

Supporting Information for:

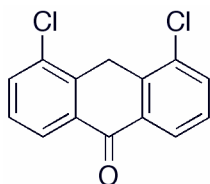
Transistors from A Conjugated Macrocyclic: Field and Photo Effects

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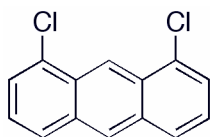
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Synthesis

General: The reagents and starting materials employed were either commercially available or prepared according to the known procedures as noted below. Anhydrous and oxygen free THF was distilled from sodium. Unless otherwise noted, all reactions were run in oven-dried glassware, and monitored by TLC using silica gel 60 F₂₅₄ precoated plated (Merck). Column chromatography was carried out under positive pressure on MN Kieselgel 60M 230-400 mesh silica. ¹H NMR(300MHz) spectra were recorded on a Bruker DPX spectrometer and ¹³C NMR(100.7MHz) spectra were recorded on a Varian Inova 400 spectrometer at. Mass spectra were recorded on Thermo Finnigan MAT 95 XL spectrometer. Thermal reactions of **1a** and **1b** were monitored using Perkin Elmer Differential Scanning Calorimeter Pyris 1. Melting point of other compounds was measured using a Nikon Polarizing Microscope ECLIPSE 50i POL equipped with an INTEC HCS302 heating stage.

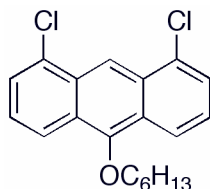


4,5-Dichloro-9-anthrone was synthesized according to Helge, P.; Wolfgang, W.; Müllen, K. *J. Org. Chem.* **1996**, 61, 2853–2856.

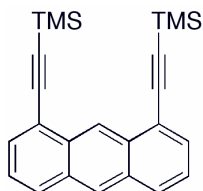


1,8-Dichloro-anthracene (2a): To a stirred suspension of 4,5-dichloro-9-anthrone (762mg, 2.9mmol) in *i*-PrOH (80ml) was added NaBH₄ (549mg, 14.5mmol) in small portions over 30mins. The mixture was further stirred for 1h at room temperature and poured into 100ml of saturated NH₄Cl aqueous solution. The organic layer was separated and the aqueous layer was further extracted with dichloromethane (80ml). The organic layers were combined, dried with anhydrous Na₂SO₄, concentrated under reduced pressure. Column chromatography (10% dichloromethane in hexanes) on silica gel yielded 1,8-dichloro-anthracene (694mg, 97%) as yellow crystalline powder: ¹H-NMR(CDCl₃) δ(ppm): 9.23 (s, 1H), 8.44 (s, 1H), 7.92 (d, J=8.6Hz, 2H), 7.61 (dd, J₁=7.1Hz, J₂=0.7Hz, 2H), 7.40 (dd, J₁=8.5Hz, J₂=7.2Hz, 2H); ¹³C-NMR(CDCl₃) δ(ppm): 132.6, 132.4, 129.5, 127.6, 127.3, 126.0, 125.6, 121.0. HRMS (EI⁺): calcd. for C₁₄H₈Cl₂: 245.9998, found 245.9988. These data are consistent with those reported in House,

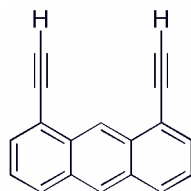
H.O.; Koepsell, D.; Jaeger, W. *J. Org. Chem.* **1973**, 38, 1167-1173.



1,8-Dichloro-10-hexyloxanthracene (2b): To a mixture of 4,5-dichloro-9-anthrone (1.010g, 3.84mmol) and K_2CO_3 (798mg, 5.8mmol) in 100ml of DMF, which was purged with nitrogen for 30 minutes, was added 1-bromohexane (0.81ml, 5.8mmol) via a syringe under a nitrogen atmosphere at room temperature. The resulting solution was stirred under a N_2 atmosphere at 55 °C overnight and poured into 1L of water and extracted with 200ml of diethyl ether. The organic layer was separated and the aqueous layer was further extracted with 50ml of diethyl ether for three times. The organic layer was combined, washed with brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography on silica gel (10% of CH_2Cl_2 in hexanes) yielded 1,8-dichloro-10-hexyloxanthracene (915.5mg, 70%) as yellow powder: mp: 61~63°C; 1H -NMR ($CDCl_3$) δ (ppm): 9.05 (s, 1H), 8.22 (d, $J=8.7$ Hz, 2H), 7.62 (d, $J=7.2$ Hz, 2H), 7.40 (dd, $J_1=8.7$ Hz, $J_2=6.9$ Hz, 2H), 4.15 (t, $J=6.9$ Hz, 2H), 2.03 (m, 2H), 1.65 (m, 2H), 1.43 (m, 4H), 0.98 (t, $J=6.9$ Hz, 3H); ^{13}C -NMR ($CDCl_3$) δ (ppm): 152.4, 132.8, 129.9, 126.0, 125.9, 125.0, 121.6, 116.2, 76.7, 31.7, 30.5, 25.8, 22.6, 14.1; HRMS (MALDI-TOF): cald. for $C_{20}H_{20}OCl_2$: 346.0885, found 346.0881.

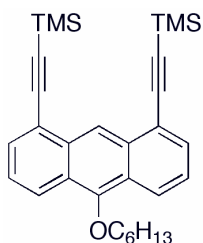


(1,8-Anthracenediyl-diethynylene)bis(trimethylsilane) was synthesized according to: Katz, H.E. *J. Org. Chem.* **1989**, 54, 2179-2183.

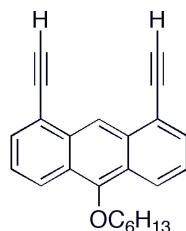


1,8-Diethynylantracene (3a): To a solution of (1,8-anthracenediyl-diethynylene)-bis(trimethylsilane) (295mg, 0.8mmol) in THF (20ml) was added 2ml of 2M KOH aqueous solution. The resulting yellow solution was stirred overnight at room temperature. Then 100ml of saturated NH_4Cl aqueous solution was added. The organic layer was separated and the aqueous layer was further extracted with dichloromethane (20ml). The organic layers were combined, dried with anhydrous Na_2SO_4 , concentrated under reduced pressure. Column chromatography (10% of CH_2Cl_2 in hexanes) on silica gel yielded 1,8-diethynylantracene (175mg, 97%) as crystalline yellow powder: 1H -NMR ($CDCl_3$) δ (ppm): 9.43 (s, 1H), 8.45 (s, 1H), 8.02 (d, $J=8.6$ Hz, 2H), 7.79 (d, $J=6.8$ Hz, 2H), 7.45 (dd, $J_1=8.6$ Hz, $J_2=6.9$ Hz, 2H), 3.61 (s, 2H); ^{13}C -NMR ($CDCl_3$) δ (ppm): 131.5, 131.3, 129.4, 127.5, 124.9, 123.7, 120.3, 82.6, 81.7. These data are

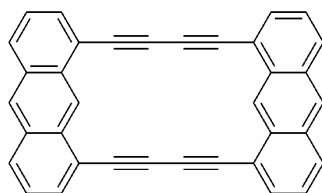
consistent with those reported in Katz, H. E. *J. Org. Chem.* **1989**, 54, 2179-2183.



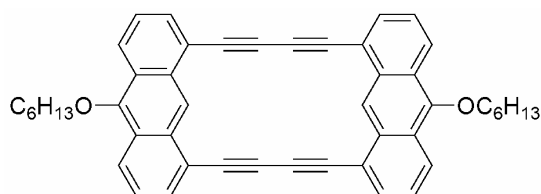
10-Hexyloxy-1,8-anthracenediyldiethynylene-bis(trimethylsilane): To a solution of (trimethylsilyl)acetylene (2.0ml, 8.9mmol) in 15ml of anhydrous and oxygen free THF was added a 3M diethyl ether solution of methylmagnesium bromide (4.4ml, 13.2mmol) under a nitrogen atmosphere at 0°C. The resulting solution was stirred for 45 mins at room temperature. To the solution were added 1,8-dichloro-10-hexyloxyanthracene (900mg, 2.63mmol), Ni(acac)₂ (6mg, 0.023mmol), and PPh₃ (12mg, 0.033mmol). The reaction mixture was refluxed for 72h under a nitrogen atmosphere, cooled to room temperature and 50ml of saturated NH₄Cl aqueous solution was added. The organic layer was separated and the aqueous layer was further extracted with 50ml of dichloromethane. The organic layers were combined, dried with anhydrous Na₂SO₄, concentrated under reduced pressure. Column chromatography (10% CH₂Cl₂ in hexanes) on silica gel yielded 10-hexyloxy-1,8-anthracenediyldiethynylene-bis(trimethylsilane) (757mg, 61%) as yellow powder: mp: 133~135°C; ¹H-NMR (CDCl₃) δ(ppm): 9.13 (s, 1H), 8.27 (d, J=8.7Hz, 2H), 7.78 (dd, J₁=6.9Hz, J₂=0.9Hz, 2H), 7.42 (dd, J₁=8.7Hz, J₂=6.9Hz, 2H), 4.14 (t, J=6.9Hz, 2H), 1.95 (m, 2H), 1.56 (m, 2H), 1.33 (m, 4H), 0.95 (t, J=6.9Hz, 3H); ¹³C-NMR(CDCl₃) δ(ppm): 152.5, 132.5, 131.9, 124.6, 124.6, 123.5, 121.6, 119.4, 103.7, 100.0, 76.7, 31.8, 30.6, 25.9, 22.7, 14.1, 0.4; HRMS (EI⁺): calcd. for C₁₈H₁₀OSi₂: 470.2456, found 470.2434.



1,8-Diethynyl-10-hexyloxyanthracene (3b) To a solution of 10-hexyloxy-1,8-anthracenediyldiethynylene-bis(trimethylsilane) (757mg, 1.6mmol) in 10ml of THF was added 2M KOH aqueous solution (4.8ml, 9.6mmol) at room temperature. The resulting solution was stirred overnight at room temperature, and then poured into 25ml of saturated NH₄Cl aqueous solution. The organic layer was separated and the aqueous layer was further extracted with 20ml of CH₂Cl₂. The organic layers were combined, dried with anhydrous Na₂SO₄, concentrated under reduced pressure. Column chromatography on silica gel (100% hexanes) yielded 1,8-diethynyl-10-hexyloxyanthracene (685.7mg, 99%) as yellow powder: mp: decomposed above 159°C; ¹H-NMR (CDCl₃) δ(ppm): 9.24(s, 1H), 8.31(d, J=8.7Hz, 2H), 7.79 (d, J=6.9Hz, 2H), 7.45 (dd, J₁=8.7Hz, J₂=6.9Hz, 2H), 4.17 (t, J=6.6Hz, 2H), 2.04 (m, 2H), 1.64 (m, 2H), 1.43 (m, 4H), 0.95 (t, J=6.9Hz, 3H); ¹³C NMR (CDCl₃) δ(ppm): 152.6, 132.2, 131.7, 125.2, 124.6, 123.8, 120.6, 119.2, 82.8, 81.8, 76.8, 31.7, 30.6, 25.8, 22.6, 14.1; HRMS (EI⁺): calcd. for C₂₄H₂₂O: 326.1665, found 326.1669.



Cyclic-bis(1,8-diethynyl-anthracene) (1a) was synthesized according to : Akiyama, S.; Misumi, S.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1960**, 346-347 and yielded as orange crystals: mp: polymerized at 402°C; ^1H -NMR (d_5 - PhNO_2 , 150°C) δ (ppm): 9.49 (s, 2H), 8.53 (s, 2H), 7.93 (d, J =6.8Hz, 4H), 7.54 (d, J =7.8Hz, 4H). Five peaks are expected to be found in ^1H NMR of **1a**. The missing peak should be hidden in the intense peaks from solvent molecules and can not be distinguished. ^{13}C -NMR was not taken due to low solubility of the product. HRMS (EI+): cald. for $\text{C}_{36}\text{H}_{16}$: 448.1247, found 448.1242. HRMS (MALDI-TOF) cald. for $\text{C}_{36}\text{H}_{16}$: 448.1247, found 448.1247.



Cyclic-bis(1,8-diethynyl-10-hexyloxy-anthracene) (1b): To a solution of 1,8-diethynyl-10-hexyloxyanthracene (647mg, 2.0mmol) in 56ml of pyridine and 4.4ml of CH_3OH was added $\text{Cu}(\text{OAc})_2$ (12.012g, 60mmol) and the resulting mixture was stirred at 55°C overnight. Then the reaction mixture was cooled to room temperature and 60ml of methanol was added into the solution. The mixture was filtered and the resulting solid was washed thoroughly with water, methanol and ether successively. Recrystallization of crude product from 1,2,4-trichlorobenzene yielded cyclic-bis(1,8-diethynyl-10-hexyloxy-anthracene) as orange crystals (405mg, 68%): mp: polymerized at 320°C; ^1H -NMR (CDCl_3) δ (ppm): 9.30 (s, 2H), 8.36 (d, 3J =8.8Hz, 4H), 7.90 (d, J =6.3Hz, 4H), 7.51 (dd, J_1 =8.8Hz, J_2 =7.0Hz, 4H), 4.20 (t, J =6.7Hz, 4H), 2.05 (m, 4H), 1.70 (m, 4H), 1.44 (m, 8H), 0.97 (t, J =7.0Hz, 6H). ^{13}C -NMR was not taken due to relatively low solubility of the product. HRMS (EI+): cald. for $\text{C}_{48}\text{H}_{40}\text{O}_2$: 648.3023, found 648.3010.

Characterization of solids and films

UV-visible spectra were taken on a Virian Cary 1E UV-Visible Spectrophotometer. Differential Scanning Calorimetry (DSC) was performed on Perkin Elmer Differential Scanning Calorimeter Pyris 1. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance Diffractometer with high-intensity $\text{Cu K}\alpha 1$ irradiation (λ =1.5406Å). X-ray crystallography was taken on a Bruker KAPPA APEX2 with Mo irradiation (λ =1.71073Å). Micrographs of crystals and thermal products were taken on Nikon ECLIPSE 50iPOL microscope with a SPOT Insight IN1820 CCD camera and an INSTRON HCS302 heating stage.

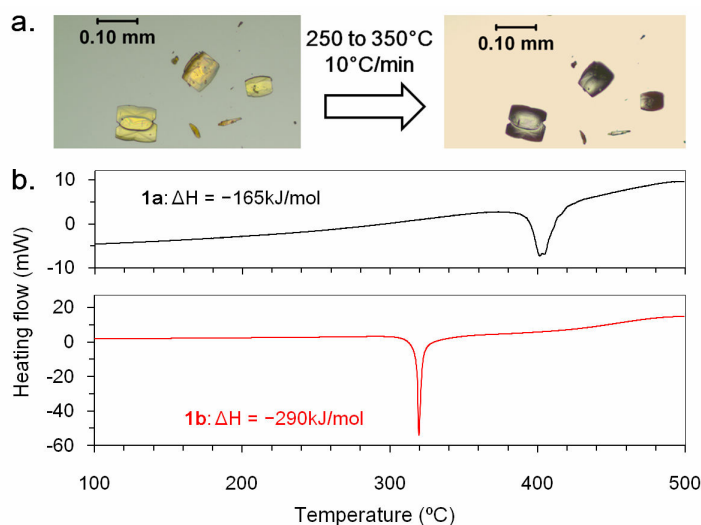


Figure S-1 Thermal reactions of **1a** and **1b** monitored by polarized microscopy and DSC: (a) micrographs (reflection mode) of **1b** before and after being heated; (b) DSC thermograms of **1a** and **1b** showing exothermal transition in the heating cycle at a heating rate of 10°C/min.

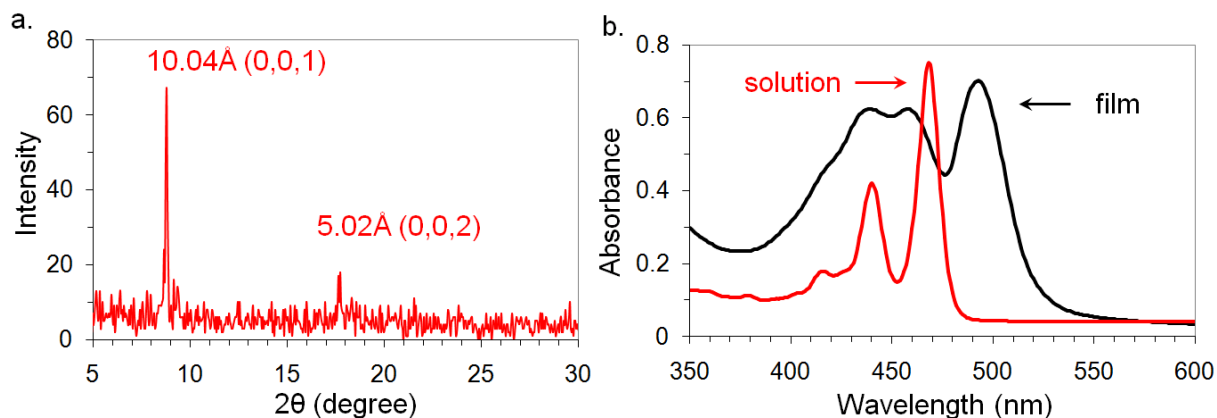


Figure S-2 (a) X-ray diffractogram from a thermal evaporated film of **1a**. (b) UV-vis absorption of **1a** from a solution in 1,2,4-trichlorobenzene (3×10^{-5} M) and from a thermal evaporated film of 150 nm thick on glass.

Wafer cleaning and SiO₂ surface modification with OTS

An oxidized silicon wafer (Si is highly n-doped with resistivity smaller than 0.005 Ω·cm and the thermally grown SiO₂ is 300 nm thick) was used as substrates for organic thin film transistors. The following surface treatments of the SiO₂ were performed on the dielectric surface before vacuum sublimation of the semiconductor film: a 10 min sonication in acetone, followed by a 70:30 H₂SO₄/H₂O₂ (piranha) etch for 1 hour at 100°C, then a 1:1:5 NH₃/H₂O/H₂O₂/deionized H₂O wash for 20 min at 70°C, and finally a soak in a 2.5 mM solution of octadecyltrichlorosilane (OTS) in toluene at 28°C for 1 hour. The dielectric surface was characterized using contact angle measurements, which were <5° after cleaning and >105° after OTS monolayer formation. The contact angle of the OTS monolayer confirms a tight-packed hydrophobic surface.

Transistor fabrication, capacitance measurement, and transistor measurements

1a was not further purified before vacuum-deposition. The thin films composed of **1a** were vacuum-deposited by an Edwards Auto 306 vacuum coater with the Turbomolecular pump at a pressure of 2.0×10^{-6} Torr or lower, with a deposition rate of ca. $1 \text{ \AA/s}$ to the desired thickness. During vacuum deposition the distance between source and substrate was 18cm. Different substrate temperatures for deposition were achieved using a radiant heater and measured with a thermocouple. Top-contact drain and source gold electrodes were vacuum-deposited through a shadow mask onto the films of **1a** in the same vacuum chamber, and the resulting semiconducting channels were $50\mu\text{m(L)} \times 1\text{mm(W)}$, $100\mu\text{m(L)} \times 1\text{mm(W)}$, $50\mu\text{m(L)} \times 2\text{mm(W)}$ and $100\mu\text{m(L)} \times 2\text{mm(W)}$. In these transistors highly n-doped silicon functioned as gate electrode and SiO_2 of 300nm thick (untreated or treated with octadecyl trichlorosilane) functioned as dielectrics.

The current-voltage measurement for thin-film transistors was carried out on a probe station using a HP 4145B semiconductor parameter analyzer. During the measurement, the samples were kept at room temperature in the ambient atmosphere. Several LED lamps, which were attached to the microscope of probe station, were used as source of visible light with varied colors.

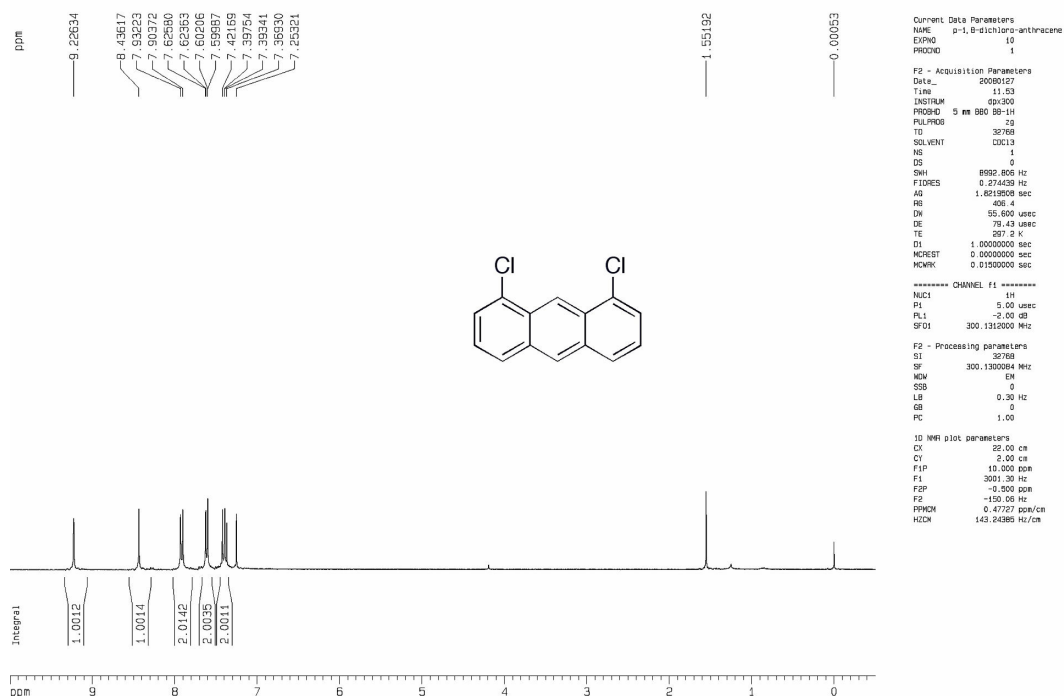
Transistor characteristics with different substrates and temperatures for **1a**

The field-effect mobility is measured in the saturation regime using the equation: $I_{\text{DS}} = (\mu_{\text{FET}} C_i / 2L)(V_{\text{G}} - V_{\text{T}})^2$ and C_i of 11 nF/cm^2 for 300nm SiO_2 . The ratio of the width to the length (W/L) of the channel was 40, 20 and 10. The on/off ratios were measured between gate biases of 0 and -50 V .

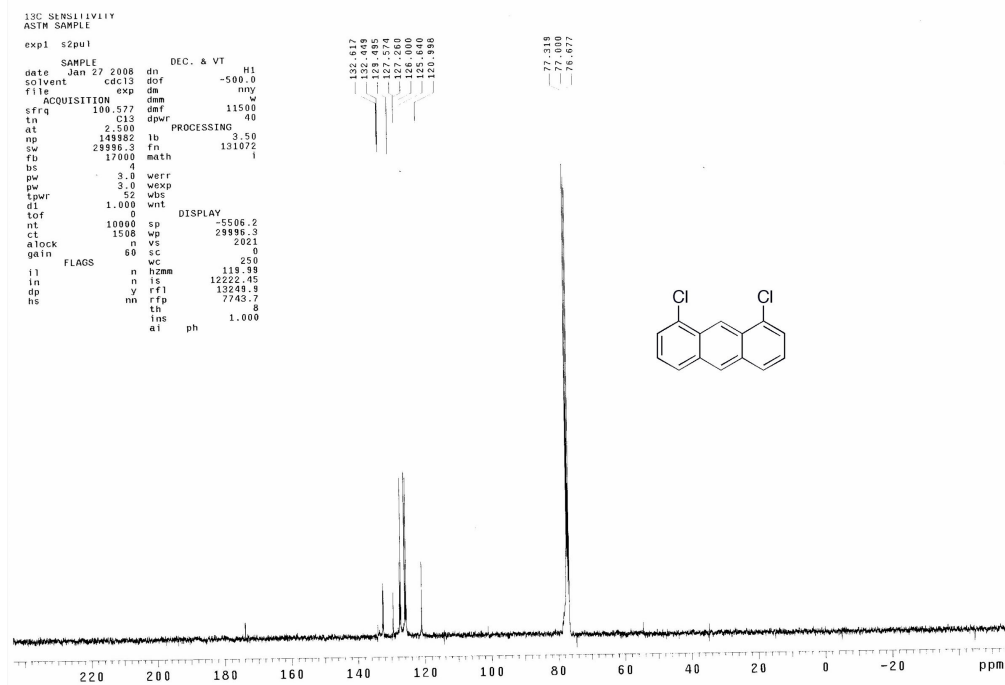
Table S-1. Summary of electrical characteristics for thin film transistors of **1a** deposited on two types of dielectric surfaces at varied temperature of substrate (T_{D}).

$T_{\text{D}} (^{\circ}\text{C})$	SiO_2		OTS-treated SiO_2	
	$\mu_{\text{FET}} (\text{cm}^2 \cdot \text{V}^{-1} \text{s}^{-1})$	On/Off ratio	$\mu_{\text{FET}} (\text{cm}^2 \cdot \text{V}^{-1} \text{s}^{-1})$	On/Off ratio
20	$3 \times 10^{-6} \sim 5 \times 10^{-6}$	10^2	$1 \times 10^{-5} \sim 2 \times 10^{-5}$	10^3
60	$1 \times 10^{-5} \sim 2 \times 10^{-5}$	10^2	$1 \times 10^{-3} \sim 2 \times 10^{-3}$	10^2
80	$9 \times 10^{-5} \sim 1 \times 10^{-4}$	10^2	$3 \times 10^{-3} \sim 6 \times 10^{-3}$	10^5
100	$1 \times 10^{-3} \sim 2 \times 10^{-3}$	10^4	$2 \times 10^{-2} \sim 3 \times 10^{-2}$	10^5
110	$1 \times 10^{-3} \sim 2 \times 10^{-3}$	10^4	$2 \times 10^{-2} \sim 7 \times 10^{-2}$	10^5
120	$1 \times 10^{-3} \sim 2 \times 10^{-3}$	10^4	$2 \times 10^{-2} \sim 7 \times 10^{-2}$	10^5
130	$1 \times 10^{-3} \sim 2 \times 10^{-3}$	10^4	$2 \times 10^{-2} \sim 6 \times 10^{-2}$	10^5
140	$1 \times 10^{-4} \sim 2 \times 10^{-4}$	10^3	$7 \times 10^{-3} \sim 2 \times 10^{-2}$	10^5

1,8-dichloro-anthracene

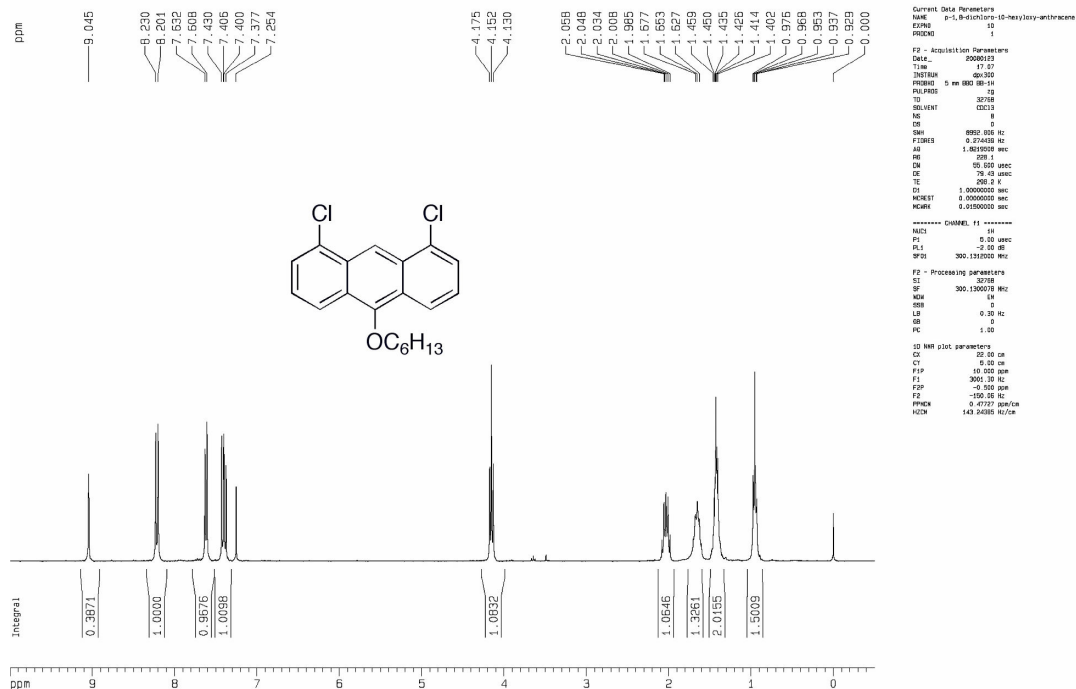


¹H NMR of 1,8-dichloro-anthracene

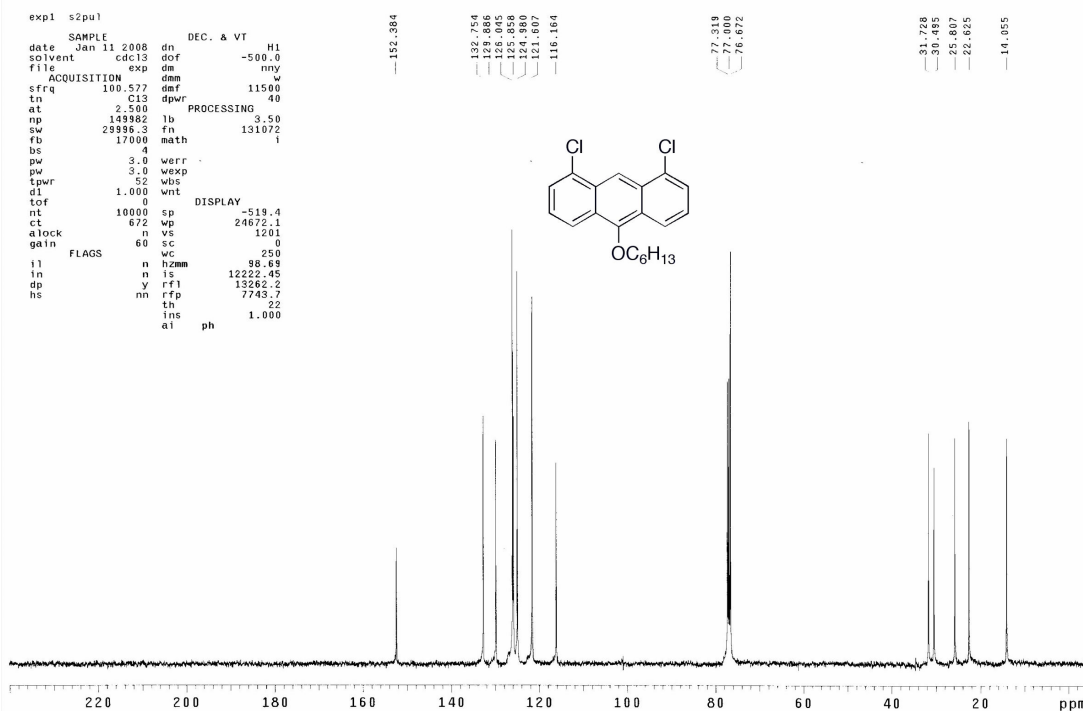


¹³C NMR of 1,8-dichloro-anthracene

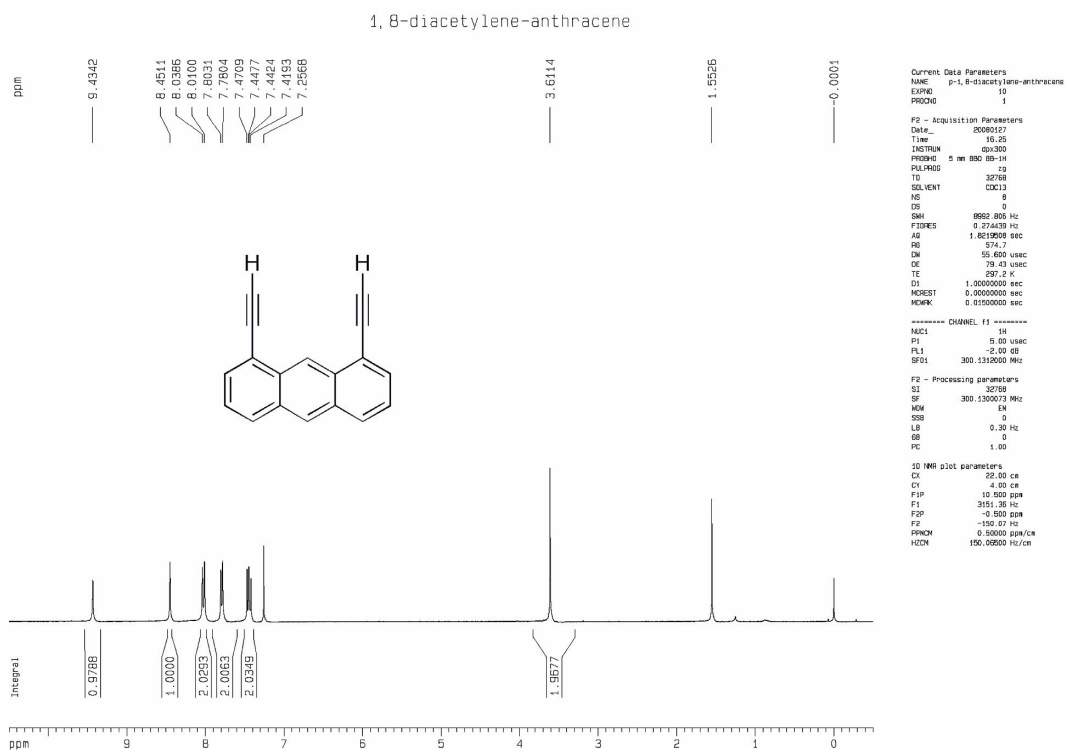
1,8-dichloro-10-hexyloxy-anthracene



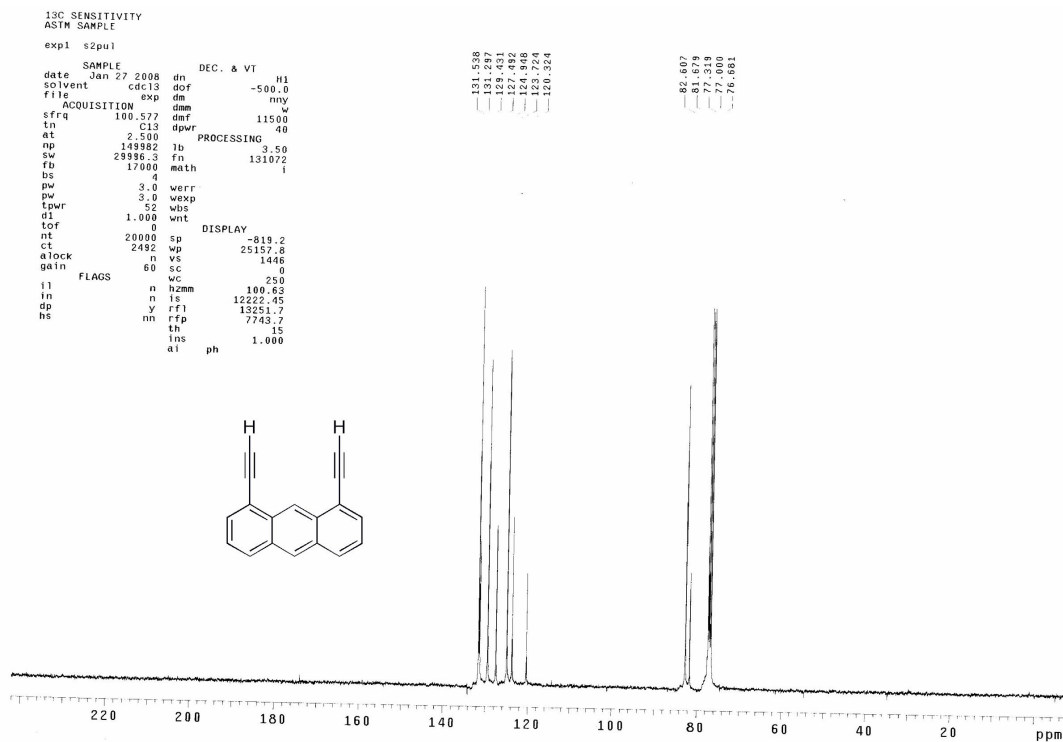
¹H NMR of 1,8-dichloro-10-hexyloxyanthracene



¹³C NMR of 1,8-dichloro-10-hexyloxyanthracene

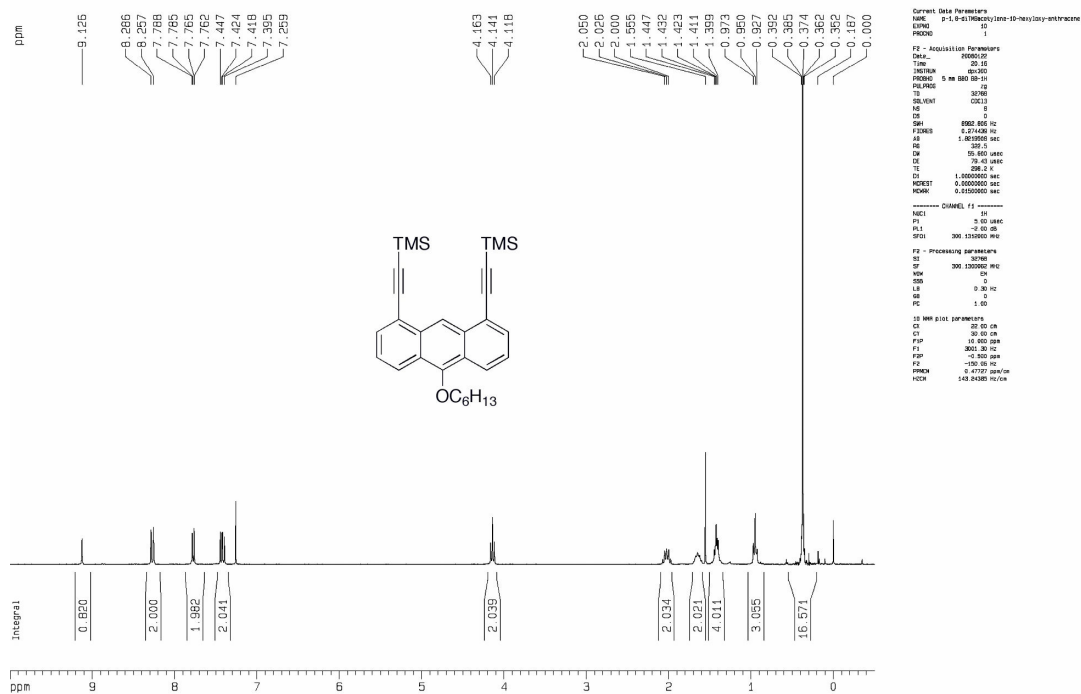


¹H NMR of 1,8-diethynylantracene

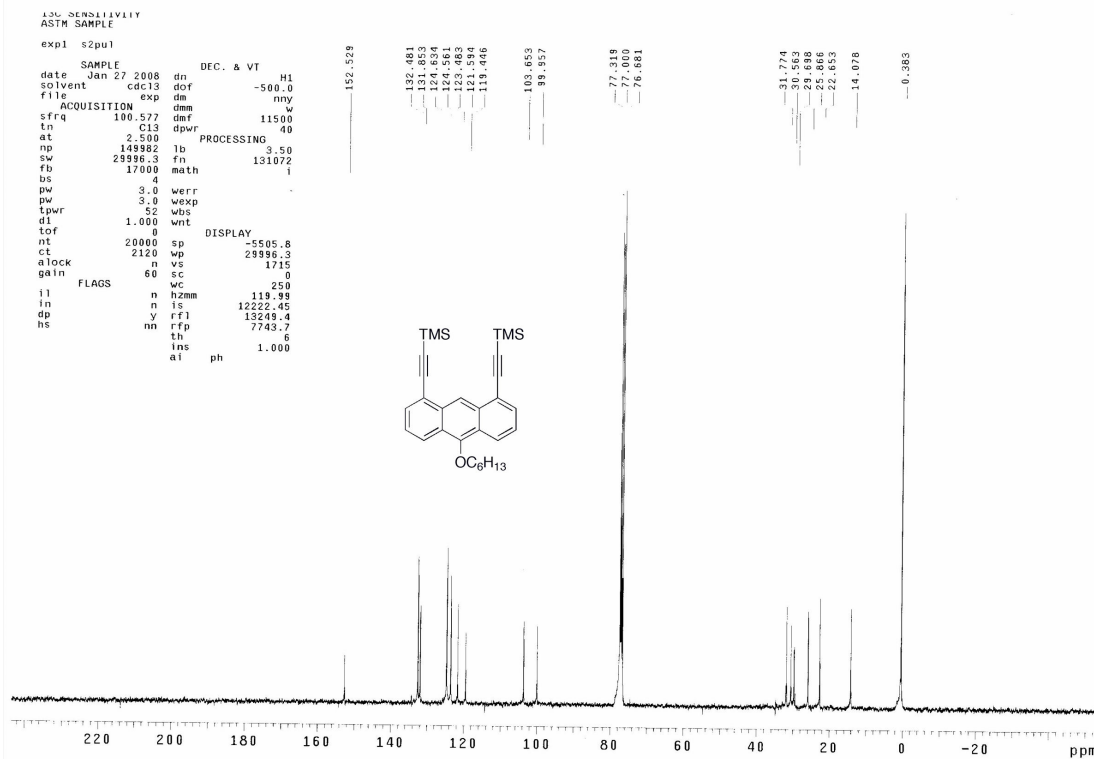


¹³C NMR of 1,8-diethynylantracene

1,8-diTMSacetylene-10-hexyloxy-anthracene

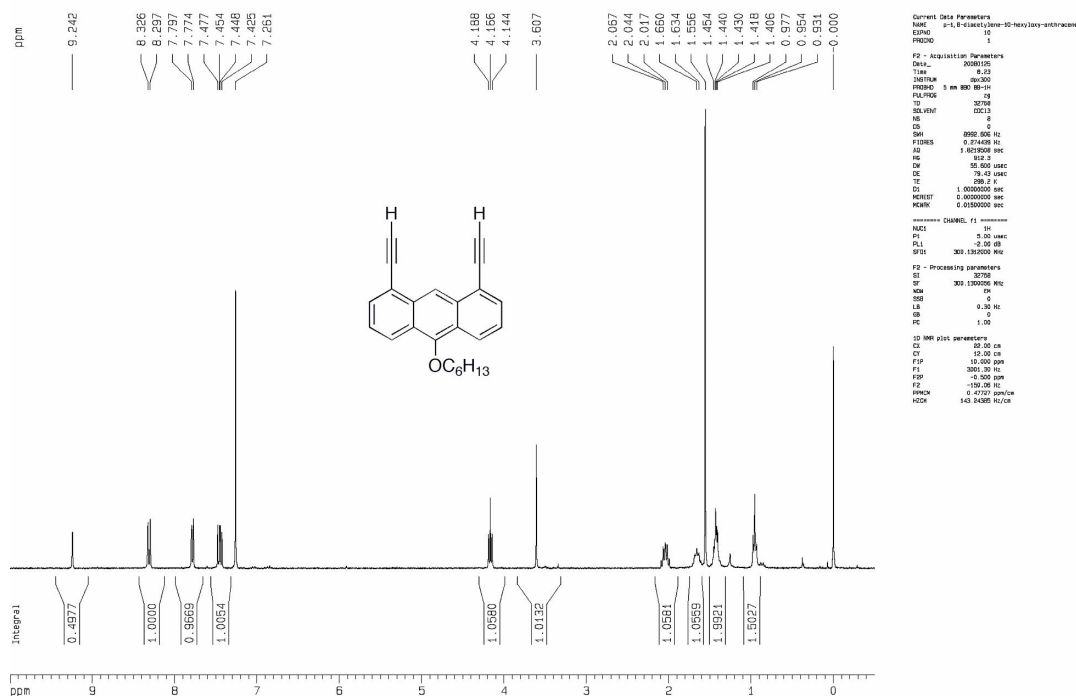


¹H NMR of 10-hexyloxy-1,8-anthracenediethynylene-bis(trimethylsilane)

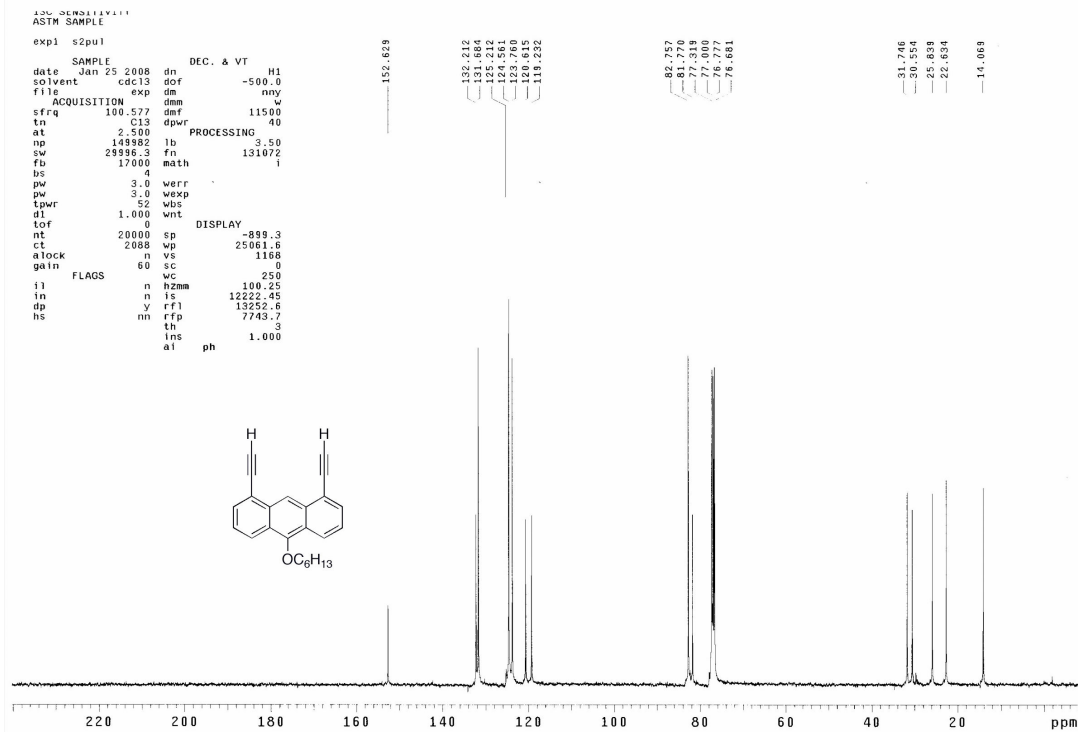


¹³C NMR of 10-hexyloxy-1,8-anthracenediethynylene-bis(trimethylsilane)

1,8-diacylene-10-hexyloxy-anthracene



¹H NMR of 1,8-diethynyl-10-hexyloxyanthracene



¹³C NMR of 1,8-diethynyl-10-hexyloxyanthracene

