Supplementary information

Synthesis and photophysical properties of regioregular low bandgap copolymers with controlled 5-fluorobenzotriazole orientation for photovoltaic application

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Experimental details

All chemicals and reagents were grade and purchased from Aldrich or Acros companies and used without further purification. Toluene tetrahydrofuran were freshly distilled before use. 4,4'-Bis(2-ethylhexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole (M1) [1] 2-hexyl-4,7-dibromo-5-fluorobenzo-1,2,3-triazole (M2) [2] was preparation according to a report literature.

¹H NMR and ¹³C-NMR spectra were recorded at 400 MHz and 100 MHz on Bruker AVANCE spectrometer using CDC₃ as the solvent and tetramethlsilane (TMS) as the internal standard. The elemental analysis was performed with an Elementar Vario EL III element analyzer for C, H, N, S determination. Absorption spectra were measured with a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. The molecular weights of the polymers were measured by GPC method on Waters 515-2410 with polystyrenes as standard and chloroform as an eluent. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 in a nitrogen atmosphere and a heating rate of 10°Cmin^{-1.}The DSC analysis was performed on a DSC Q600 under nitrogen atmosphere at a heating rate of 10°Cmin^{-1.} Cyclic votammetry was performed under an inert atmosphere at a scan 0.1Vs⁻¹ and 0.1M Bu₄NPF₆ in acetonitrile as the electrolyte. An ITO glass slide covered with a thin layer polymer (20nm) was used as the working electrode. The counter and reference electrode were a Pt wire and Ag/Ag^{+,} respectively. All potentials were referenced against Fc/Fc⁺. The redox potential of the F_c/F_c^{+.} Internal reference is 0.4V vs Ag/Ag⁺.

5-difluorobenzene-1,2-diamine (2) [2]. 5-fluoro-2-nitroaniline (1) (4.496 g, 0.0288 mol) was dissolved in concentrated HCl (150 mL). At 0^oC tin (16.56 g, 0.140 mol) was added in small portions over 15 minutes. The reaction mixture was stirred at room temperature until all the tin was dissolved, and was further stirred for another one hour after which it was refrigerated overnight. The reaction mixture was poured into deionized water and a solution of NaOH (4 M) was added gradually until the solution reached pH 10. The organic phase was extracted with ethyl acetate (4 x 100 mL), washed with water (4 x 100 mL), and dried over anhydrous MgSO₄. The solution was concentrated in vacuum to obtain 2.54 g of yellow crystals (70%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 6.75-6.60 (m, 1H), 6.52-6.40 (m,2H), 3.31 (s,4H)

5-Fluorobenzo[*c*][1,2,5]thiadiazole(3)[2]. In a three-neck round-bottom flask 4-fluoro-1,2-benzenediamine (2) (5.5 g, 43.6 mmol) was fully dissolved in chloroform (500 mL) and triethylamine (30 mL). Thionyl chloride (7 mL, 96.0 mmol) was added dropwise via syringe. The solution stirred at 80 °C overnight. The reaction was allowed to cool and 250 mL of deionized water was added. The mixture was transferred to a separatory funnel and washed several times with water. The organic phase was collected and dried over magnesium sulfate. The solution was filtered, concentrated and used directly. Recovered yield: 4.75 g (70 %). ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.15-7.95 (m, 1H), 7.70-7.55 (m, 1H), 7.50-7.40 (m, 1H)..¹⁹F NMR (100 MHz, CDCl₃, δ ppm): - 9.37 (s, 1F).

4,7-Dibromo-5-fluorobenzo[*c*][**1,2,5]thiadiazole** (**4**) [**2**]. A round-bottom flask was charged with **3** (2.23 g, 14.5 mmol) followed by 48 % hydrobromic acid (30 mL). Molecular bromine (7.47 mL, 145 mmol) was added dropwise and the reaction refluxed

for 48 h. The reaction was allowed to cool to room temperature and diluted with chloroform and deionized water. The biphasic mixture was transferred to a separatory funnel and washed several times with water, rinsed with saturated sodium sulfite and rinsed with saturated sodium bicarbonate. Organics were collected and dried over magnesium sulfate. The solution was filtered and concentrated with silica. The compound was purified by flash column chromatography using a hexanes / chloroform gradient. Isolation of pure fractions afforded a white solid. Yield: 2.58g (57 %). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, 1H, J = 8.4 Hz).

3,6-Dibromo-4-fluoro-1,2-phenylendiamine (5)[2]. 4,7-dibromo-5-fluoro-2,1,3benzothiadiazole (4) (5g, 0.016mol) was dissolved in ethanol (150ml), then sodium borohydride (12.1g, 0.32mol) was added portion wise at 0°C and the reactants were stirred for 20h at room temperature. After evaporation of the solvent 160ml water was added , and the mixture was extracted with ethyl acetate. The extract was washed with brine and dried over MgSO₄. Residue was purified by column chromatography on silica gel using hexane/ethyl acetate (25:1) mixture as eluent to afford 3,6-dibromo-4-fluoro-1,2-phenylendiamine (3.5g) a pale solid in 78% yield. Elemental analysis: C₆H₅Br₂N₂F (%). Calcd. C: 25.38; H: 1.78; N: 9.87; Found C: 24.29; H: 1.81; N: 10.14; ¹H NMR (400 MHz, CDCl₃, δ ppm): 6.81 (d, 1H), 3.86(s, 4H).

6-Fluorobenzo-1,2,3-triazole, and 5- fluorobenzo-1,2,3-triazole (6)[2]. In a 150mL round bottom flask 3,6-dibromo-4-fluoro-1,2-phenylendiamine (**5**) (2.4g, 8mmol) was dissolved in 100 mL of AcOH at room temperature. A solution of NaNO₂ (2.76 g, 40 mmol) in 29 mL of H₂O was added within 20 min. The mixture was stirred at room temperature for 1h and precipitated into ice water. The resulting brown solid was filtered and recrystallized from water, and used for next step without further purification. ¹H NMR (400 MHz, acetone-*d*₆, δ ppm): 7.74 (d, 1H), 15.63 (s, 1H).

2-(Hexyl)-4,7-dibromo-5-fluorobenzo-1,2,3-triazole (M2)[2]. The crude fluorobenzo-1,2,3-triazole (52.28 g, 177.3 mmol), potassium *tert*-butoxide (201.0 g, 179 mmol), and 1-bromohexane (29.56 g, 179 mmol) were dissolved in methanol (445 mL) under argon

atmosphere. The reaction mixture was refluxed for 48 h and then poured into a saturated NH₄Cl aqueous solution. The mixture was extracted with methylene dichloride for three times, washed with deionized water for three times. The combined organic extractions were dried over anhydrous MgSO₄, and the solvent was evaporated off under reduced pressure. The compound 7 was purified by column chromatography (silica gel; eluent: methylene dichloride-hexane = 2:1, v/v) and was obtained as pale-yellow solid with a 20% yield. ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.48 (d, 1H), 4.76 (t, 2H), 2.14 (m, 2H), 1.14 (m, 6H), 0.89 (t, 3H).



Figure S1. 1H NMR spectrum of M2.

4,4'-Bis(2-ethylhexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole (M1)[1]. A solution of n-BuLi (40 ml, 62.85 mmol, 1.6M, 2.2 eqv) was slowly added dropwise to a solution of 4,4'-bis(2-ethylhexyl)-5,5'-dibromo-dithieno[3,2-b:2',3'-d]silole (16.473 mmol, 28.57 eqv) in 400 ml of dry THF at -80°C. After the addition was completed, the reaction mixture was stirred at that temperature for additional 40 min, then a solution of Cl-SnMe₃ (13.67 g, 68.6 mmol, 2.4 eqv) was added, the mixture was allowed to warm to room temperature, and stirred for 2 h. Water (300 ml) was added, layers were separated, water phase extracted with ethter. Combined organic phases were washed with water,

dried over MgSO₄, filtrated and evaporated to dryness. The product was used without further purification. The yield is 20 g (94%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.13 (s, 1H), 1.50-1.00 (m, 9H), 1.00-0.70 (m, 9H), 0.43 (t, 9H). ¹³C NMR (150 MHz, CDCl₃, δ ppm): 154.69 (br. m), 143.90 (t), 137.94 (br. m), 137.42 (br. s), 35.93, 35.63, 28.99, 28.90, 23.05, 17.82, 14.25, 10.90, 8.14 (t).



Figure S2 ¹H NMR spectrum of 4,4'-bis(2-ethylhexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole (**M1**).



Figure S3 ¹³C NMR spectrum of 4,4'-bis(2-ethylhexyl)-5,5'-bis(trimethyltin)dithieno[3,2-b:2',3'-d]silole (**M1**)

2,6-Bis(7-bromo-6-fluoro-2-hexyl-2H-benzotriazol-4-yl)-4,4-bis(2-ethylhexyl)-4H-

silolo[3,2-*b*:4,5-*b*']dithiophene (M3). A mixture of compound M1(4.0 g, 5.374 mmol), compound M2 (5.093 g, 13.435 mmol) and Pd(PPh₃)₄ (621 mg, 0.537 mmol) in toluene (120 мл) was stirred at 90°C for 100 h, then cooled to room temperature. The solvent was evaporated and residue was purified on SiO₂ using hexane-CHCl₃ mixture as eluent. The title compound was obtained as red solid (3.1 g, 57%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.11 (c, 1H), 7.43 (d, 1H), 4.82 (t, 2H), 2.21 (m, 2H), 1.50-0.75 (m, 26H). 19F NMR (100 MHz, CDCl₃, δ ppm): 110.61 (s). Elemental analysis: C₄₈H₆₄Br₂F₂N₆S₂Si (%). Calcd. C: 56.80; H: 6.36; N: 8.28; Br: 15.74; S: 6.32. Found C: 56.65; H: 6.60; N: 8.30; Br: 15.86; S: 6.42.



Figure S4 ¹H NMR spectrum of 2,6-bis(7-bromo-6-fluoro-2-hexyl-2*H*-benzotriazol-4-yl)-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*]dithiophene (**M3**)



Figure S5¹³C NMR spectrum of M2 and M3



Figure S6 Partial density of states of (a) P1, and (b) P2 (calculated using the M06 functional).



Figure S7 Theoretical UV/Vis absorption spectrum of P1 and P2 (calculated using the B3LYP functional).

Table SI-1

Electronic excitations of **P1** (with non-negligible oscillator strengths, f), and the corresponding major contributions. Calculated using the M06 functional (and CF for solvent).

No.	Wavelength r	Main	
	(nm)	J	Contributions
1	576	2.059	H→L (96%)
2	436	0.139	H→L+1 (93%)
3	430	0.044	H−1→L (94%)
4	368	0.053	H→L+2 (85%)
5	353	0.091	H−1→L+1 (87%)
6	343	0.022	H→L+3 (84%)
7	334	0.032	H−2→L (93%)
13	290	0.038	H−8→L (18%)
			H–4→L (44%)
			H−2→L+1 (12%)
14	290	0.137	H−8→L (17%)
			H–4→L (44%)
			H−2→L+1 (14%)
15	285	0.057	H−2→L+1 (44%)
			H−1→L+3 (24%)
16	284	0.028	H−8→L (13%)
			H−2→L+1 (10%)
			H−1→L+3 (49%)
17	279	0.144	H−9→L (23%)
			H→L+4 (43%)
19	267	0.067	H→L+5 (62%)
20	263	0.045	H–6→L+1 (10%)
			H−3→L+1 (15%)
			H→L+6 (38%)
25	257	0.052	H−7→L+1 (12%)
			H−5→L+1 (12%)
			H−3→L+1 (29%)
			H→L+6 (11%)

Table SI-2

Electronic excitations of **P2** (with non-negligible oscillator strengths, f), and the corresponding major contributions. Calculated using the M06 functional (and CF for solvent).

No.	Wavelength	f	Main
	(nm)	J	Contributions
1	574	2.074	H→L (97%)
2	441	0.130	H→L+1 (96%)
3	424	0.050	H−1→L (96%)
5	351	0.112	H−1→L+1 (82%)
6	344	0.029	H→L+3 (82%)
12	295	0.106	H−7→L (32%)
			H−2→L+1 (43%)
14	287	0.067	H−8→L (48%)
			H−7→L (13%)
			H–6→L (16%)
15	287	0.029	H−7→L (24%)
			H–6→L (15%)
			H−2→L+1 (45%)
16	281	0.079	H−1→L+3 (67%)
			H→L+4 (16%)
17	279	0.138	H−1→L+3 (16%)
			H→L+4 (64%)
19	268	0.056	H→L+5 (55%)
20	266	0.029	H−3→L+1 (72%)
			H→L+5 (12%)
22	262	0.062	H−8→L (13%)
			H→L+6 (60%)
26	255	0.027	H−10→L (37%)
			H–9→L+1 (23%)

1 (a) L. Huo, H.-Y. Chen, J. Hou, T. L. Chen and Y. Yang, Chem. Commun., 2009, 5570–5572; (b) J. Hou, H.-Y. Chen, Shaoqing Zhang, Gang Li and Yang Yang, J. Am. Chem. Soc. 2008, 130, 16144

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