Supporting information for

Monodispersed molecular donors for bulk hetero-junction solar cells: from molecular properties to device performances

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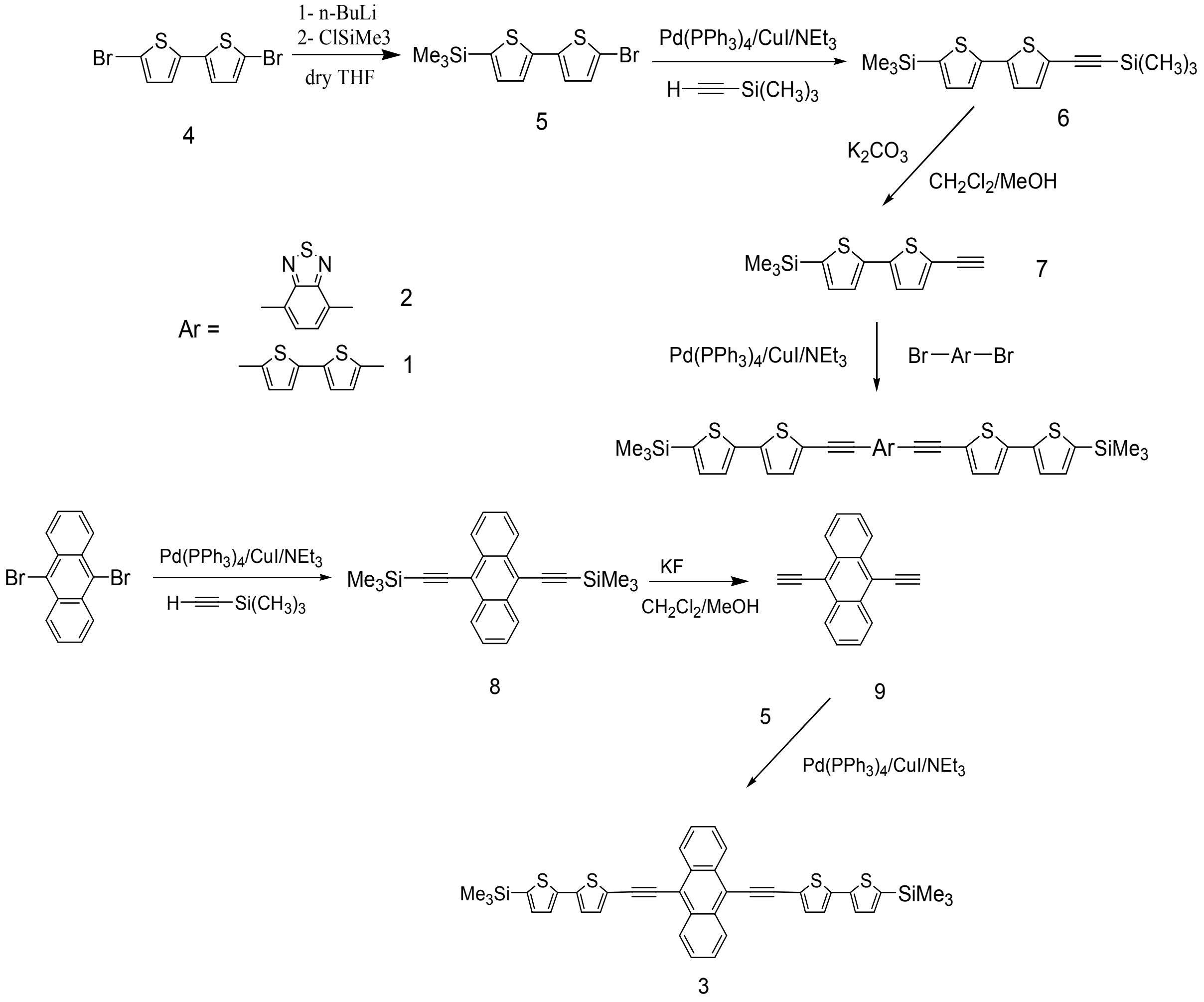


Figure S1. Synthesis of **1-3** .

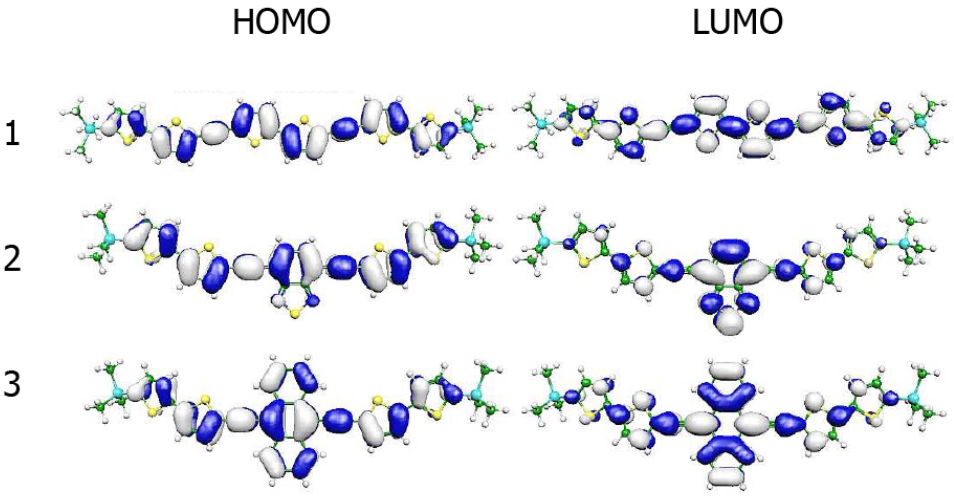


Figure S2. Frontier molecular orbitals in the ground-state configuration for **1-3**.

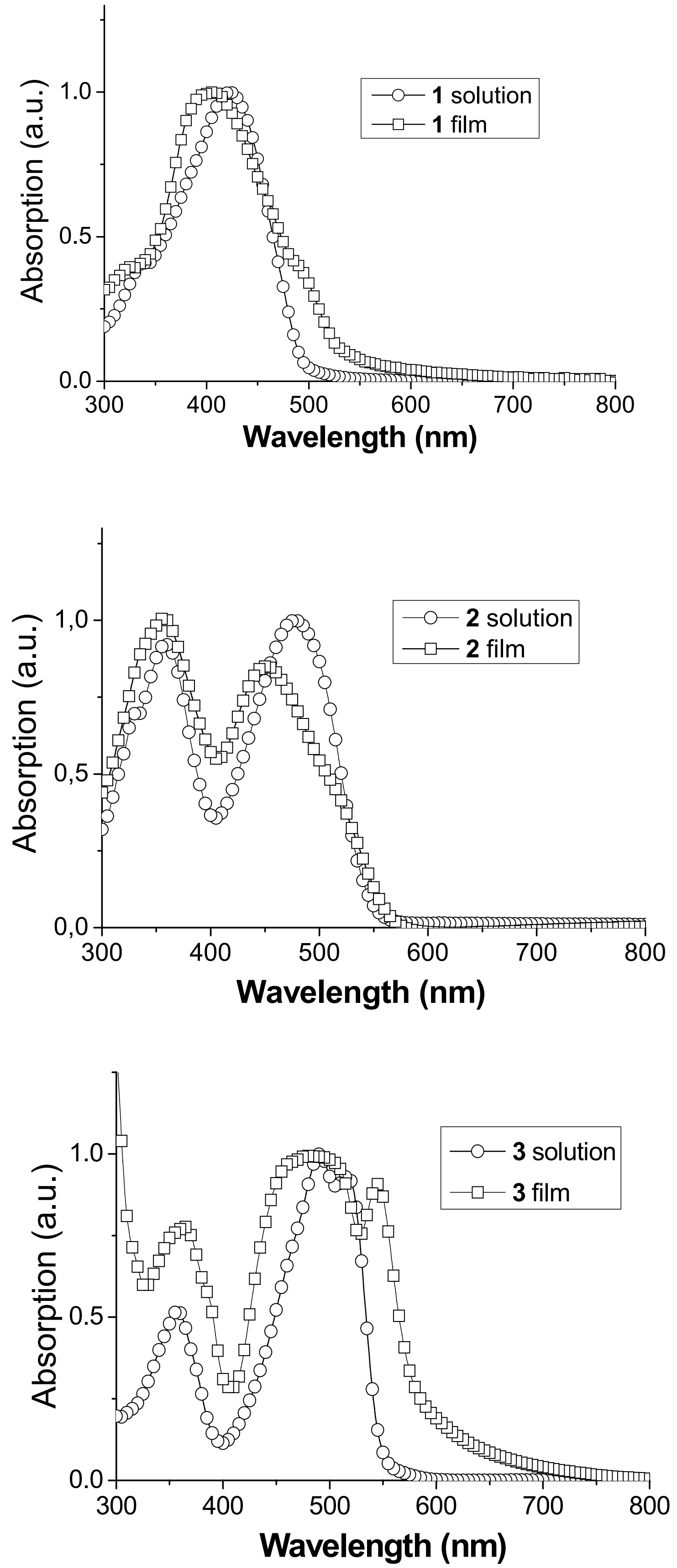
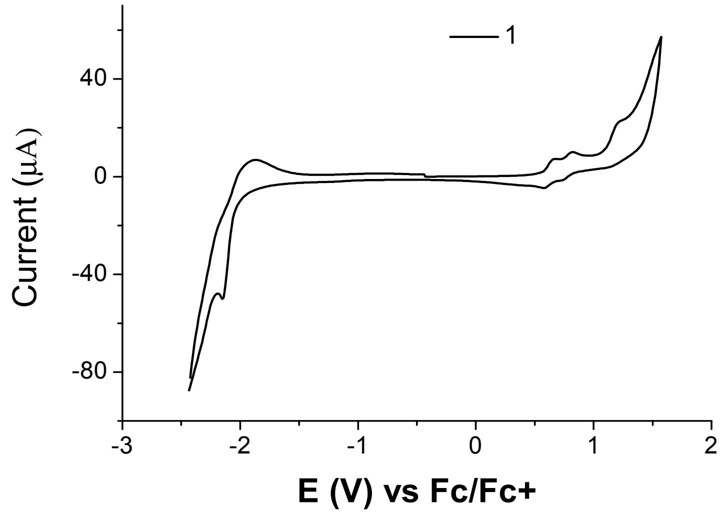
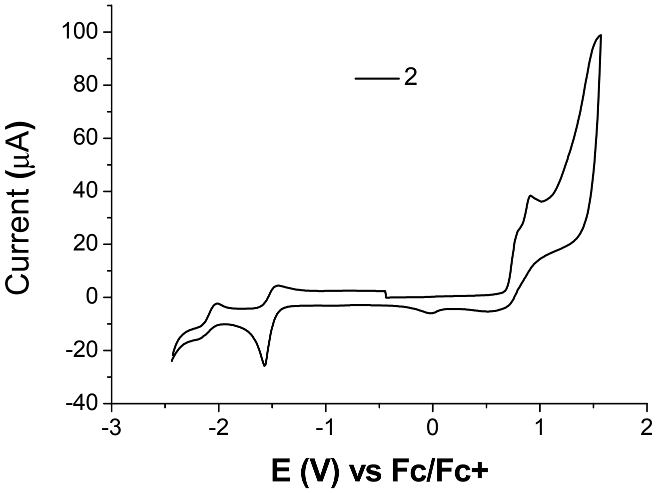


Figure S3. Optical density of **1**-**3** in dichloromethane and as spin-coated film on quartz.





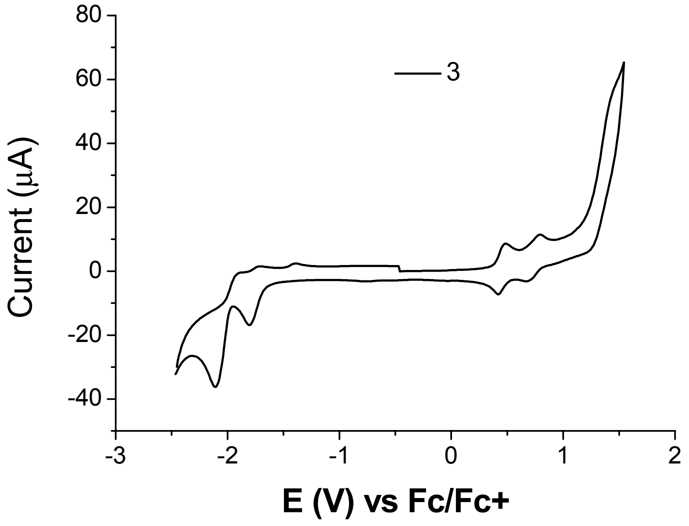


Figure S4. CV scans recorded for **1-3** compounds.

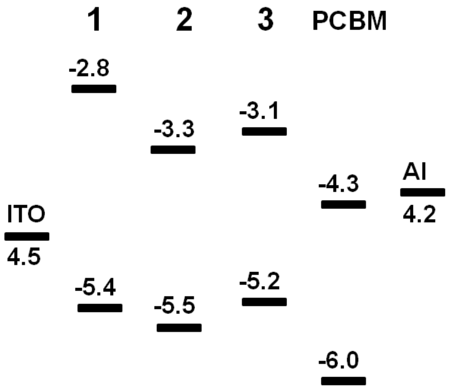


Figure S5. Experimental values obtained for the energy levels of **1**-**3** and PCBM.

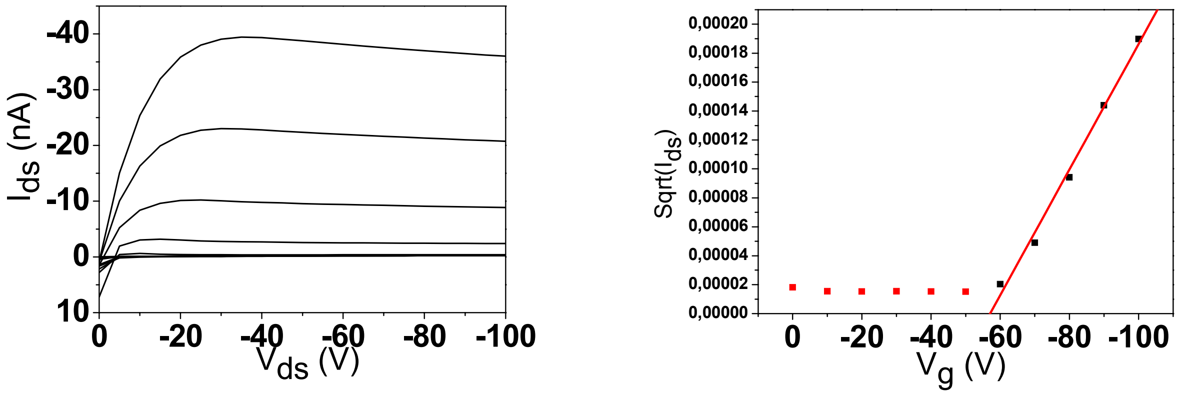


Figure S6. OTFT I_{ds} *vs*. V_{ds} current – voltage characteristics and square-root of I_{ds} vs. gate bias for compounds **3**. The extracted field effect mobility is $\mu = 2.09 *10\text{-}4\ cm^2/V{\cdot}s$, the threshold voltage is $V_t = 57.07$ V while the on/off ratio is 109.56

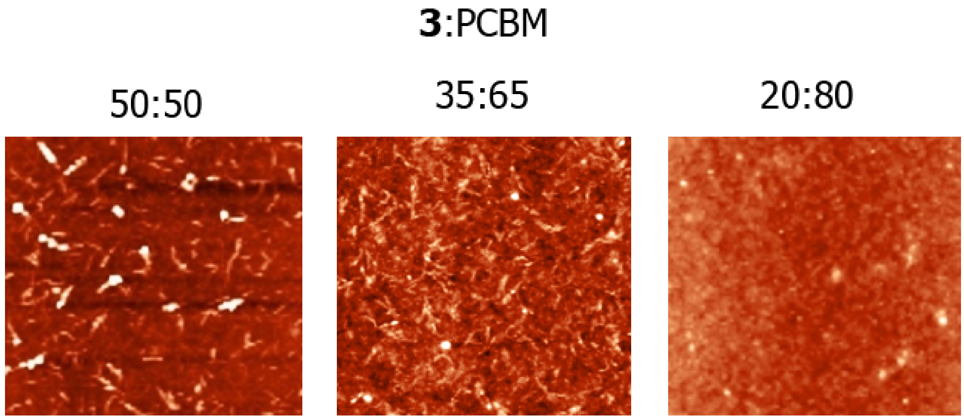


Figure S7. Tapping mode AFM topography images (10 µm x 10 µm) of **3**/PCBM at different PCBM concentrations.

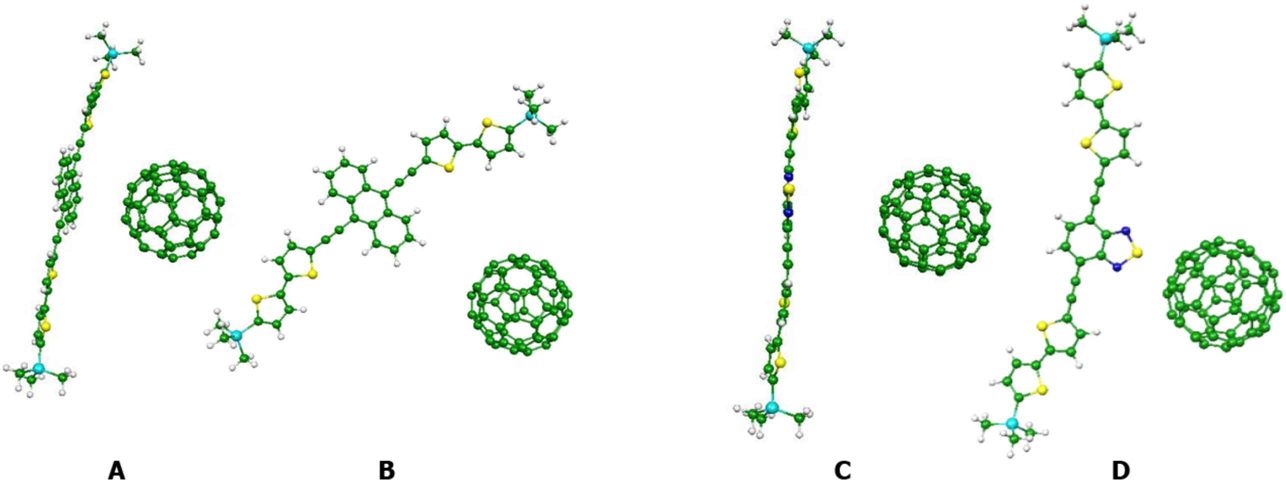


Figure S8. Molecular modeling of complexes: **3**-C_{60} in π-π configuration (molecular distance 5.20 Å) (A) and T-type configuration (molecular distance 5.32 Å) (B); **2**-C_{60} in π-π configuration (molecular distance 5.30 Å) (C) and T-type configuration (molecular distance 2.93 Å) (D).

	PCE (%)	**FF**	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**
3/PCBM (40%)	0.23	0.25	0.84	1.1
3/PCBM (50%)	0.56	0.28	0.90	2.24
3/PCBM (65%)	1.00	0.31	0.98	3.41
3/PCBM (80%)	0.70	0.30	0.89	2.65

Table S1. Photovoltaic responses properties of BHJ devices **3**/PCBM with different PCBM concentrations.

Material synthesis

All reagents were analytical grade and used as received. The solvents were carefully dried and freshly distilled prior to use according to common laboratory practice.[1] All reactions were performed under inert atmosphere using standard Schlenk techniques. Flash chromatography was performed with silica gel 60 (particle size 63 – 200 μm, 230 – 400 mesh, Merck®). NMR spectra were recorded at 295 K on a Bruker Avance 400 MHz. The chemical shifts (δ)are given in ppm and referenced to Me_4Si. Mass analyses were performed by direct injection on an Agilent HPLC system equipped with a MS systems (Agilent 1200/6320 LC-MS) and an APCI interface.

5,5'-Dibromo-[2,2']bithiophene (4). To a solution of [2,2']bithiophene (6.01 g, 36.1 mmol) in dry DMF (80 ml) NBS (12.8 g, 72.2 mmol) was slowly added at 0°C. The mixture was allowed to reach r.t., stirred for 12 h and then quenched with water. The solid was filtered and extracted from dichloromethane and water, dried with Na2SO4, filtered and concentrated under vacuum, to afford compound **4** in 92% yield.

5-bromo-5'-trimethylsilyl-[2,2']bithiophene (5). To a solution of **4** (8.75 g, 27 mmol) in freshly distilled THF (180 ml), a solution of n-BuLi (1.6 M in hexane, 16.8 mL, 27 mmol) was slowly added at -78°C. The mixture was stirred for 30 minutes and then chloro trimethyl silane (3.77 ml, 29.7 mmol) was slowly added. The reaction mixture was allowed to reach r.t., stirred for 12 h and then quenched with water. The aqueous layer was extracted with dichloromethane, dried (Na_2SO_4), filtered, and concentrated under vacuum. The crude product was purified by chromatograpy on silica gel (hexane) to afford 5-bromo-5'-trimethylsilyl-[2,2']bithiophene (**5**) as a white solid (70% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) 7.16 - 7.15 (d, *J* = 4, 1 H), 7.13-7.12 (d, *J* = 4, 1 H), 6.97 - 6.96 (d, *J* = 4, 1 H), 6.92-6.91 (d, *J* = 4, 1 H), 0.33 (s, 9 H).

5-trimethylsilanyl-5'-trimethylsilyl-ethynyl-bithiophene (6). Dry triethylamine (50 ml), 5-bromo-5'-trimethylsilyl-[2,2']bithiophene (**5**) (5.4 g, 17 mmol), CuI (0.16 g, 0.85 mmol) and $Pd(PPh_3)_4$ (0.98 g, 0.85 mmol) were placed in a flask and degassed with nitrogen. Trimethylsilyl ethyne (3.4 ml, 23.8 mmol) was then added and the mixture was refluxed for 3 h. The solvent was then evaporated to dryness and the crude product was purified by column chromatography (SiO_2, hexane) to afford **6** (21% yield, yellow solid); ^{1}H NMR ($CDCl_3$, 400 MHz) 7.24 - 7.23 (d, *J* = 3.6, 1 H), 7.15-7.14 (d, *J* = 3.6, 2 H), 7.03 – 7.02 (d, *J* = 3.6, 1 H), 0.35 (s, 9 H), 0.28 (s, 9 H).

5-trimethylsilyl-5'-ethynyl-bithiophene (7). A solution of **6** (1.1 g 3.28 mmol) and K_2CO_3 (0.45 g, 3.28 mmol) in distilled methanol (15 ml) and DCM (40 ml), was stirred at r.t. for 24 h. The crude mixture was purified by column chromatography on silica using CH_2Cl_2:Hex (1:1) as eluent and washed with methanol to give compound **7** (95% yield, pale yellow solid); ^{1}H NMR ($CDCl_3$, 400 MHz) 7.24 – 7.23 (d, *J* = 3.6, 1 H), 7.18 - 7.17 (d, *J* = 4, 1 H), 7.14 – 7.13 (d, *J* = 3.2, 1 H), 7.03 – 7.02 (d, *J* = 4, 1 H), 3.4 (s, 1 H), 0.33 (s, 9 H). ^{13}C NMR ($CDCl_3$, 400 MHz) 141.31, 140.9, 139.2, 134.76, 133.96, 125.62, 123.26, 120.46, 82.14, 76.92.

9,10-Bis-trimethylsilylethynyl-anthracene (8). Dry triethylamine (50 ml), 9,10-dibromo anthracene (5 g, 14.9 mmol), CuI (0.14 g, 0.75 mmol) and $Pd(PPh_3)_4$ (0.85 g, 0.75 mmol) were placed in a flask and degassed by freeze and pump. Trimethylsilyl ethyne (4.2 ml, 29.8 mmol) was then added and the mixture was refluxed for 3 h. The solvent was then evaporated to dryness, extract by DCM/water and the crude product was purified by column chromatography (SiO_2, hexane) to afford **8** (45%, red solid). ^{1}H NMR ($CDCl_3$, 400 MHz) 8.59 – 8.57 (dd, J = 3.35, 6.7, 4 H), 7.63-7.60 (dd, J = 3.35, 6.7, 4 H), 0.43 (s, 18 H).

9,10-Diethynyl-anthracene (9). To a solution of **8** (0.6 g 1.62 mmol) in distilled DCM (5 ml) a solution of anhydrous KF (0.94 g, 16.2 mmol) in distilled methanol (5 ml) was added and refluxed for 12 h. The crude mixture was purified by column chromatography on silica using CH_2Cl_2 as eluent to give compound **9** (40% yield, dark red solid); ^{1}H NMR ($CDCl_3$, 400 MHz) 8.62 – 8.60 (dd, J = 3.35, 6.7, 4 H), 7.63-7.61 (dd, J = 3.0, 6, 4 H), 4.1 (s, 2 H).

Compound 1. A solution of 5,5'-dibromo-dithiophene **4** (0.123 g, 0.38 mmol), 5-trimethylsilyl-5'-ethynyl-dithiophene **7** (0.210 g, 0.8 mmol), CuI (0.007 g, 0.038 mmol) and $Pd(PPh_3)_4$ (0.044 g, 0.038 mmol) in dry triethylamine (5 ml), were placed in a flask and degassed with freeze and pump techniques. The solution was refluxed for 24 h, the solvent was then evaporated to dryness and the crude product, after extraction by DCM/water, was purified by column chromatography (SiO_2, Petroleum ether:DCM = 1:1) to afford **3** (37%, reddish brown solid). ^{1}H NMR (CD_2Cl_2, 400 MHz) 7.30 – 7.29 (d, J = 3.2, 2 H), 7.23 - 7.22 (d, J = 4, 4 H), 7.19 - 7.18 (d, J = 3.2, 2 H), 7.15-7.12 (m, 4 H), 0.37 (s, 18 H). MS (m/z) 687 (M+ [H^+]).

Compound 2. A solution of 4,7-dibromo-benzothiadiazole (0.111 g, 0.38 mmol), 5-trimethylsilyl-5'-ethynyl-dithiophene **7** (0.210 g, 0.8 mmol), CuI (0.007 g, 0.038 mmol) and $Pd(PPh_3)_4$ (0.044 g, 0.038 mmol) in dry triethylamine (5 ml), were placed in a flask and degassed by freeze and pump. The solution was refluxed for 24 h, the solvent was then evaporated to dryness and the crude product, after extraction by DCM/water, was purified by column chromatography (SiO_2, Petroleum ether:DCM = 4:1) to afford **2** (27%, orange solid). ^{1}H NMR (CD_2Cl_2, 400 MHz) 7.79 (s, 2 H), 7.37 - 7.36 (d, J = 4, 2 H), 7.33 - 7.32 (d, J = 3.2, 2 H), 7.20-7.17 (m, 4 H), 0.35 (s, 18 H). ^{13}C NMR ($CDCl_3$, 400 MHz) 154.6, 142.0, 141.7, 141.0, 135.5, 134.8, 132.6, 126.3, 124.4, 121.3, 117.2, 91.2, 91.0, 0. MS (m/z) 657.1 (M+ [H^+]).

Compound 3. A solution of 9,10-diethynyl-anthracene **9** (0.106 g, 0.47 mmol), 5-bromo-5'-trimethylsilyl-[2,2']bithiophene **5** (0.313 g, 0.99 mmol), CuI (0.009 g, 0.047 mmol) and $Pd(PPh_3)_4$ (0.054 g, 0.047 mmol) in dry triethylamine (5 ml), were placed in a flask and degassed by freeze and pump. The solution was refluxed for 48 h, the solvent was then evaporated to dryness and the crude product, after extraction by DCM/water, was purified by column chromatography (SiO_2, Petroleum ether : DCM = 4:1) to afford **1** (31%, red solid). ^{1}H NMR (CD_2Cl_2, 400 MHz) 8.62 – 8.60 (dd, J = 3.35, 6.7, 4 H), 7.69 - 7.67 (dd, J = 3.35, 6.7, 4 H), 7.45 - 7.44 (d, J = 4, 2 H), 7.36-

7.35 (d, *J* = 3.2, 2 H), 7.23 – 7.21 (m, 4 H), 0.37 (s, 18 H). ^{13}C NMR ($CDCl_3$, 400 MHz) 141.9, 141.8, 140.4, 135.5, 134.0, 132.3, 127.6, 126.2, 124.5, 122.1, 118.6, 96.5, 92.2, 0.065. MS (m/z) 699.1 (M+ [H^+]).

Experimental details

PV Device Fabrication and Testing

All compounds have been tested in photovoltaic devices with structure ITO/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (40 nm)/**1**-**2**-**3** : PCBM (~100nm)/Ca (25 nm)/Al (150 nm). The layer thickness was measured with a Tencor Alpha-Step 500 Surface Profiler. Organic BHJ PV cells were fabricated on patterned ITO-coated glass substrates as the anode. The substrates were cleaned by ultrasonication in acetone, water and isopropanol. The ITO surface was then modified by spin-coating of a conductive poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) thin film (~40nm) purchased by HC Starck, followed by a baking at 140°C in nitrogen atmosphere for 15 minutes.

Compounds **2** and **3** were blended with PCBM in chloroform with a concentration of 16mg/ml, while the **1**:PCBM blend was prepared with a concentration of only 8mg/ml because of its lower solubility. Device fabrication was completed by thermal evaporation deposition of the cathode (25nm of calcium and 150nm of aluminum) in a Cluster Tool Kurt J. Lesker UHV with a base pressure of ~10^{-7} mbar. The solar cells, with an active area of 25 mm^2, were encapsulated before testing in air. Current-voltage (I-V) characteristics and IPCE measurements were recorded using a computer-controlled Keithley 2400 source meter while the solar cells where illuminated by a Spectra Physics Oriel 150W Solar Simulator at 100 mWcm^{-2} (AM1.5D) white light, or by monochromatic light using a DK240 monochromator.

Organic Thin-Film Transistor fabrication

The semiconducting properties of compounds were investigated by fabricating OTFT devices in top contact bottom gate configuration. The active layers were deposited by spin coating from 2 mg mL^{-1} chloroform solutions onto a SiO_2 (300 nm)/n-doped Si substrate. The SiO_2 surface was alkylated by treatment in 1,1,1,3,3,3-hexamethyldisilazane saturated vapours for 24 h. A series of 30 gold source (S) and drain (D) contacts were defined, by thermal evaporation through a shadow mask, directly on the organic films. The transistor characteristics were measured by polarizing the devices up to −100 V. Since p-type behavior was expected, negative source-drain and gate voltage biases were applied. The field effect mobility was extracted as reported elsewhere.[2]

Electrochemical, optical and morphological characterization

Cyclic voltammetry (CV) experiments were carried out in a dry dichloromethane solution of concentration $\sim 10^{-3}$M at room temperature in nitrogen atmosphere using a computer-controlled Autolab PGSTAT100 Potentiostat. The supporting electrolyte was tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 98% Aldrich, ~0,1M). Platinum disk was used as working electrode (WE), platinum wire as counter electrode (CE) and Ag/AgCl as reference electrode (RE). Ferrocene redox couple (Fc/Fc^+) was used as internal standard.[3]

The electronic absorption spectra were recorded on a Varian Cary 5000 double beam UV-Vis-NIR spectrometer and baseline corrected. AFM has been carried out on a Solver PRO Scanning Probe Microscope (NT-MDT). Images were acquired in tapping mode. Confocal laser scanning microscopy was carried out on an Olympus FluoView1000 instrument.

Computational details

Density-functional theory calculations employing the B3LYP[4] functional and the TZVP basis set[5] were performed to optimize and compute the ground-state geometric and electronic structure of isolated compounds **1**,**2** and **3**.

To study the **2**-C_{60} and **3**-C_{60} complexes relevant p-p and T-type configurations were optimized at the PBE/TZVP level of theory[6] including empirical dispersion corrections.[7] The binding energy of the complexes were obtained by applying a counter-poise procedure.[8] Starting configurations for geometry optimization were sampled at the AM1 level.[9]

All DFT calculations were performed with the TURBOMOLE[10] program package. AM1 calculations were performed with the Gaussian03 program.[11]

References for supporting informations

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