**SUPPORTING INFORMATION**

# A [3,2-*b*]thienothiophene-*alt*-benzothiadiazole copolymer for photovoltaic applications : design, synthesis, material characterization and device performances

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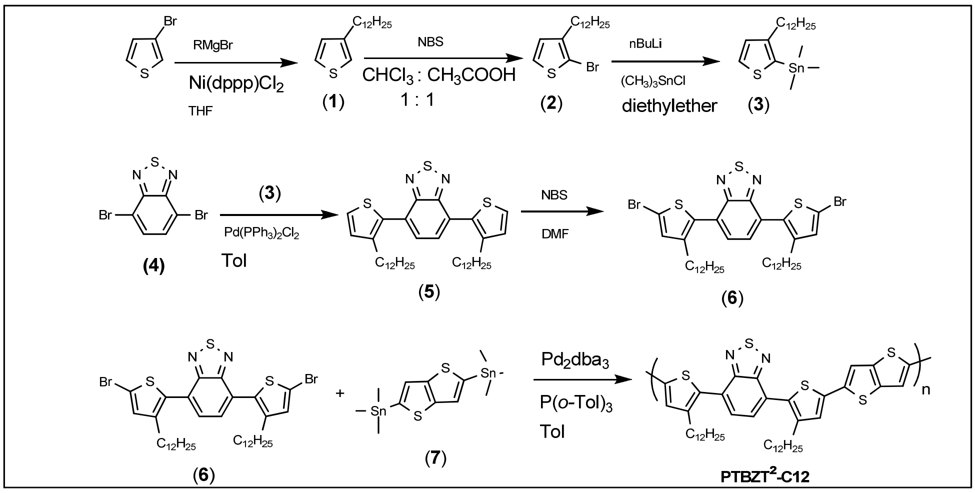
## Experimental details for material characterizations and device elaboration

### Material characterizations

**$^1$H, $^{13}$C NMR** spectra were recorded on a Bruker 300 UltrashieldTM 300 MHz NMR spectrometer and a Bruker 400 UltrashieldTM 400 MHz NMR spectrometer, with an internal lock on the 2H-signal of the solvent ($CDCl_3$).
**Gel permeation chromatography** measurements were performed in chloroform (HPLC grade) with two PL-gel 5 $\mu$m mixed-C, a 5 $\mu$m 100 Å, and a 5 $\mu$m Guard columns in a Shimadzu LC-10AD liquid chromatograph equipped with a Shimadzu RID-10A refractive index detector and a Shimadzu SPD-M10A diode array (UV) detector.
**UV-visible absorption spectroscopy** measurements were done using a Shimadzu UV-2101 spectrophotometer. The PTBzT$^2$-C12 absorption spectra were measured in solution and in spin-coated thin films.
**Photoluminescence spectra** were measured on a SPEX Florolog-2 spectrofluorometer and a B&WTEK CCD array spectrometer using an 532 nm excitation wavelength.
**Cyclic voltammetry analyses** of polymers were carried out with a BioLogic VSP potentiostat using platinum electrodes at scan rates of 50 mV/s. The measurements were performed on thin films drop-cast from chloroform solutions onto a platinum working electrode. We used a Pt wire counter electrode and a $Ag/Ag^+$ reference electrode in a 0.1 mol.L$^{-1}$ solution of tetrabutylammonium perchlorate in acetonitrile. Ferrocene was used as internal standard to convert the values obtained in reference to $Ag/Ag^+$ to the saturated calomel electrode scale (SCE).
**Thermogravimetric analyses** were performed on a Hi-Res TGA 2950 apparatus from TA Instruments. The analyses were carried out under a mixture of 75% $N_2$ and 25% $O_2$ at a heating rate of 20 °C min$^{-1}$.

### Materials

Tetrahydrofuran (ACS grade) was distilled over sodium, while toluene (ACS grade) and *N,N*-dimethylformamide (ACS grade) were distilled over $CaH_2$, prior to use. All other chemicals were purchased from Aldrich and used without further purification. The synthesis of 4,7-dibromobenzothiadiazole[1] **4** and 2-5-bis-trimethylstannyl-thieno[3,2-*b*]thiophene[2] **7** have been described previously.



**Scheme 1** Synthetic route for PTBzT$^2$-C12

**3-dodecylthiophene (1).** To magnesium turnings (9.70 g, 0.40 mol) in dry THF (5 mL) was added 1-bromododecane (89 mL, 0.37 mol) in THF (90 mL) at a rate sufficient to maintain reflux. The reflux was maintained for 1 h after the end of addition. The Grignard reagent was then added dropwise to a solution of 3-bromothiophene (50.00 g, 0.31 mol) and Ni(dppp)$Cl_2$ (3.07 mmol) in THF (180 mL). Finally, the mixture was refluxed under argon and stirred overnight. Then, the mixture was hydrolyzed by careful addition of water followed by 38% aqueous HCl and extracted with methylene chloride. The brown organic phase was washed with saturated sodium chloride and then with water and dried over sodium sulfate. After removing the solvent under reduced pressure, the crude product was distilled to provide a colorless oil. (bp 111-117 °C at 1.3 mbar). (54.5 g, 70%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 7.26 (dd, 1H, $^3J$ = 4.9 Hz, $^4J$ = 2.1 Hz), 6.95 (m, 2H), 2.65 (t, 2H, $^3J$ = 7.5 Hz), 1.65 (q, 2H, $^3J$ = 7.4 Hz, $^3J$ = 7.3 Hz), 1.30 (m, 18H), 0.90 (t, 3H, $^3J$ = 7.0 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ = 143.25, 128.29, 125.03, 119.79, 32.03, 30.67, 30.38, 29.79, 29.78, 29.76, 29.72, 29.59, 29.47, 22.79, 14.19.

**2-bromo-3-dodecylthiophene (2).** To a solution of 3-dodecylthiophene (30 g, 0.12 mol) in chloroform (135 mL) and acetic acid (135 mL) was added *N*-bromosuccinimide (NBS) (20.91 g, 0.12 mol) dropwise, in the dark and the mixture was stirred for 1 h. Then, it was extracted with chloroform and the organic phase washed with potassium hydroxide (10% wt) and water and dried over sodium sulfate. The crude product was distilled to provide a colorless oil. (bp 156 °C at 1.3 mbar). (33.8 g, 86%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 7.20 (d, 2H, $^3J$ = 5.6 Hz), 6.81 (d, 2H, $^3J$ = 5.6 Hz), 2.58 (t, 2H, $^3J$ = 7.4 Hz), 1.59 (q, 2H, $^3J$ = 7.3 Hz, $^3J$ = 7.3 Hz), 1.28 (m, 18H), 0.90 (t, 3H, $^3J$ = 6.9 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ = 141.99, 128.23, 125.10, 31.92, 29.71, 29.63, 29.56, 29.40, 29.34, 29.21, 22.68, 14.10.

**2-(trimethylstannyl)-3-dodecylthiophene (3).** Under an argon atmosphere, a solution of 2-bromo-3-dodecylthiophene (4.00 g, 12.07 mmol) in THF was cooled to -78°C. Then, *n*BuLi 2.5 M in hexane (5.3 mL, 13.28 mmol) was added dropwise and the reaction was stirred at -78°C for 2 h. Then, trimethyltin chloride 1 M in THF (18.1 mL, 18.11 mmol) was added dropwise. The cooling bath was removed and the mixture was stirred under argon overnight at room temperature. Water was then added under vigorous stirring. The mixture was extracted with diethyl ether and the organic phase washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure and was further dried under high vacuum providing the desired compound (4.5 g, 90%). It should be noted that, although slightly contaminated with 3-dodecylthiophene, this monostannylated compound was used without further purification. $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 7.54 (d, 1H, $^3J$ = 4.7 Hz), 7.10 (d, 1H, $^3J$ = 4.7 Hz), 2.64 (t, 2 H, $^3J$ = 7.7 Hz), 1.58 (m, 2H, $^3J$ = 7.6 Hz), 1.28 (m, 18H), 0.91(t, 3H, $^3J$ = 6.9 Hz), 0.39 (s, 9H ).

**4,7-bis(3-dodecylthiophen-2-yl)-benzothiadiazole (5).** 4,7- dibromobenzothiadiazole (2.13 g, 7.24 mmol) and 2-(trimethylstannyl)-3-dodecylthiophene (9.02 g, 21.73 mmol) were dissolved in dry toluene (75 mL). Then, $Pd(PPh_3)_2Cl_2$ (0.254 g, 0.362 mmol) was added and the reaction mixture was stirred at 110 °C for 48 h under argon atmosphere. Then, the reaction mixture was filtered through a pad of celite and the toluene solution was evaporated and dried under high vacuum. The crude product was purified by column chromatography on silica gel with cyclohexane/toluene 9:1

as eluent, to give compound **5** as an orange solid (1.5 g, 32.5%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 7.67 (s, 1H), 7.47 (d, 2H, $^3$J = 5.2 Hz), 7.14 (d, 2H, $^3$J = 5.2 Hz), 2.68 (t, 2H, $^3$J = 7.6 Hz), 1.62 (q, 2H, $^3$J = 7.5 Hz, $^3$J = 7.3 Hz), 1.26 (m, 18H), 0.89 (t, 3H, $^3$J = 7.0 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ = 154.44, 141.85, 132.33, 130.03, 129.37, 127.62, 125.99, 32.06, 30.86, 29.81, 29.77, 29.68, 29.59, 29.53, 29.49, 22.82, 14.26.

**4,7-bis(5-bromo-3-dodecylthiophen-2-yl)-benzothiadiazole (6).** Compound **5** (1.50 g, 2.36 mmol) was solubilized in DMF (60 mL) under argon in the dark. *N*-bromosuccinimide (NBS) (0.84 g, 4.72 mmol) was added portionwise. The resulting solution was stirred at room temperature under argon overnight. Water (240 mL) and diethylether (250 mL) were added and the resulting solution was stirred for 2 h. The organic phase was separated from the water phase and extracted with brine (3 x 100 mL). The organic phase was dried with sodium sulfate, filtered and the solvent evaporated under reduced pressure and further dried under high vacuum. The yellow-greenish solid formed was washed with methanol, filtered and dried under high vacuum, to give compound **6** as a greenish solid (1.64 g, 87%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 7.62 (s, 1H), 7.08 (s, 1H), 2.63 (t, 2H, $^3$J = 7.7 Hz), 1.62 (q, 2H, $^3$J = 6.9 Hz, $^3$J = 8.2 Hz ), 1.28 (m, 18H), 0.90 (t, 3H, $^3$J = 6.9 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ = 154.08, 142.60, 133.71, 132.14, 129.83, 126.78, 113.34, 32.07, 30.66, 29.81, 29.78, 29.65, 29.56, 29.49, 22.83, 14.26.

Elemental analysis found : C, 56.9; H, 6.75; S, 13.75; Br, 18.62; N, 3.61. Calc. for $C_{38}H_{54}Br_2N_2S_3$ : C 57.4; H, 6.85; S, 12.1; Br, 20.1; N, 3.5.

**Poly[4,7-bis(3-dodecylthiophen-2-yl)benzothiadiazole-*co*-thieno[3,2-*b*]thiophene] (PTBzT²-C12).** 2-5–bis-trimethylstannyl-thieno[3,2-*b*]thiophene **7** (0.36 g, 0.77 mmol) and 4,7-bis(5-bromo-3-dodecylthiophen-2-yl)-benzothiadiazole **6** (1.00 g, 0.77 mmol) were dissolved in dry toluene (45 mL). Then, tris(dibenzylideneacetone)dipalladium(0) ($Pd_2dba_3$) (0.02 eq) and tri-*o*-tolyl-phosphine (P(*o*-tol)$_3$) (0.08 eq) were added and the reaction mixture was stirred at 110 $^o$C under argon atmosphere for 72 h. Then, the toluene solution was evaporated, the mixture was solubilised in $CHCl_3$ and filtered through a pad of celite. The polymer was purified by precipitation in methanol, filtered and washed on Soxhlet apparatus with methanol, cyclohexane and chloroform. The chloroform fraction was evaporated under reduced pressure and the polymer was precipitated in methanol, filtered and finally dried under high vacuum, providing a film with a metallic shine (409 mg, 57.4%).

$^1$H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.72 (s, 1H), 7.41 (s, 1H), 7.26 (s, 1H), 2.71 (m, 2H), 1.71 (m, 2 H,), 1.27 (m, 18H), 0.89 (m, 3 H).

## Photovoltaic cells:

**Bulk heterojunction devices** were elaborated from PTBzT$^2$-C12 blended with $C_{61}$-PCBM (purchased from Solenne BV). The structure of the photovoltaic devices was glass/ITO/PEDOT:PSS/PTBzT$^2$-C12:PCBM/Al with four diodes (active area of 9 mm²) on each device. The Indium Tin Oxide (purchased from PGO, Precision Glass&optics) coated glass substrates with a surface resistance lower than 20 Ω/sq and a ITO thickness of 110 nm, were cleaned by ultrasonic treatment, in acetone, isopropyl alcohol, and deionised water sequentially. Subsequently the substrates were cleaned for 15 minutes in an ultra-violet ozone system and highly conductive polyethylenedioxythiophene/polystyrenesulphonate PEDOT:PSS (Baytron PS) was spincoated (2500 rpm: 40 nm) from an aqueous solution (after passing a 0.45 $\mu$m nylon filter). The substrates were dried for 30 minutes at 120°C under vacuum and then transferred to a nitrogen filled glove box to spin-coat the active layer. The anhydrous dichlorobenzene solutions comprising PTBZT$^2$-C12:PCBM were stirred at 40°C for 24 hours and finally heated at 70°C and stirred for 6 hours before deposition (without any filtration) by spin-coating. Unless otherwise stated, the solution had a total concentration of 40 mg/mL with a relative weight concentration of PTBzT$^2$-C12:PCBM ranging from 1:0.5 to 1:4. Finally, a 80 nm thick aluminium layer was thermally evaporated and used as cathode.

**Current density versus Voltage (J-V) characteristics** were measured using an Agilent 4155B source measurement unit. The Oriel 150 W AM1.5 solar simulator using a filtered Xe lamp was calibrated before each measurement with a THORLABS optical power meter.

**External Quantum Efficiency** measurements were carried out with an Oriel 75 W lamp using a Spectral Products Dk 120 monochromator. The emission spectrum of the system was calibrated using an OLM 130 CHORUS reference photodiode.

## Additionnal results

### Photovoltaic performances as a function of the polymer:fullerene mass ratio:

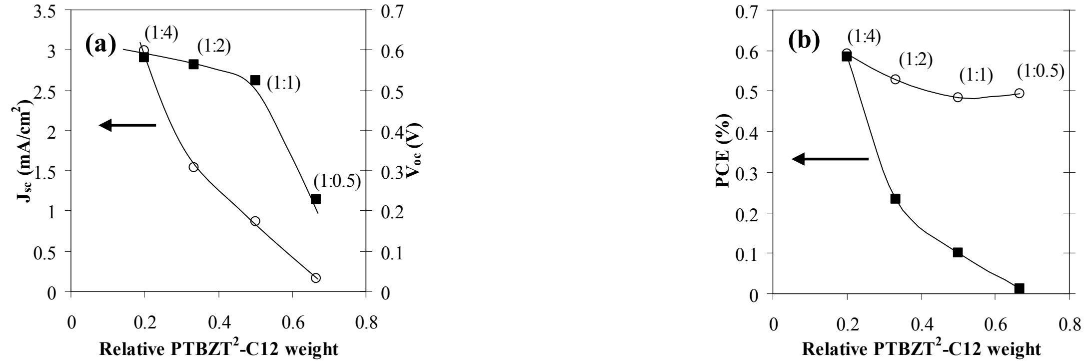


**Fig 1** (a) Evolution of the average values of Jsc (open circles) and Voc (closed squares) as a function of the relative PTBzT2-C12 weight. (b) Evolution of the average values of FF (open circles) and PCE (closed squares) as a function of the relative PTBzT2-C12 weight. The PTBzT2-C12:PCBM weight ratio are included in the figure.

### Active layer thickness versus polymer:fullerene mass ratio:

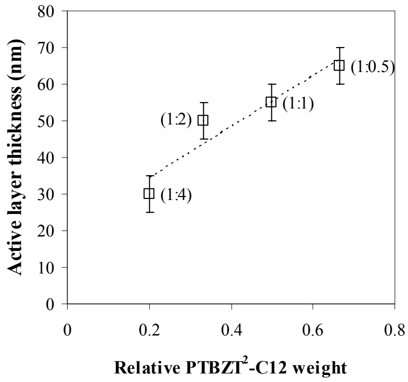


**Fig.2** Evolution of the thickness of the active layer as a function of the relative PTBzT$^2$-C12 weight. The thickness uncertainty is equal to 5 nm and the PTBzT$^2$-C12:PCBM ratio are included in the figure.

### Photovoltaic performances of a 1:4 device as a function of the active layer thickness:

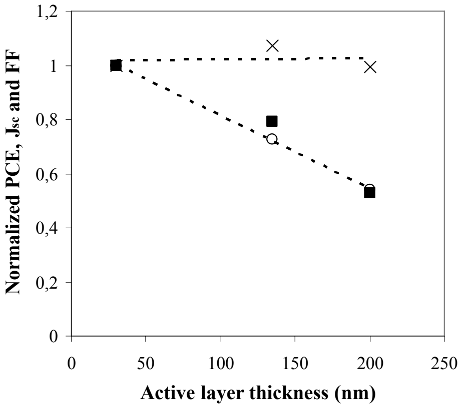


**Fig.3** Evolution of the PCE (closed squares), $J_{sc}$ (open circles) and FF (crosses) as a function of the active layer thickness for a constant PTBzT$^2$-C12:PCBM relative weight ratio of 1:4. The values for PCE, FF and $J_{sc}$ were normalized relative to their values for an active layer thickness of 30 nm. For a 30 nm thick active layer, the PCE is equal to 0.6 %, the $J_{sc}$ is equal to 3 mA/cm$^2$ and the FF is equal to 29 %.

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[2] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee and M. F. Toney, Nat. Mater., 2006, **5**, 328-333.