Supporting information for

Conjugated Anthracene Derivatives as Donor Materials for Bulk-Heterojunction Solar Cells: Olefinic *versus* Acetylenic Spacers

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General remarks. Melting points were determined on a Buchi melting point apparatus and are uncorrected. Chromatography was performed on Riedel de Haën silica gel (230-400 mesh ASTM). NMR spectra were recorded on a Varian Associates VXR-400 multinuclear instrument (internal Me_4Si). UV-vis spectra were recorded on a Cary Model 1 UV-vis spectrophotometer. Commercially available reagents were purchased from Sigma-Aldrich Co. and utilized without further purification, unless otherwise noted. PCBM was purchased from American Dye Source, Inc. (ADS) and was further purified by several cycles of sonication in toluene followed by filtration, and then sonication in pentane, followed by centrifugation. Petroleum ether as the 40°-60°C boiling fraction was used. Electrochemistry was performed on a C3 Cell Stand Electrochemical Station equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN) in an electrolyte solution of 0.1M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) in dry dichloromethane. Platinum wire or carbon electrodes were used as working electrodes, platinum wire was used as counter electrodes, and a silver wire was used as the pseudo-reference electrode. A ferrocene/ferrocenium redox couple was used as an internal standard and the potential values obtained in reference to the silver electrode were converted to the vacuum scale. TGA analyses were performed under nitrogen on a TA Instruments Q50 instrument (scan rate 10°C/min).

BHJ OPV device fabrication and Thin Film Characterization. Devices were fabricated by spin-coating at 6000 rpm (60”) under air a blend of **1-4 :** PCBM in a 1:1 ratio (16mg/mL total for **1**,**2** and **4**, and 8mg/ml total for **3**; dry chloroform as solvent) on anodes consisting of glass substrates pre-coated with indium tin oxide (ITO). Before device fabrication, the ITO-coated (~150 nm) glass substrates were cleaned by ultrasonic treatment in detergent, deionized water and soap, deionized water, isopropyl alcohol, methanol and acetone sequentially and finally in a UV-ozone cleaner for 30 minutes under ambient atmosphere. A thin layer (~30 nm) of PEDOT/PSS (Baytron P VP A1 4083) was then spin-coated on the anode to modify the ITO surface, followed by baking at 150 °C for 15 min. Immediately after the spin-coating, the films were kept in a covered glass petri dishes for drying. In a nitrogen-filled glove box (<1 ppm O_2 and H_2O), LiF/Al (~0.12 nm / ~150 nm) cathodes were next deposited sequentially without breaking vacuum using a thermal evaporator. The deposition rates used were 0.1 Å/s for LiF (Acros, 99.98%) and ~2 Å/s for Al (Sigma-Aldrich, 99.999%), with a chamber pressure of 1.1×10^{-6} Torr. Finally, the completed solar cells were encapsulated with a glass slide using UV-curable epoxy (Electron-lite Corp., ELC-2500) which was cured in a UV chamber inside the glove box.

Atomic force microscopic (AFM) images were obtained using a JEOL-5200 Scanning Probe Microscope with silicon cantilevers in the tapping mode, using WinSPM Software.

BHJ OPV I-V characterization. Device evaluation was performed at 298K using a Class A Spectra-Nova Technologies solar cell analyzer having a xenon lamp that simulates AM1.5G light from 400 – 1100 nm. The instrument was calibrated with a monocrystalline Si diode fitted with a KG3 filter to bring spectral mismatch to unity. The calibration standard was calibrated by the National Renewable Energy Laboratory (NREL). Four-point contacts were made to the substrate with Ag paste and copper alligator clips. Individual devices were isolated by a mask during testing to avoid current collection from adjacent devices and edge effects.

Materials Synthesis.

3,4-(Bishexyloxy)-styrene (5). To a solution of trimethylphosphonium bromide (0.5 g, 1.4 mmol) in dry THF (12 ml) a solution of n-BuLi (1.6 M in hexane, 0.63 mL, 1.0 mmol) was slowly added at 0°C. The mixture was stirred for 3 h and then 3,4-(bishexyloxy)-benzaldehyde[1] (0.15 g, 0.49 mmol) was added. The reaction mixture was allowed to stand at r.t., stirred for 12 h and then quenched with water. The aqueous layer was extracted with dichloromethane, washed with water and brine, dried (Na_2SO_4), filtered, and concentrated under vacuum. The crude product was purified by chromatograpy on silica gel (hexane/dichloromethane 4:1) to afford 3,4-(bishexyloxy)-styrene **5** as a colorless oil (91% yield); (Found: C, 79.13; H,10.58. Calcd. for: $C_{20}H_{32}O_2$: C, 78.90; H, 10.59%); δ_H ($CDCl_3$) 0.85 (m, 6H), 1.30 (m, 8H), 1.42 (m, 4H), 1.76 (m, 4H), 3.95 (m, 4H), 5.07 (d, 1H, J=10.8 Hz), 5.53 (d, 1H, J= 17.0 Hz), 6.58 (m, 1H), 6.77 (d, 1H, H= 8.2 Hz), 6.86 (m, 1H), 6.92 (d, 1H, J= 1.9 Hz) ; δ_C ($CDCl_3$) 149.1, 136.5, 130.7, 119.5, 113.6, 111.5, 111.3, 69.2, 31.6,29.2, 25.7, 22.6, 14.0.

Compound 7. To a solution of trimethylphosphonium bromide (0.64 g, 1.78 mmol) in dry THF (13 ml) a solution of n-BuLi (1.6 M in hexane, 0.8 mL, 1.28 mmol) was slowly added at 0°C. The mixture was stirred for 3h and then compound **6** (0.25 g, 0.62 mmol) was added. The reaction mixture was allowed to warm at r.t., stirred for 12 h and then quenched with water. The aqueous layer was extracted with dichloromethane, washed with water and brine, dried (Na_2SO_4), filtered, and concentrated under vacuum. The crude product was chromatographed on silica gel eluting with petroleum ether/dichloromethane (7:3) to afford stilbene-like compound **7** as a pale yellow solid (60% yield); (Found: C, 82.52; H, 9.43. Calcd. for: $C_{28}H_{38}O_2$: C, 82.71; H, 9.42 %); mp 70-71°C (from MeOH); δ_H ($CDCl_3$) 0.86 (m, 6H), 1.36 (m, 12H), 1.79 (m, 4H), 3.96 (m, 4H), 5.18 (d, 1H, J= 10.8 Hz), 5.70 (d, 1H, J= 17.0 Hz), 6.66 (m, 1H), 6.80 (d, 1H, J= 8.2 Hz), 6.88 d, 1H, J= 16.2 Hz), 6.99 (m, 3H), 7.37 (m, 4H); δ_C ($CDCl_3$) 149.3, 149.2, 137.2, 136.5, 130.4, 128.5, 126.5, 126.3, 126.2, 120.0, 113.7, 113.4, 111.5, 69.3, 69.2, 31.6, 29.3, 29.2, 25.7, 22.6, 14.0.

Compounds 1,2,6. General Procedure. The Heck reaction procedure[2] described for preparing **1** is that used for preparing compounds **2** and **6**.

A dried flask was charged under Ar with K_3PO_4 (0.09 g, 0.42 mmol), and DMF (1.5 ml). Next, 9,10-dibromoanthracene (0.05 g, 0.15 mmol) and the respective terminal alkene 3,4-(bishexyloxy)-styrene (0.108 g, 0.36 mmol) were added. A solution of $Pd(OAc)_2$ in DMF (0.01 M, 30μL, 0.0003 mmol) was then added via syringe. The flask was sealed under Argon and placed in an oil bath preheated to 140°, and the reaction mixture was stirred for 24 h at this temperature. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate. The combined extracts were washed with brine, dried and concentrated to dryness under vacuum. The crude product was purified by column chromatography on silica gel to afford the desired product.

1: purified by column chromatography (hexane/dichloromethane 7:3); yellow solid (70% yield); (Found: C, 83.36; H,9.07. Calcd. for: $C_{57}H_{74}O_4$: C, 83.16; H, 9.06%); mp 118-119°C (from ethyl acetate); δ_H ($CDCl_3$) 0.86 (m, 12H), 1.32 (m, 16H), 1.47 (m, 8H), 1.82 (m, 8H), 4.04 (m, 8H), 6.79 (d, 2H, J= 16.5 Hz), 6.90 (d, 1H, J=8.3 Hz), 7.12 (m, 2H), 7.42 (m, 4H), 7.71 (d, 2H, J= 16.3 Hz), 8.35 (m, 4H); δ_C ($CDCl_3$) 149.5, 137.2, 132.7, 130.6, 129.6, 126.5, 125.1, 122.9, 120.0, 113.9, 111.7, 69.5, 69.4, 31.6, 29.3, 29.2, 25.7, 22.6, 14.0; λ_{max} ($CHCl_3$)/nm 267 (logε 5.0), 317 (4.4), 417 (4.3).

2: Prepared by coupling 9,10-dibromoanthracene and compound **7** (1/2.3); purified by column chromatography (petroleum ether/dichloromethane 1:1); yellow solid (60% % yield); (Found: C, 84.89; H, 8.38. Calcd. for: $C_{70}H_{82}O_4$: C, 85.15; H, 8.37 %); mp 205-206°C (from toluene); δ_H ($CDCl_3$) 0.87 (m, 12H), 1.031 (m, 16H), 1.45 (m, 8H), 4.02 (m, 8H), 6.95 (m, 12H), 7.43 (m, 4H), 7.53 (d, 4H, J= 8.3 Hz), 7.62 (d, 4H, J= 8.3 Hz), 7.90 (d, 2H, J=16.4 Hz), 8.36 (m, 4H); δ_C ($CDCl_3$) 149.2, 137.4, 137.1, 136.1, 132.7, 130.4, 129.6, 128.7, 126.9, 126.6, 126.5, 126.1, 125.2, 124.7, 120.1, 113.6, 111.4, 69.3, 69.2, 31.6, 29.3, 29.2, 25.7, 28.6$_9$, 22.6, 14.0; ; λ_{max} ($CHCl_3$)/nm 268 (logε 4.9), 349 (4.8), 423 (4.7).

6: Prepared by coupling 4-bromobenzaldehyde and 3,4-(bishexyloxy)-styrene (1/1.2); purified by column chromatography (petroleum ether/dichloromethane 1:1); yellow solid (80% % yield); (Found: C, 79.52; H,8.87. Calcd. for: $C_{27}H_{32}O_3$: C, 79.37; H, 8.88%); mp 66°C (from MeOH); δ_H ($CDCl_3$) 0.86 (m, 6H), 1.36 (m, 12H), 1.77 (m, 4H), 6.81 (d, 1H, J= 8.3 Hz), 6.93 (d, 1H, J= 16.3 Hz), 7.00 (m, 2H), 7.14 (d, 1H, J= 16.3 Hz), 7.57 (d, 2H, J= 8.3 Hz), 7.80 (d, 2H, J= 8.3 Hz); δ_C ($CDCl_3$) 191.5, 149.9, 149.3, 143.8, 132.1, 132.2, 129.5, 126.5$_4$, 125.1, 120.7, 113.4, 111.7, 69.4, 69.2, 31.5, 29.2, 25.7, 22.6, 14.0.

Compound 9. Dry toluene (7 ml), 4-(iodophenylethynyl)trimethylsilane (0.46 g, 1.53 mmol), CuI (0.0052 g, 0.03 mmol), $Pd(PPh_3)_4$ (0.032 g, 0.03 mmol) and diisopropylamine (3 ml) were placed in a flask and degassed with argon at 0°C. 3,4-(Bishexyloxy)-ethynylbenzene **8** (0.42 g, 1.4 mmol) was then added and the mixture was kept at 45°C for 18 h. The solvent was then evaporated to dryness and the crude product was purified by column chromatography (SiO_2, petroleum ether/dichloromethane 3:1) to afford **9** (99% yield, pale yellow crystals); (Found: C, 78.66; H, 8.93. Calcd. for: $C_{31}H_{42}O_2Si$: C, 78.43; H, 8.92 %); mp 57-58°C (from MeOH); δ_H ($CDCl_3$) 0.19 (s, 9H), 0.85 (m, 6H), 1.28 (m, 8H), 1.42 (m, 4H), 1.76 (m, 4H), 3.97 (m, 4H), 6.77 (d, 1H, J= 8.3 Hz), 6.97 (d, 1H, J= 1.9), 7.03 (dd, 1H, J= 1.9, 8.3 Hz), 7.37 (m, 3H); δ_C ($CDCl_3$) 148.8, 148.7, 131.8, 131.1, 125.0, 122.5, 116.6, 115.7, 113.2, 104.74, 96.0, 91.7, 87.4, 69.1, 31.5, 29.1, 25.6, 22.5, 14.0, -0.3.

Compound 10. To a solution of **9** (0.51 g, 1.07 mmol) in dry THF (6 ml) was added tetrabutylamoniumfluoride (1.61 ml, 1.51 mmol). The mixture was kept under nitrogen and magnetically stirred at 25°C for 15 h. The solvent was then removed *in vacuo*. The residue was chromatographed on silica gel (eluent: hexane/dichloromethane 3:1) to obtain compound **10** (93% yield) as white solid; (Found: C, 83.28; H,8.50. Calcd. for: $C_{28}H_{34}O_2$: C, 83.54; H, 8.51 %); mp 70-71°C (from MeOH); δ_H ($CDCl_3$) 0.86 (m, 6H), 1.27 (m, 8H), 1.44 (m, 4H), 1.77 (m, 4H), 3.01 (s, 1H), 3.66 (m, 4H), 6.77 (d, 1H, J= 8.3 Hz), 6.97 (d, 1H, J= 1.9_8 Hz), 7.04 (dd, 1H, J= 1.9_8, 8.3 Hz), 7.39 (m, 3H); δ_C ($CDCl_3$) 149.9, 148.7, 132.0, 131.2, 125.0, 124.1, 121.4, 116.6, 114.9, 113.2, 91.8, 87.3, 83.3, 78.7, 69.2, 69.1, 31.5, 29.1_3, 29.1_1, 25.6, 22.6, 14.0.

Compound 3. Dry toluene (4.2 ml), 9,10-dibromoanthracene (0.13 g, 0.38 mmol), CuI (0.003 g, 0.015 mmol), $Pd(PPh_3)_4$ (0.018 g, 0.015 mmol), and diisopropylamine (1.8 ml) were placed in a flask and degassed with argon at 0°C. Compound **10** (0.312, 0.77 mmol) was then added and the mixture was kept at 60°C for 18 h. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel (elution: hexane/dichloromethane 7:3) to give compound **3** (80% yield) as an orange solid; (Found: C, 86.03; H,7.63. Calcd. for: $C_{70}H_{74}O_4$: C, 85.85; H, 7.62 %); mp 167-170°C (from ethyl acetate); δ_H ($CDCl_3$) 0.87 (m, 12H), 1.30 (m, 16H), 1.44 (m, 8H), 1.79 (m, 8H), 3.99 (m, 8H), 6.80 (d, 2H, J= 8.4Hz), 7.02 (m, 2H), 7.08 (m, 2H), 7.54 (d, 4H, J=8.16Hz), 7.61 (m, 4H), 7.70 (dd, 4H, J=8.16Hz), 8.64 (m, 4H); δ_C ($CDCl_3$) 149.9, 148.7, 132.1,131.5, 127.2, 126.9, 125.1, 123.9, 122.7, 118.4, 116.6, 114.9, 113.2, 103.0, 102.4, 92.1, 88.2, 87.6, 69.2, 69.1, 31.6, 29.2, 25.7, 22.6, 14.0; ; λ_{max} ($CHCl_3$)/nm 279 (logε 5.0), 331 (4.8), 350 (4.7), 464 (4.9), 488 (4.8).

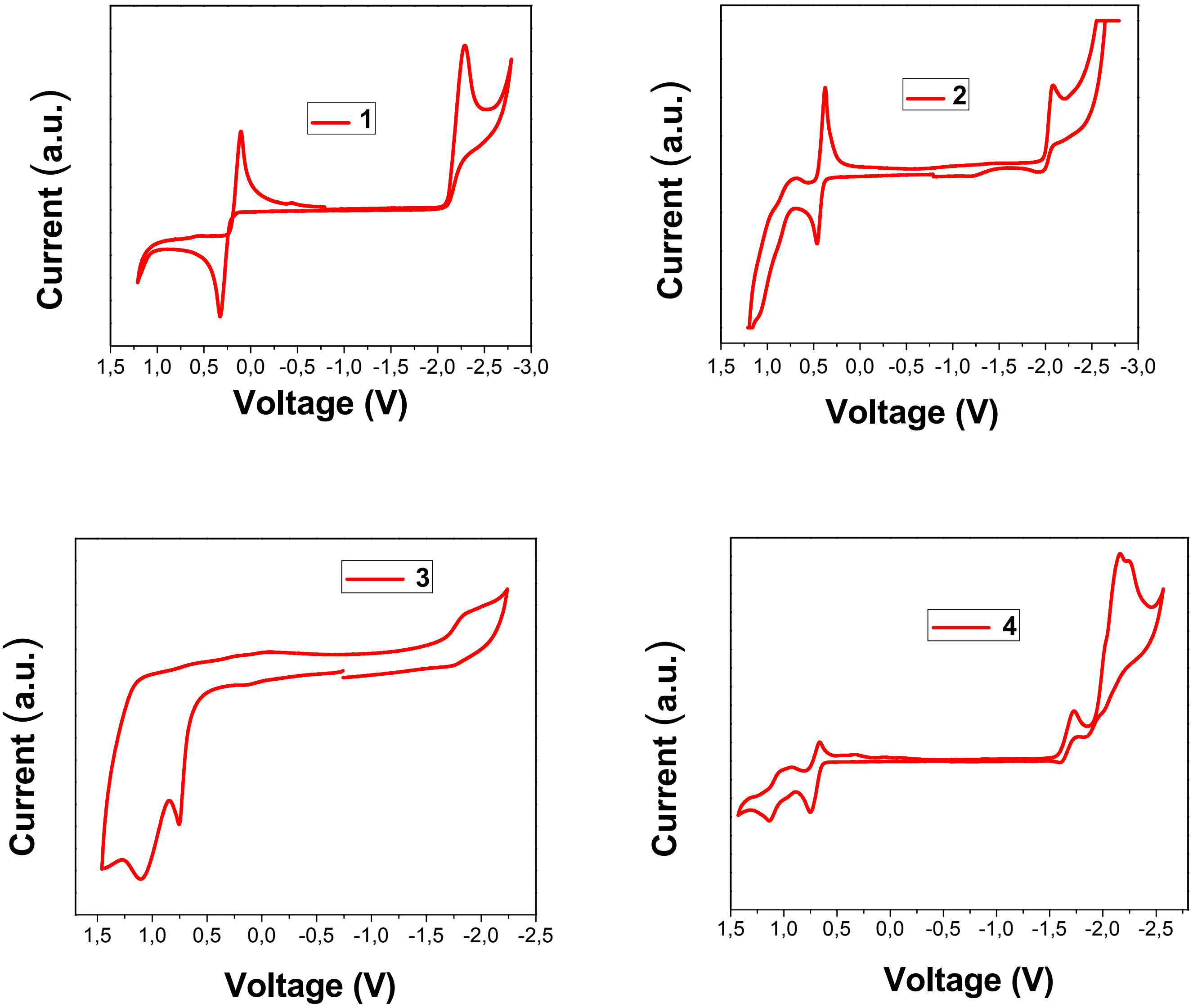

Figure S1. CV curves of anthracene derivatives **1-4** in 0.1 M $Bu_4N^+PF_6^-$ solution in CH_2Cl_2 at a scan rate of 100 mV/s. Ferrocene was used as internal standard.

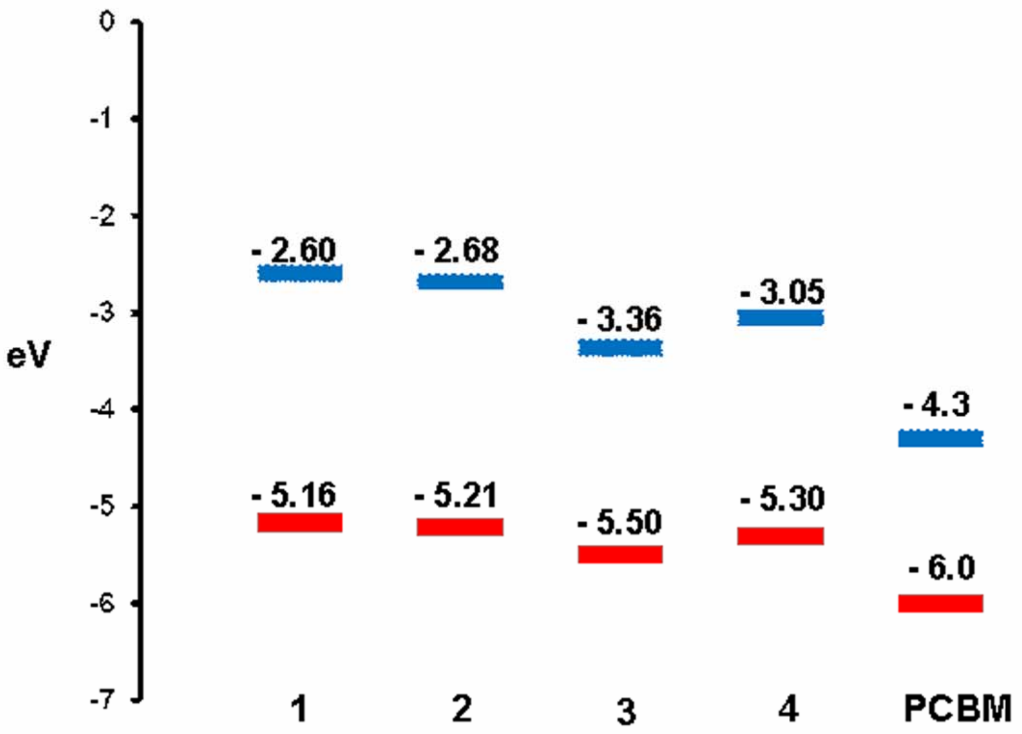

Figure S2. Energy band diagram with HOMO/LUMO levels of the donor derivatives **1**-**4** and the PCBM acceptor estimated from CV data.

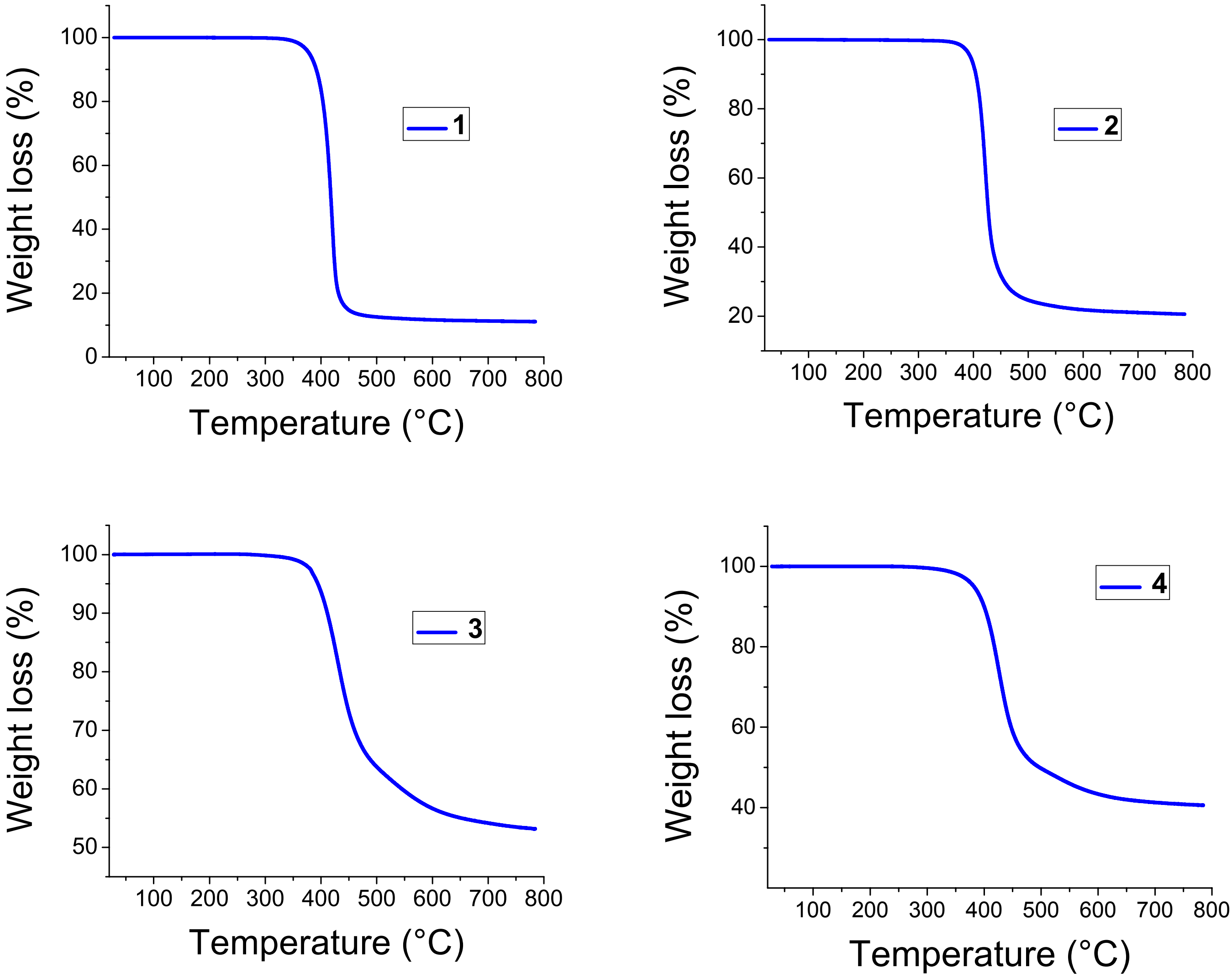

Figure S3. TGA plots obtained for the anthracene derivatives **1-4**

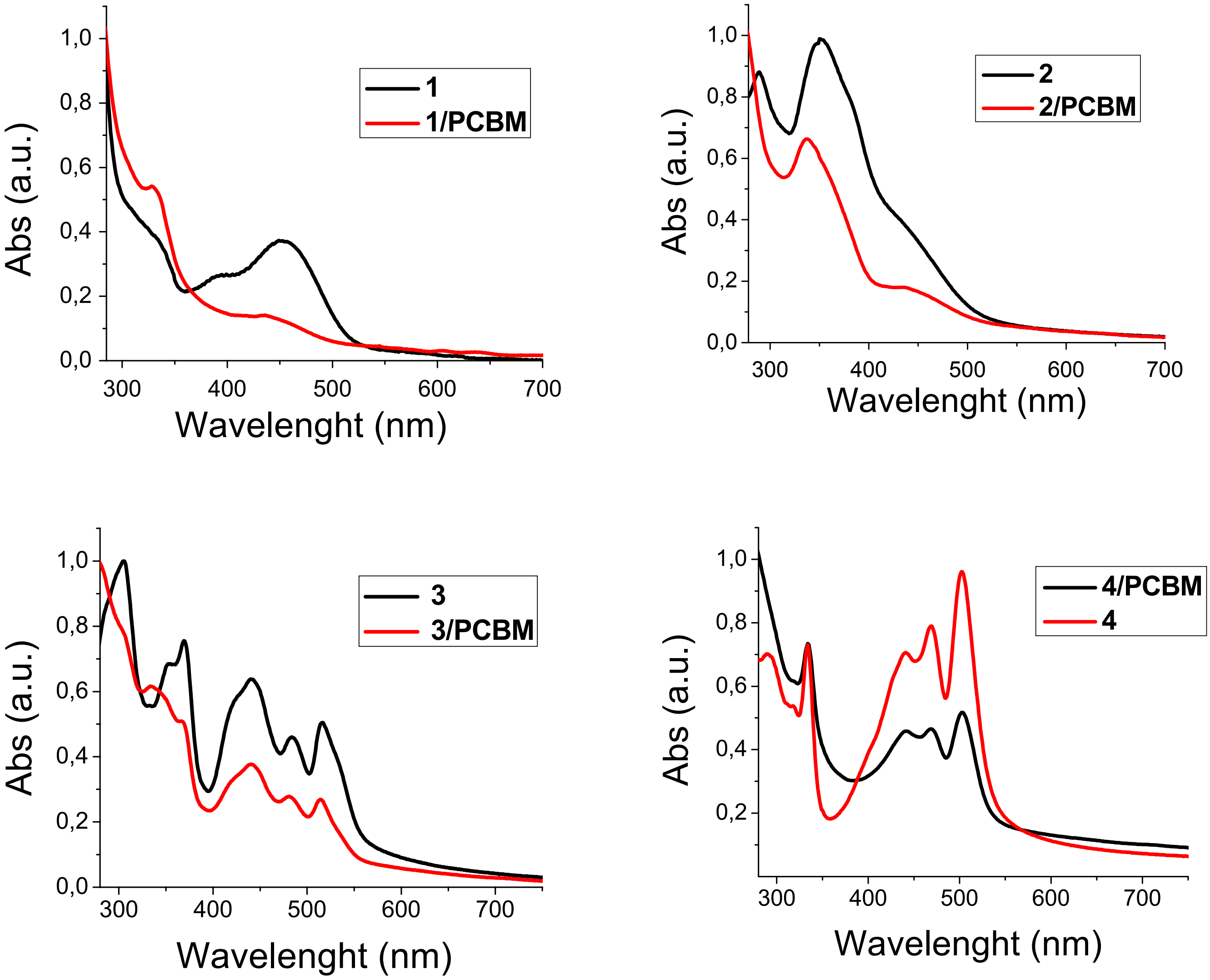

Figure S4. Absorption spectra for pristine **1**-**4**, **1**/PCBM, **2**/PCBM, **3**/PCBM and **4**/PCBM (1:1 wt/wt) thin films.

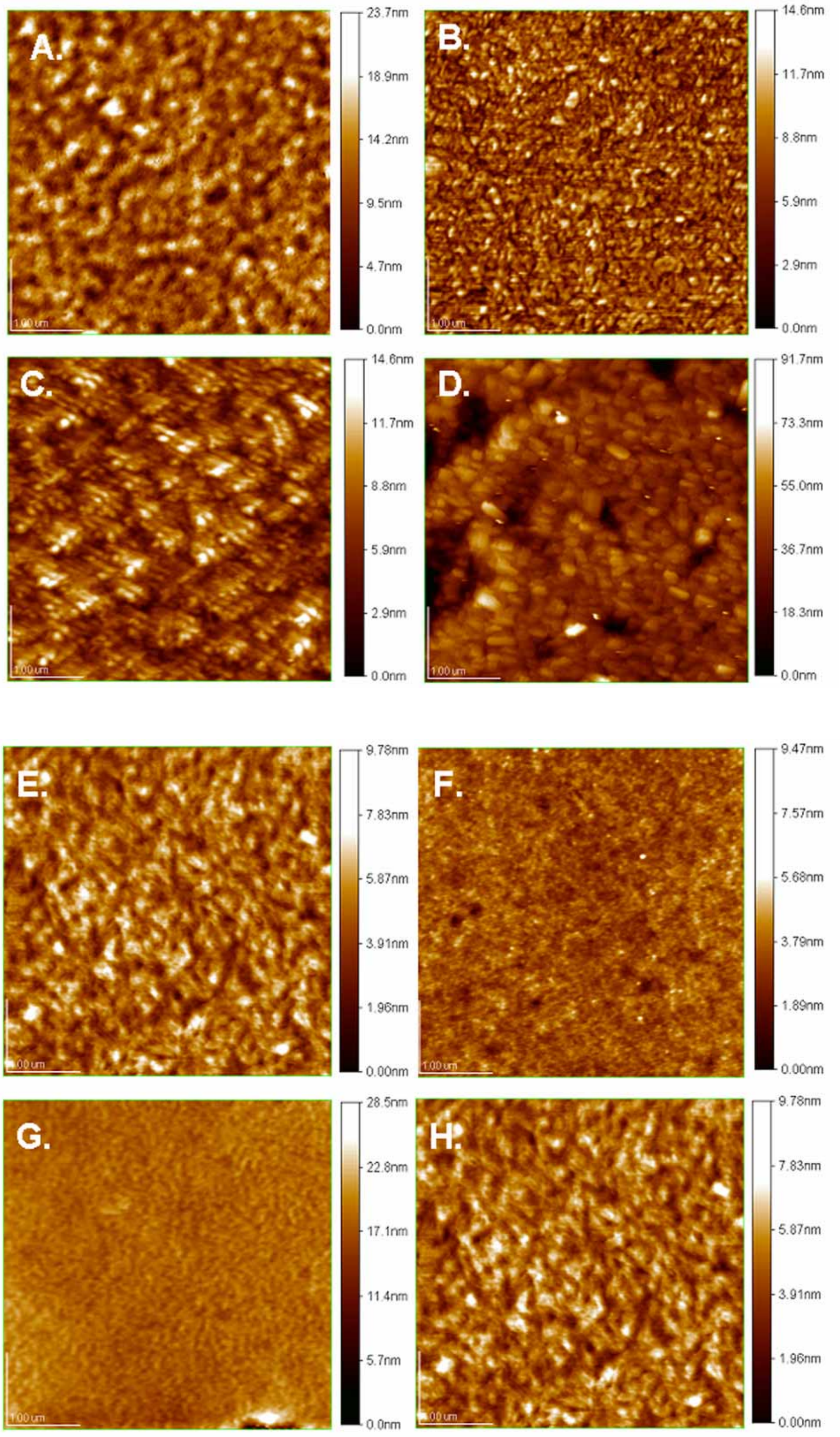

Figure S5. Tapping mode AFM images (100um x 100um) of spin-coated films. A.) **1**; B.) **2**; C.) **3**; D.) **4**; E.) **1**/PCBM; F.) **2**/PCBM; G.) **3**/PCBM; H.) **4**/PCBM

References

1. F.Kostein, G.Zerban and H.Meier, *Chem. Ber.* 1992, **125**, 893.
2. Q.Yao, E.P.Kinney and Z.Yang, *J.Org.Chem*., 2003, **68**, 7528.