

Supporting Information

General remarks. Melting points were determined on a Büchi melting point apparatus and are uncorrected. Adsorption chromatography was carried out on Riedel de Haën silica gel (32-63 μm ; 230-400 mesh ASTM). UV-VIS spectra in solution were recorded on a Kontron Uvikon 923 spectrophotometer. NMR spectra were recorded on a Varian Associates VXR-400 multinuclear instrument (internal Me_4Si). Petroleum ether as 40-60° boiling fraction was used.

{[*m,p*-bis(hexyloxy)phenyl]ethynyl}(trimethyl)silane (3).

Dry toluene (17.5 ml), 1,2-bis(hexyloxy)-4-iodobenzene **2** (1.5g, 3.7 mmol), CuI (0.057 g, 0.30 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.350 g, 0.30 mmol) and diisopropylamine (7.5 ml) were placed in a flask and degassed with Ar at 0°C. Trimethylsilylacetylene (2.1 ml, 14.9 mmol) was then added and the mixture was kept at 30°C overnight. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel (elution: hexane/dichloromethane 85:15) to afford compound **3** (98%) as pale yellow oil. $^1\text{H-NMR}$ (CDCl_3) δ 0.19 (s, 9H), 0.85 (m, 6H), 1.34 (m, 12H), 1.75 (m, 4H), 3.92 (m, 4H), 6.71 (d, 1H, $J=8.3\text{Hz}$), 6.91 (d, 1H, $J=1.9\text{Hz}$), 6.98 (dd, 1H, $J=1.9, 8.3\text{Hz}$); $^{13}\text{C-NMR}$: (CDCl_3): δ 149.8, 148.5, 125.4, 116.9, 115.1, 113.0, 92.0, 69.1, 69.0, 31.5, 29.1, 29.0, 25.6, 22.5, 14.0, 0.04. An. Calcd. for $\text{C}_{23}\text{H}_{38}\text{O}_2\text{Si}$: C, 73.74; H, 10.22. Found: C, 73.55 ; H, 10.21%.

***m,p*-Bis(hexyloxy)ethynylbenzene (4).**

To a solution of **3** (1.40g, 3.8 mmol) in 20 ml of THF was added Bu_4NF (4.9 ml, 1.0 M solution in THF). The reaction mixture was stirred at room temperature for 20 h under a nitrogen atmosphere. The solvent was evaporated under vacuum and the residue purified by column chromatography on SiO_2 (elution: hexane/dichloromethane 85/15) to give compound **4** as a pale yellow oil in 92%; $^1\text{H-NMR}$: (CDCl_3): δ 0.85 (m, 6H), 1.34 (m, 12H), 1.75 (m, 4H), 2.93 (s, 1H), 3.92 (m, 4H), 6.73 (d, 1H, $J=8.2\text{Hz}$), 6.94 (m, 1H) 7.00 (dd, 1H, $J=1.9, 8.2\text{Hz}$); $^{13}\text{C-NMR}$: (CDCl_3): δ 150.0, 148.6, 125.5, 117.1, 114.0, 113.0, 83.9, 75.4, 69.2, 69.1, 31.5, 29.0, 25.6, 22.6, 14.0; An. Calcd. for $\text{C}_{20}\text{H}_{30}\text{O}_2$: C, 79.42; H, 10.00. Found: C, 79.60; H, 10.01 %.

9,10-Bis{[*m,p*-bis(hexyloxy)phenyl]ethynyl}anthracene (1).

Dry toluene (6ml), 9,10-dibromoanthracene **5** (0.15 g, 0.45 mmol), CuI (0.004 g, 0.02 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.026 g, 0.02 mmol), compound **4** (0.34g, 1.1 mmol) and diisopropylamine (3 ml) were placed in a flask and degassed

with Ar at 0°C. The mixture was kept at 55°C overnight. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel (elution: petroleum ether/dichloromethane 75:25) to give compound **1** (98%) as bright orange solid. M.p. (ethyl acetate) 131-132°C; $^1\text{H-NMR}$ (CDCl_3) δ 0.87 (m, 12H), 1.33 (m, 16H), 1.46 (m, 8H), 1.82 (m, 8H), 4.03 (m, 8H), 6.88 (d, 2H, $J=8.4\text{Hz}$), 7.20 (m, 2H), 7.29 (d, 2H, $J=8.4\text{Hz}$), 7.58 (m, 4H), 8.65 (m, 4H); $^{13}\text{C-NMR}$ (CDCl_3) δ 150.1, 148.9, 132.0, 127.3, 126.6, 125.2, 118.4, 116.7, 115.5, 113.3, 102.7, 85.0, 69.4, 69.2, 31.6, 29.2, 29.1, 25.7, 22.6, 14.0; UV-Vis (CHCl_3) [λ_{max} nm (log ϵ): 277 (4.93), 322 (4.42), 457 (4.64); An. Calcd. for $\text{C}_{54}\text{H}_{66}\text{O}_4$: C, 83.25; H, 8.54. Found: C, 83.50 ; H, 8.55 %.

Cyclic voltammetry measurements were carried out using a Pt disk working electrode and a Pt counter electrode vs saturated calomel electrode. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte. Scan rate was 100 mV/s. The cyclic voltammograms for the oxidation of compound **1** in 0.1 M TBAP/ CH_2Cl_2 displayed the following data: $E_{\text{ox}}^{\text{I}} = 0.99\text{V}$; $E_{\text{ox}}^{\text{II}} = 1.33\text{V}$.

A Perkin-Elmer Lambda 35 UV spectrophotometer was used to monitor the absorption spectra of neat molecule and blends. The spectra were performed on the films used to prepare the active layer.

The solar cell were fabricated with the structure of ITO/poly(3,4-ethylenedioxythiophene (PEDOT):poly(styrenesulfonate) (PSS)/Active layer/Al. The ITO glass was previously pre-cleaned and plasma treated in oxygen atmosphere (5 min., 8.0×10^{-2} Torr, -300V bias substrate) and modified by a thin layer of PEDOT:PSS (Baytron P®) which was spin-cast (4000 rpm) from a PEDOT:PSS aqueous solution on the plasma treated ITO substrate, and was dried subsequently at 150 °C for 10 min in air. The thickness of the PEDOT: PSS layer was 50 nm. The photosensitive layer was prepared by spin-coating (2000 rpm) the CHCl_3 solution of the 1/PCBM (1:0.88, 1:1.17, 1:1.46 weight ratio) blends with the solution concentration of 20mg/ml on the ITO/PEDOT:PSS electrode. The thickness of the photosensitive layer was optimized to 150 nm by adjusting the rotating speed of the spin-coating, and was measured with an atomic force microscopy. Then the top metal electrode, which is made up of LiF and Al, was deposited on the active layer by vacuum evaporation ($\approx 10^{-6}$ Torr) with an optimized thickness of 0.7 nm and 60 nm, respectively. Fifteen electrodes with an effective area of 3 mm² were deposited for each sample. The current-voltage (*I-V*) measurement of the devices was conducted on a computer-controlled Keithley 4200 Source Measure Unit. An halogen tungsten lamp was used as the white light source, and the optical power at the sample was 41 mW/cm².

