

**5,6-Bis(octyloxy)-2,1,3-benzoxadiazole-based (X-DADAD)<sub>n</sub> polymers incorporating electron-donor building blocks used as photoactive materials in organic solar cells**

**Irina V.Klimovich, Fedor A. Prudnov, Liana N. Inasaridze, Iliya E. Kuznetsov, Alexander S. Peregudov and Pavel A. Troshin**

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## Synthesis of monomer **M1**

(2,5-bis(7-(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[2,1,3]oxadiazol-4-yl)thiophene)

[Solar Energy Materials and Solar Cells, 2016, 378-386]

5,6-Bis(octyloxy)benzoxadiazole (2.0 g, 3.76 mmol), 2-(tributylstannyl) thiophene (0.85 g, 1.27 mmol) and 2,5-bis(tributylstannyl) thiophene (3.35 g, 9.04 mmol) were dissolved in anhydrous toluene (50 mL) in a three necked round-bottom flask. The mixture was deaerated and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.023 g, 0.02 mmol) was added under argon. The mixture was heated at reflux for 24 h and then cooled to the room temperature. The target compound (2,5-bis(7-(thiophen-2-yl)-5,6-bis(octyloxy)benzo[2,1,3]oxadiazol-4-yl)thiophene (0.428 g, 33%) was separated from the 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[2,1,3]oxadiazole side product (yield 1.02 g, 52%) by column chromatography on SiO<sub>2</sub> (light petroleum-toluene as eluent) and further purified by preparative GPC. Further bromination was carried out by dissolving 1.0 mmol of (2,5-bis(7-(thiophen-2-yl)-5,6-bis(octyloxy)benzo[2,1,3]oxadiazol-4-yl)thiophene in 40–80 mL of warm 1,2-dichlorobenzene, adding 2.0 mmol of NBS (N-bromosuccinimide) and stirring the reaction mixture at 40 °C for 1 h. Following concentration of the reaction mixture to dryness and washing the residue with methanol produced pure **M1** in 90–96% yield.

**(2,5-bis(7-(thiophen-2-yl)-5,6-bis(octyloxy)benzo[2,1,3]oxadiazol-4-yl)thiophene** : yield 33%

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 8.51 (s, 2H), 8.49 (d, J = 3.7 Hz, 2H), 7.51 (d, J = 5.1 Hz, 2H), 7.23 (t, J = 5.0 Hz, 2H), 4.20 (m, 8H), 2.05 (m, 8H), 1.50 (m, 8H), 1.30 (m, 32H), 0.91 (t, J = 6.8 Hz, 6H), 0.85 (t, J = 6.8 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): d (ppm) 152.41, 151.85, 146.93, 146.89, 135.56, 133.06, 131.13, 131.09, 128.39, 127.36, 113.45, 113.18, 74.83, 74.66, 32.01, 31.99, 30.53, 30.49, 29.80, 29.73, 29.48, 29.47, 26.13, 26.08, 22.83, 22.80, 14.27, 14.22.

ESI-MS *m/z* C<sub>56</sub>H<sub>76</sub>N<sub>4</sub>O<sub>6</sub>S<sub>3</sub> [M]<sup>-</sup> 997, [M-C<sub>8</sub>H<sub>17</sub>]<sup>-</sup> 883

**Compound M1**: yield 90% <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 8.51 (s, 2H), 8.28 (d, J = 4.1 Hz, 2H), 7.19 (d, J = 4.1 Hz, 2H), 4.22 (t, J = 7.2 Hz, 4H), 4.18 (t, J = 7.2 Hz, 4H), 2.04 (m, 8H), 1.38 (m, 40H), 0.91 (t, J = 6.7 Hz, 6H), 0.85 (t, J = 6.7 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): d (ppm) 152.11, 151.70, 146.92, 146.39, 135.65, 134.57, 131.29, 130.22, 116.47, 113.50, 112.77, 74.93, 74.90, 31.99, 31.98, 30.50, 30.51, 29.77, 29.67, 29.74, 26.08, 26.06, 22.85, 22.80, 14.27, 14.23.

ESI-MS *m/z* C<sub>56</sub>H<sub>74</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>6</sub>S<sub>3</sub> [M]<sup>-</sup> 1154, [M-C<sub>8</sub>H<sub>17</sub>]<sup>-</sup> 1041

# NMR and ESI-MS spectra of M1

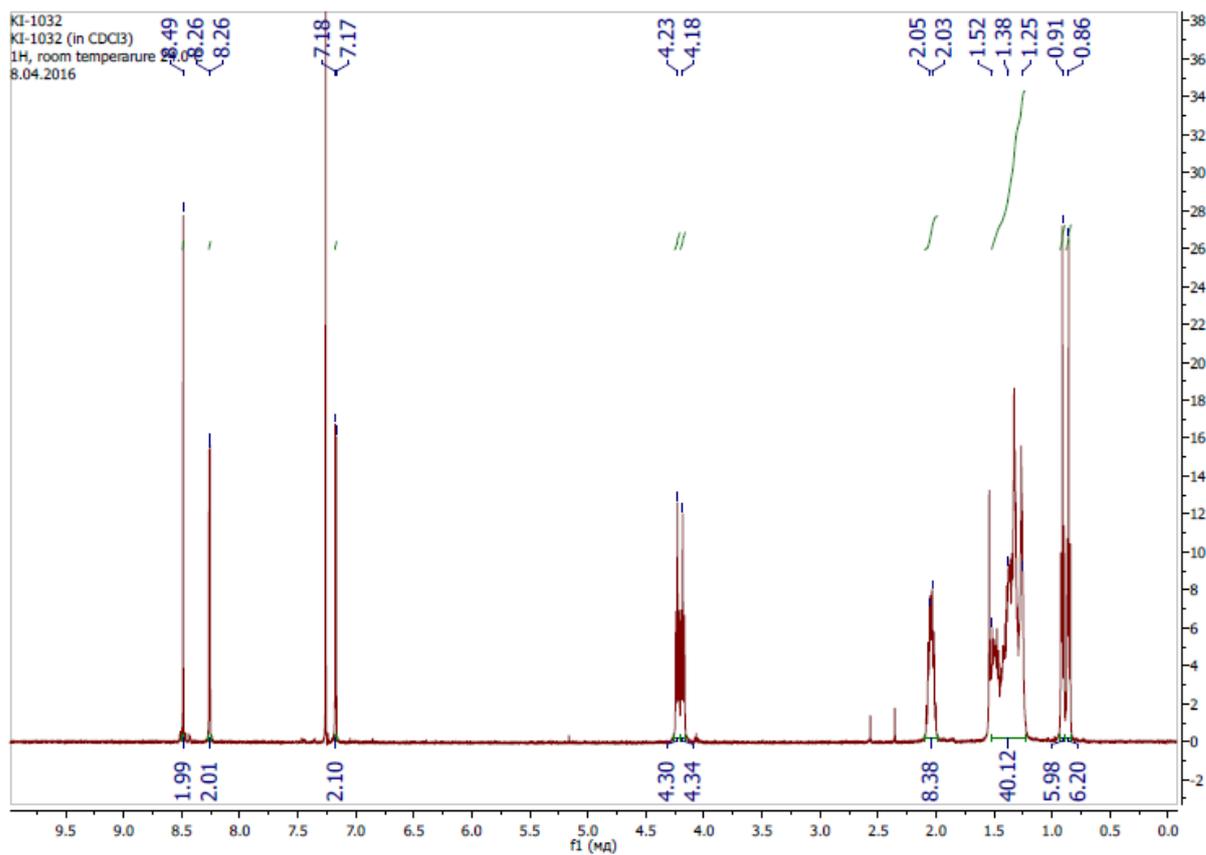


Figure S1  $^1\text{H}$  NMR spectrum of M1.

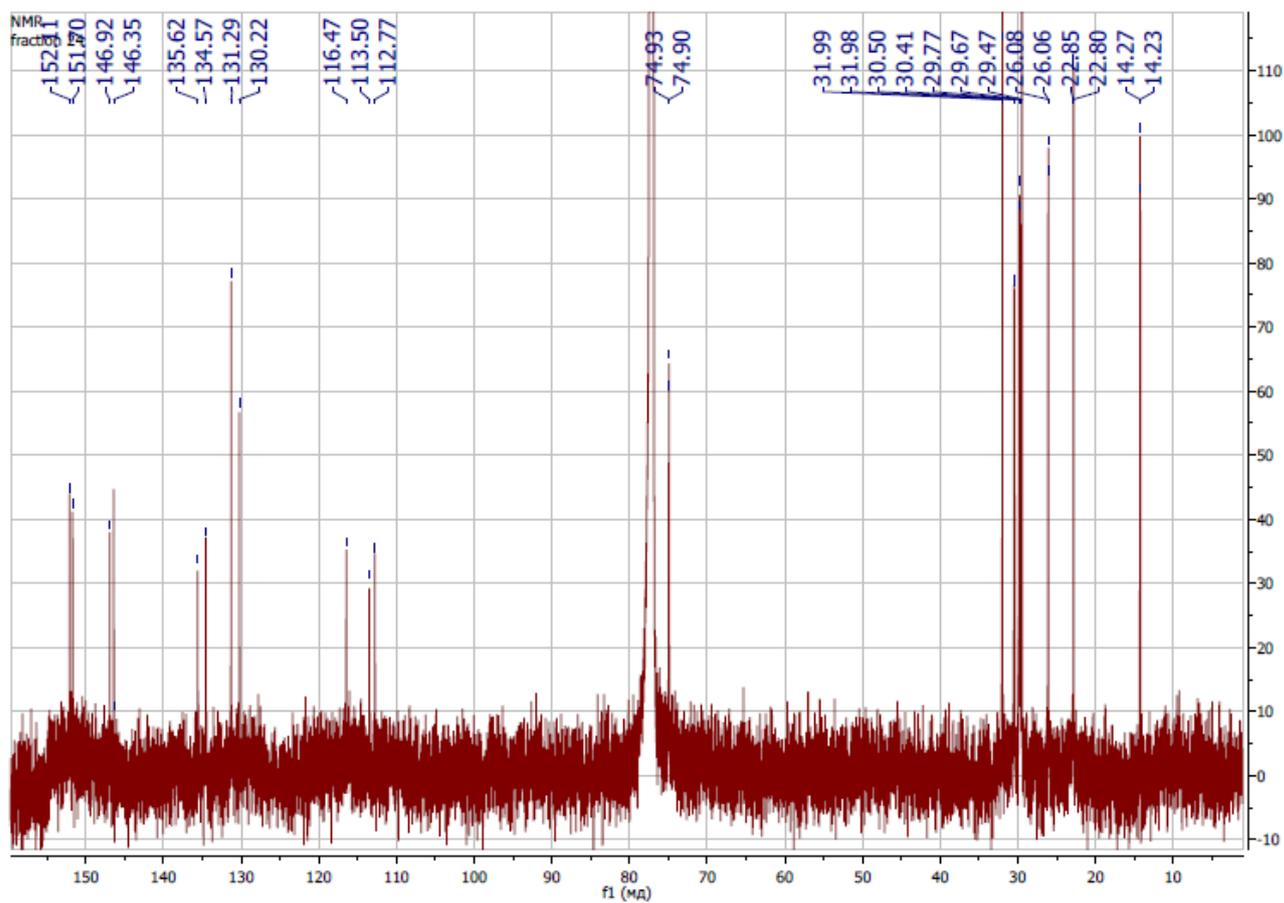
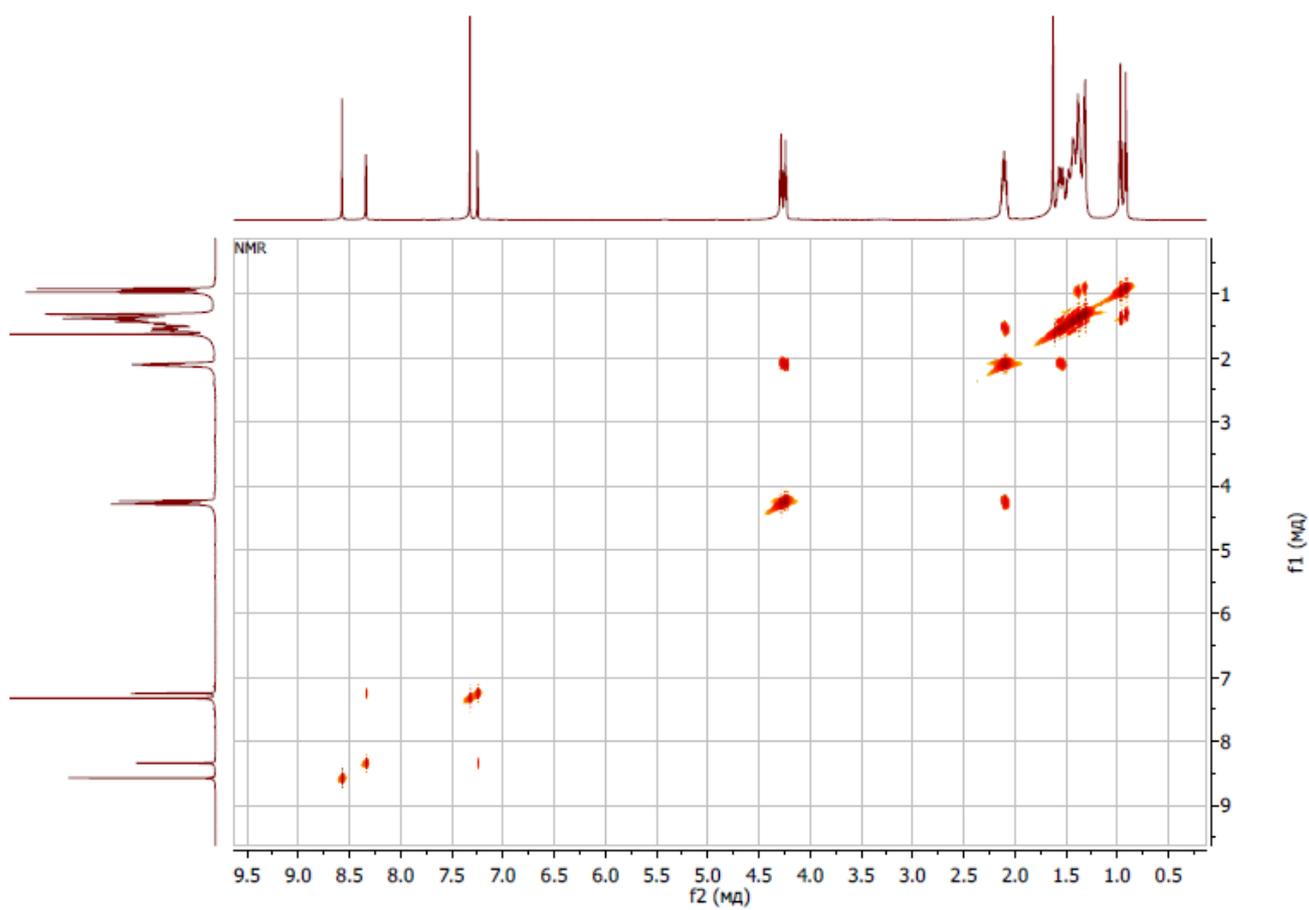
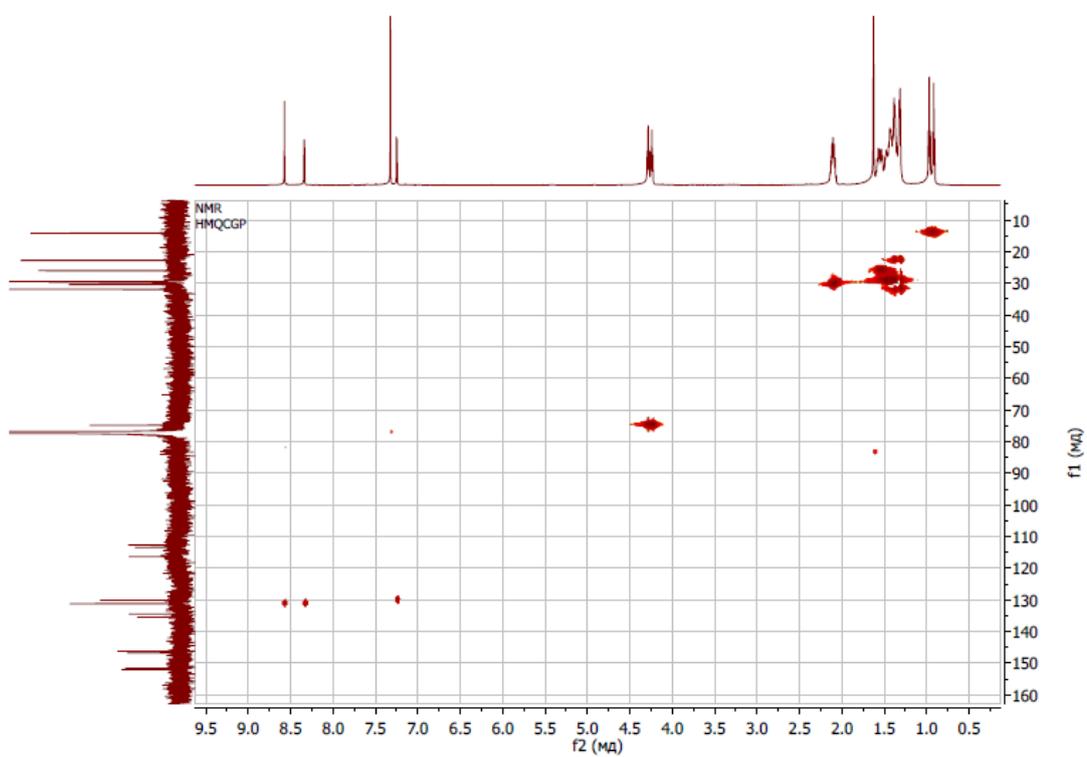


Figure S2  $^{13}\text{C}$  NMR spectrum of M1.



**Figure S3**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **M1**.



**Figure S4**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **M1**.

==== Shimadzu LabSolutions Data Report ====

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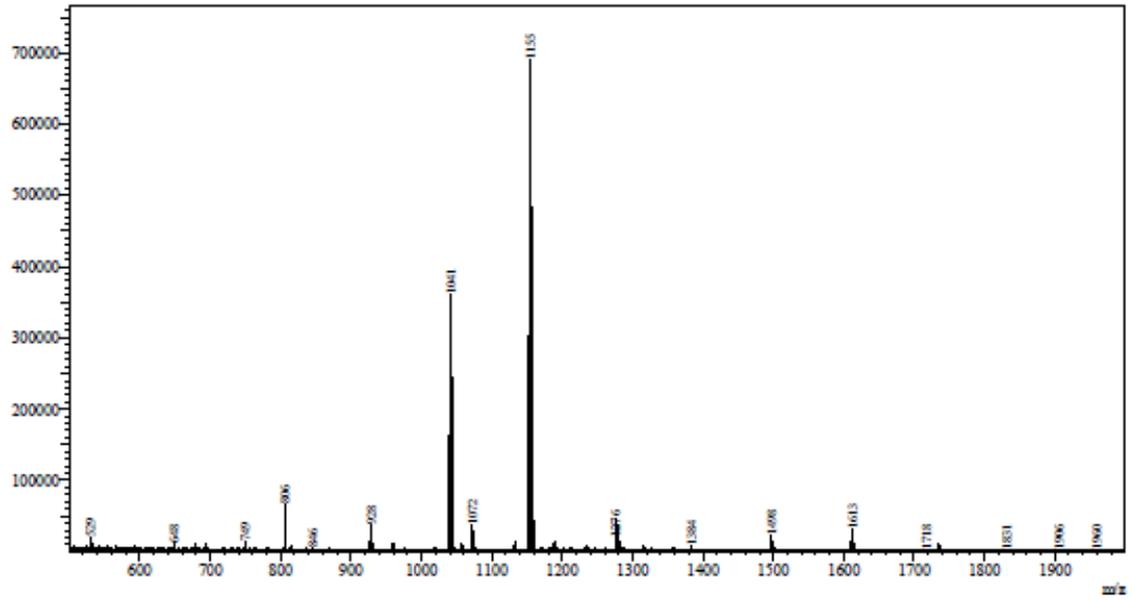


Figure S5 ESI-MS of M1.

## General procedure for synthesis of conjugated polymers

Poly(thiophene-*alt*-2,5-bis(7-(thiophen-2-yl)-5,6-bis(octyloxy)benzo[2,1,3]oxadiazol-4-yl)thiophene) (**P1**)

Poly(4,8-bis(4,5-didecylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-*alt*-2,5-bis(7-(thiophen-2-yl)-5,6-bis(octyloxy)benzo[2,1,3]oxadiazol-4-yl)thiophene) (**P2**)

Poly(9,9-dioctyl-9H-fluorene-*alt*-2,5-bis(7-(thiophen-2-yl)-5,6-bis(octyloxy)benzo[2,1,3]oxadiazol-4-yl)thiophene) (**P3**)

Polymers **P1** and **P2**: Monomers **M1** (0.13 mmol) and **M2/M3** (0.130 mmol) taken in precise stoichiometric amounts were introduced into a 50 ml round-bottom three necked flask equipped with a thermometer and reversed condenser. Toluene (15 ml) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were added. The reaction mixture was deaerated, immersed into an oil bath and heated at reflux for 3-6 h. The molecular weight characteristics of the formed product were controlled every 30 min. The reaction was stopped when product started to form a precipitate on the walls of the flask. To terminate the reaction, we introduced 0.1 mmol of bis(trimethylstannyl)thiophene, heated the mixture at reflux for additional 0.5 h and then introduced 2 mmol of bromobenzene and continued the heating for additional 0.5 h.

Polymer **P3**: Monomers **M1** (0.13 mmol) and **M4** (0.130 mmol) taken in precise stoichiometric amounts were introduced into a 50 ml round-bottom three necked flask equipped with a thermometer and a reversed condenser. Toluene (15 ml), 2M K<sub>2</sub>CO<sub>3</sub> (3 ml), aliquat 336 (25 mg) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were added. The reaction mixture was deaerated, immersed into an oil bath and heated at reflux for 3-6 h. The molecular weight characteristics of the formed product were controlled every 30 min. The reaction was stopped when product started to form a precipitate on the walls of the flask. To terminate the reaction, we introduced 0.1 mmol of phenyl boronic acid, heated the mixture at reflux for additional 0.5 h and then introduced 2 mmol of bromobenzene and continued the heating for additional 0.5 h.

## General procedure for purification of conjugated polymers

The reaction mixture was cooled down to room temperature, the polymer was extracted with 200 ml of toluene, the resulting solution was washed 3 times with deionized water (250 ml), dried and concentrated in vacuum (rotary evaporator) to 40 ml. Addition of 150 ml of methanol precipitated the crude polymer. Subsequent purification was achieved using several additional dissolving/precipitation cycles. Finally, the precipitated polymer flakes were filtered to the cellulose thimble and processed using Soxhlet extraction with hexanes (12 h), acetone (12 h), dichloromethane (12 h) and chlorobenzene (12 h). The chlorobenzene extract was concentrated in vacuum and precipitated in methanol. The obtained solid was collected by filtration and dried in vacuum. The resulting crude polymer was further purified from the residual Pd catalyst as described (K. T. Nielsen, K. Bechgaard and F. C. Krebs, *Macromolecules*, 2005, 38, 658 and K.T. Nielsen, K. Bechgaard and F.C. Krebs, *Synthesis*, 2006, 10, 1639). The total yield of the purified polymers varied between 60 and 90% depending on the initial molecular weight and number of the applied

dissolving/precipitation cycles. All prepared polymer samples were transferred immediately inside argon glove box where they were stored in the absence of direct light.

## Materials and instrumentation

All solvents and reagents were purchased from Sigma-Aldrich or Acros Organics and used as received or purified according to standard procedures. Starting monomers **M1**, **M2** and **M3** were synthesized according to the procedures described in the literature [I. V. Klimovich, D. K. Susarova, F. A. Prudnov, L. N. Inasaridze, O. A. Mukhacheva, A. V. Chernyak and P. A. Troshin, *Sol. Energy Mater. Sol. Cells*, 2016, **155**, 378; R. Tkachov, V. Senkovskyy, H. Komber and A. Kiriya, *Macromolecules*, 2011, **44**, 2006; L. Huo, J. Hou, S. Zhang, H.-Y. Chen and Y. Yang, *Angew. Chem. Int. Ed.* 2010, **49**, 1500]. AFM images were obtained using a NTEGRA PRIMA instrument (NT-MDT, Russia). Absorption spectra (for solutions of polymers in DCB and thin films) and PL spectra were obtained using an Avantes AvaSpec-2048 optical fiber spectrometer. Molecular weight characteristics of conjugated polymers were obtained using a Shimadzu LC20 instrument equipped with a Phenomenex Luna Phenogel 5u column (0.78×30 cm, 5-500 kDa). The measurements were performed using freshly distilled toluene as eluent (flow rate 0.5 ml min<sup>-1</sup>). The column was calibrated using custom-made F8BT standards with PDI <1.5 (toluene used as eluent). Molecular weights of the F8BT standards were cross-checked additionally using a Waters Alliance GPCV 2000 instrument equipped with multi-angle scattering detector HELEOS II (Wyatt). Each polymer sample was analyzed in several (3-5) concentrations to discriminate effects of aggregation on the molecular weight characteristics of the material. All polymers showed very weak (or no) aggregation when they were analyzed in toluene at low concentrations.

## Cyclic voltammetry measurements

The cyclic voltammetry measurements were performed for thin films (150-250 nm thick) of polymers **P1-P3** deposited on glassy carbon disc electrode (working electrode, d=5 mm, BAS Inc.) by drop casting from 1,2-dichlorobenzene, chlorobenzene, chloroform or their mixtures. The measurements were performed in a three-electrode electrochemical cell using 0.1 M solution of Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile as supporting electrolyte, platinum wire as a counter electrode and a silver wire immersed in 0.01 M solution of AgNO<sub>3</sub> in 0.1 M TBAP (CH<sub>3</sub>CN) as a reference Ag/Ag<sup>+</sup> electrode (BAS Inc.). Ferrocene was used as internal reference. The electrolyte solution was purged with argon before the measurements. The voltammograms were recorded using an ELINS P-30SM instrument at room temperature with a potential sweep rate of 50 mV s<sup>-1</sup>.

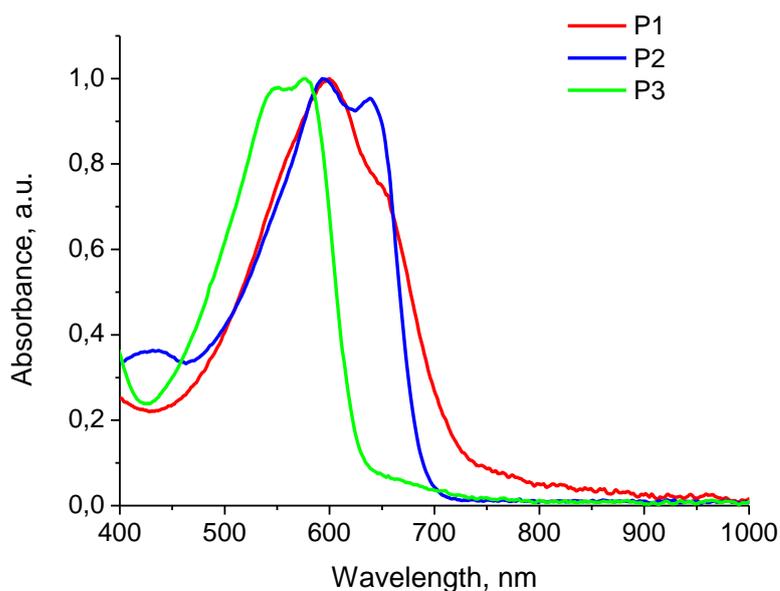
## Fabrication of photovoltaic devices

The conjugated polymers **P1**, **P2** or **P3** (8 mg) and PC<sub>61</sub>BM (16 mg) were dissolved together in 1 mL of 1,2-dichlorobenzene while stirring at room temperature for 48 h. The obtained solution was filtered through a PTFE 0.45 mm syringe filter and subjected to spin-coating at 700–1300 rpm for 150 s on the top of the annealed PEDOT:PSS (Clevios HTL) films deposited on the patterned ITO electrodes. The obtained films were transferred immediately inside the glove box and thermally annealed in an argon atmosphere at 90 °C for 15 min (**P1**), 95 °C for 10 min (**P2**), 95 °C for 5 min (**P3**). The top electrode comprising Mg (75/50/ 25 nm for **P1/P2/P3**) and Ag (145/140/100 nm for

**P1/P2/P3**) was deposited by thermal evaporation at the pressure below  $4 \times 10^{-6}$  mbar in a vacuum chamber integrated inside the MBraun glove box. The size of the active area in photovoltaic cells was  $\sim 0.5 \text{ cm}^2$  as it was defined by a shadow mask.

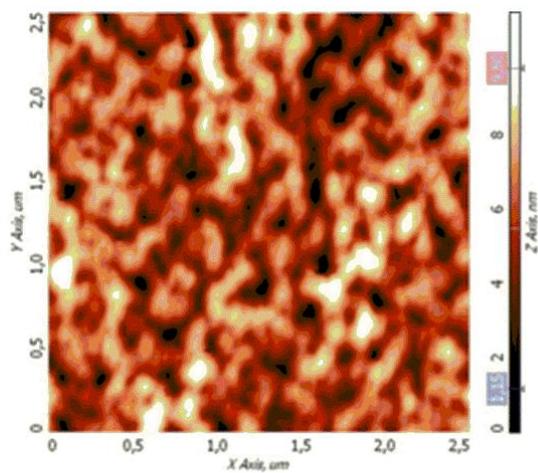
### Characterization of organic solar cells

The current-voltage (I-V) characteristics of the devices were obtained in dark and under the simulated  $100 \text{ mW cm}^{-2}$  AM1.5 solar irradiation provided by a KHS Steuernagel solar simulator integrated in MBraun glove box. The intensity of the illumination was checked every time before the measurements using a calibrated silicon diode with a known spectral response. The I-V curves were recorded in inert atmosphere using a Kethley 2400 source-measurement unit. The active areas of all devices were measured with a good accuracy just after the J-V measurements to estimate the short circuit current densities. The obtained  $J_{\text{SC}}$  values were reconfirmed by integrating the external quantum efficiency (EQE) spectra against standard AM1.5 spectrum. The EQE spectra were measured in ambient atmosphere without applying any special encapsulation or protection to the photovoltaic devices using specially designed setup, LOMO instruments, Russia.

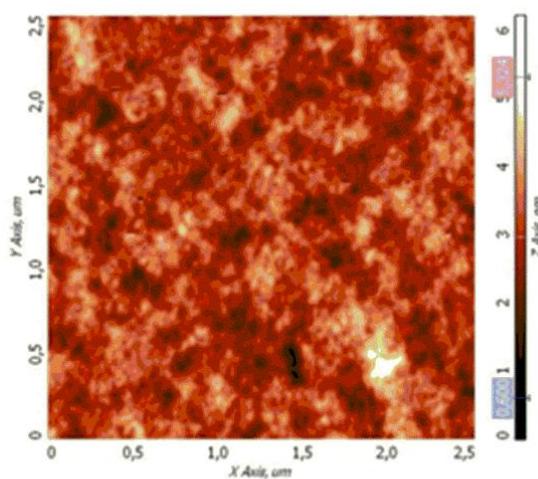


**Figure S6** Absorption spectra of **P1-P3** in 1,2-DCB.

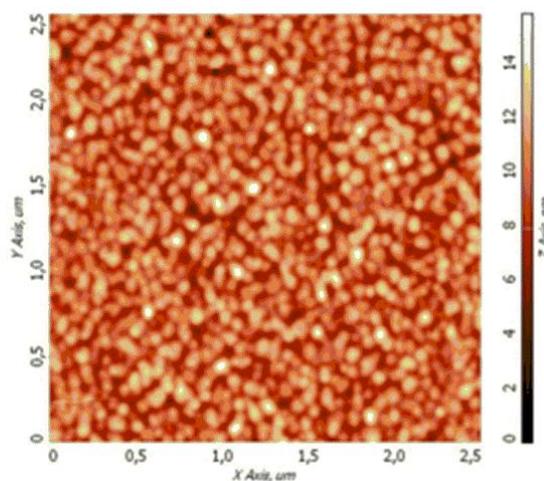
**P1/[60]PCBM**



**P2/[60]PCBM**



**P3/[60]PCBM**



**Figure S7** AFM images of thin films of **P1-P3** blended with [60]PCBM.