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Efficient truxenone-based acceptors for organic photovoltaics

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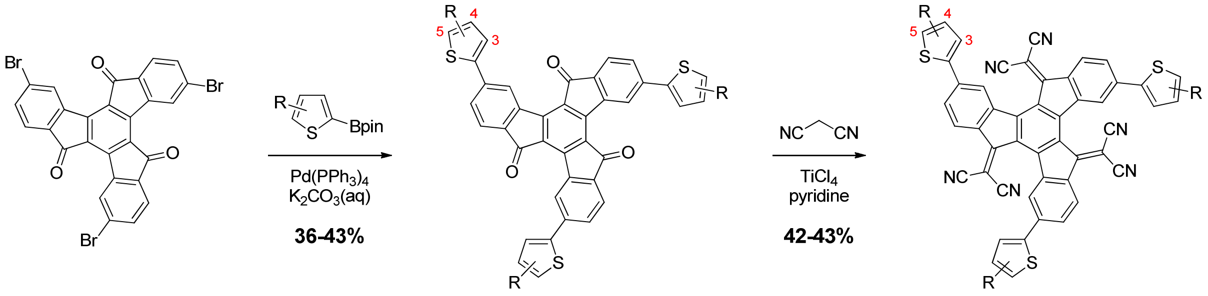
Supporting Information

Experimental Section

All chemicals were purchased from commercial suppliers unless otherwise specified. 4,9,14-Tribromotruxenone was synthesised according to a literature procedure.[1] ^{1}H NMR spectra were recorded on a BRUKER 400 spectrometer in $CDCl_3$ solution at 298 K unless otherwise stated. UV-Vis absorption spectra were recorded on a UV-1800 Shimadzu UV-Vis spectrophotometer. Cyclic voltammetry was performed with a standard three-electrode setup with a Pt-disk working electrode and an Ag/Ag^+ reference electrode calibrated against Fc/Fc^+ using an Autolab PGSTAT101 potentiostat. The measurements were carried out with 3×10^{-4} M solutions of **2a** and **2b** in anhydrous and deoxygenated dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. HOMO and LUMO energy values were obtained using the following equations: $E_{LUMO} = -(E_{red} - E_{Fc} + 4.8)$ eV and $E_{HOMO} = -(E_{ox} - E_{Fc} + 4.8)$ eV.



1a R = 5-hexyl
1b R = 3-hexyl

2a R = 5-hexyl
2b R = 3-hexyl

4,9,14-Tris(5-hexyl-2-thienyl)truxenone (1a). To a degassed solution of 4,9,14-tribromotruxenone (0.62 g, 1.0 mmol), 5-hexyl-2-thiopheneboronic acid pinacol ester (1.2 ml, 4.0 mmol), tetrakis(triphenylphosphine)palladium(0) (149 mg, 0.13 mmol) and Aliquat 336 (two drops) in toluene (60 ml) was added a degassed potassium carbonate solution (2.0 M, 10 ml). The resulting biphasic mixture was heated to reflux for 24 hours with vigorous stirring. The reaction mixture was subsequently quenched with water, extracted with toluene, dried over anhydrous magnesium sulphate and concentrated in vacuo to afford the crude product. Purification by column chromatography (silica, chloroform) and subsequent recrystallisation (toluene/methanol) afforded the title compound (0.32 g, 0.36 mmol, 36 % yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.70 (d, 1H, J = 1.5 Hz), 7.15 (d, 1H, J = 7.6 Hz), 6.99 (dd, 1H, J = 7.6 Hz, 1.5 Hz), 6.97 (d, 1H, J = 3.5 Hz), 6.53 (d, 1H, J = 3.5 Hz), 2.70

(t, 2H), 1.67 (m, 2H), 1.37 (m, 6H), 0.96 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 189.80, 147.56, 145.68, 141.44, 140.42, 140.31, 133.30, 129.73, 126.60, 125.30, 125.15, 124.07, 123.82, 31.83, 31.57, 30.50, 29.19, 22.86, 14.32.

4,9,14-Tris(3-hexyl-2-thienyl)truxenone (1b). To a degassed solution of 4,9,14-tribromo-truxenone (0.90 g, 1.45 mmol), 3-hexyl-2-thiopheneboronic acid pinacol ester (1.75 ml, 5.85 mmol), tetrakis(triphenylphosphine)palladium(0) (266 mg, 0.23 mmol) and Aliquat 336 (two drops) in toluene (75 ml) was added a degassed potassium carbonate solution (2.0 M, 10 ml). The resulting biphasic mixture was heated to reflux for 24 hours with vigorous stirring. The reaction mixture was subsequently quenched with water, extracted with toluene, dried over anhydrous magnesium sulphate and concentrated in vacuo to afford the crude product. Purification by column chromatography (silica, chloroform) and subsequent recrystallisation (toluene/methanol) afforded the title compound (0.55 g, 0.62 mmol, 43 % yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 9.35 (d, 1H, *J* = 1.5 Hz), 7.72 (d, 1H, *J* = 7.7 Hz), 7.54 (dd, 1H, *J* = 7.7 Hz, 1.5 Hz), 7.34 (d, 1H, *J* = 5.2 Hz), 7.05 (d, 1H, *J* = 5.2 Hz), 2.83 (t, 2H), 1.73 (m, 2H), 1.31 (m, 6H), 0.84 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 190.85, 146.93, 142.22, 141.94, 140.93, 136.88, 134.26, 131.83, 130.43, 128.84, 125.35, 124.15, 31.87, 31.03, 29.51, 22.80, 14.27.

4,9,14-Tris(5-hexyl-2-thienyl)-1,6,11-tris(dicyanomethylene)truxene (2a). To a solution of **1a** (100 mg, 0.113 mmol) and malononitrile (280 mg, 4.24 mmol) in anhydrous chlorobenzene (10 ml) cooled to 0°C was added titanium tetrachloride (0.20 ml, 1.8 mmol) and pyridine (0.20 ml, 2.5 mmol). The dark reaction mixture was allowed to react for 30 min at 0°C and then purified by column chromatography (silica, hexane/dichloromethane) and subsequently by reprecipitation from dichloromethane into methanol to afford the title compound (49 mg, 0.048 mmol, 42% yield) as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.39 (d, 1H, *J* = 8.4 Hz), 7.75 (s, 1H), 7.66 (d, 1H, *J* = 8.4 Hz), 7.31 (d, 1H, *J* = 3.7 Hz), 6.83 (d, 1H, *J* = 3.7 Hz), 2.88 (t, 2H), 1.75 (m, 2H), 1.39 (m, 6H), 0.93 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 161.47, 150.29, 143.96, 139.84, 139.42, 139.08, 134.23, 132.97, 128.52, 126.55, 126.42, 123.77, 113.96, 113.27, 76.84, 31.71, 31.67, 30.62, 29.00, 22.76, 14.26.

4,9,14-Tris(3-hexyl-2-thienyl)-1,6,11-tris(dicyanomethylene)truxene (2b). To a solution of **1b** (300.8 mg, 0.3406 mmol) and malononitrile (0.87 g, 13 mmol) in anhydrous chlorobenzene (30 ml) cooled to 0°C was added titanium tetrachloride (0.60 ml, 5.5 mmol) and pyridine (0.60 ml, 7.4 mmol). The dark reaction mixture was allowed to react for 30 min at 0°C and then purified by column chromatography (silica, hexane/dichloromethane) and subsequently by reprecipitation from dichloromethane into methanol to afford the title compound (152 mg, 0.148 mmol, 43% yield) as a red solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.45 (d, 1H, J = 8.1 Hz), 7.76 (d, 1H, J = 1.4 Hz), 7.66 (dd, 1H, J = 8.1 Hz, 1.4 Hz), 7.41 (d, 1H, J = 5.0 Hz), 7.08 (d, 1H, J = 5.0 Hz), 2.78 (t, 2H), 1.68 (m, 2H), 1.31 (m, 6H), 0.85 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.49, 144.26, 141.59, 140.98, 139.33, 135.57, 135.30, 133.90, 132.35, 130.57, 127.99, 126.57, 126.22, 113.83, 112.87, 78.42, 31.78, 31.13, 29.36, 29.29, 22.74, 14.19.

Device preparation

The substrates used in this study are glass substrates with 110 nm thick pre-patterned ITO (Kintec). Substrate cleaning consisted of sonication in detergent, deionized water and acetone, followed by submersion in hot isopropanol. Upon cleaning, ZnO is deposited from a Zn(acac) precursor solution in air and annealed at 300C for 10 min. Truxenone and PCBM (Solenne bv.) layers are deposited from a chloroform solution under N_2 atmosphere. Materials were dissolved in a concentration of 10 mg/ml. The substrates with the acceptors were transferred in thermal evaporation chamber and left outgassing overnight at 10^{-7} Torr.
The donor materials, ZnPc (Sigma-Aldrich) and SubPc (Lumtec Corp.), were purified once using thermal gradient sublimation, and MoO_3 and Ag were used as received. Organic thin films were deposited by thermal evaporation in a high vacuum evaporator with a base pressure 10^{-7} Torr and growth rate of 1 Å/s, as monitored by a quartz crystal microbalance, and the substrate temperature was fixed to room temperature. The Ag cathode is evaporated through a shadow mask, defining an active area of 0.134 cm^2.

Thin film and device characterization

Current-voltage characteristics of photovoltaic cells were measured in dark and under simulated solar light, using a Keithley 2602 in combination with an Abet solar simulator, calibrated to produce 100 mW cm^{-2} AM1.5G illumination. In the spectral response and reflection setup, light from Xe and quartz halogen lamps were coupled into a monochromator and their intensities calibrated with a Si photodiode. The light incident on the device was chopped and the modulated current signal detected with current-voltage and lock-in amplifiers. Reflection measurements were conducted with an integrating sphere. AFM images were collected using a Picoscan PicoSPM LE scanning probe operated in the tapping mode. Layer thickness of solution processed layers were measured with a Dektak profilometer.

References

1) C. Lambert, G. Nöll, E. Schmälzlin, K. Meerholz and C. Bräuchle, *Chem.--Eur. J.*, 1998, **4**, 2129-2135

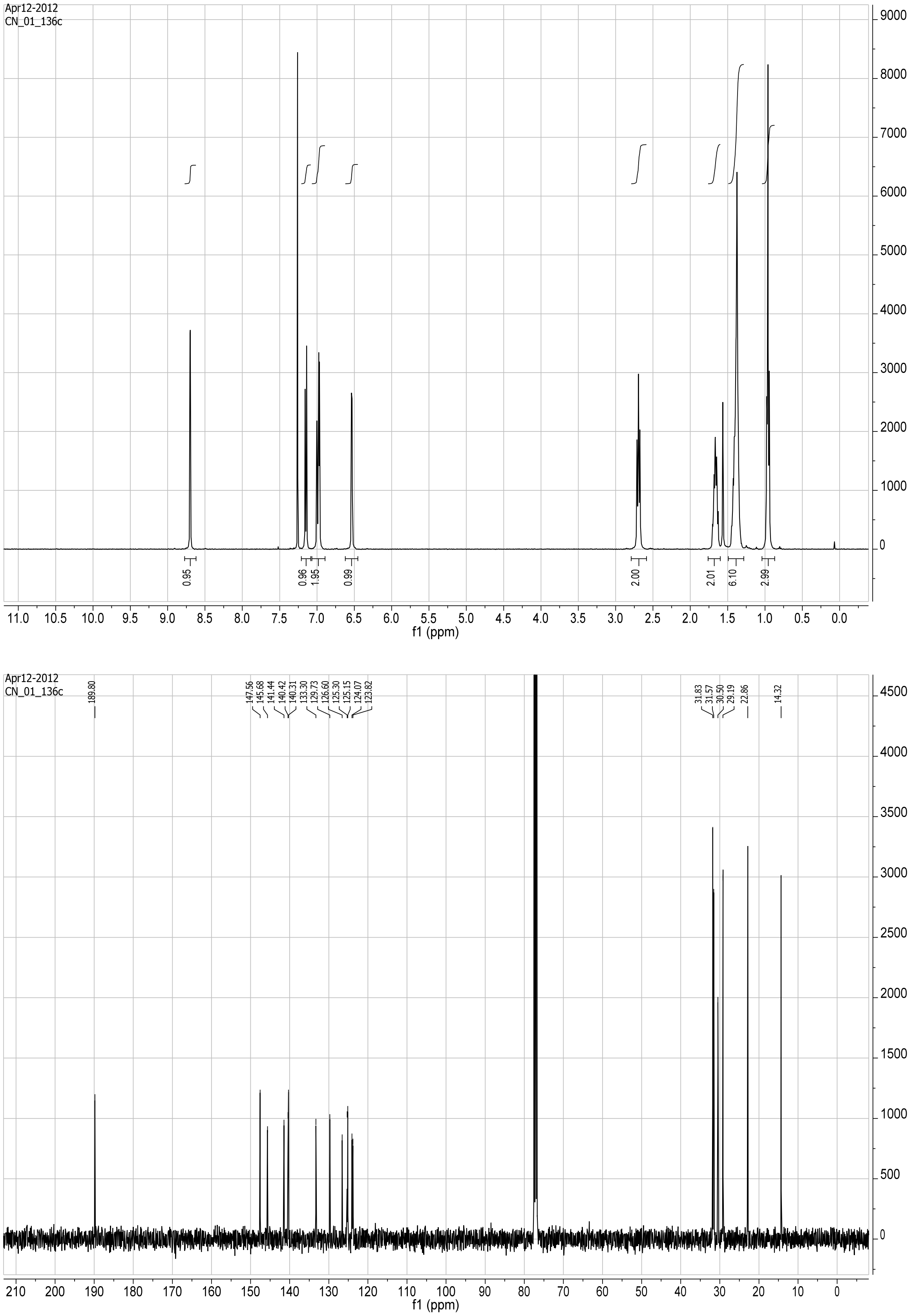


Figure S1 ^{1}H and ^{13}C NMR spectra of **1a**.

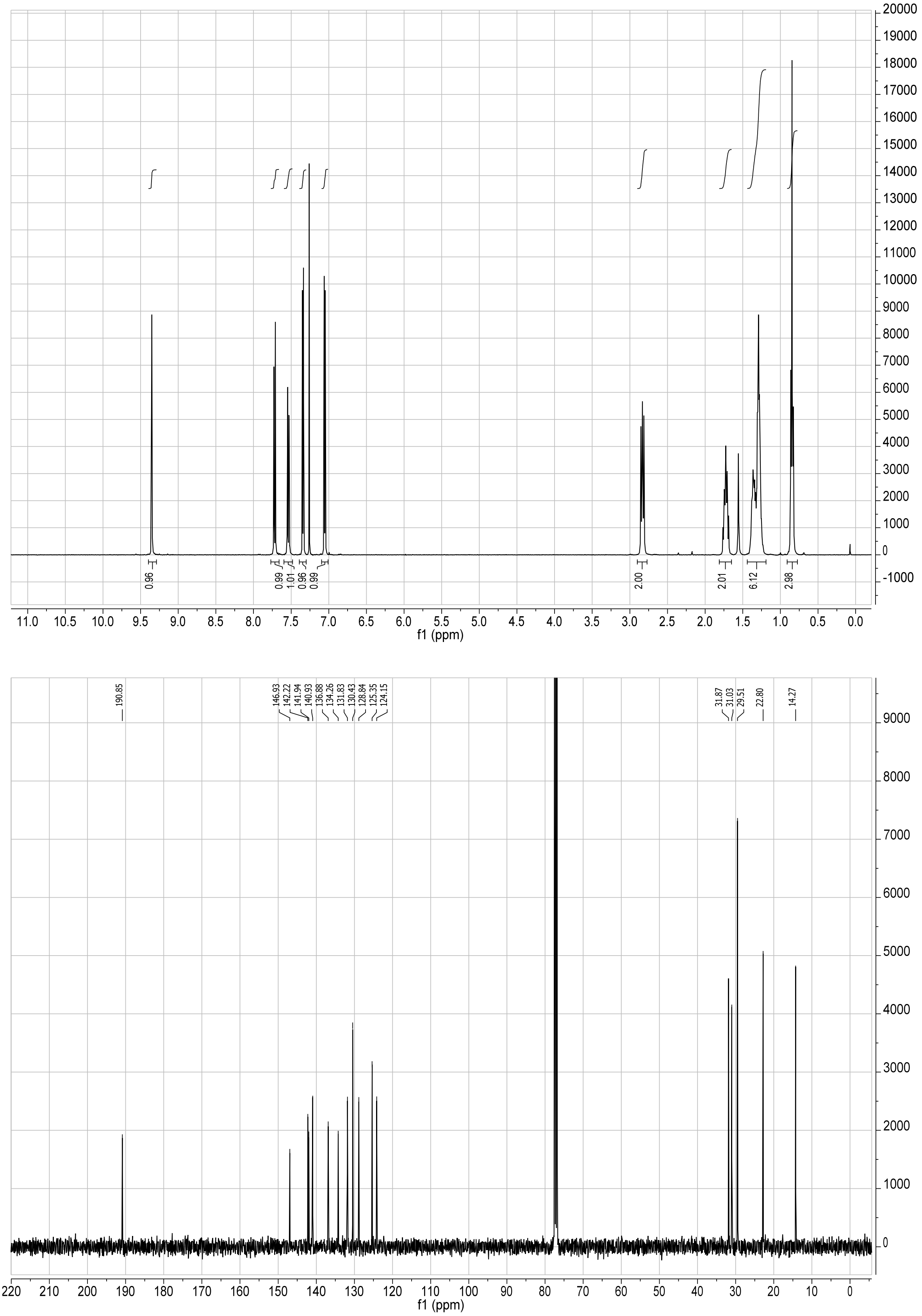


Figure S2 ^{1}H and ^{13}C NMR spectra of **1b**.

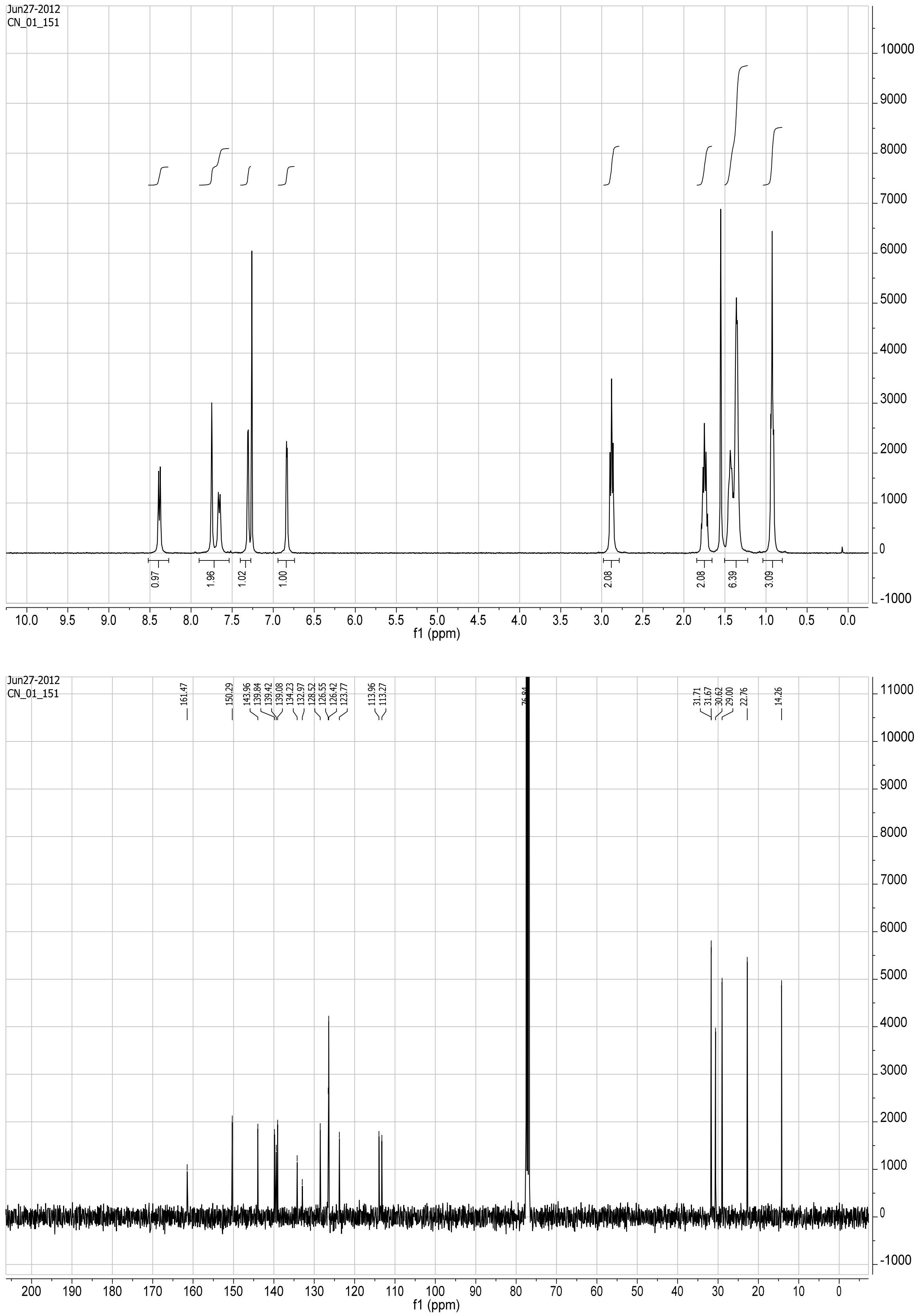


Figure S3 ^{1}H and ^{13}C NMR spectra of **2a**.

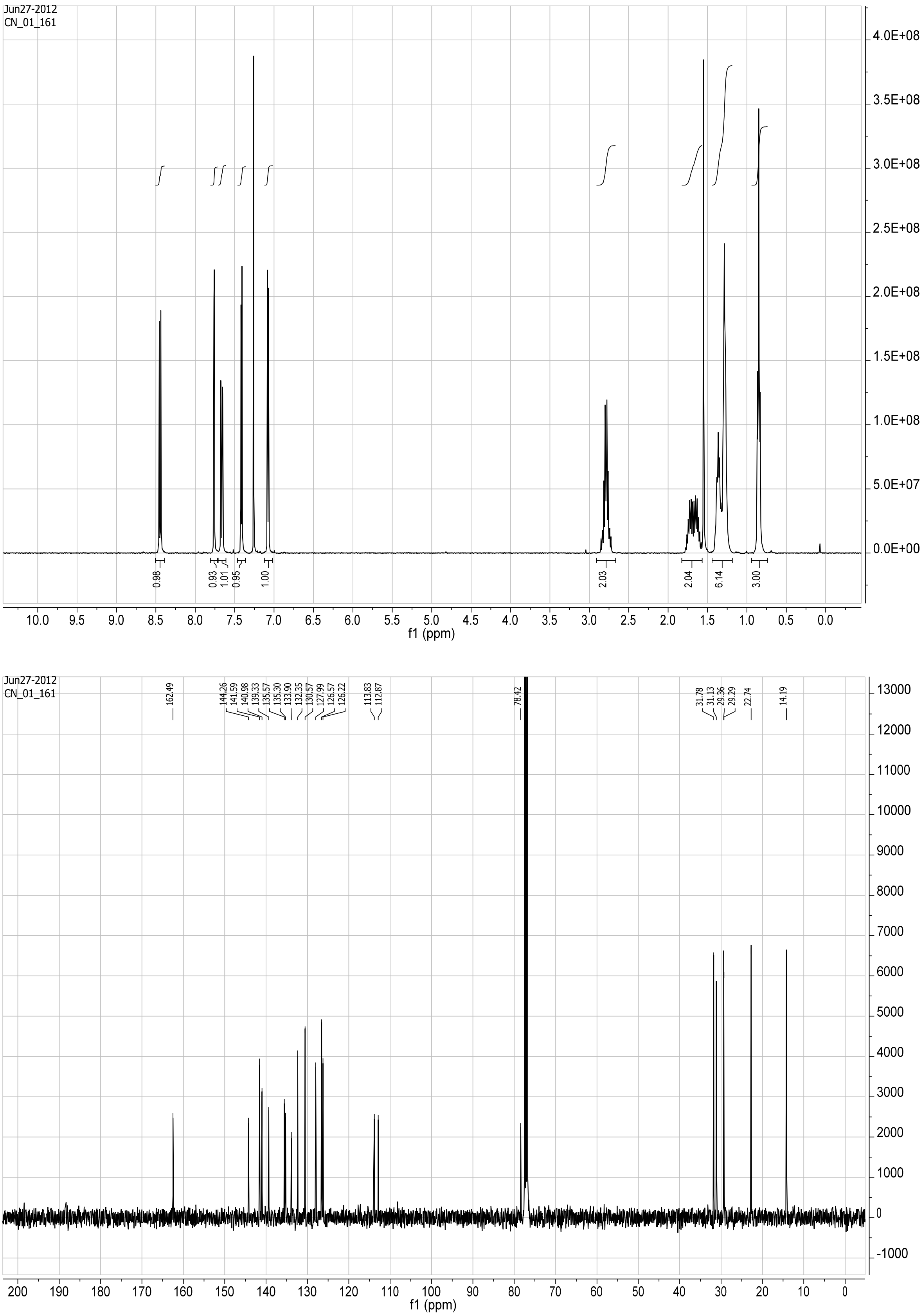


Figure S4 ^{1}H and ^{13}C NMR spectra of **2b**.

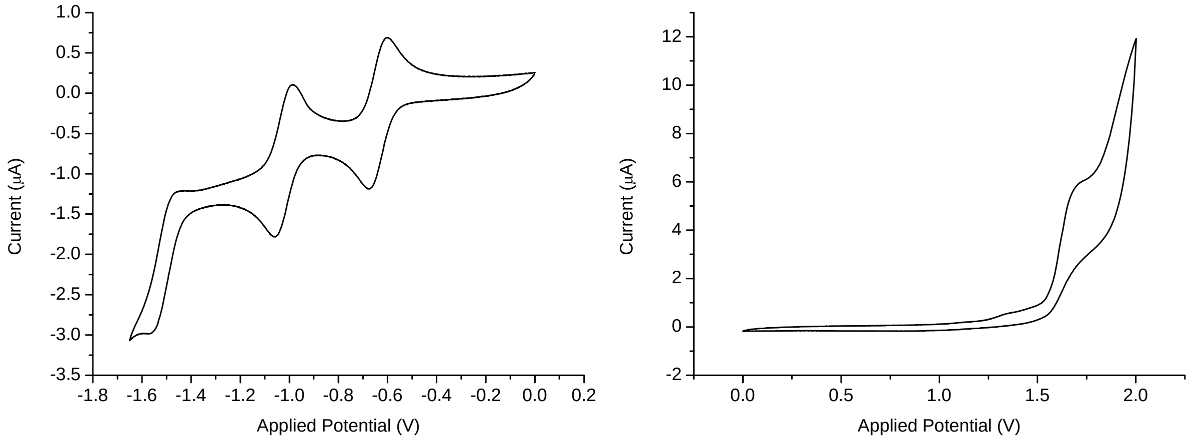


Figure S5 Cyclic voltammograms for PC$_{61}$BM reduction (left) and oxidation (right).

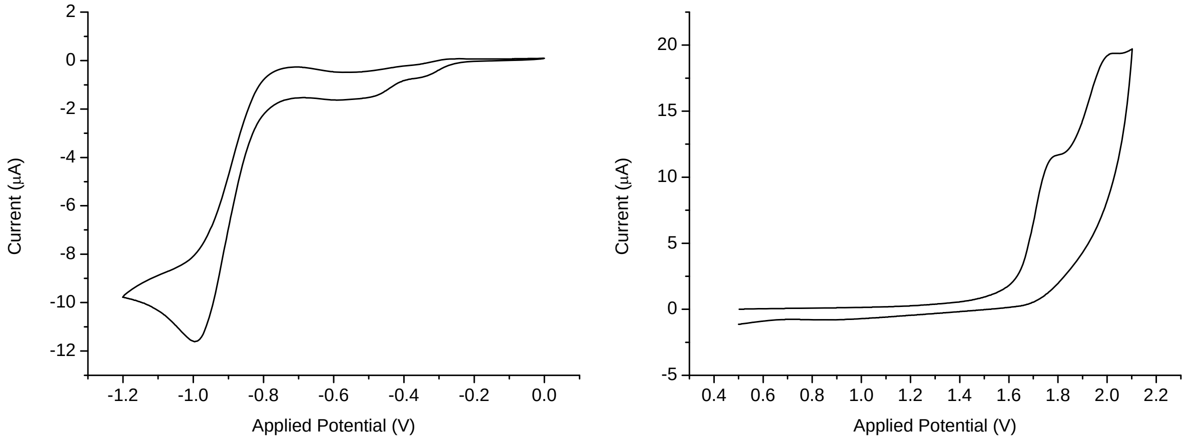


Figure S6 Cyclic voltammograms for **2a** reduction (left) and oxidation (right).

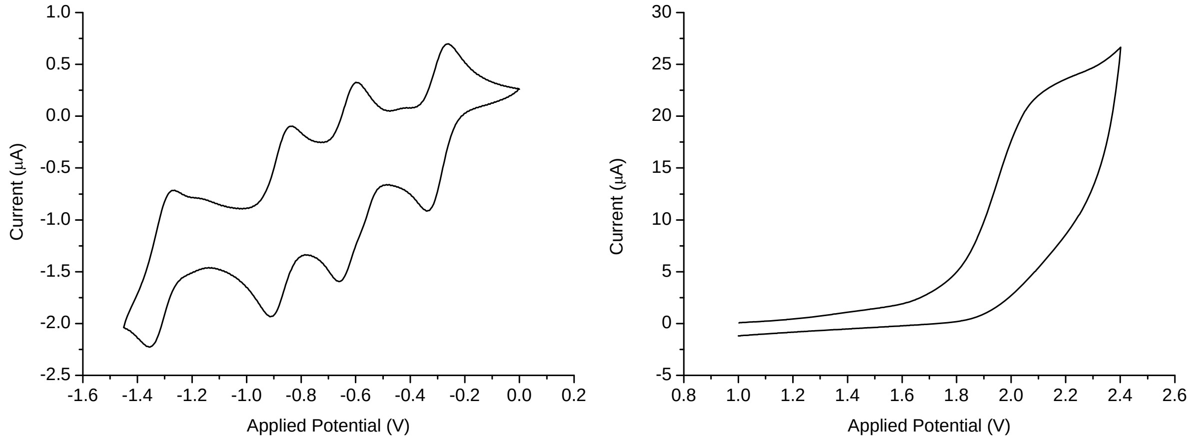


Figure S7 Cyclic voltammograms for **2b** reduction (left) and oxidation (right).

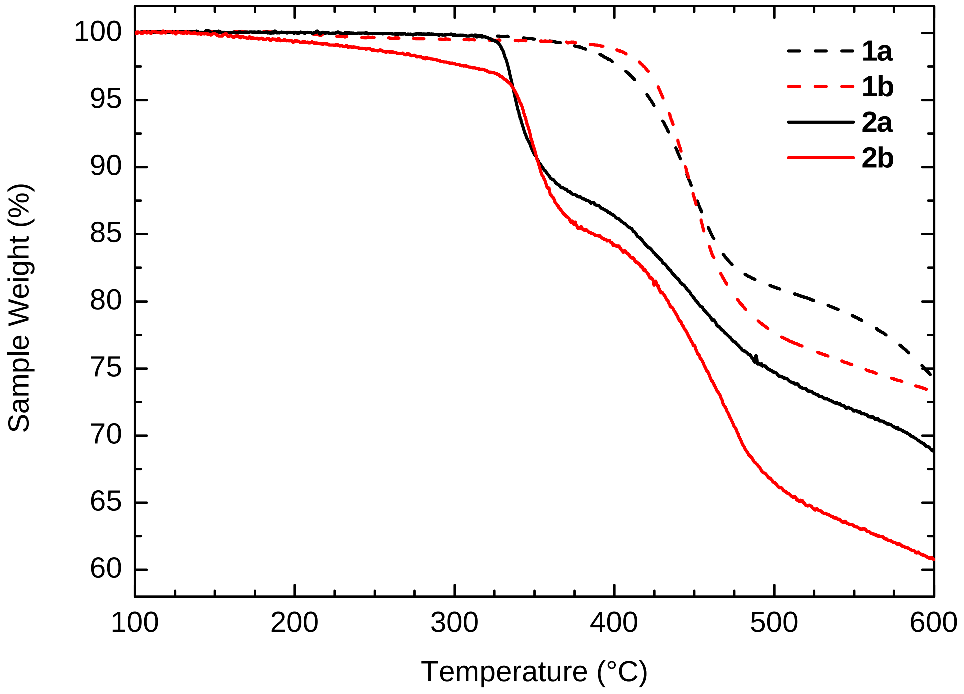


Figure S8 Thermal Gravimetric Analysis (TGA) traces recorded on a Pyris 1 Thermogravimetric Analyzer from Perkin Elmer at a rate of 10°C/min under nitrogen.

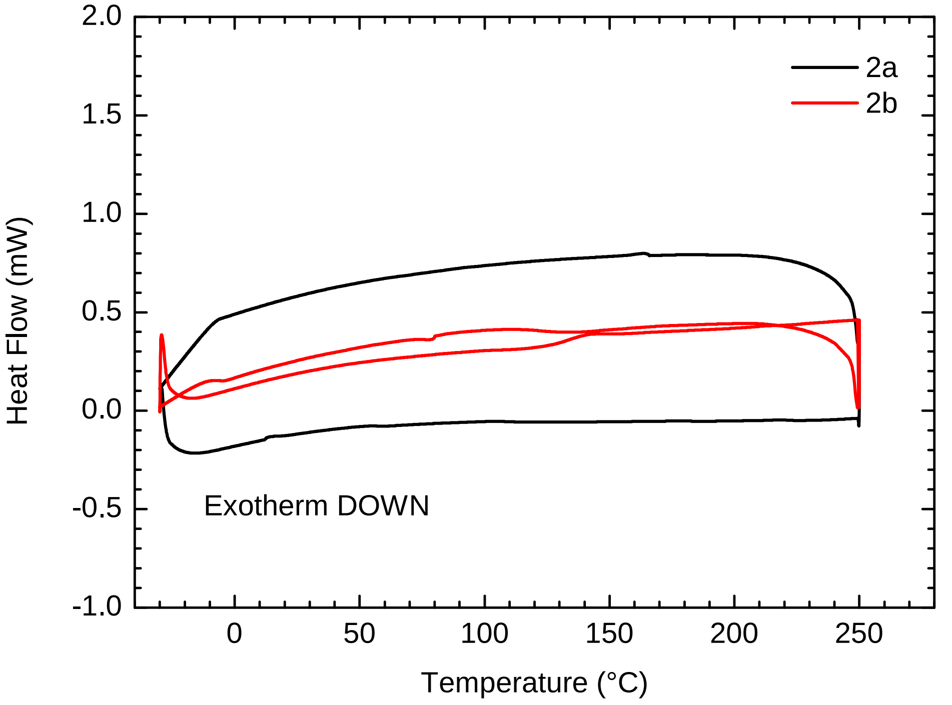
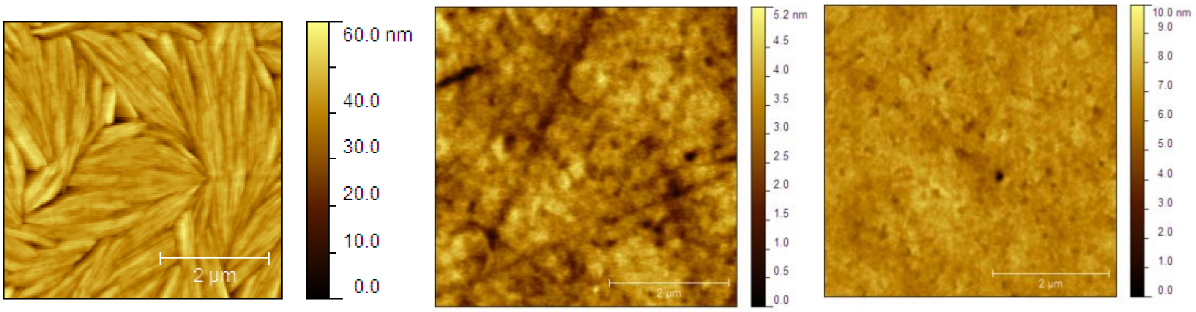


Figure S9 Differential Scanning Calorimetry (DSC) traces recorded on a Q20 Differential Scanning Calorimeter from TA Instruments at a rate of 10°C/min.



(a) (b) (c)

Figure S10 Topography scan by AFM of the solution processed truxenones **2a** (a), **2b** (b), and PCBM (c) layers.

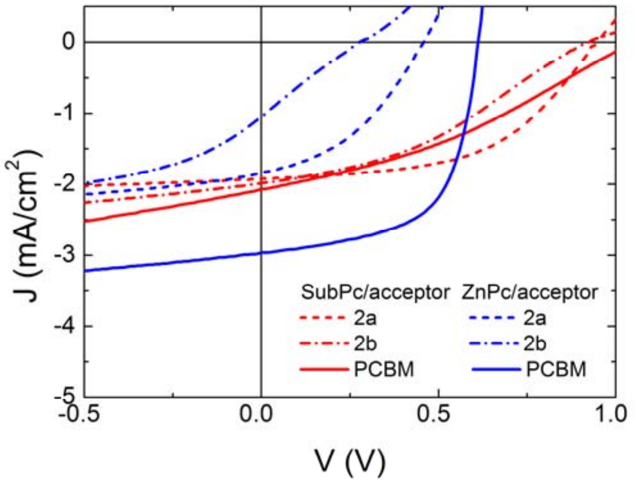


Figure S11 Current density-voltage (*J*-*V*) characteristics of the different devices measured under 100 mW/cm^2 intensity AM1.5G spectrum solar radiation.

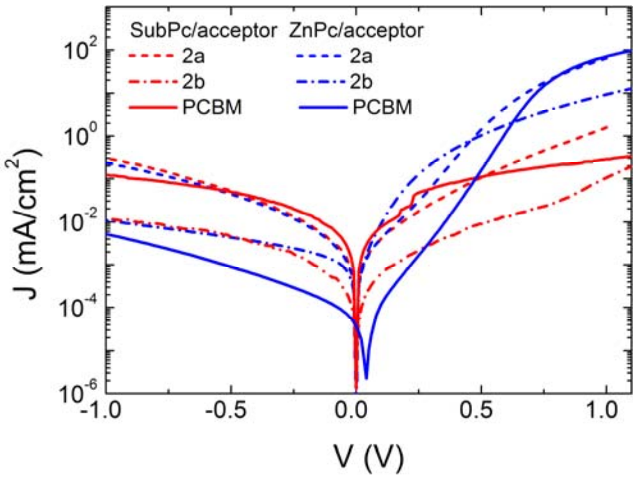


Figure S12 Current density-voltage (*J*-*V*) characteristics of the different devices measured in dark.