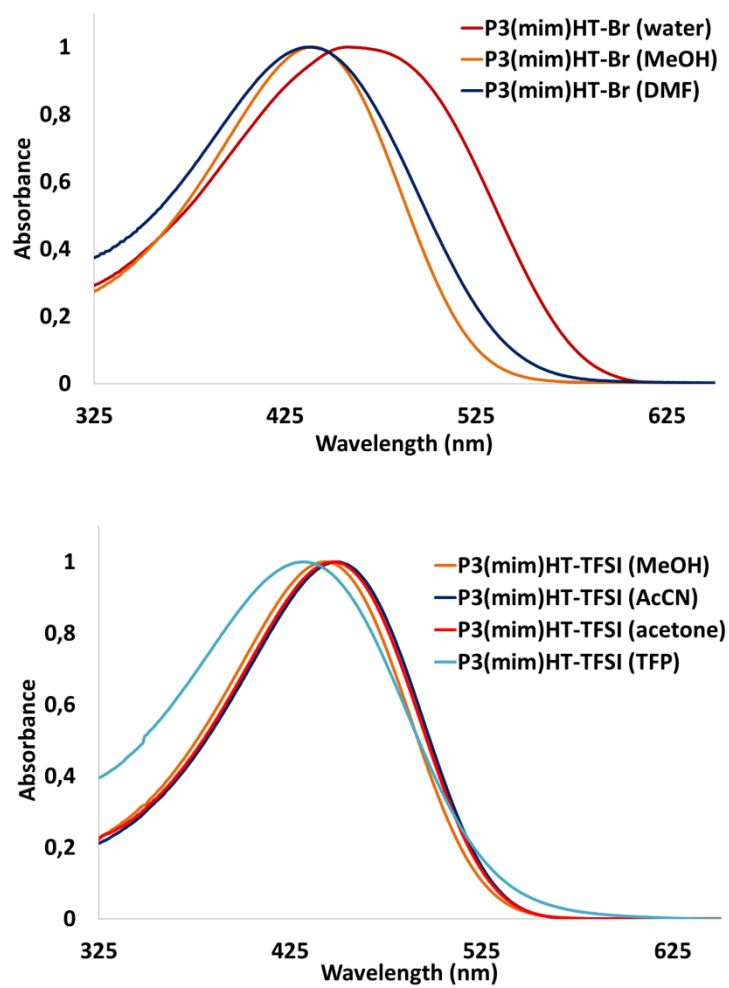


Fig. S2 UV-Vis spectra of the ionic polythiophenes in polar solvents.

4. Bi-layer integrity study

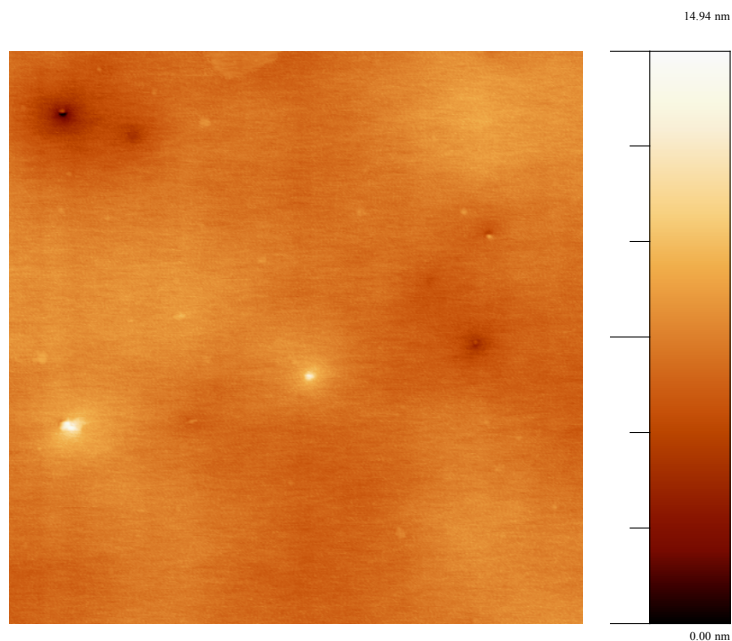


Fig. S3 AFM image of a **P3(mim)HT-TFSI** film (RMS roughness 0.8 nm).

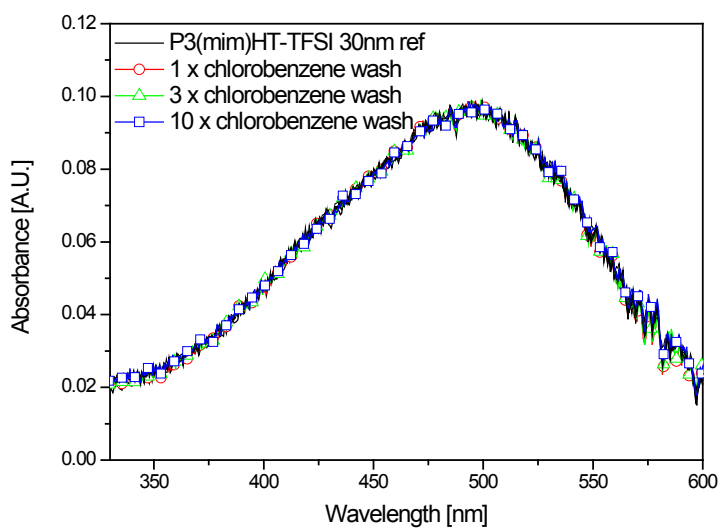


Fig. S4 Absorption spectrum of the **P3(mim)HT-TFSI** layer before and after chlorobenzene washes.

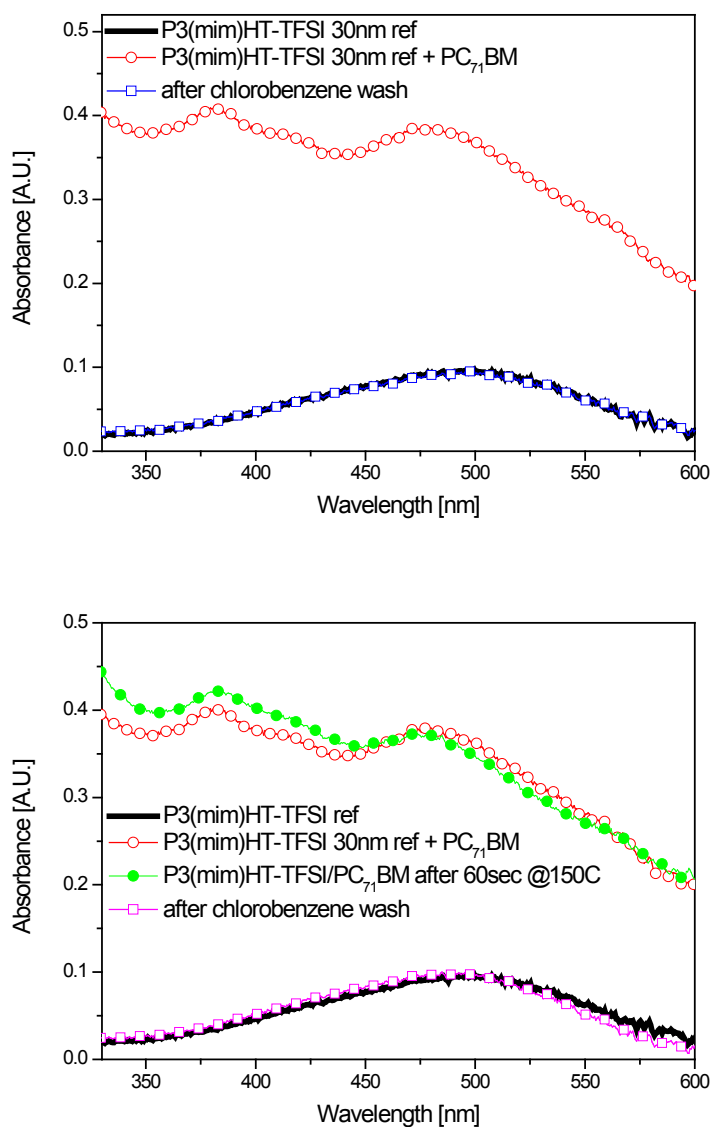


Fig. S5 Absorption spectra of **P3(mim)HT-TFSI** alone, **P3(mim)HT-TFSI** with PC₇₁BM on top, and the same **P3(mim)HT-TFSI** after removal of the PC₇₁BM layer by a chlorobenzene wash, either without heating step (top) or with short annealing of the **P3(mim)HT-TFSI/PC₇₁BM** bi-layer (bottom).

5. Reproducibility data for bi-layer devices based on P3(mim)HT-TFSI

Table S1 Reproducibility data for **P3(mim)HT-TFSI/PC₆₁BM** bi-layer devices.

P3(mim) HT-TFSI [nm]	PC₆₁BM [nm]	PCE [%]	FF [%]	V_{oc} [V]	J_{sc} [mA/cm²]
50	40	0.49	61	0.61	1.3
50	40	0.45	63	0.61	1.2
50	40	0.54	63	0.61	1.4
50	40	0.47	62	0.61	1.3
50*	40*	0.49*	62*	0.61*	1.3*
50	35	0.42	62	0.61	1.1
50	35	0.4	64	0.6	1
50	35	0.41	65	0.6	1.1
50	35	0.35	62	0.6	1
50*	35*	0.4*	63*	0.6*	1.1*
50	30	0.3	61	0.59	0.85
50	30	0.33	61	0.6	0.9
50*	30*	0.32*	61*	0.6*	0.9*
50	50	0.41	64	0.6	1.1
50	50	0.42	66	0.59	1
50*	50*	0.41*	65*	0.6*	1*
50	60	0.23	60	0.61	0.61
50	60	0.31	60	0.61	0.84
50*	60*	0.27*	60*	0.61*	0.72*

* Average values.

Table S2 Reproducibility data for **P3(mim)HT-TFSI/PC₇₁BM** bi-layer devices.

P3(mim) HT-TFSI [nm]	PC₇₁BM [nm]	PCE [%]	FF [%]	V_{oc} [V]	J_{sc} [mA/cm²]
40	40	1.5	55	0.65	4.3
40	40	1.3	56	0.66	3.5
40	40	1.8	55	0.64	5.2
40	40	1.6	56	0.65	4.3
40	40	1.7	59	0.65	4.5
40	40	1.5	60	0.65	3.9
40	40	1.6	57	0.64	4.4
40	40	1.5	60	0.65	3.9
40	40	1.5	56	0.66	4
40	40	1.4	57	0.66	3.8
40	40	1.9	57	0.65	5.1
40	40	1.6	56	0.66	4.2
40*	40*	1.6*	57*	0.65*	4.26*

* Average values.

6. Absorption data for bi-layer devices using different P3(mim)HT-TFSI thicknesses

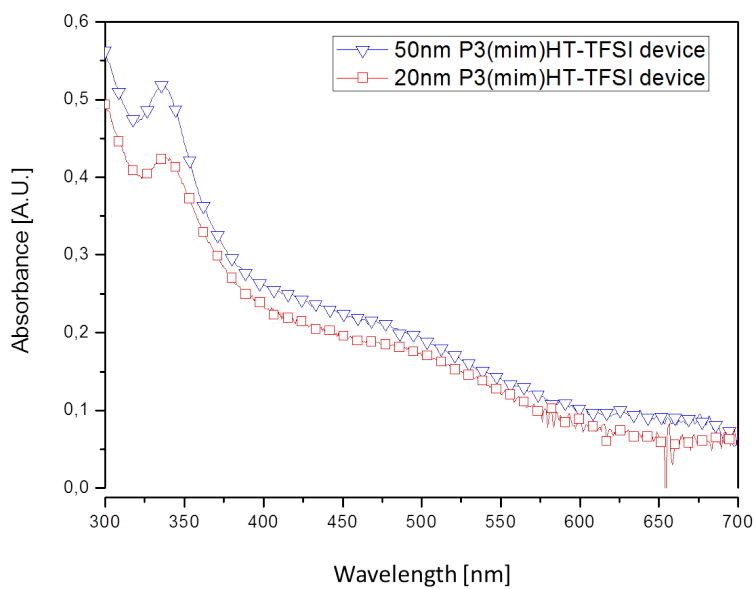


Fig. S6 Absorption versus wavelength for bi-layer devices using different P3(mim)HT-TFSI thicknesses.

7. Transfer matrix optical simulation

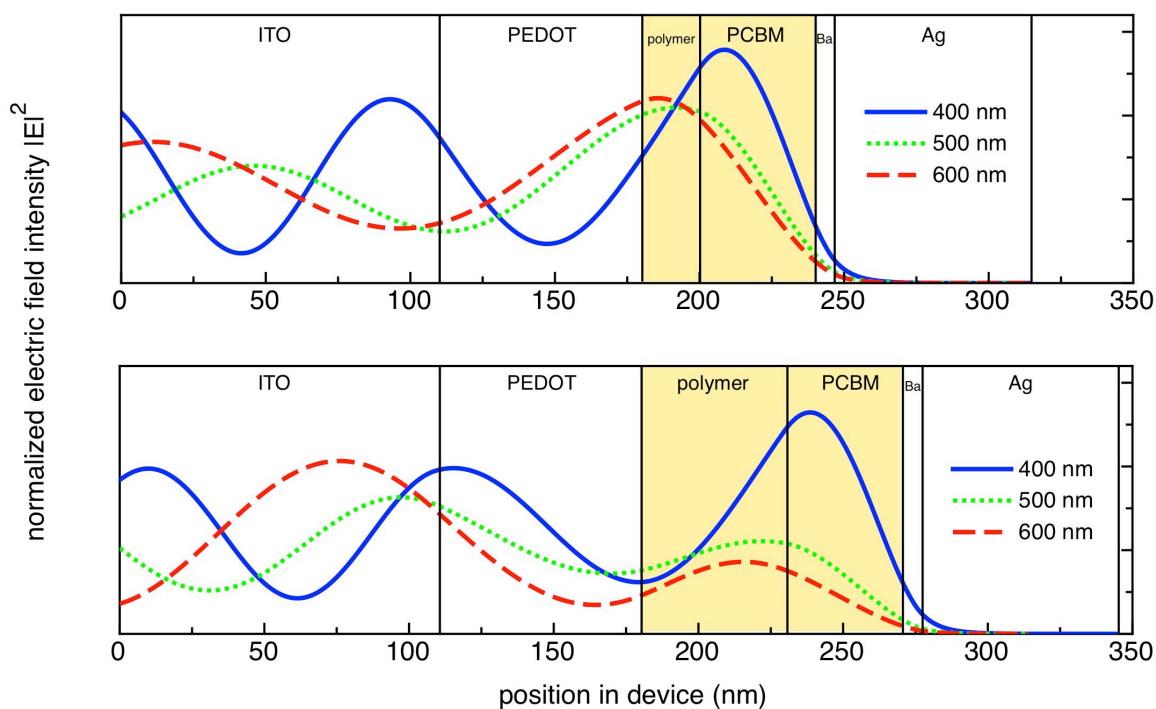


Fig. S7 Normalized electric field intensity for 400, 500 and 600 nm light, inside a device stack that contains a 20 nm (top) and 50 nm (bottom) polymer layer, as calculated with the transfer matrix optical simulation Matlab package provided by the McGehee group (<http://www.stanford.edu/group/mcgehee/transfermatrix/index.html>).³ The active layer (polymer + PC₆₁BM) is highlighted in yellow.⁴

³ G. F. Burkhard, E. T. Hoke and M. D. McGehee, *Adv. Mater.*, 2010, **22**, 3293.

⁴ As precise optical parameters (refractive index) are not available yet for the **P3(mim)HT-TFSI** polymer, an approximation was made using standard P3HT as the polymer donor material.