Electronic supporting information

Solution processed ter-anthrylene-ethynylenes for annealing-activated organic field-effect transistors: a structure-performance correlation study

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1. Materials and Methods

Reactants were purchased from commercial sources and used without further purification; 9,10-dibromoanthracene (**1**),[1] [(trimehylsilyl)ethynyl]zinc,[2] 10-bromoanthracene-9-carbonyl chloride (**2**),[3] and $Pd(PPh_3)_4$,[4] were synthesized according to literature procedures. All manipulations were carried out under inert nitrogen atmosphere using standard Schlenk techniques unless otherwise specified. All solvents used were carefully dried and freshly distilled according to standard laboratory practice. Chromatography was performed using Merck®Kieselgel 60 (230–400 mesh) silica gel. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 or Bruker Avance 700 MHz and are reported in ppm relative to tetramethylsilane. FT-IR spectra (in KBr or as neat films between NaCl plates) were recorded on a Bruker Vector 22 spectrophotometer. UV-Vis spectra were measured on a Kontron Uvikon 942. Fluorescence spectra were obtained on a Varian Cary Eclipse spectrofluorimeter. GC-MS data (EI, 70 eV) were acquired on a HP 6890 instrument equipped with a HP-5MS capillary column (crosslinked 5% Ph Me siloxane) 30.0 m×250 µm×0.25 µm coupled with a HP 5973 mass spectrometer. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere (flow of 40 mL min^{-1}) with a Perkin-Elmer Pyris 6 TGA in the range from 30 to 800 °C with a heating rate of 10°C min^{-1}. Cyclic voltammetry was carried out on a Metrohm Autolab PGSTAT 302-N potentiostat. The materials were drop cast on a glassy carbon working electrode. Measurements were carried at 25 °C in acetonitrile solution containing 0.10 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. The potentials were measured versus Ag/Ag^+ as the quasi-reference electrode. After each experiment, the potential of

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[1] C. C. Price and C. Weaver, *J. Am. Chem. Soc.*, 1939, **61**, 3360.
[2] A. O. King and E.-I. Negishi, J. *Org. Chem.*, 1978, **43**, 358.
[3] S. M. A. Karim, R. Nomura, F. Sanda, S. Seki, M. Watanabe and T. Masuda, *Macromolecules*, 2003, **36**, 4786.
[4] D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.

the Ag/Ag^+ electrode was calibrated against the ferrocene/ferrocenium redox couple.[5] Elemental analyses were obtained on a EuroVector CHNS EA3000 elemental analyser. The high resolution mass spectrometry (HRMS) analysis of **E1-3** was performed using a Bruker microTOF QII mass spectrometer equipped with an electrospray ion source operated in positive ion mode. The sample solutions ($CHCl_3$/CH_3OH) were introduced by continuous infusion at a flow rate of 180 µL min^{-1} with the aid of a syringe pump. The instrument was operated with end-plate offset and capillary voltages set to −500 V and −4500 V respectively. The nebulizer pressure was 0.8 bar (N_2), and the drying gas (N_2) flow rate was 7.0 L min^{-1}. The capillary exit and skimmer 1 voltages were 90 V and 30 V respectively. The drying gas temperature was set at 180°C. The calibration was carried out with sodium formiate.

OFET devices were fabricated in top-contact bottom-gate configuration on heavily n-doped silicon wafers (resistivity: 0.02-1 Ω cm^{-1}) with 300-nm-thick thermally grown SiO_2 (C_i=9 nF cm^{-2}). Prior to **E1-E3** films deposition the substrates were sonicated in isopropanol and methanol for 10 min, rinsed in acetone and deionized water and then dried with a dinitrogen flow. Organic semiconductors were deposited by spin-coating from anhydrous $CHCl_3$ solutions ($0.05_{w/w}$ for **E1** and 0.10 $\%_{w/w}$ for **E2-E3**) at 2000 rpm for 30 seconds and, when needed, annealed at 100°C for 30 min under high vacuum condition (10^{-5} torr). Gold drain and source electrodes (W=4 mm L=200 µm) were fabricated on the organic layer by thermal evaporation through a shadow mask. The gate was a gold ohmic contact created onto the silicon substrate. The I_{ds}-V_{ds} current-voltage characteristics were measured under dinitrogen atmosphere using an Agilent 4155C semiconductor parameter analyzer. The field-effect mobility (μ_{FET}) in saturation regimes was extracted using the equation:

$$I_{ds} = C_i \mu \frac{W}{2L} \cdot (V_g - V_{th})^2 \quad \text{at} \quad V_{ds} > V_g$$

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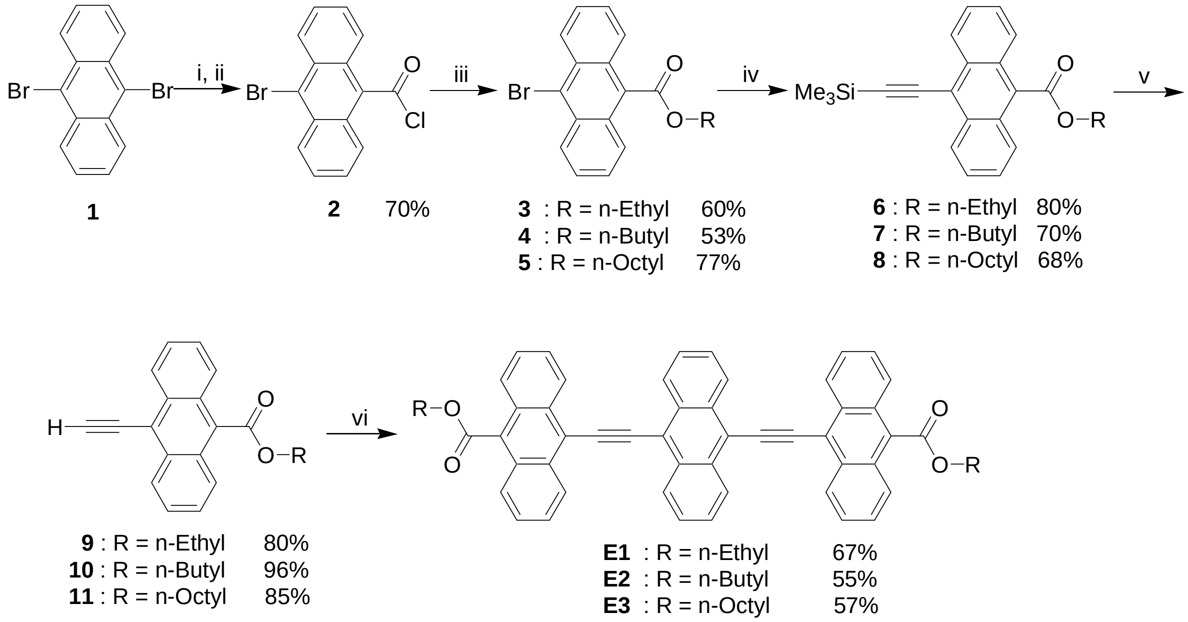
[5] For nonaqueous electrochemistry, IUPAC recommends the use of a redox couple such as ferrocene/ferrocenium ion (Fc/Fc^+) as an internal (or marker) standard: a) G. Gritzner and J. Kůta, *Pure Appl. Chem.*, 1984, **56**, 461; b) G. Gritzner, *Pure Appl. Chem.*, 1990, **62**, 1839.

where I_{ds} is the drain-source current, C_i is the capacitance per unit area of the SiO_2 dielectric, V_g is the gate voltage and V_{th} is the threshold voltage. The V_{th} was extrapolated from the $(I_{ds})^{1/2}$ vs. V_g plot. The statistics was performed on five devices.

XSR measurements were performed in coupled detector/sample scan mode (2θ/θ scans) on a D8 Discover diffractometer by Bruker, equipped with a Göbel mirror, using CuKα radiation. XRD measurements were performed in detector scan mode (2θ scans) at a fixed incidence angle of approximately 2°, by employing a diffractometer equipped with a Rigaku 200H rotating anode X-ray source, using CuKα radiation monochromatized by a Ge single crystal (111 reflection).

2. Synthesis and characterization of building blocks and E1-E2 and E3

The synthetic approach followed for the preparation of **E1-E3** is described in scheme S1 and follows the previously published strategy for the obtainment of alkyl functionalised ter(anthrylene-ethynylene)s which was successfully adapted for the preparation of their ester functionalised congeners. [6,7]



Scheme S1: Synthetic route for the obtainment of **E1-E3**. Reagents and conditions: (i) 1) BuLi (1 equiv)/Et_2O/–78°C 2) CO_2/H^+; (ii) $SOCl_2$/reflux; (iii) ROH/pyridine/THF; (iv)

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[6] P. Keg, A. Dell’Aquila, F. Marinelli, O. L. Kapitanchuk, D. Fichou, P. Mastrorilli, G. Romanazzi, G.P. Suranna, L. Torsi, Y. M. Lam and S. G. Mhaisalkar, *J. Mater. Chem.*, 2010, **20**, 2448.

[7] A. Dell'Aquila, F. Marinelli, J. Tey, P. Keg, Y. M. Lam, O. L. Kapitanchuk, P. Mastrorilli, C. F. Nobile, P. Cosma, A. Marchenko, D. Fichou, S. G. Mhaisalkar, G. P. Suranna and L. Torsi, *J. Mater. Chem.*, 2008, **18**, 786.

[(trimehylsilyl)]ethnyl]zinc chloride in THF, $Pd(PPh_3)_4$, toluene, 80°C, overnight; (v) *n*-Bu_4NF 1.0 M in THF, 0°C, 20 min; (vi) **1** 0.5 equiv, CuI, $Pd(PPh_3)_4$, $HNEt_2$, reflux, overnight.

The 9,10-dibromoanthracene (**1**) was monometallated with buthyl-lythium and subsequently reacted with carbon dioxide, followed by protonation. Subsequent treatment with $SOCl_2$ permitted the obtainment of the corresponding chloride **2** that was reacted with ethanol, n-buthanol, n-octanol to yield the corresponding bromoesters (**3**, **4**, or **5**) under classic Schotten–Baumann conditions. These building blocks were subjected to a Negishi coupling with (trimethylsilyl)ethynyl zinc(II) chloride to obtain the corresponding trimethylsilyl-ethynyl derivatives (**6**, **7** and **8**). Deprotection of the aforementioned trimethylsilylacetylene derivatives with tetrabutylammonium fluoride gave the corresponding terminal alkynes (**9**, **10** and **11**) that were employed in the final reaction step. The Sonogashira cross coupling between **1** and two equivalents of the terminal alkynes **9**, **10** and **11** afforded the desired oligomers **E1-3** in 67, 55 and 57% yield respectively. The products precipitated from the reaction medium as red powders and were purified by subsequent Soxhlet washings (methanol, acetone, and hexane) and multiple reprecipitations from chloroform-methanol.

2.1 Ethyl 10-bromoanthracene-9-carboxylate (3)

A THF solution (25 mL) containing ethanol (345 mg, 7.50 mmol), **2** (1.60 g, 5.00 mmol) and pyridine (791 mg, 10.00 mmol) was stirred at room temperature overnight. The solution was then poured into a 10 %w HCl solution and extracted with dichloromethane. The collected organic layers were dried over anhydrous Na_2SO_4, and the solvent removed *in vacuo*. The crude residue was then purified by flash chromatography on silica gel using dichloromethane as eluent affording **3** (988 mg, 60%) as pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.60 (d, J=8.62 Hz, 2H), 8.01 (d, J=8.61, 2H), 7.66-7.56 (m, 4H), 4.70 (q, J=7.14 Hz, 2H), 1.54 (t, J=7.12 Hz, 3H). $^{13}C\{^1H\}$ NMR

(101 MHz, $CDCl_3$, δ): 169.44, 130.08, 129.19, 128.67, 128.32, 127.36, 127.21, 125.49, 125.40, 62.17, 14.52. FT-IR (KBr): ν = 3069, 2978, 2935, 2872, 1942, 1720, 1550, 1522, 1484, 1442, 1286, 1264, 1215, 1175, 1029, 908, 753, 638, 602, 577 cm^{-1}. EIMS (m/z): 328 (M^+).

2.2 Butyl 10-bromoanthracene-9-carboxylate (4)

The synthesis of **4** was carried out by the same procedure outlined for **3** using 1.60 g (5.00 mmol) of 10-bromoanthracene-9-carbonyl chloride (**2**), 556 mg (7.50 mmol) of butan-1-ol, 791 mg (10.00 mmol) of pyridine and 25 mL of THF respectively. The product was purified by column chromatography (silica gel, petroleum ether 40–60 °C/CH_2Cl_2 = 3:1) to afford **4** (947 mg, 53%) as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.61-8.59 (m, 2H), 8.01-7.99 (m, 2H), 7.67-7.56 (m, 4H), 4.64 (t, J=6.68 Hz, 2H), 1.91-1.84 (m, 2H), 1.58-1.47 (m, 2H), 1.01 (t, J=7.50 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.54, 130.10, 129.52, 129.34, 128.69, 128.30, 127.35, 127.18, 124.43, 66.06, 30.80, 19.34, 13.80. FT-IR (KBr): ν = 3077, 2956, 2930, 2872, 2363, 1944, 1812, 1722, 1549, 1522, 1441, 1211, 1157, 1029, 751, 638, 602, 575 cm^{-1}. EIMS (m/z): 356 (M^+).

2.3 Octyl 10-bromoanthracene-9-carboxylate (5)

The synthesis of **5** was carried out by the same procedure outlined for **3** using 1.60 g (5.00 mmol) of 10-bromoanthracene-9-carbonyl chloride (21), 977 mg (7.50 mmol) of octan-1-ol, 791 mg (10.00 mmol) of pyridine and 25 mL of THF respectively. The product was purified by column chromatography (silica gel, petroleum ether 40–60 °C/CH_2Cl_2 = 4:1) to afford **5** (1.59 g, 77%) as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.61-8.59 (m, 2H), 8.02-7.99 (m, 2H), 7.67-7.57 (m, 4H), 4.63 (t, J=6.39 Hz, 2H), 1.92-1.85 (m, 2H), 1.54-1.44 (m, 2H), 1.42-1.28 (m, 8H), 0.89 (t, J=6.32 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.55, 130.10, 129.35, 128.69, 128.30, 127.35, 127.15, 125.45, 66.31, 31.83, 29.26, 29.25, 28.78, 26.11, 22.71, 14.17. FT-IR (KBr): ν = 3075, 2989, 2925, 2853, 1950, 1817, 1717, 1617, 1483, 1470, 1376, 1240, 1215, 1156, 1028, 892, 756, 645, 602, 576 cm^{-1}. EIMS (m/z): 412 (M^+).

2.4 Ethyl 10-[(trimethylsilyl)ethynyl]anthracene-9-carboxylate (6)

A three-necked round bottomed flask was added of 900 mg (2.73 mmol) of ethyl 10-bromoanthracene-9-carboxylate (**3**), 158 mg (0.14 mmol) of $Pd(PPh_3)_4$, 15 mL of toluene and a solution of 3.00 mmol of [(trimethylsilyl)]ethynyl]zinc(II) chloride in THF respectively. The mixture was kept under stirring overnight at 80 °C. The reaction mixture was then poured into 100 mL of 1.0 N HCl and repeatedly extracted with diethyl ether. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, petroleum ether 40–60 °C/CH_2Cl_2 = 2:1) to afford **6** (757 mg, 80%) as orange solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.60-8.63 (m, 2H), 8.03-8.00 (m, 2H), 7.64-7.54 (m, 4H), 4.69 (q, J=7.12 Hz, 2H), 1.55 (t, J=7.12 Hz, 3H), 0.44 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.50, 132.24, 129.29, 127.70, 127.32, 127.12, 126.74, 125.39, 120.00, 108.05, 101.01, 62.06, 14.54, 0.24. FT-IR (KBr): ν = 3062, 2960, 2900, 2148, 1948, 1726, 1624, 1441,1414, 1381, 1283, 1211, 1166, 1022, 851, 769, 727, 645 cm^{-1}. EIMS (m/z): 346 (M^+).

2.5 Butyl 10-[(trimethylsilyl)ethynyl]anthracene-9-carboxylate (7)

The synthesis of **7** was carried out following the same procedure reported for **6** using 900 mg (2.52 mmol) of butyl 10-bromoanthracene-9-carboxylate (**4**), 150 mg (0.13 mmol) of $Pd(PPh_3)_4$, 14 mL of toluene and a solution of 2.77 mmol of [(trimethylsilyl)]ethnyl]zinc chloride in THF respectively. The crude was purified by column chromatography (silica gel, petroleum ether 40–60 °C/CH_2Cl_2 = 3:1) to afford **7** (661 mg, 70%) as orange solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.61-8.59 (m, 2H), 8.01-7.99 (m, 2H), 7.67-7.56 (m, 4H), 4.64 (t, J=6.68 Hz, 2H), 1.91-1.84 (m, 2H), 1.58-1.47 (m, 2H), 1.01 (t, J=7.50 Hz, 3H), 0.46 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.52, 132.23, 129.29, 127.71, 127.32, 127.12, 126.74, 125.39, 120.01, 108.05, 101.01, 66.05, 30.80, 19.35, 13.80, 0.24. FT-IR (KBr pellet): ν = 3063, 2964, 2874, 2150, 2126, 1936, 1718, 1442, 1200, 1070, 1019, 856, 752, 653, 647 cm^{-1}. EIMS (m/z): 374 (M^+).

2.6 Octyl 10-[(trimethylsilyl)ethynyl]anthracene-9-carboxylate (8)

The synthesis of **8** was carried out by the same procedure reported for **6** using 1.40 g (3.39 mmol) of octyl 10-bromoanthracene-9-carboxylate (24), 196 mg (0.17 mmol) of $Pd(PPh_3)_4$, 18 mL of toluene and a solution of 3.73 mmol of [(trimethylsilyl)]ethnyl]zinc chloride in THF respectively. The product was purified by column chromatography (silica gel, petroleum ether 40–60 °C/CH_2Cl_2 = 4:1) to afford **8** (993 mg, 68%) as orange solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.63-8.61 (m, 2H), 8.02-8.00 (m, 2H), 7.65-7.53 (m, 4H), 4.62 (t, J=6.78 Hz, 2H), 1.92-1.85 (m, 2H), 1.53-1.46 (m, 2H), 1.43-1.23 (m, 8H), 0.89 (t, J= 6.79 Hz, 3H), 0.44 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.63, 132.55, 129.77, 127.63, 127.17, 127.07, 126.93, 125.43, 118.84, 108.02, 101.03, 66.23, 31.83, 29.26, 28.80, 26.11, 22.70, 14.16, 22.70, 14.16, 0.24. FT-IR (KBr): ν = 3068, 2949, 2920, 2854, 2150, 1720, 1470, 1441, 1287, 1262, 1217, 1015, 841, 766, 728, 659 cm^{-1}. EIMS (m/z): 430 (M^+).

2.7 Ethyl 10-ethynylanthracene-9-carboxylate (9)

2 mL of a 1.0 M solution of anhydrous tetrabutylammonium fluoride in THF was added to a 10 mL THF solution of 693 mg (2.00 mmol) of ethyl 10-((trimethylsilyl)ethynyl)anthracene-9-carboxylate (**6**) kept in a two-necked flask protected from light by an aluminium foil. The reaction mixture was stirred at 0 °C for 20 min. The mixture was then poured in water and extracted with diethyl ether. The collected organic phases were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The crude was eventually purified by column chromatography (silica gel, petroleum ether 40–60°C/CH_2Cl_2 = 2:1) to afford **9** (439 mg, 80%) as a reddish solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.67-8.61 (m, 2H), 8.05-7.98 (m, 2H), 7.65-7.54 (m, 4H), 4.70 (q, J=7.28 Hz, 2H), 4.06 (s, 1H), 1.55 (t, J=7.32 Hz 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.40, 132.55, 129.77, 127.63, 127.17, 127.07, 126.93, 125.43, 118.84, 89.67, 79.94, 62.10, 14.53. FT-IR (KBr): ν = 3278, 3059, 2979, 2933, 2901, 2874, 1895, 1709, 1624, 1561, 1490, 1442, 1378, 1283, 1025, 868, 768, 651, 626 cm^{-1}.

2.8 Butyl 10-ethynylanthracene-9-carboxylate (10)

The synthesis of **10** was carried out by the same procedure reported for **9** using 600 mg (1.60 mmol) of butyl 10-((trimethylsilyl)ethynyl)anthracene-9-carboxylate (**7**), 8 mL of THF and 1.6 mL of a 1.0 M solution of anhydrous tetrabutylammonium fluoride in THF respectively. The product was purified by column chromatography (silica gel, petroleum ether 40–60°C/CH_2Cl_2 = 3:1) to afford **10** (465 mg, 96%) as reddish solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.67-8.61 (m, 2H), 8.05-7.98

(m, 2H), 7.65-7.54 (m, 4H), 4.63 (t, J=6.68 Hz, 2H), 4.06 (s, 1H), 1.97-1.89 (m, 2H), 1.58-1.48 (m, 2H), 1.02 (t, J=6.73 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.40, 132.55, 129.77, 127.63, 127.17, 127.07, 126.93, 125.43, 118.84, 89.67, 79.94, 66.09, 30.94, 19.46, 14.01. FT-IR (KBr): ν = 3274, 3064, 2956, 2931, 2873, 1721, 1442, 1399, 1208, 1020, 833, 765, 751 cm^{-1}.

2.9 Octyl 10-ethynylanthracene-9-carboxylate (11)

The synthesis of **11** was carried out by the same procedure reported for **9** using 950 mg (2.20 mmol) of octyl 10-((trimethylsilyl)ethynyl)anthracene-9-carboxylate (**8**), 11 mL of THF and 2.2 mL of a 1.0 M solution of anhydrous tetrabutylammonium fluoride in THF respectively. The product was purified by column chromatography (silica gel, petroleum ether 40–60 °C/CH_2Cl_2 = 3:1) to afford **11** (670 mg, 85%) as reddish solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.64-8.61 (m, 2H), 8.03-8.01 (m, 2H), 7.66-7.53 (m, 4H), 4.62 (t, J=6.78 Hz, 2H), 4.04 (s, 1H), 1.92-1.85 (m, 2H), 1.53-1.46 (m, 2H), 1.43-1.23 (m, 8H), 0.89 (t, J= 6.79 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.39, 132.55, 129.77, 127.63, 127.17, 127.07, 126.93, 125.43, 118.84, 89.67, 79.94, 66.31, 31.83, 29.26, 29.25, 28.78, 26.11, 22.71, 14.16. FT-IR (KBr pellet): ν = 3257, 3079, 2990, 2926, 2866, 2853, 2098, 1714, 1455, 1440, 1372, 1279, 1124, 1019, 812, 768, 721, 662, 642, 620 cm^{-1}.

2.10 9,10-bis[(10-carboethoxyanthracen-9-yl)ethynyl]anthracene (E1)

A three-necked flask was added of 412 mg (1.50 mmol) of ethyl 10-ethynylanthracene-9-carboxylate (**9**), 229 mg (0.68 mmol) of 9,10-dibromoanthracene (**1**), 25.9 mg (0.14 mmol) of CuI, 10 mL of diethylamine and 162 mg (0.14 mmol) of $Pd(PPh_3)_4$ respectively. The mixture was then heated at reflux and kept under stirring overnight. After cooling to room temperature, the product formed as a red precipitate was collected and washed on a Soxhlet using hot methanol, acetone and hexane. Finally the product was extracted using chloroform and precipitated twice from chloroform-methanol to afford **E1** as a red powder (329 mg, 67%). ^{1}H NMR (700 MHz, $CDCl_3$, δ): 9.04-9.00 (m, 8H), 8.14 (d, J=8.7, 4H), 7.82-7.78 (m, 4H), 7.76-7.73 (m, 4H), 7.70-7.66 (m, 4H), 4.77 (q, J=7.1 Hz, 4H), 1.61 (t, J=7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, δ): 169.52, 132.54, 132.26, 129.83, 127.53, 127.44, 127.32, 127.24, 127.13, 125.70, 120.10, 119.05, 99.06, 98.85, 62.08, 14.53. FT-IR (KBr): ν = 3055, 2981, 2933, 1942, 1793, 1715, 1432, 1365, 1280, 1210, 1040, 847, 790, 769, 639 cm^{-1}. HRMS (ESI, m/z): $[M]^+$ calcd for $C_{52}H_{34}O_4$, 722.2452; found 722.2453, Anal. calcd for $C_{52}H_{34}O_4$: C 86.41, H 4.74; found: C 85.67, H 4.82.

2.11 9,10-bis[(10-carbo-1-butoxyanthracen-9-yl)ethynyl]anthracene (E2)

The synthesis of **E2** was carried out by the same procedure outlined for **E1** using 450 mg (1.48 mmol) of butyl 10-ethynylanthracene-9-carboxylate (**10**), 225 mg (0.67 mmol) of 9,10-dibromoanthracene (**1**), 24.8 mg (0.13 mmol) of CuI, 10 mL of diethylamine and 150 mg (0.13 mmol) of $Pd(PPh_3)_4$ respectively. The product was collected and washed on a Soxhlet using hot methanol, acetone and hexane. Finally the product was extracted using chloroform and precipitated twice from chloroform-methanol to afford **E2** as a red powder. (287 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.04-8.97 (m, 8H), 8.12 (d, J=8.76, 4H), 7.82-7.77 (m, 4H), 7.77-7.71 (m, 4H), 7.71-7.64 (m, 4H), 4.69 (t, J=6.64 Hz, 4H), 1.97-1.89 (m, 4H), 1.60-1.54(m, 4H), 1.05 (t, J=7.69 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 169.62, 132.57, 132.31, 129.94, 128.02, 127.58, 127.51, 127.38, 127.31, 127.21, 125.78, 120.12, 119.09, 99.06, 98.96, 66.09, 30.94, 19.46, 14.01. FT-IR (KBr): ν = 3055, 2956, 2874, 1943, 1793, 1715, 1653, 1560, 1487, 1433, 1279, 1204, 1039, 768, 743, 636, 611 cm^{-1}. HRMS (ESI, m/z): $[M + Na]^+$calcd for $C_{56}H_{42}O_4$, 801.2975; found, 801.2981. Anal. Calcd for $C_{56}H_{42}O_4$: C 86.35, H 5.43; found: C 85.37, H 5.62.

2.12 9,10-bis[(10-carbo-1-octlyoxyanthracen-9-yl)ethynyl]anthracene (E3)

The synthesis of **E3** was carried out by the same procedure outlined for **E1** using 650 mg (1.81 mmol) of octyl 10-ethynylanthracene-9-carboxylate (**11**), 275 mg (0.82 mmol) of 9,10-dibromoanthracene (**1**), 30.5 mg (0.16 mmol) of CuI, 10 mL of diethylamine and 185 mg (0.16 mmol) of $Pd(PPh_3)_4$ respectively. The product was collected and washed on a Soxhlet using hot methanol, acetone and hexane. Finally the product was extracted using chloroform and reprecipited twice from chloroform-methanol to afford **E3** as a red powder. (417 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.03-8.98 (m, 8H), 8.12 (d, J=8.64, 4H), 7.83-7.76 (m, 4H), 7.76-7.70 (m, 4H), 7.70-7.63 (m, 4H), 4.68 (t, J=7.11 Hz, 4H), 1.97-1.92 (m, 4H), 1.58-1.48 (m, 4H), 1.46-1.24 (m, 16H), 0.91 (t, J=6.62 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 169.63, 132.55, 129.94, 128.03, 127.54, 127.37, 127.30, 127.22, 125.80, 120.12, 119.09, 99.07, 98.96, 66.37, 31.87, 29.30, 28.85, 26.16, 22.75, 14.50. FT-IR (KBr): ν = 3055, 2951, 2928, 2869, 1719, 1522, 1472, 1433, 1401, 1274, 1202, 1028, 762, 744, 636 cm^{-1}. HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{64}H_{58}O_4$, 913.4227; found, 913.4212. Anal. calcd for $C_{64}H_{58}O_4$: C 86.26, H 6.56; found: C 85.33, H 6.51.

3. TGA traces of E1-E3

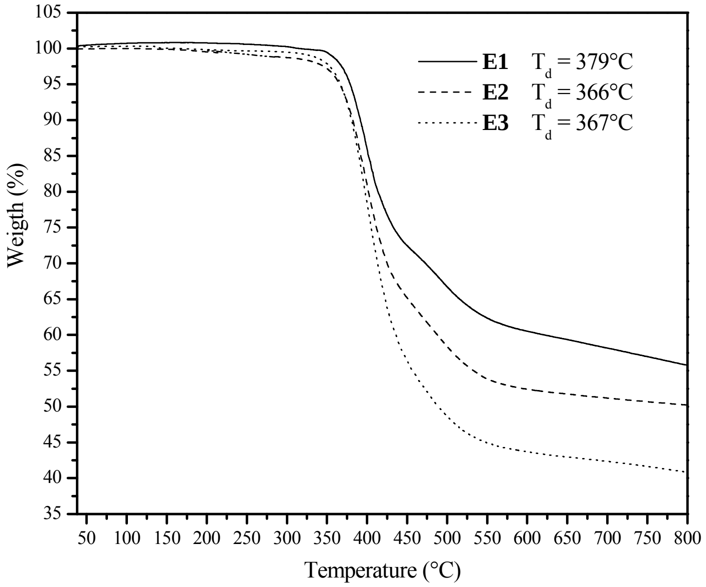

Figure S1: TGA traces obtained for **E1-E3**. The 5% weight loss temperatures are also reported.

4. Optical properties of E1-E3

Table S1. Optical properties of **E1-E3** in solution and in the solid state.

Molecule	λ_{max} [nm] [a]	λ_{max} [nm] [b]	λ_{em} [nm] [a]	λ_{em} [nm] [b]	E_g^{solid} [eV] [c]
E1	500	–[d]	561	–[d]	–[d]
E2	500	512, 552	561	650	2.1
E3	500	492, 550	561	653	2.1

[a] Maximum absorption and emission wavelength in dilute $CHCl_3$ solutions (~10^{-6} M). [b] Thin films. [c] Estimated from the onset of the UV–Vis absorption spectra of thin films. [d] Not recorded due to the low quality of film.

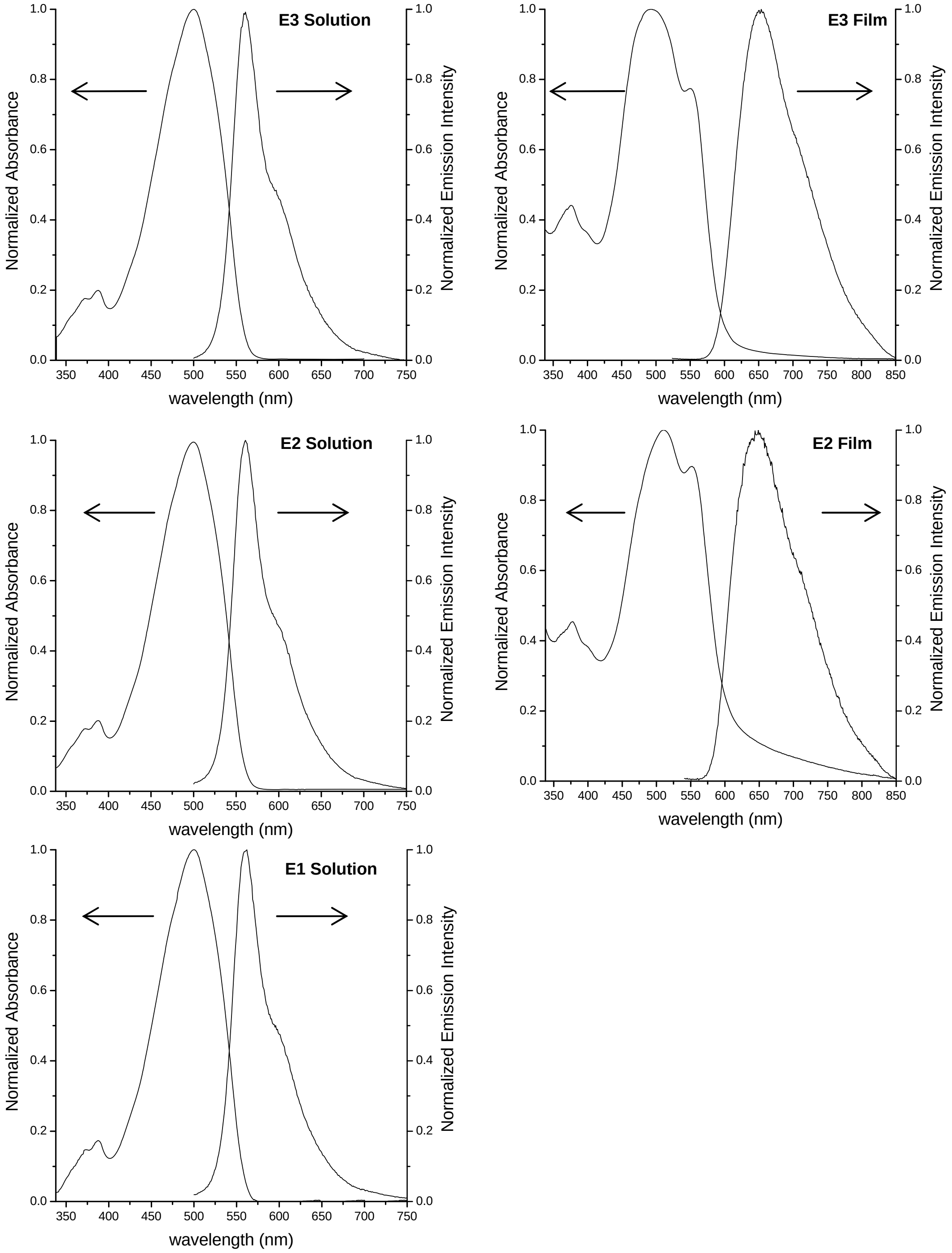

Figure S2: UV–Vis absorption and PL spectra of **E1-E3** in $CHCl_3$ solution and of **E2** and **E3** as thin film.

5. Cyclic voltammograms

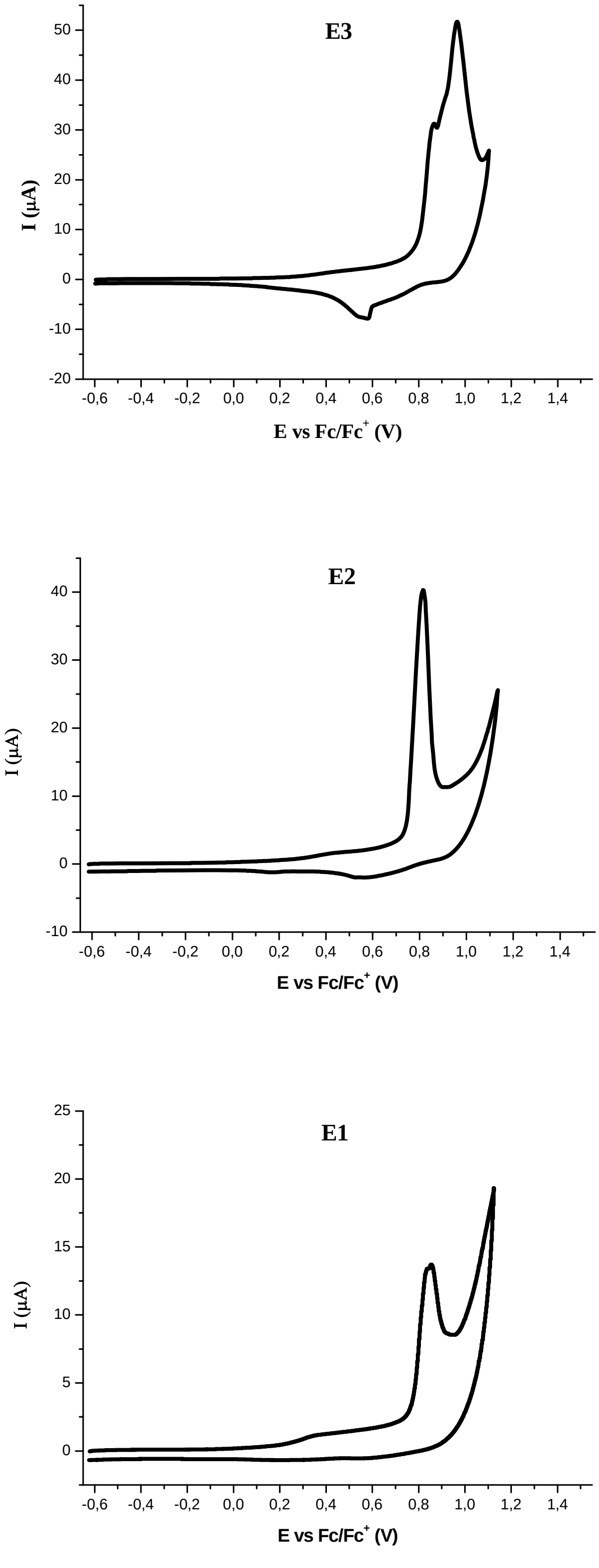

Figure S3: A representative cyclic voltammogram (anodic region, scan rate 100 mV s^{-1}) obtained for a film of **E1-E3**.

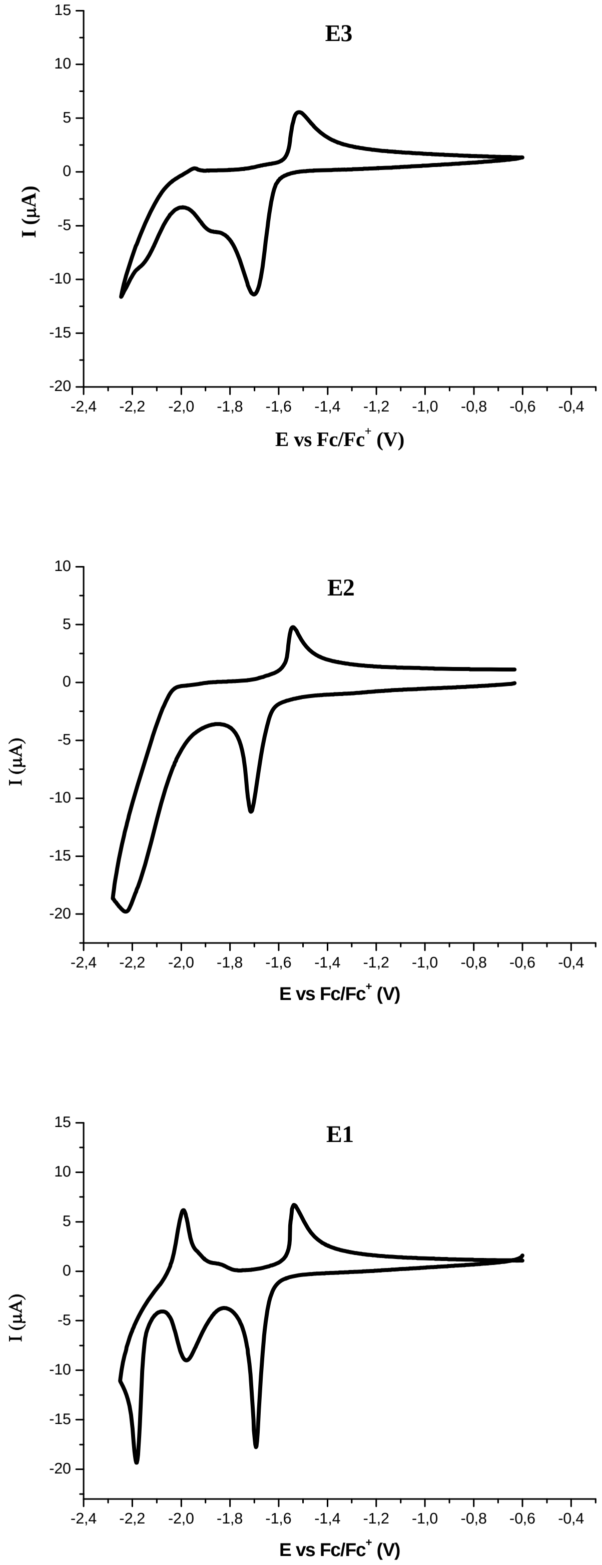

Figure S4: A representative cyclic voltammogram (cathodic region, scan rate 100 mV s^{-1}) obtained for a film of **E1-E3**.

6. Output characteristics for the not-annealed OFETs

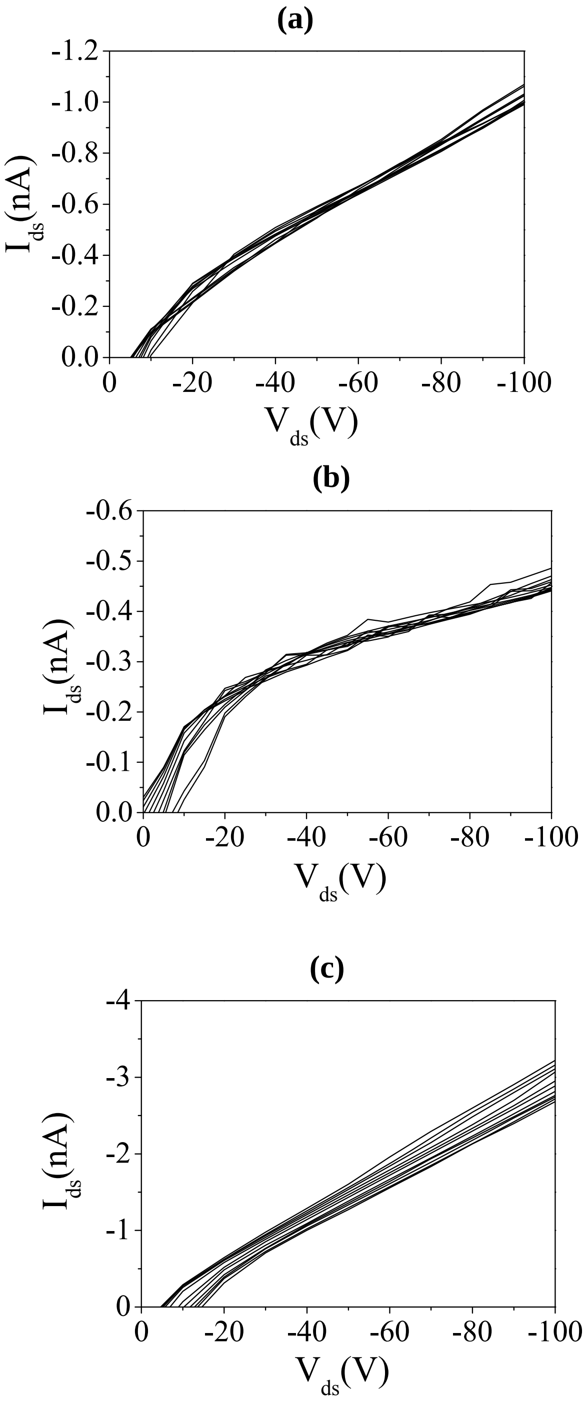

Figure S5 Output characteristics for the not-annealed top contact OFET with (a) **E1**, (b) **E2**, and (c) **E3** as active layers.

7. Output characteristics for an E2-based OFET

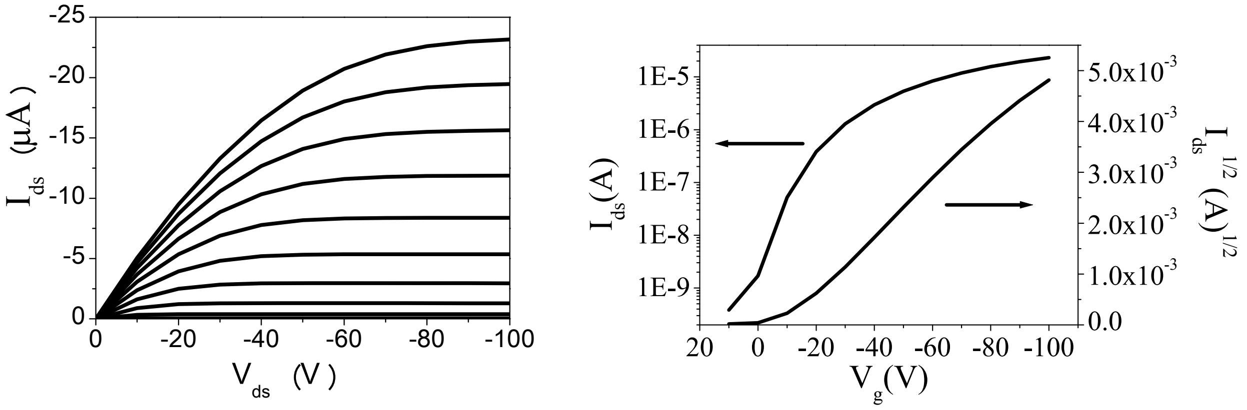

Figure S6. Output characteristics (left) and transfer characteristics at V_{ds} = -100 V (right) for the annealed top contact OFET embodying **E2** as active layer. The output characteristics were measured at gate voltages ranging from 0 V to –100 V in steps of –10 V. The resulting μ_{FET} was $3.1\cdot10^{-2}$ cm^{2}V^{-1}s^{-1}, with an on/off of 10^4 and a threshold value of –6.9 V.