Acetylide-bridged tetracene dimers

Supporting information

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Monomer and starting materials Synthesis:

5,12-diphenyltetracene. (1) To a 250 ml three necks round flask was added 5,12 naphtacenequinone (1g, 3.87 mmol) following by freshly distilled THF (60 ml). Phenylmagnesium bromide (10 ml, 1.0 M in THF) was added drop to drop at -78°C (acetone dry ice bath) and the reaction mixture was allowed to warm to room temperature overnight. Thus, a solution of 10 % aqueous HCl (100 ml) saturated with $SnCl_2$ was added carefully under vigorous agitation. The reaction mixture was stirred 1h. The solution turns yellow. Organic phase was extracted with DCM with a separation funnel and distilled under reduce pressure. The solid was dissolved in DCM and washed with water (3x). The solution was distilled under reduce pressure and purified by chromatography on silica gel with hexane to give 1.2 g of a yellow powder (3.15 mmol, 82%) following by train sublimation (x2).
^{1}H NMR *($CDCl_3$,400MHz)* δ 8.32 (s, 2H), 7.78 (dd, 2H), 7.70-7.55 (m, 2H, *J* = 8.6Hz), 7.31-7.24 (m, 4H, *J* = 8.4Hz) ^{13}C NMR *($CDCl_3$,400MHz)* δ 131.51, 128.52, 128.39, 127.57, 126.97, 125.67, 125.17, 124.73. Anal Calcd exact mass: 380.16 Anal. Calcd for $C_{30}H_{20}$: C 94.70; H 5.30. Found: C 94.53; H 4.97 Mp: 206 °C.

5,12-diphenylpentacene. (2) ^{1}H NMR *(C_6D_6, 500MHz)* δ 8.60 (s, 4H), 7.58 (m, 4H), 7.45 (m, 4H), 7.40 (m, 4H), 7.36 (m, 4H), 6.89 (m, 4H) ^{13}C NMR *(C_6D_6,500MHz)* δ 139.7, 137.2, 131.9, 131.1, 128.8, 128.7, 127.9, 125.7, 125.4 Anal Calcd exact mass: 430.17 Maldi-TOF/MS: 430.17. Calcd for $C_{34}H_{22}$: C 94.85; H 5.15. Found: C 94.83; H 5.17 Mp: 254 °C.

5,12-bis(triethylsilylethynyl)tetracene (4) was prepared following up the general procedure described by S.A. Odom et al.[1] and purify by recrystallization from DCM: EtOH (Yield: 72%).
^{1}H NMR *($CDCl_3$, 500MHz)* δ 9.26 (s, 2H), 8.60 (dd, 2H, *J* = 3.5Hz), 8.04 (dd, 2H, *J* = 3.5Hz), 7.54 (dd, 2H, *J* = 3.5Hz), 7.47 (dd, 2H, *J* = 3.5Hz), 1.24 (t, 18H, *J* = 7.8Hz), 0.91 (t, 12H, *J* = 7.8Hz) ^{13}C NMR *($CDCl_3$, 500MHz)* δ 132.16, 132.53, 130.16, 128.58, 127.58, 126.67, 126.21, 125.98, 118.47, 106.86, 103.19, 7.82, 4.73 Anal Calcd exact mass: 504.27 Maldi-TOF/MS: 504.16. Calcd for $C_{34}H_{40}Si_2$: C 80.89; H 7.99. Found: C 80.80; H 7.84 Mp: 104 °C.

5,12-bis(triethylsilylethynyl)pentacene (5) was prepared following up the general procedure described by J. E. Anthony et al.[2] and purify by recrystallization from DCM: EtOH (Yield: 64%).
^{1}H NMR *(CDCl$_3$, 500MHz)* δ 9.26 (s, 4H), 8.00 (dd, 4H, *J* = 3.3Hz), 7.41 (dd, 4H, *J* = 3.3Hz), 1.30 (t, 18H, *J* = 7.8Hz), 0.96 (t, 12H, *J* = 7.8Hz) ^{13}C NMR *(CDCl$_3$, 500MHz)* δ 132.27, 130.48, 128.66, 126.22, 126.00, 118.24, 108.17, 7.88, 4.79, Calcd exact mass: 554.91 Maldi-TOF/MS: 554.06. Anal. Calcd for $C_{38}H_{42}Si_2$: C 82.25; H 7.63 Si 10.12. Found: C 82.23; H 7.66 Si 10.11 Mp: 194 °C.

12-Phenyl-12H-naphthacen-5-one To a 250 ml three necks round flask was added 5,12 naphtacenequinone (1 eq.) following by freshly distilled THF. Phenylmagnesium bromide (1 eq., 1.0 M in THF) was added drop to drop at -78°C (acetone dry ice bath) and the reaction mixture was allowed to warm to room temperature overnight. Thus, a solution of 10 % aqueous HCl (100 ml) saturated with $SnCl_2$ was added carefully under vigorous agitation. The reaction mixture was stirred 1h. Organic phase was extracted with DCM with a separation funnel and distilled under reduce pressure. The solid was dissolved in DCM and washed with water (3x). The solution was distilled under reduce pressure. 5-phenylnaphtacenequinone was separated by chromatography on silica gel with hexane:DCM (1:1) to give 1.2 g of a white/yellowish powder (3.15 mmol, 71%).
^{1}H NMR *(CDCl$_3$,400MHz)* δ 8.87 (s, 1H), 8.33 (d, 1H, *J* = 8.6Hz), 8.14 (s, 1H,), 8.02 (d, 1H, *J* = 8.4Hz) 7.83 (d, 1H, *J* = Hz) 7.73 (d, 1H, *J* = Hz) 7.54 (d, 4H, *J* = Hz) 7.38 (d, 2H, *J* = Hz) 7.21 (m, 2H, *J* = 8.4Hz) 7.13 (m, 1H, *J* = 8.4Hz) ^{13}C NMR *(CDCl$_3$,600MHz)* δ 184.13, 147.90, 146.91, 143.32, 135.94, 134.26, 132.26, 132.18, 130.39, 129.73, 128.95, 128.73, 128.33, 128.20, 128.10, 128.05, 127.84, 127.56, 127.04, 126.95, 126.74, 125.38, 73.Anal. Calcd for $C_{24}H_{16}O$: C 89.57; H 5.03; O 4.99. Found: C 88.6; H 4.48 Mp: 230°C.

Acene dimer synthesis:

General procedure. All reagents were obtained from the Sigma Aldrich Co. and used as received. Moisture sensitive reaction was performed under dry nitrogen atmosphere in a 250 ml three necks round flask previously dried under vacuum.
To the three neck round flask under N2 was added 65 mL of freshly distilled THF following by appropriate acetylene (3.4 eq.). Then, n-BuLi (1.6M in hexane, 2.7 eq.) was added drop to drop to the stirred solution cooled down to -78°C and the resulting reaction mixture stirred and allowed to warm to room temperature during 2h. Appropriate quinone (1 eq.) was added slowly and the system was kept stirring overnight. A x % HCl aq. solution saturated with SnCl2 was added to the reaction flask and the resulting mixture was stirred 30 min. Then, after pulling off THF, organic phase was extracted with DCM, washed with water following by NH4Cl/H2O and dried on MgSO4. Most of the ethylene linked acene dimers presented were not stable on silica gel column, therefore to separate dimer from residual monomer, the crude solution in DCM was precipitated in MeOH to yield a solid.

(triethylsilylethynyl) tetracene dimer (**6**) ^{1}H NMR *(CDCl$_3$,400MHz)* δ 9.68 (s, 2H), 9.35 (s, 2H), 9.04 (d, 2 H, *J* = 8.5Hz), 8.71 (d, 2H, *J* = 8.7Hz), 8.12 (m, 4H, *J* = 9.4-

17.1Hz), 7.66 (m, 4H, *J* = 5.4-11.3Hz), 7.51 (m, 4H, *J* = 3.4-6.3Hz), 1.25 (t, 18H, *J* = 7.8Hz), 0.96 (q, 12H, *J* = 7.6,7.9Hz) ^{13}C NMR *(CDCl$_3$,400MHz)* The product was unsufficiently soluble for meaningful analysis by ^{13}C NMR spectroscopy. Anal Calcd exact mass: 754.35 Maldi-TOF/MS: 753.96. Mp: 251 °C.

(triisopropylsilylethynyl) tetracene dimer ^{1}H NMR *(CDCl$_3$,400MHz)* δ 9.76 (s, 2H), 9.42 (s, 2H), 9.06 (d, 2H, *J* = 8.6Hz), 8.75 (d, 2H, *J* = 8.6Hz), 8.08 (m, 4H, *J* = 7.7-9.9Hz), 7.71 (m, 4H, *J* = 8.1-14.7Hz), 7.53 (m, 4H, *J* = 3.9-5.6Hz), 1.37 (m, 25H) The product was unsufficiently soluble for meaningful analysis by ^{13}C NMR spectroscopy. Anal Calcd exact mass: 838.44 Maldi-TOF/MS: 837.84. Anal. Mp: 300°C.

(trimethyldiphenylethynyl) tetracene dimer ^{1}H NMR *(CDCl$_3$,500MHz)* δ 9.70 (s, 2H), 9.33 (s, 2H), 9.06 (d, 2H, *J* = 8.6Hz), 8.74 (d, 2H, *J* = 8.4Hz), 8.12 (m, 2H), 8.03 (m, 2H), 7.94 (m, 6H, *J* = 15.0-30.0Hz), 7.70 (t, 2H) , 7.64 (t,2H), 7.51 (m, 12H) , 1.03 (s, 6H) ^{13}C NMR *(CDCl$_3$,400MHz)* The product was unsufficiently soluble for meaningful analysis by ^{13}C NMR spectroscopy. Anal Calcd exact mass: 918.31 Maldi-TOF/MS: 918.38 Mp: 420°C

(diphenylethynyl) tetracene dimer (3) ^{1}H NMR *(CDCl$_2$,400MHz)* δ 9.81 (s, 2H), 9.15 (d, 2H, J=), 8.40 (s, 2H), 8.13 (d, 2H, *J* =), 7.89 (d, 2H), 7.78 (d, 2H, J=), 7.65 (m, 6H), 7.60 (m, 4H) , 7.41 (m, 8H). Anal Calcd exact mass: 630.23 Maldi-TOF/MS: 629.61.

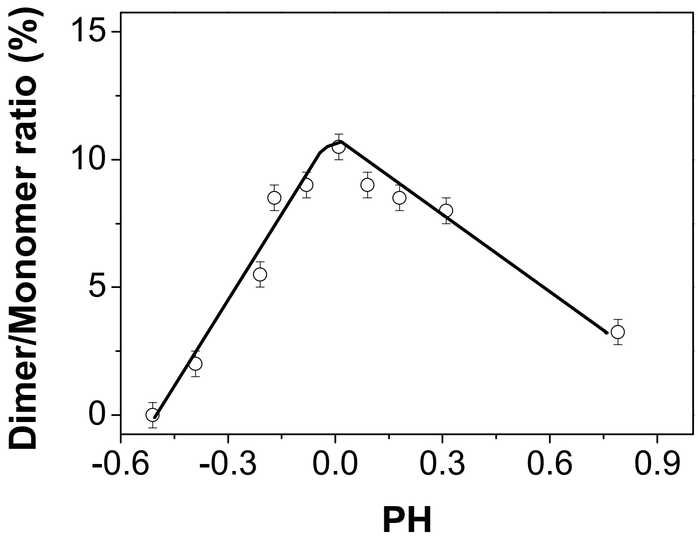

Figure S1. Ratio dimer/monomer vs. pH for 6 synthesis based on ^{1}H NMR (CDCl$_3$, 400MHz) analysis before purification process

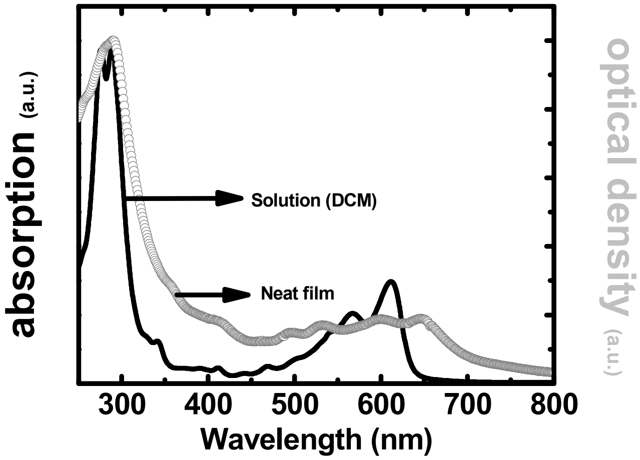

Figure S2. Absorption spectra of 6 in solution (solid black line) and in solution and in neat film (grey open circle)

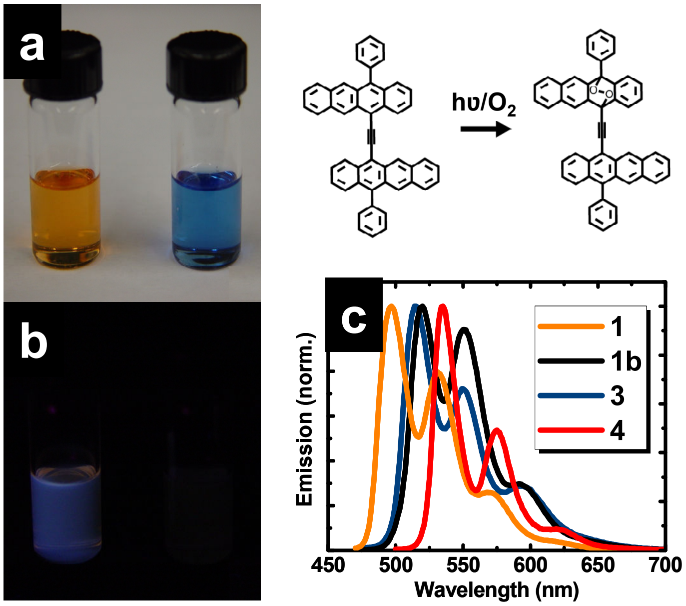

Figure S3. Absorption (a) and emission (λ_{ex}=365nm) (b) illustrations of 3 (left) and TEST-D (right) in DCM after exposure overnight to white light/air atmosphere condition; emission spectra of 1, Triethyl-(12-phenyl-naphthacen-5-ylethynyl)-silane (1b), 4 and 3 after exposure overnight to white light/air atmosphere condition

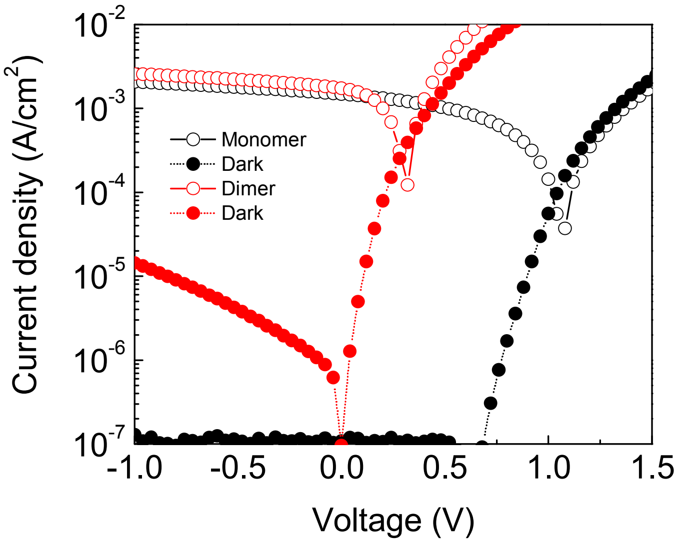

Figure S4. **Semi-log scale plot of current-density as a function of applied voltage for photovoltaic devices with 4 (black squares) and 6 (red circles) donor layers in the dark (filled symbols) and under illumination (open symbols).**

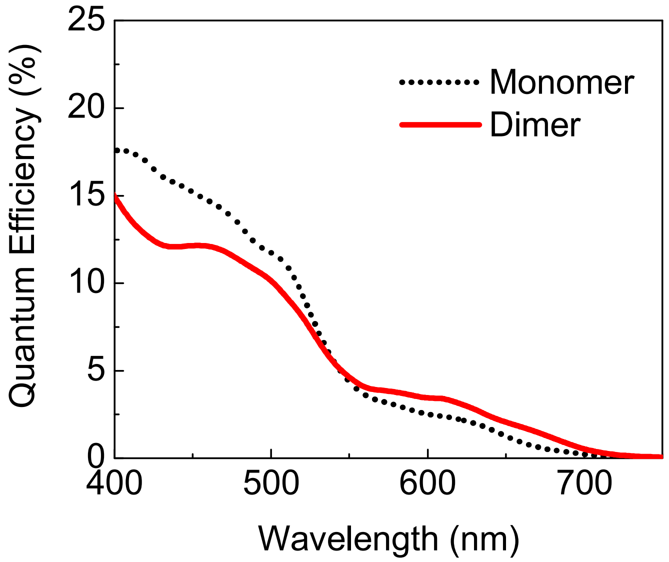

Figure S5. **Quantum efficiency traces for devices comprise ITO/ MoO_3 (100Å)/ Donor (100Å)/ C_{60} (400Å)/ BCP (100Å)/ Al, where Donor is either 4 (dotted black line) or 6 (solid red line).**

1. **S. A. Odom, S. R. Parkin and J. E. Anthony, *Organic Letters*, 2003, 5, 4245-4248.**
2. **J. E. Anthony, D. L. Eaton and S. R. Parkin, *Organic Letters*, 2001, 4, 15-18.**