Supporting information

Synthesis of new D-A1-D-A2 type low bandgap terpolymers based on different thiadiazoloquinoxaline acceptor units for efficient polymer solar cells

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Synthesis of materials

Isopropyl 2-bromobenzoate (2). 2-Bromobenzoic acid (**1**, 150.0 g, 746 mmol) and propan-2-ol (896 g, 15 mol) were mixed in the flask and the mixture was cooled to 0°C. To this mixture $SOCl_2$ (177 г, 1.5 mol) was added dropwise at 0…+5°C, than the mixture was warmed to room temperature and stirred overnight. Solvents were evaporated in vacuum, the dark residue was passed through SiO_2. After evaporation the product was obtained as yellow oil with the yield of 175.0 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.40 (d, *J*=6.36 Hz, 6H), 5.29 (m, 1H), 7.33 (m, 2H), 7.65 (m, 1 H), 7.75 (m, 1 H).

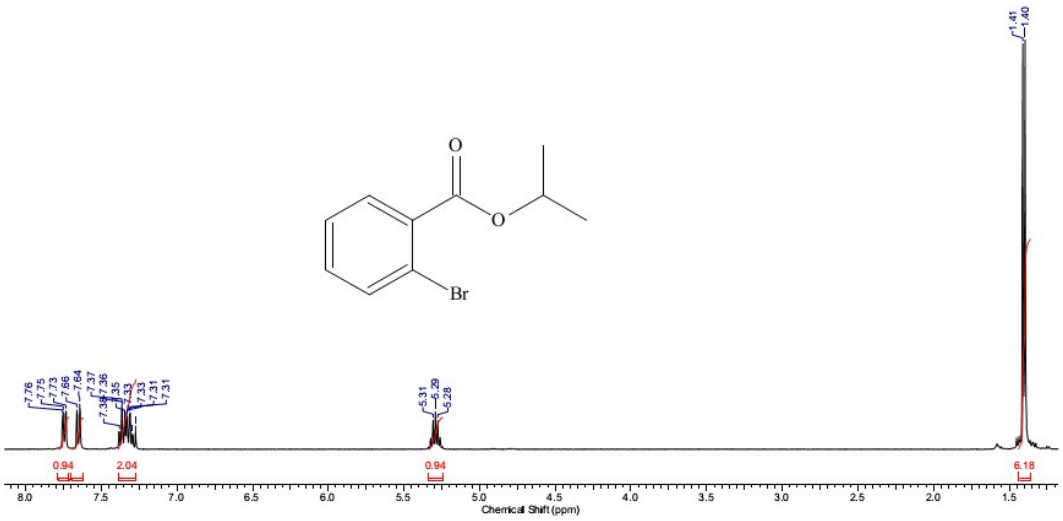

Fig S1. ^{1}H NMR spectrum of compound **2**.

Isopropyl 4'-fluorobiphenyl-2-carboxylate (3). A mixture of isopropyl 2-bromobenzoate (**2**) (16.5 g, 68 mmol), *para*-fluorophenylboronic acid (10.6 g, 76 mmol), dioxane (100 ml) and aqueous solution of Na_2CO_3 (16.5 g, 155 mmol) was purged with Ar during 20 min, then $PdCl_2$*dppf (1.2 g, 1.64 mmol) was added, and the mixture was heated at 90°C for 8 h. After cooling the reaction mixture was diluted with ether (200 ml), organic layer was separated, washed with water (2×100 ml) and evaporated. The residue was purified by chromatography using the Biotage SP1 instrument and $CHCl_3$ as an eluent. After evaporation of the solvent 15.0 g (86%) of compound **3** was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.07 (m, 5H), 5.02 (m, 1H), 7.10 (m, 2H), 7.19 (m, 1H), 7.31 (m, 3H), 7.43 (m, 1H), 7.52 (m, 1H), 7.84 (m, 1H).

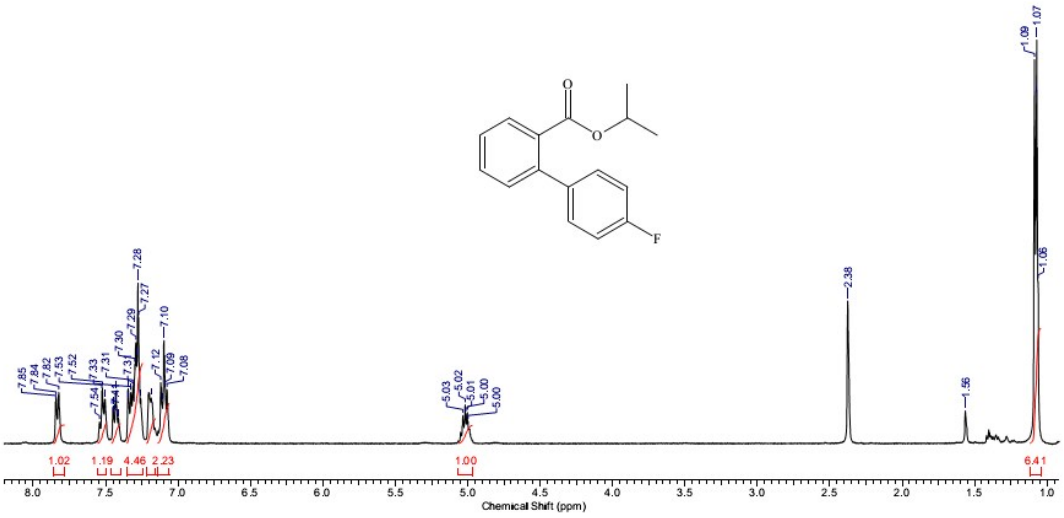

Fig S2. ^{1}H NMR spectrum of compound **3**.

4'-Fluorobiphenyl-2-carboxylic acid (4). A mixture of LiOH (5.6 g, 232 mmol), KOH (13.0 g, 232 mmol), water (100 ml), THF (100 ml) and isopropyl 4'-fluorobiphenyl-2-carboxylate (**3**) (15.0 g, 58 mmol) was refluxed for 4 h and cooled to room temperature. Organic solvents were removed in vacuum, and residue was acidified until pH 2 by addition of conc. HCl with good stirring. Reaction mixture was stirred for 2 h, filtrated, and solids were washed with water (3x150 мл) and dried in vacuum. The yield of compound **4** is 12.0 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.03 (m, 2H), 7.21 (m, 2H), 7.31 (d, *J*=7.52 Hz, 1H), 7.49 (m, 1H) 7.51 (t, *J*=7.49 Hz, 1H), 7.98 (d, *J*=7.83 Hz, 1H).

4'-fluorobiphenyl-2-carbonyl chloride (5). A mixture of 4'-fluorobiphenyl-2-carboxylic acid (**4**) (12.0 g, 55 mmol), $CHCl_3$ (100 ml) and $SOCl_2$ (19.8 g, 166 mmol) were stirred for 5 min, then DMF (2 drops) was added and the mixture was refluxed for 4 h. After evaporation of the solvent dark oil was obtained with the yield of 13.0 g (99%), which was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.15 (m, 2H), 7.32 (m, 2H), 7.40 (dd, *J*=7.58, 0.86 Hz, 1H), 7.53 (m, 1H), 7.64 (td, *J*=7.52, 1.22 Hz, 1H), 8.06 (dd, *J*=7.89, 0.92 Hz, 1H).

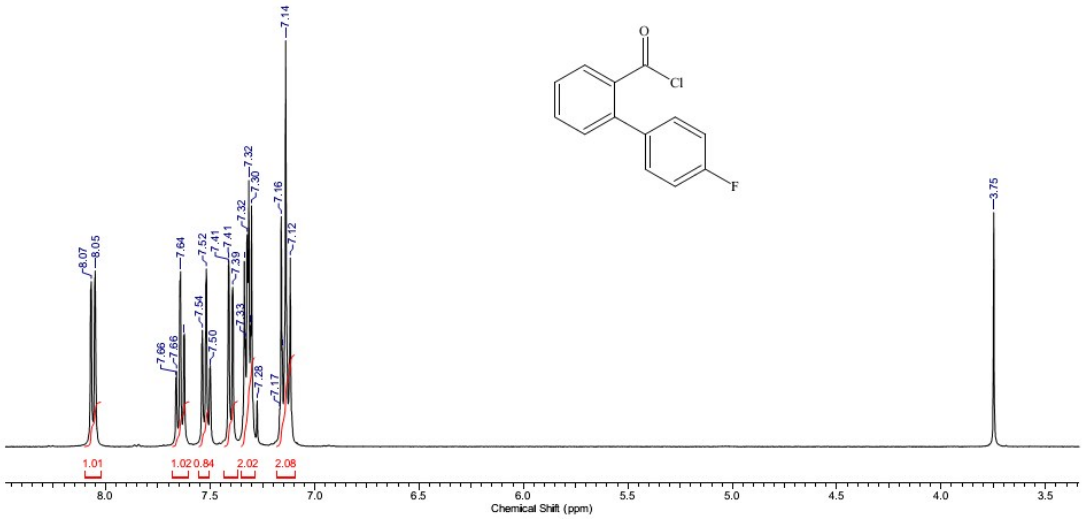

Fig S3 ^{1}H NMR spectrum of compound **5**.

2-fluoro-9*H*-fluoren-9-one (6). Aluminum chloride (8.9 g, 67 mmol) was added portion wise to a cooled solution of 4'-fluorobiphenyl-2-carbonyl chloride (**5**) (13.0 g, 55 mmol) in 200 ml of dichloromethane with good stirring. The mixture was stirred for 2 h at room temperature and then 3 h at 40°C. The reaction mixture was poured into acidified ice-water mixture, and dichloromethane was added. Organic layer was separated, dried with Na_2SO_4 and evaporated. Residue was purified by flash-chromatography with a mixture $CHCl_3$-hexane = 80:20 as an eluent. After evaporation 9.6 g (87%) of compound **6** as yellow crystals were obtained. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.17 (m, 1H), 7.28 (m, 1H), 7.34 (dd, *J*=7.27, 2.38 Hz, 1H), 7.49 (m, 3H), 7.66 (d, *J*=7.21 Hz, 1H).

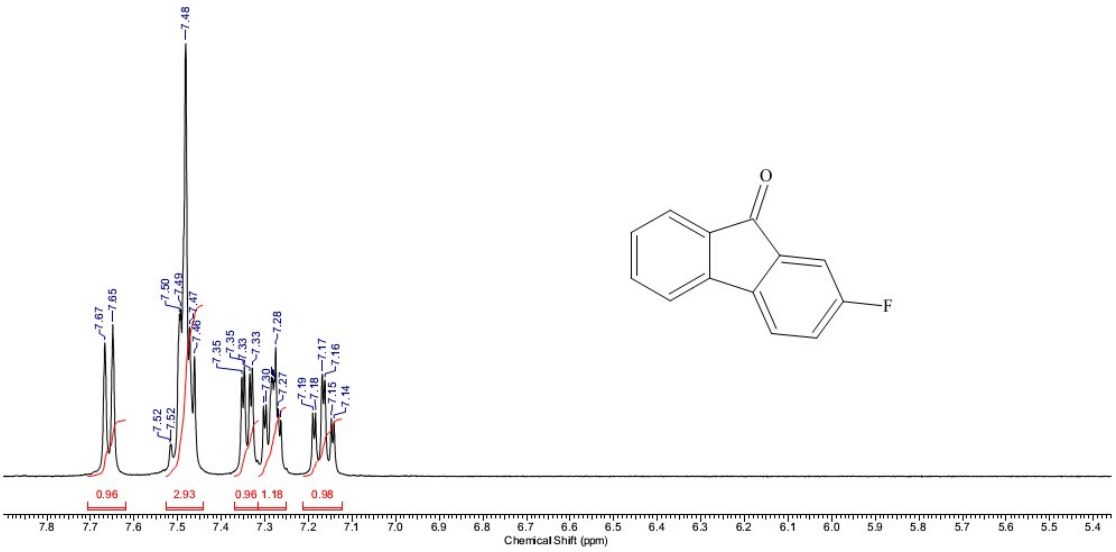

Fig S4. ^{1}H NMR spectrum of compound **6**.

2-fluoro-9*H*-fluorene (7). A mixture of 2-fluoro-9*H*-fluoren-9-one (**6**) (30 g, 151 mmol), diethylene glycol (600 ml) and hydrazine hydrate (38 g, 757 mmol) was heated at 80°C for 2 h and then refluxed for additional 1 h. After cooling to 25°C a solution of KOH (43 g, 757 mmol) in water (70 ml) was added in one portion and the reaction mixture was refluxed for 2.5 h. During the reaction the product **7** sublimed on the cold parts of reactor. The mixture was cooled to 25°C, poured into 1 L of ice water, stirred for 20 min, and filtrated. The yield is 27.7 g (99%) of pure compound **7**. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.90 (s, 2H), 7.11 (m, 1H), 7.30 (m, 2H), 7.41 (t, *J*=7.46 Hz, 1H), 7.56 (d, *J*=7.46 Hz, 1H), 7.74 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$, δ ppm): -116.00 (s).

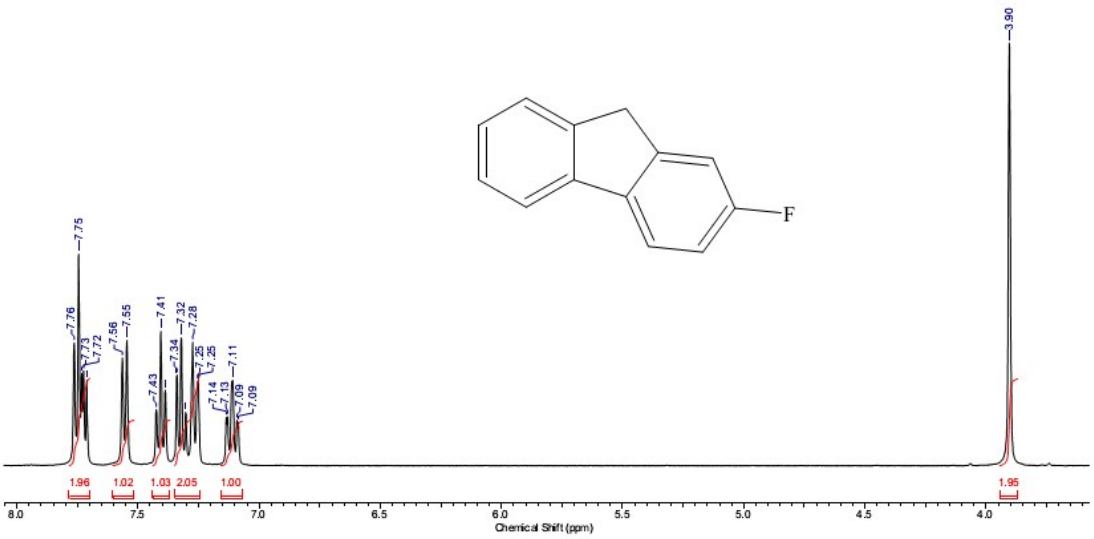

Fig S5. ^{1}H NMR spectrum of compound **7**.

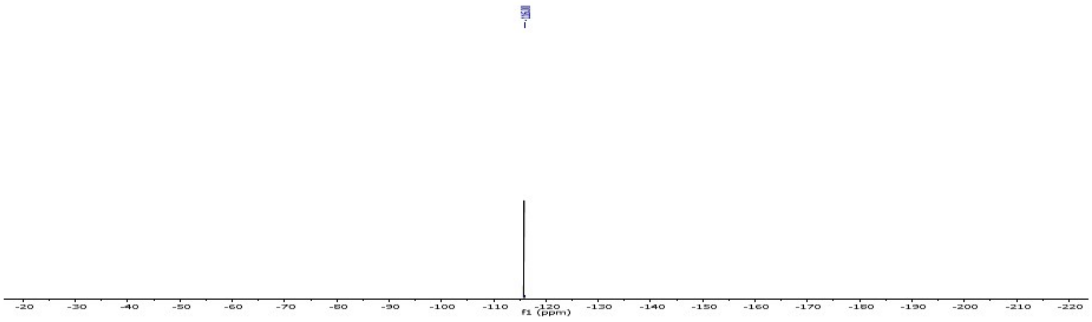

Fig S6.. ^{19}F NMR spectrum of compound **7**.

9,9-didodecyl-2-fluoro-9*H*-fluorene (8). A mixture of 2-fluoro-9*H*-fluorene (**7**) (29.0 g, 158 mmol), THF (150 ml) was cooled to -60°C and then LDA solution (346 mmol, 2 M in THF/heptanes/ethylbenzene) was added dropwise. After stirring for 20 min at that temperature, a solution of 1 bromododecane (86 g, 346 mmol) in THF (60 ml) was added dropwise. The reaction mixture was warmed to 25°C and stirred overnight. Then the mixture was poured into saturated ammonium chloride solution, and extracted with hexane (2 x 200 ml), organic phase was washed with water several times, dried with Na_2SO_4 and evaporated. The residue was purified by chromatography using gradient

mixture of hexane to hexane-CH_2Cl_2 = 70:30. Compound **8** was obtained as oil with the yield of 78 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.63 (s, 4H), 0.89 (m, 6H), 0.98-1.34 (m, 40H), 1.95 (m, 4H), 7.04 (m, 2H), 7.32 (m, 4H), 7.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.00, 161.56, 153.16, 150.46, 140.27, 137.07, 126.84, 126.68, 122.80, 120.62, 120.53, 119.32, 113.88, 113.66, 110.27, 110.05, 55.26, 40.37, 31.92, 29.98, 29.61, 29.55, 29.34, 29.26, 23.68, 22.69, 14.13. ^{19}F NMR (282 MHz, $CDCl_3$, δ ppm): -115.08 (s).

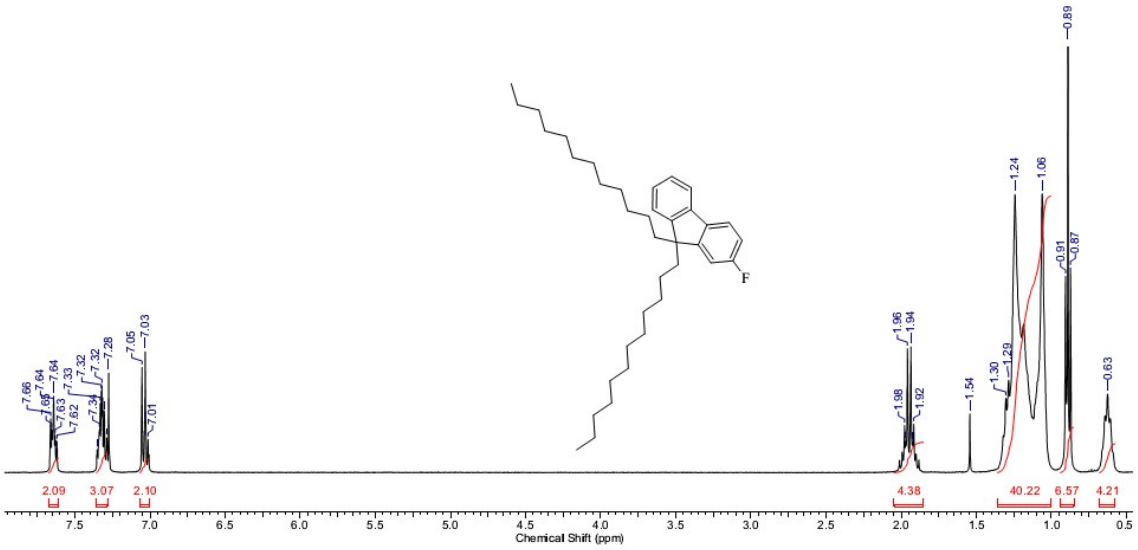

Fig S7. ^{1}H NMR spectrum of compound **8**.

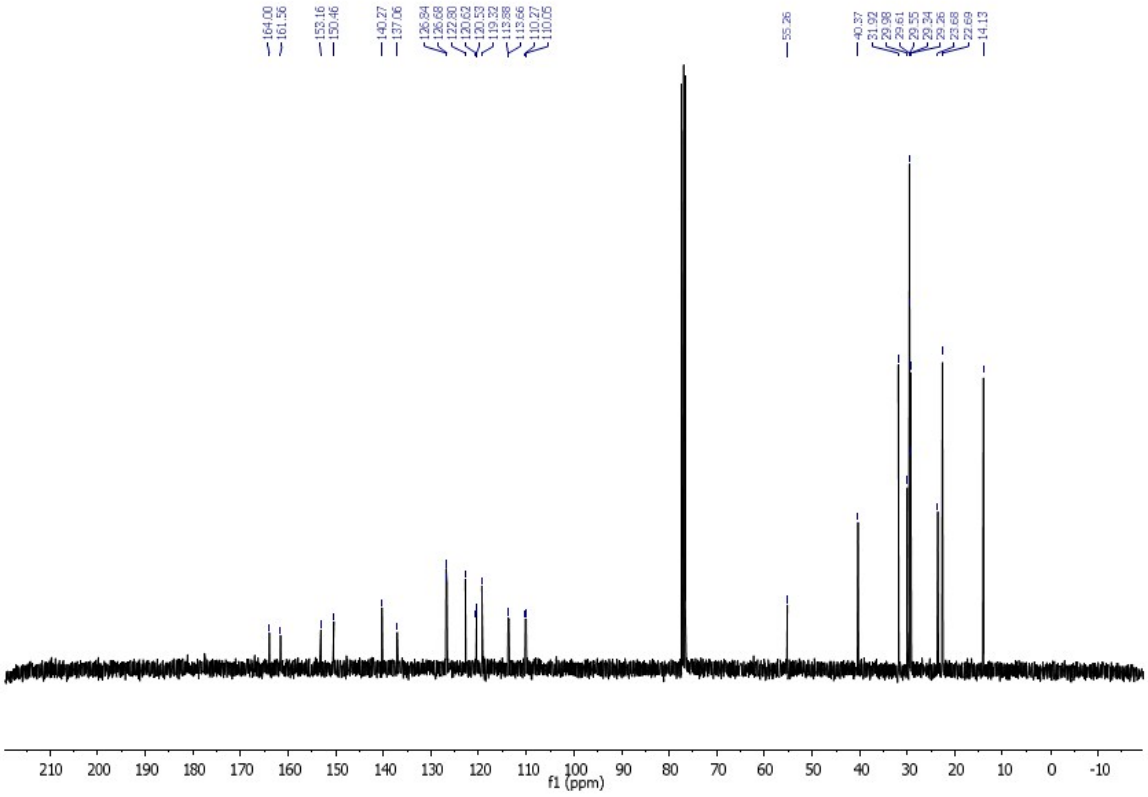

Fig S8. ^{13}C NMR spectrum of compound **8**.

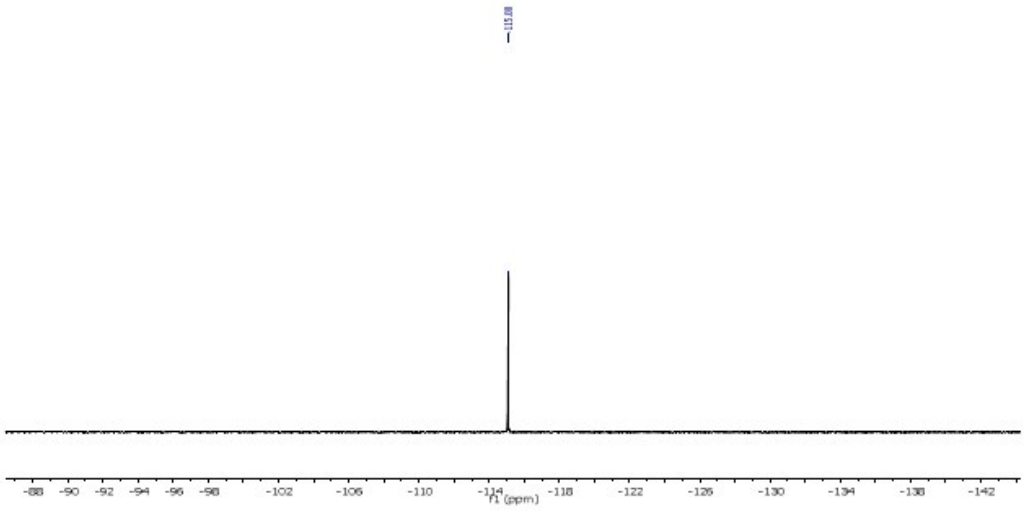

Fig. S9. ^{19}F NMR spectrum of compound **8**.

1,2-bis(9,9-didodecyl-7-fluoro-9*H*-fluoren-2-yl)ethane-1,2-dione (9). A suspension of $AlCl_3$ (10.4 g, 78 mmol) in 1,2-dichloroethane (20 ml) was cooled to -30°C and a

solution of oxalyl chloride (2.64 g, 21 mmol) in 1,2-dichloroethane (5 ml) was added dropwise and stirred for 5 min. To this mixture a solution of 9,9-didodecyl-2-fluoro-9*H*-fluorene (**8**) (18.0 g, 35 mmol) in 1,2-dichloroethane (17 ml) and pyridine (2.74 g, 35 mmol) was added in one portion. After the addition the temperature of the mixture rose to 0°C. The reaction mixture was stirred in cooling bath until the temperature dropped to -5°C, then the cooling bath was removed, the reaction mixture was warmed to 10°C, and stirred at this temperature for 1 h. The reaction mixture was poured onto 100 ml of ice and extracted with dichloromethane (3x100 ml). Organic phase was washed with water, dried with Na_2SO_4, and evaporated. The residue was purified by chromatography with a mixture of hexane-ethylacetate = 80:20 as an eluent. The yield of compound **9** was 7.2 g (38%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.61 (s, 8H), 0.88 (m, 12H), 0.98-1.35 (m, 80H), 2.00 (m, 8H), 7.09 (m, 4H), 7.72 (m, 4H), 7.90 (d, *J*=7.95 Hz, 2H), 8.08 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 194.97, 164.91, 162.94, 155.05, 154.99, 151.40, 146.99, 135.39, 131.53, 130.81, 123.34, 122.41, 122.34, 119.46, 114.74, 114.56, 110.64, 110.46, 55.73, 55.72, 40.11, 31.92, 29.90, 29.62, 29.56, 29.35, 29.29, 23.78, 22.70, 14.13. ^{9}F NMR (282 MHz, $CDCl_3$, δ ppm): -111.25 (s).

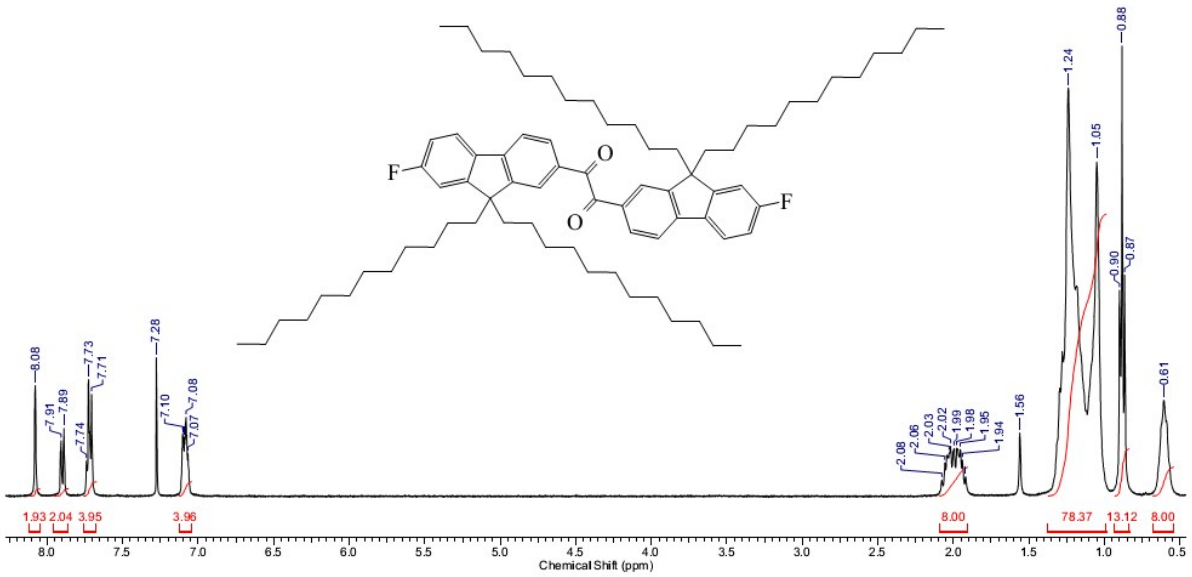

Fig S10. ^{1}H NMR spectrum of compound **9**.

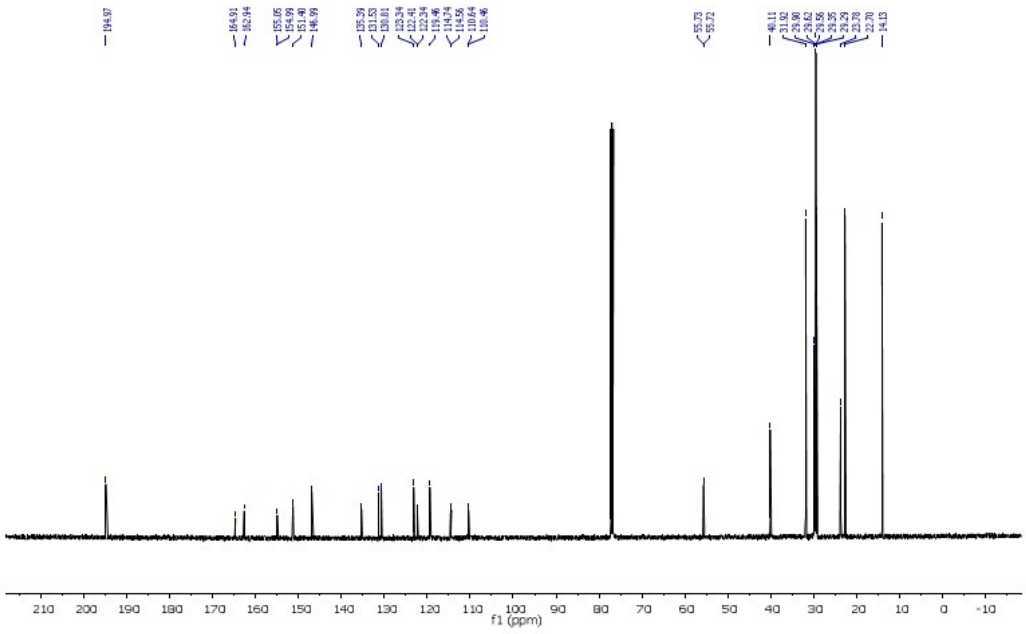

Fig.S11. ^{13}C NMR spectrum of compound **9**.

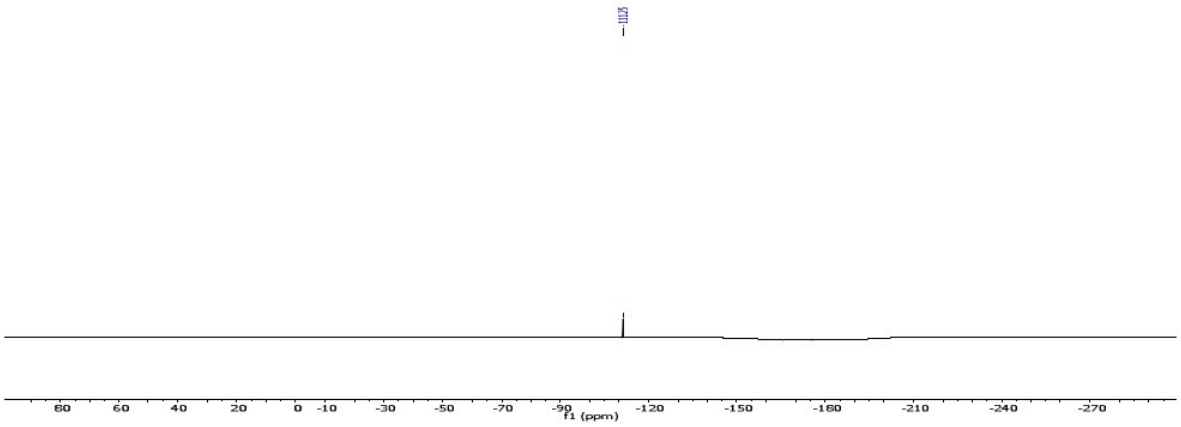

Fig.S12 ^{19}F NMR spectrum of compound **9**.

4,9-dibromo-6,7-bis(9,9-didodecyl-7-fluoro-9*H*-fluoren-2-yl)[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (M2). A mixture of 1,2-bis(9,9-didodecyl-7-fluoro-9*H*-fluoren-2-yl)ethane-1,2-dione (**9**) (6.35 g, 58 mmol), 4,7-dibromo-2,1,3-benzothiadiazole-5,6-diamine (**10**) (2.45 g, 7.6 mmol), acetic acid (100 ml) and dioxane (60 ml) was purged

with Ar and heated at 125°C overnight. After cooling the reaction mixture was evaporated, residue was purified by chromatography using a mixture of hexane-CH_2Cl_2 as an eluent. The title compound **M2** was obtained as very viscous red oil with the yield of 7.0 g (67%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.66 (m, 8H), 0.87 (m, 12H), 1.02 (s, 8H), 0.98-1.35 (m, 80H), 1.86 (t, *J*=8.19 Hz, 8H), 7.05 (m, 4H), 7.64 (m, 4H), 7.83 (d, *J*=8.44 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.35, 162.39, 156.25, 154.16, 154.10, 152.36, 150.65, 142.77, 138.10, 136.20, 135.96, 129.62, 124.93, 121.60, 121.53, 119.35, 114.38, 114.20, 113.73, 110.45, 110.27, 55.46, 55.45, 40.23, 31.91, 29.70, 29.68, 29.66, 29.64, 29.36, 23.94, 22.68, 14.11. ^{9}F NMR (282 MHz, $CDCl_3$, δ ppm): -112.94 (s).

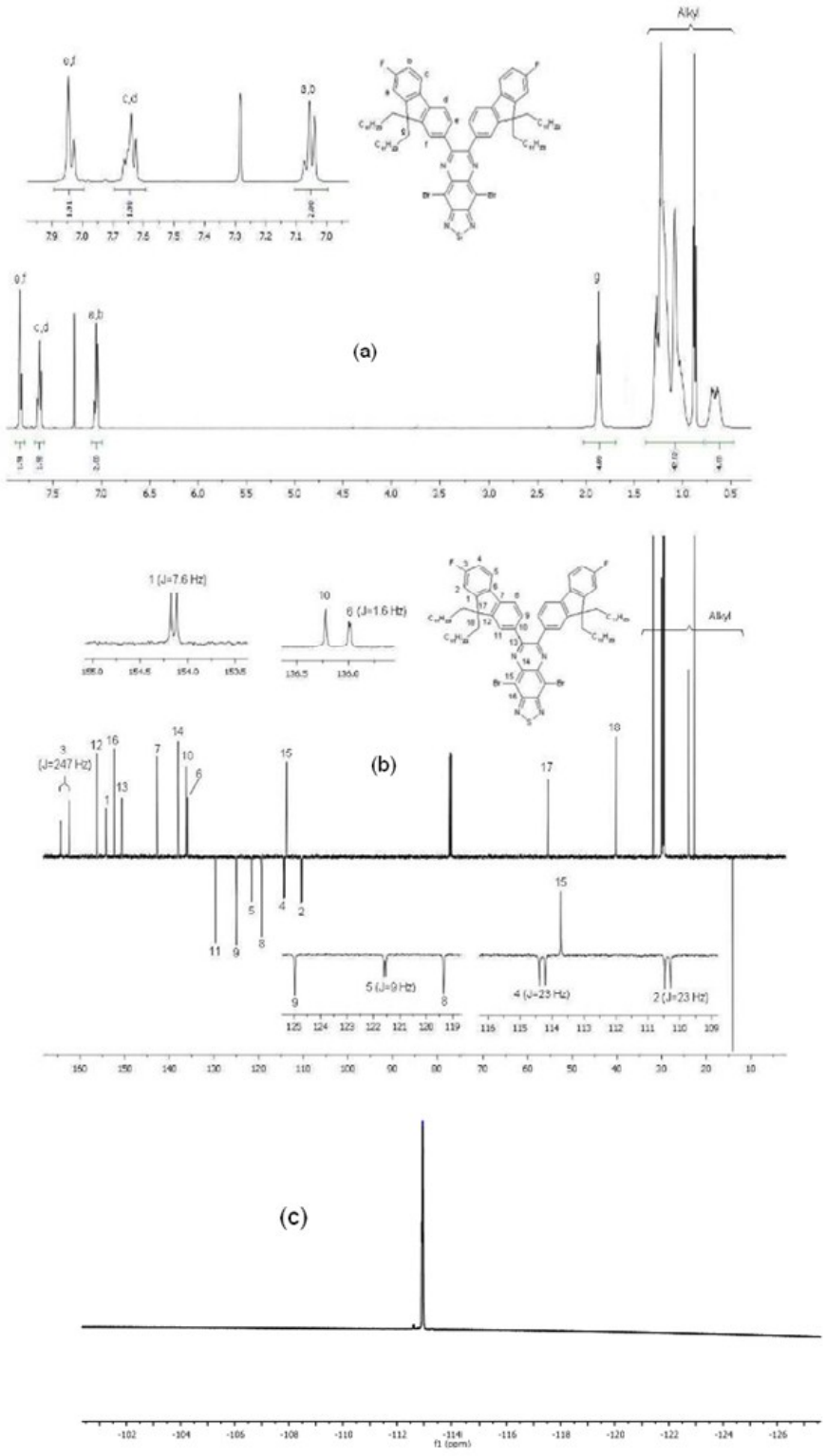

Fig. S13 Spectra ^{1}H NMR (a), ^{13}C NMR (b) and ^{19}F NMR (c) of M2

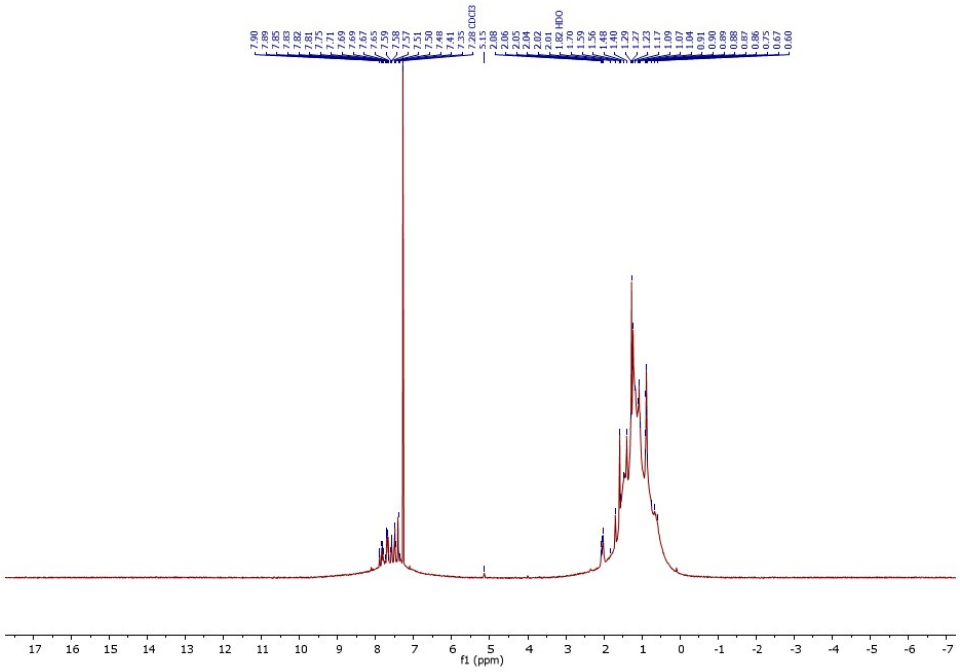

Fig S14 (a) ^{1}HNMR of copolymer **P1**

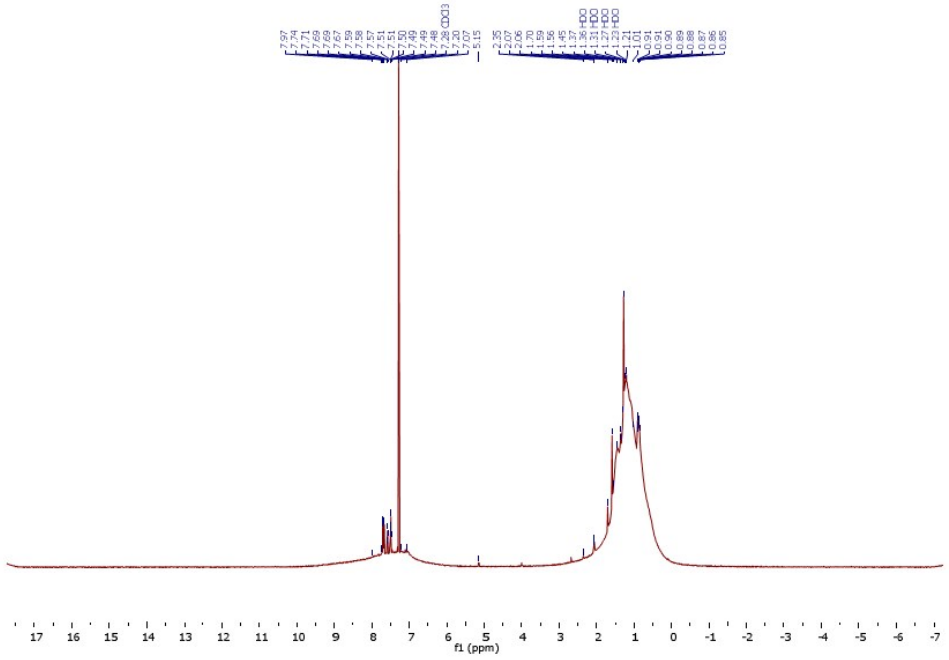

Fig S14 (b) ^{1}HNMR of polymers **P2**

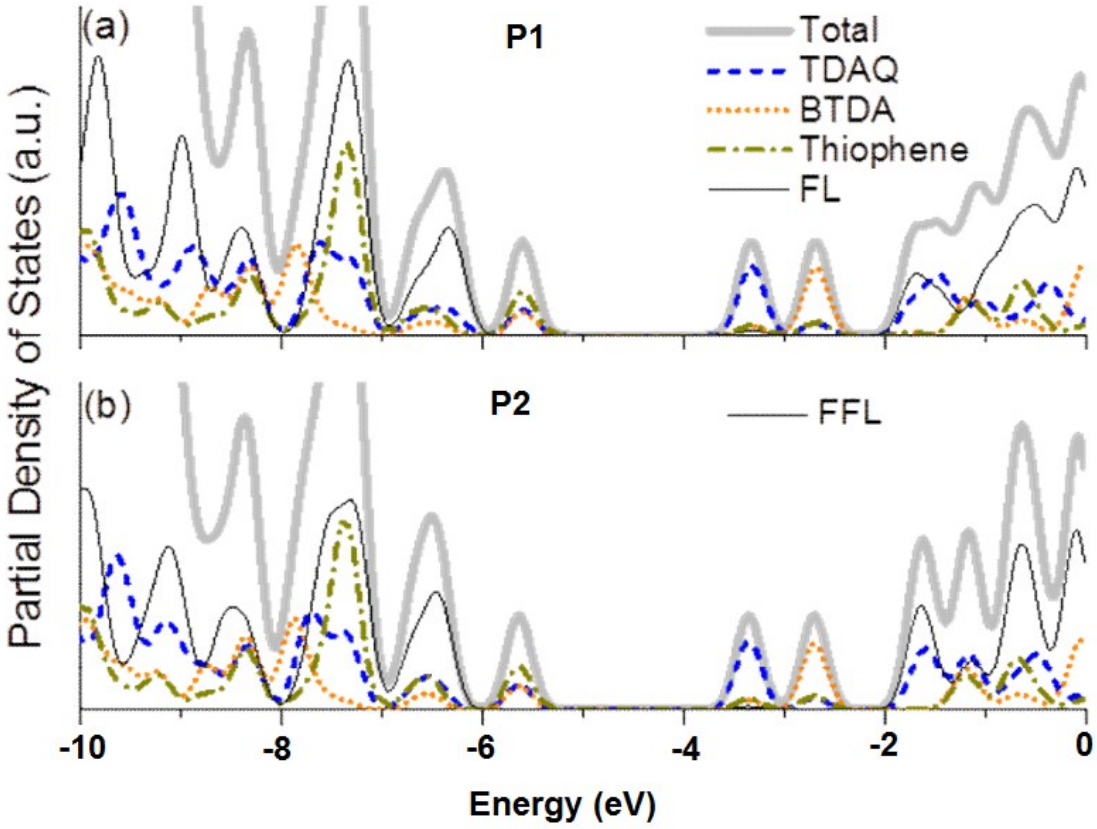

Fig. S15 Total and partial density of states of (a) **P1**, and (b) **P2** (calculated using the M06 functional)

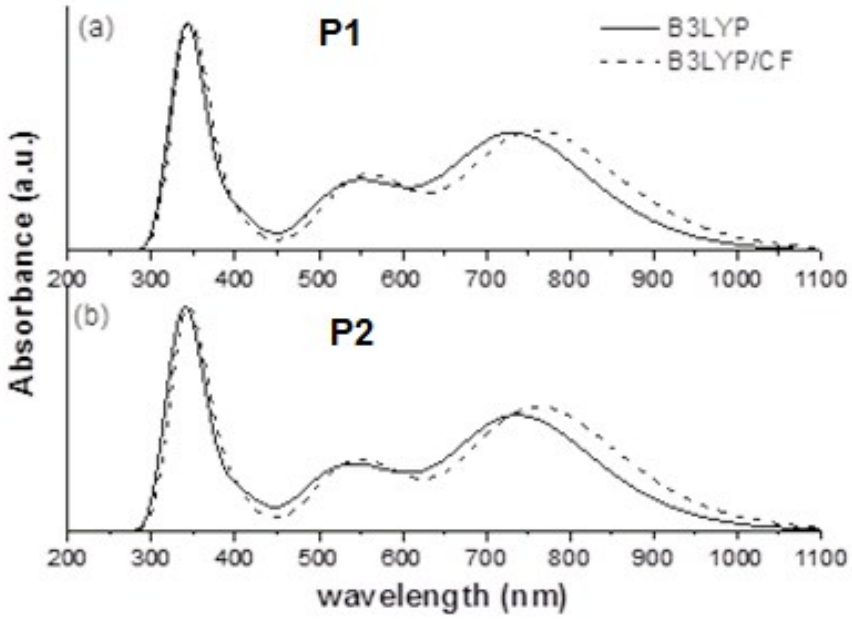

Fig. S16 Theoretical UV/Vis absorption spectrum of (a) **P1**, and (b) **P2** (calculated using the B3LYP functional).

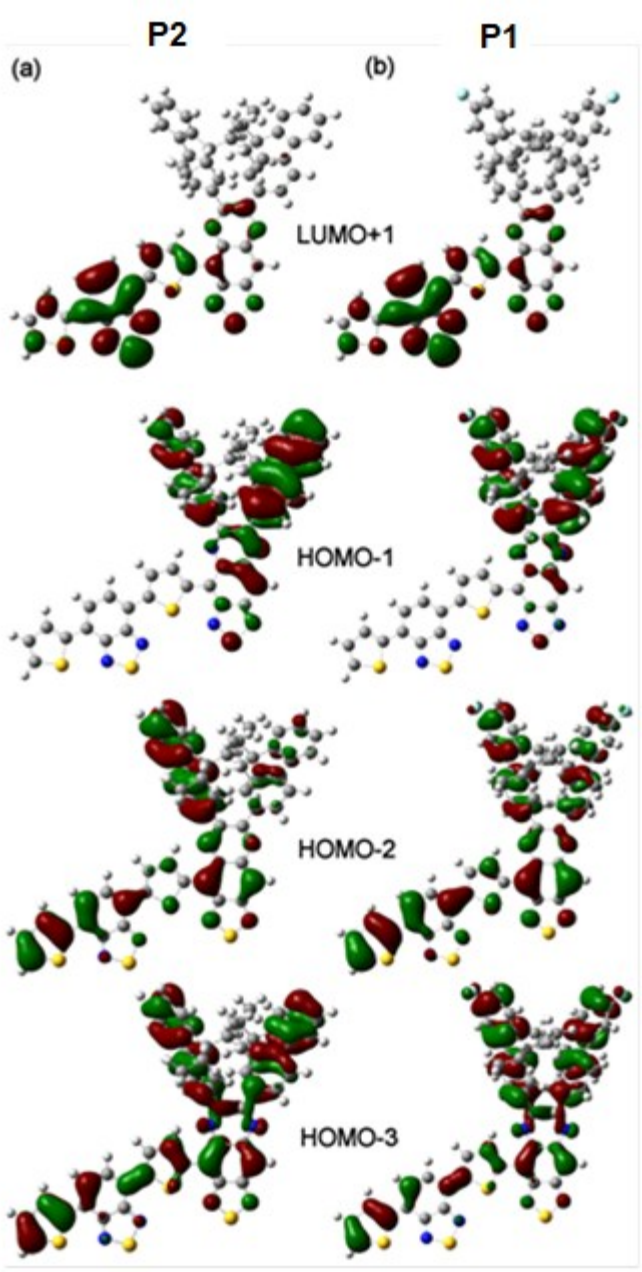

Figure S17 Near frontier orbitals of (a) **P1** and (b) **P2**

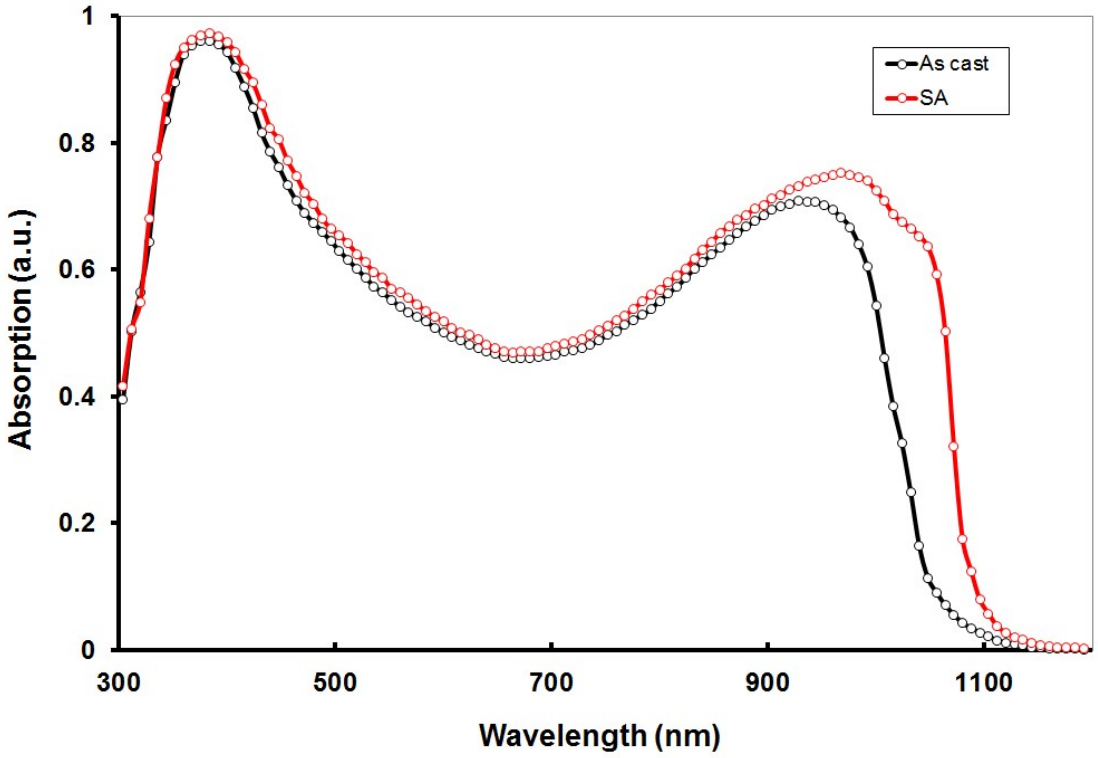

Figure S18 Normalized absorption spectra of as cast and SA treated P2:PCBM thin films

1. M.L Keshtov, S.A. Kuklin, N.A.Radychhev, A.Y.Nikolaev, E.N.Koukaras, A.Snarma, G.D. Snarma, *RSC Advances, DOI*: 10.1039/c5ra24364e

2. Zhou E., Hashimoto K., Tajima K., *Polymer.2013,54,6501-6509*

3. J.-F. Jheng, Y.-Y. Lai, J.-S. Wu, Y.-H. Chao, C.-L. Wang and C.-S. Hsu, *Adv. Mater., 2013, 25, 2445-2451.*