Supporting Information for

Acetylene-bridged Dyes with High Open Voltage for Dye-Sensitized Solar Cells

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Spectral and electrochemical measurements:

^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 MHz. chemical shifts for ^{1}H NMR spectra are referenced in the deuterated solvent ($CHCl_3$ $\delta = 7.26$ ppm for ^{1}H and $\delta = 77$ ppm for ^{13}C). Spectra were recorded at room temperature, chemical shifts are written in ppm and coupling constants in Hz. UV-visible spectra (Varian Cary 50), emission spectra (a JASCO FP-6000 spectrofluorometer) and mass spectra (Finnigan TSQ Ultra EMR, Triple Quadrupole, LC/ESI/APCI/MS) operating in the positive ion detection mode were recorded. Electrochemistry (Cyclic Voltammetry) was performed with a three-electrode potentiostat (CH Instruments, Model 750A) in CH_3CN deoxygenated by purging with prepurified dinitrogen gas. Cyclic voltammetry was conducted with the use of a home-made three-electrode cell equipped with a BAS glassy carbon (0.07 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode, and a home-made Ag/AgCl (saturated) reference electrode. The reference electrode is separated from the bulk solution by a double junction filled with electrolyte solution. Potentials are reported *vs.* NHE and referenced to the ferrocene/ferrocenium (Fc/Fc$^+$) couple which occurs at $E_{1/2} = +0.63$ V *vs.* Ag/AgCl (saturated). The working electrode was polished with 0.03 μm alumina on Buehler felt pads and washed with deionized water prior to each experiment. The reproducibility of individual potential values was within ±5 mV.

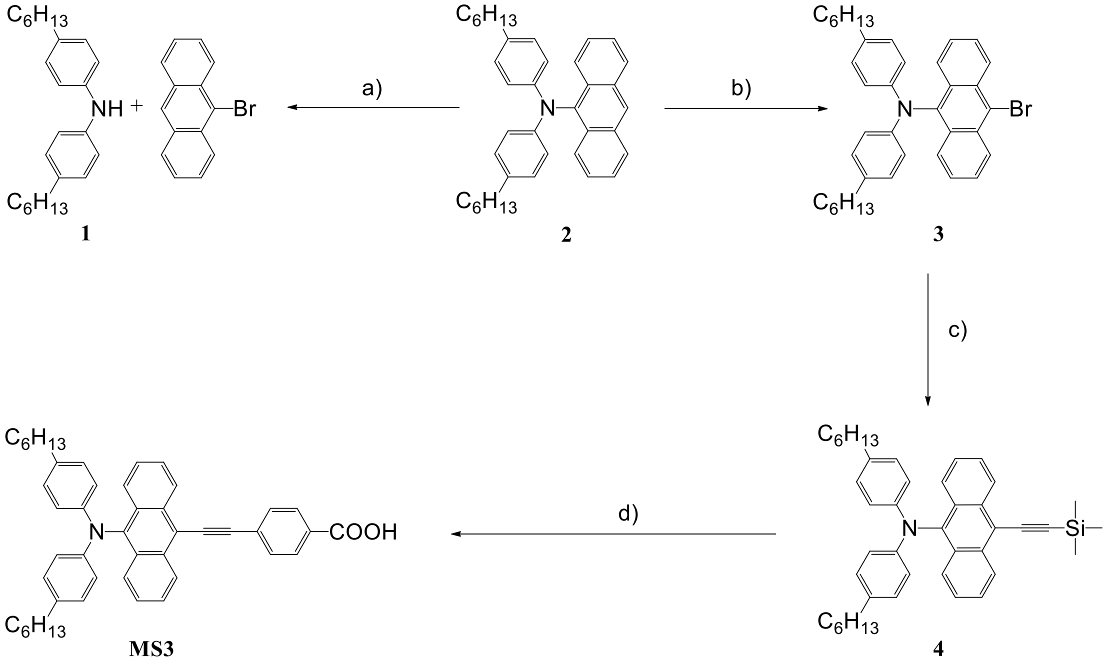
Materials and Syntheses.

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. THF was dried over sodium/ benzophenone and freshly distilled before use. Tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) was recrystallized twice from absolute ethanol and further dried for four days under vacuum. Column chromatography was performed on silica gel (Merck, 70-230 Mesh ASTM). **MS3** was synthesized according to the route in Scheme S1. Amination[1] of bis(4-hexylphenyl)amine **1** with 9-bromoanthracene afforded **2**; subsequent bromination[2] of **2** with NBS gave **3** in satisfactory yield. Sonogashira coupling[3] of **3** with silylated acetylene produced intermediate **4.** Deprotection of **4** with TBAF followed by Sonogashira coupling to 4-iodobenzoic acid produced **MS3**.

Electrode Preparation and Device Fabrication

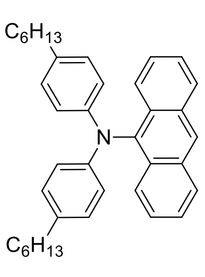
The photoanode were prepared used the transparent TiO_2 electrodes comprising 8 μm mesoporous TiO_2 layer (particle size, 20 nm, 24 nm pore size) were prepared by screen-printing onto fluorine doped thin oxide (FTO, 4 mm thickness, 10 Ω/sq, Nippon Sheet Glass, Japan) conducting glass. In order to render high PCE, a scattering layer (5 μm) (400 nm diameter, Catalysts & Chemicals Ind. Co. Ltd. (CCIC), HPW-400) was deposited on the transparent layer. Sintering was carried out at 500 °C for 15 min. The films were soaked in the solution of 40 mM aqueous $TiCl_4$ for 30 min at 70 °C. After being washed with deionized water and fully rinsed with ethanol, the films were heated again at 500°C for 15 min. The TiO_2 electrodes were immersed into a 0.3 mM solution of a dye with 2.0 mM of chenodeoxycholic acid in $CHCl_3$/EtOH mixture (1: 4, *v*/*v*) and kept for 12 h at room temperature. The Pt counter electrodes were prepared by placing drops of an H_2PtCl_6 solution (2 mg Pt in 1 mL ethanol) onto FTO glass and heating at 400 °C for 15 min. The two electrodes were assembled into a cell of sandwich type and sealed with a 25 μm hot-melt film (Surlyn, Dupont) by heating the system at 100°C. The electrolyte solution for **MS1**, **MS2** and **MS3** used electrolyte (Z959) for the device fabrication contains 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.03 M iodine , 0.5 M *tert*-butylpyridine, and 0.1 M guanidinium thiocyanate (GNCS) in the mixed solvent of acetonitrile and valeronitrile (85/15, *v/v*).[4, 5]

Synthetic procedures



Scheme S1. Synthetic route of organic dye **MS3**. (a) $Pd(OAc)_2$, $P(t\text{-}Bu)_3$, NaO-*t*-Bu, toluene (83%). (b) NBS, CH_2Cl_2 (96%). (c) Ethynyltrimethylsilane, $Pd(PPh_3)_2Cl_2$, CuI, THF, Et_3N (47%). (d) i) TBAF/THF; ii) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF (62%).

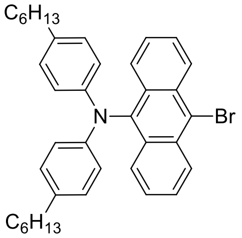
N,N-Bis(4-*n*-hexylphenyl-9-amino)anthracene (2)



A solution of the bis(4-hexylphenyl)amine **1**[6] (144 mg, 0.43 mmol) 、 9-bromoanthracene (100 mg, 0.39 mmol) with $Pd(OAc)_2$ (0.9 mg, 0.004 mmol) 、 $P(t\text{-}Bu)_3$ (0.9 mg, 0.005 mmol) and NaO-*t*-Bu (50 mg, 0.47 mmol) in 10 mL of toluene was refluxed for 12 h under nitrogen atmosphere. The solvent was removed in vacuo, and the residue was purified on a column chromatograph (silica gel) using hexanes as eluent to give fluorescent yellow solid (166 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta_H = 8.48$ (s, 1H), 8.14 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.48-7.34

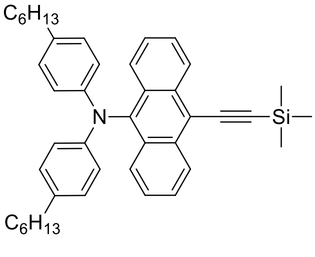
(m, 4H), 7.01-6.90 (m, 8H), 2.48 (t, J = 7.6 Hz, 4H), 1.63-1.47 (m, 4H), 1.39-1.19 (m, 12H), 0.96-0.78 (m, 6H). ^{13}CNMR (101 MHz, CDCl$_3$) δ_C = 145.7, 137.7, 135.3, 132.8, 130.8, 128.9, 128.8, 126.5, 125.4, 124.6, 119.9, 35.2, 31.7, 31.5, 29.1, 22.6, 14.1. ESI(MS): m/z: Calcd for $C_{38}H_{43}N$: 513.8 $[M]^+$ Found: 513.5.

10-Bromo-N,N-Bis(4-*n*-hexylphenyl-9-amino)anthracene (3)



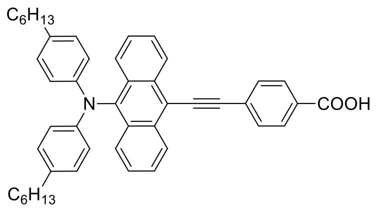
To a stirred solution of compound **2** (100 mg, 0.22 mmol) in CHCl$_3$ (5.0 mL) was slowly added a solution of NBS (42 mg, 0.24 mmol) in CHCl$_3$ (3.0 ml) was gently refluxed for 4 h under nitrogen atmosphere. After the reaction was quenched with acetone, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using hexanes as eluent to afford the fluorescent yellow solid product **3** (111 mg, 96 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ_H = 8.59 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 7.61-7.52 (m, 2H), 7.44-7.36 (m, 2H), 6.94 (s, 8H), 2.47 (t, J = 7.6 Hz, 4H), 1.55-1.46 (m, 4H), 1.36-1.18 (m, 12H), 0.92-0.79 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ_C = 145.5, 138.3, 135.7, 131.7, 129.0, 128.4, 127.2, 126.8, 125.1, 120.0, 35.2, 31.7, 31.4, 29.0, 22.6, 14.1. ESI (MS): m/z: Calcd for $C_{38}H_{42}BrN$: 592.7 $[M]^+$ Found: 593.4.

***N*,*N*-Bis(4-*n*-hexylphenyl)-10-(trimethylsilylethynyl)anthracen-9-amine (4)**



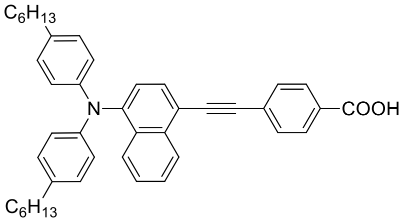
A solution of compound **3** (100 mg, 0.17 mmol) 、trimethylsilylacetylene (83 mg, 0.84 mmol) 、Pd(PPh$_3$)$_2$Cl$_2$ (11.8 mg, 0.017 mmol) and CuI (3.3 mg, 0.017 mmol) in a mixture of THF (4.0 mL) and NEt$_3$ (1.0 mL) was gently refluxed for 12 h under nitrogen atmosphere. The solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) using hexanes as eluent give the product (48 mg, 47%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.72 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.02 (s, 8H), 2.55 (t, *J* = 7.6 Hz, 4H), 1.69-1.54 (m, 4H), 1.42-1.26 (m, 12H), 1.01-0.87 (m, 6H), 0.52 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 145.6, 139.0, 135.6, 134.1, 130.4, 129.0, 127.4, 126.7, 125.0, 120.1, 106.9, 101.6, 35.2, 31.7, 31.4, 29.0, 22.6, 14.1, 0.3. ESI (MS): m/z: Calcd for $C_{43}H_{51}NSi$: 610.0 $[M]^+$ Found: 609.5.

4-((10-(bis(4-*n*-hexylphenyl)amino)anthracen-9-yl)ethynyl)benzoic acid (MS3)



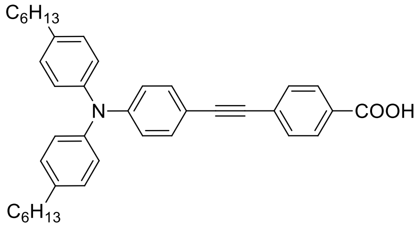
To a solution of compound **4** (116 mg, 0.19 mmol) in dry THF (3.0 mL) was added TBAF (0.28 mL, 0.948 mmol). The solution was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with H_2O and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. A Schlenk tube with the deprotected intermediate was charged with 4-iodobenzoic acid (138 mg, 0.56 mmol), $Pd_2(dba)_3$ (17 mg, 0.019 mmol) and $AsPh_3$ (57 mg, 0.186 mmol). The mixture was dissolved in a degassed mixture of THF (10.0 mL) and NEt_3 (2.0 mL) and gently refluxed for 4 h under nitrogen atmosphere. The solvent was removed under vacuum and the residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/CH_3OH (20/1) as eluent. Removal of solvent under reduced pressure and recrystallization from CH_2Cl_2/CH_3OH gave an orange solid **MS3** (76 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H= 8.69 (d, *J* = 8.8 Hz, 2H), 8.23 (dd, *J* = 8.4, 8.4 Hz, 4H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 6.95 (s, 8H), 2.48 (t, *J* = 7.6 Hz, 4H), 1.62-1.46 (m, 4H), 1.38-1.19 (m, 12H), 0.95-0.8 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 145.6, 139.6, 135.7, 134.0, 131.6, 130.5, 130.4, 129.0, 127.2, 126.9, 126.8, 125.2, 120.1, 116.4, 100.4, 89.9, 35.2, 31.7, 31.5, 29.1, 22.6, 14.1. ESI(HRMS): m/z: Calcd for $C_{47}H_{47}NO_2$: 657.36 $[M]^+$ Found: 657.35.

4-((4-(bis(4-*n*-hexylphenyl)amino)naphthalen-1-yl)ethynyl)benzoic acid (MS2)



A procedure similar to **MS3** was employed for the synthesis of **MS2** (65 %) except that the intermediate was different. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta_H = 8.42$ (d, $J = 8.4$ Hz, 1H), 8.13 (d, $J = 7.6$ Hz, 2H), 7.95 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 3H), 7.53 (t, $J = 6.8$ Hz, 1H), 7.40-7.28 (m, 1H), 7.20 (d, $J = 7.6$ Hz, 1H), 6.99 (dd, $J = 8.0$, 8.0 Hz, 8H), 2.52 (t, $J = 7.6$ Hz, 4H), 1.66-1.50 (m, 4H), 1.40-1.20 (m, 12H), 0.97-0.80 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta_C = 146.3$, 145.7, 136.7, 134.9, 131.5, 131.4, 130.6, 130.2, 129.0, 127.0, 126.5, 125.7, 125.1, 122.3, 117.3, 93.6, 35.3, 31.7, 31.5, 29.1, 22.6, 14.1. ESI (HRMS): m/z: Calcd for $C_{43}H_{45}NO_2$: 607.34 $[M]^+$ Found: 607.34.

4-((4-(bis(4-*n*-hexylphenyl)amino)phenyl)ethynyl)benzoic acid (MS1)



A procedure similar to **MS3** was employed for the synthesis of **MS1** (75 %) except that the intermediate was different. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta_H = 8.06$ (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.10 (dd, $J = 8.4$, 8.4 Hz, 8H), 6.94 (d, $J = 8.4$ Hz, 2H), 2.57 (t, $J = 7.6$ Hz, 4H), 1.69-1.54 (m, 4H), 1.45-1.23 (m, 12H), 0.95-0.84 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta_C =170.7$, 148.9, 144.5, 138.7, 132.6, 131.3, 130.1, 129.5, 129.3, 127.8, 125.3, 120.7, 113.9, 93.9, 87.7, 35.4, 31.7, 31.5, 29.1, 22.6, 14.1. ESI (HRMS): m/z: Calcd for $C_{39}H_{43}NO_2$: 557.32883 $[M]^+$ Found: 557.32879.

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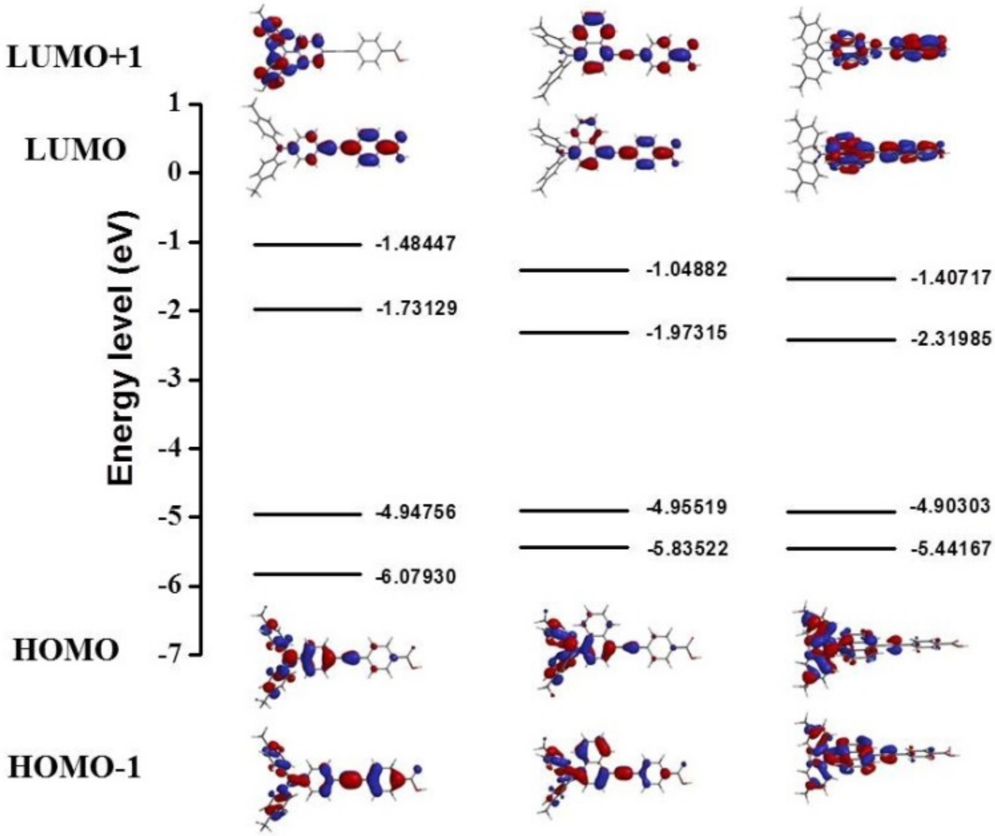

Figure S1. Energy level diagram and the corresponding molecular orbitals of **MS1**, **MS2** and **MS3** calculated at the B3LYP/6-31G(d) level of theory.