9,10-Ter-anthrylene-ethynylene: a new molecular architecture for solution processed anthracene-based thin film transistors

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This study deals with the properties of a new molecular architecture for organic thin film transistors obtained by introducing 10-decylanthr-9-yl-ethynyl moieties at the anthracene 9,10 positions. The resulting structure, formally a ter-anthrylene-ethynylene (D3ANT), is stable and endowed with sufficient solubility to guarantee the formation of good quality films. The molecule was characterised by ¹H NMR, mass spectrometry, IR, UV-vis and photoluminescence both in solution and in the solid state. Cyclic voltammetry measurements, combined with solution UV-vis, permitted the evaluation of HOMO and LUMO energy levels. A series of D3ANT-based OTFT devices were built both in bottom and top contact configurations by a spin coating technique. Top contact OTFT devices exhibited the best semiconducting characteristics, showing an average mobility of 1.2×10^{-2} cm² V⁻¹ s⁻¹ with on-off ratios higher then 10^4 , while the highest mobility obtained was 0.055 cm² V⁻¹ s⁻¹. AFM thin-film characterization showed evidence of a granular structure. High-resolution STM images of D3ANT monolayers adsorbed on Au(111) and HOPG reveal highly-ordered self-organized domains with molecules lying flat on the substrates, but, remarkably, no reflections were recorded by out-of plane GIXRD of spin coated films on SiO₂.

Introduction

The huge research efforts directed towards the synthesis of organic semiconductor materials for applications in organic thin-film transistors (OTFTs),¹ have considerably widened the library of promising structures. The building blocks acknowledged as the most promising are without doubt thiophenes and acenes.² Among the latter, pentacene, particularly as high vacuum deposited thin films, shows hole field-effect mobilities as high as 3 cm² V⁻¹ s⁻¹ and on-off ratios higher then 10⁶.³ Recently, 6,13-functionalized soluble and stable pentacenes have been prepared,⁴ exhibiting hole mobilities as high as 0.17 cm² V⁻¹ s⁻¹ for solution deposited thin films.⁵ All this calls for a focussed synthetic effort aimed at investigating compounds holding a fused aromatic system, particularly as soluble systems. Lately, the oligomerization of anthracene, which has only recently been recognized as appealing for transistor applications,⁶ has been adopted as a strategy to extend the π -system beyond the single anthracene unit.7 The introduction of solubilising chains in the anthracene 9,10 positions allowed the

obtainment of oligo-2,6-(9,10-bisalkynylanthrylene)s exhibiting a hole mobility of $\sim 3 \times 10^{-3}$ cm² V⁻¹ s⁻¹ as solution deposited thin films.8 The oligomerization of anthracenes through the 9,10 positions would be an effective alternative as a higher delocalization can in principle be achieved, besides those linking positions are the most reactive ones. To the best of our knowledge no example has been provided so far of 9,10-linked anthracenes exhibiting field-effect modulation properties, as poly and oligo-9,10-anthrylenes⁹ show a high dihedral angle between the anthracene units, hampering the effective delocalization. A viable way of easing the steric hindrance between anthracene units, while mantaining conjugation between them in a potentially planar structure, is to link them through an ethynylene bond. This concept was exploited for the synthesis of ladderlike π -conjugated poly and oligo(anthrylene-ethynylenes)¹⁰

A decyl alkyl chain functionalised 9,10-ter-anthryleneethynylene, D3ANT, is the first example of a monodispersed architecture in which three neighbouring anthracenes are chemically linked by two ethynylene bonds. The end groups provide D3ANT with a solubility allowing its deposition by wet techniques. In this study, we report D3ANT synthesis, characterization and field effect properties, as well as its morphological structure, studied by AFM and STM.

Experimental

The reactants were purchased from Aldrich or Acros and used without further purification; 9,10-dibromoanthracene¹¹ 1 and [(trimethylsilyl)ethynyl]zinc¹² were synthesized according to literature procedures. All manipulations were carried out under

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inert nitrogen atmosphere using standard Schlenk techniques unless otherwise specified. All solvents used were carefully dried and freshly distilled. Chromatography was performed using Merck[®] Kieselgel 60 (230–400 mesh) silica gel or Macherey-Nagel polygoprep[®] 60–50 C18 reversed phase silica gel. ¹H NMR and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 400 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.

LC-MS analyses were performed by direct injection on an Agilent HPLC system equipped with DAD and MS systems (Agilent 1100 LC-MS SL series) using an atmospheric pressure chemical ionization interface (APCI). APCI conditions: positive ion mode, flow rate 0.5 mL min⁻¹, nitrogen as nebulising and drying gas, nebuliser pressure 60 psi, vaporizer temperature 350 °C, corona current 4.0 μ A, drying-gas flow 5 L min⁻¹, drying gas temperature 350 °C, capillary voltage 4000 V. Mass spectrometry data were acquired in the scan mode (mass range m/z = 200-3000).

Thermogravimetric analyses (TGA) were carried out under a nitrogen flow with a Perkin Elmer Pyris 6 thermobalance at a scanning rate of 10 °C min⁻¹; differential scanning calorimetry (DSC) analyses were carried out on a DSC-Q200 TA Instruments. Cyclic voltammetry measurements were carried out under inert nitrogen atmosphere with an Autolab potentiostat PGSTAT 10 using a three-electrode cell (glassy carbon as working electrode, Ag/Ag⁺ as reference electrode, and a platinum counter electrode). The scan rate was 200 mV s⁻¹ and the supporting electrolyte was an *n*-Bu₄NClO₄ (0.1 M) solution in CH₂Cl₂. Furthermore, HOMO and LUMO energy levels have been estimated from the onset of the first oxidation and reduction.¹³

Out-of-plane grazing angle X-ray data for thin films of D3ANT were performed on a Bruker D8 Discover GADDS with a 2D detector for fast acquisition to determine the crystallinity of films. Blank silicon substrates were used for comparison. Scanning tunnelling microscopy (STM) was performed at the *n*-tetradecanesubstrate interface at room temperature in the constant current mode using a Pico-LE scanning probe microscope (Molecular Imaging/Agilent Technology). STM tips were prepared from a Pt-Ir (80 : 20) wire by mechanical cutting. Highly oriented pyrolytic graphite (HOPG) substrates (Goodfellow) were freshly cleaved using adhesive tapes prior to deposition. Au(111) thin films (150 nm) were prepared by vacuum-deposition on cleaved mica (Goodfellow) and then annealed using a butane flame to achieve surface reconstruction. A small amount of D3ANT was dissolved in n-tetradecane (n-C14H30, Aldrich, 99.99%, $\sim 0.05 \text{ mg ml}^{-1}$) prior to droplet deposition onto the substrates.

The quantum-chemical calculations were applied to the isolated **D3ANT** molecule being in neutral configuration. The procedure of full geometry optimization and all electronic structure calculations were performed at the density functional theory (DFT) level with the hybrid B3LYP of three parameter Becke functional (B3)¹⁴ and the functional of Lee, Yang, and Parr

(LYP).¹⁵ The standard basis set 6-31G(d) was used in all calculations, which were performed by the Gaussian'03 program package¹⁶ with an energy convergences parameter of 10^{-4} eV. No correction was applied for the zero energy reference, thus resulting in a shift in absolute values, which was cancelled in the determination of the energy gap.

9-Bromo-10-decylanthracene 2

To a suspension of 9,10-dibromoanthracene 1 (6.00 g, 17.85 mmol) in dry di-n-butyl ether (250 ml), a 2.0 M phenyllithium solution in di-n-butyl ether (19.63 mmol) was added at ambient temperature. After 3h stirring, 1-bromodecane was added (7.90 g, 35.70 mmol) and the resulting solution was kept under stirring overnight. The reaction mixture was poured into a saturated NH₄Cl solution and then extracted several times with diethyl ether. The collected organic phases were dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was chromatographed on reversed phase (RP-18) silica using acetonitrile as eluent affording 2 as a pale yellow solid (4.26 g, 60 %): ¹H NMR (CDCl₃) $\delta = 8.60$ (d, J = 8.83 Hz, 2H), 8.29 (d, J = 8.53, 2H), 7.61–7.58 (m, 4H), 3.59 (t, J = 8.22 Hz, 2H), 1.85-1.77 (m, 2H), 1.62-1.55 (m, 2H),1.42–1.21 (m, 12H), 0.88 (t, J = 6.70 Hz, 3H); ¹³C NMR $(CDCl_3) \delta = 136.27, 130.37, 130.32, 128.65, 126.63, 125.59,$ 124.80, 121.56, 31.88, 31.41, 30.32, 29.61, 29.32, 28.38, 22.67, 14.11; v_{max} (KBr pellet)/cm⁻¹ 3076, 3039, 2914, 2848, 1510, 1457, 1368, 1327, 1255, 1096, 1023, 893, 795, 745, 646, 575; m/z $(EI, 70 \text{ eV}) 396 (M^+), 269 (M^+ - C_9H_{19}), 189 (M^+ - C_9H_{19} - Br).$

[(10-Decylanthracen-9-yl)ethynyl]trimethylsilane 3

To a three-necked round bottomed flask was added 1.590 g (4.00 mmol) of 9-bromo-10-decylanthracene 2, 231 mg (0.2 mmol) of Pd(PPh₃)₄, 30 mL of toluene and a solution of 4.4 mmol of [(trimethylsilyl)ethynyl]zinc chloride in THF. The mixture was kept under stirring overnight at 80 °C. The reaction mixture was then poured into 100 mL of 1N HCl and repeatedly extracted with diethyl ether. The solvent was removed in vacuo and the residue was chromatographed on silica gel using petroleum ether (40-60 °C) as eluent to yield 1.327 g (80%) of **3** as a reddish oil: ¹H NMR (CDCl₃) $\delta = 8.63$ (d, J = 8.33 Hz, 2H), 8.28 (d, J = 8.33 Hz, 2H), 7.60–7.52 (m, 4H), 3.60 (t, J = 8.2 Hz, 2H), 1.84–1.76 (m, 2H), 1.61–1.35 (m, 2H), 1.44–1.20 (m, 12H), 0.89 (t, J = 6.8 Hz, 3H), 0.43 (s, 9H); ¹³C NMR $(CDCl_3) \delta = 137.61, 132.81, 129.11, 127.75, 126.20, 125.65,$ 124.88, 105.81, 102.14, 31.97, 31.55, 30.40, 29.72, 29.70, 29.64, 29.41, 28.43, 22.76, 14.21, 0.38; ν_{max} (neat)/cm⁻¹ 3084, 3064, 2964, 2923, 2853, 2135, 1945, 1816, 1705, 1621, 1561, 1522, 1467, 1440, 1410, 1378, 1249, 1153, 1077, 1040, 858, 797; m/z (EI, 70 eV) 414 (M⁺), 287 (M⁺ - C_9H_{19}).

9-Decyl-10-ethynylanthracene 4

1 mL of a 1.0 M solution of anhydrous tetrabutylammonium fluoride in THF was added to a solution of **3** (414.7 mg, 1 mmol, in 5 mL THF) kept in a two-necked flask protected from light by an aluminium foil. The reaction mixture was stirred at 0 $^{\circ}$ C for 20 min. The mixture was then poured into water and extracted with diethyl ether. The collected organic phases were dried over anhydrous Na₂SO₄ and the solvent was removed *in vacuo*. The crude was eventually chromatographed on silica gel using petroleum ether (40–60 °C) as eluent to afford 332 mg (97%) of **4** as a brown solid: ¹H NMR (CDCl₃) δ = 8.65 (d, *J* = 8.04 Hz, 2H), 8.29 (d, *J* = 8.77 Hz, 2H), 7.60–7.52 (m, 4H), 3.97 (s, 1H), 3.61 (t, *J* = 8.2 Hz, 2H), 1.84–1.76 (m, 2H), 1.62–1.55 (m, 2H), 1.46–1.21 (m, 12H), 0.89 (m, 3H); ¹³C NMR (CDCl₃) δ = 137.99, 133.07, 129.09, 127.53, 126.33, 125.70, 124.93, 87.99, 31.96, 31.55, 30.42, 29.72, 29.69, 29.63, 29.40, 28.45, 22.75, 14.20; ν_{max} (KBr pellet)/cm⁻¹ 3285, 3273, 3084, 3062, 2951, 2920, 2851, 1620, 1497, 1469, 1377, 1261, 1100, 1020, 843, 792.

9,10-Bis[(10-decylanthracen-9-yl)ethynyl]anthracene D3ANT

To a three-necked flask was added 4 (308 mg, 0.9 mmol), 9,10dibromoanthracene 1 (151.2 mg 0.45 mmol), CuI (4.3 mg, 2.25 \times 10⁻² mmol), toluene (15 mL), triethylamine (6 mL), and

 Table 1
 Electrical properties of OFET based on the ter(anthryleneethynylene)
 D3ANT

Device no.	W/L	$V_{\rm t}/{ m V}$	Mobility/cm ² V ^{-1} s ^{-1}	$I_{\rm on}/I_{\rm off}$
1 ^{<i>a</i>}	1085/5	-7.3	1.4×10^{-3}	4×10^3
2^a	1085/5	-10	1.2×10^{-3}	3×10^{3}
3 ^{<i>a</i>}	1070/2	-8.1	$1.0 imes 10^{-3}$	7×10^{4}
4 ^{<i>a</i>}	980/20	-7.6	1.6×10^{-3}	2×10^4
5^a	980/20	-8.3	1.1×10^{-3}	2×10^4
			$1.3 \pm 0.2 \times 10^{-3d}$	
6 ^{<i>ab</i>}	126880/5	-13	2.5×10^{-3}	5×10^{5}
7^{ab}	117640/10	-13	2.3×10^{-3}	6×10^{4}
8 ^{<i>ab</i>}	77600/50	-11	2.0×10^{-3}	6×10^{4}
9^{ab}	56040/100	-11	3.0×10^{-3}	2×10^4
10^{ab}	56040/100	-10	2.8×10^{-3}	6×10^4
			$2.5 \pm 0.4 \times 10^{-3d}$	
11^{bc}	1000/100	-10	1.2×10^{-2}	4×10^{5}
12^{bc}	500/150	-9.6	1.6×10^{-2}	1×10^{3}
13 ^{bc}	2000/200	-11	1.0×10^{-2}	2×10^{3}
14^{bc}	4000/200	-10	1.0×10^{-2}	5×10^{3}
15^{bc}	2000/200	-9.0	1.0×10^{-2}	1×10^{3}
			$1.2 \pm 0.3 \times 10^{-2d}$	

^a "Bottom contact" device. ^b Annealed at 100 °C for 30 min. ^c "Top contact" device. ^d Average values and standard deviations of mobilities.

Pd(PPh₃)₄ (26 mg, 2.25×10^{-2} mmol) and the mixture was stirred at reflux for 1 day. The reaction mixture was then poured in water and repeatedly extracted with chloroform. The organic phases were concentrated *in vacuo* and the crude was purified by flash chromatography on silica gel using chloroform as eluent yielding 232 mg (60%) of **D3ANT** as a violet solid: ¹H NMR (C₇D₈, 80 °C) δ = 9.19 (d, *J* = 8.48 Hz, 4H), 9.13–9.11 (m, 4H), 8.29 (d, *J* = 8.78, 4H), 7.50–7.45 (m, 8H), 7.41–7.37 (m, 4H), 3.59–3.56 (m, 4H), 1.90–1.83 (m, 4H), 1.58–1.51 (m, 4H), 1.43–1.24 (m, 24H), 0.90 (bt, *J* = 6.72 Hz, 6H); ν_{max} (KBr pellet)/cm⁻¹ 3079, 3038, 2948, 2919, 2848, 1619, 1525, 1463, 1438, 1326, 1401, 1256, 1028, 926, 798, 757, 721, 672, 650; *m*/*z* (APCI) 859.5 ([M + H]⁺ requires 859.52).

Organic thin-film transistor (OTFT) devices were fabricated in "bottom" and "top" contact configurations. Top contact devices were fabricated using a highly n-doped silicon wafer (resistivity: 20 Ohm cm) as the gate electrode on which 100 nm of dielectric (SiO₂) were thermally grown. All the Si/SiO₂ substrates were cleaned as follows: the wafers were first immersed in a piranha solution for 8 min in order to remove traces of adsorbed organic materials, rinsed with deionised water and eventually dried with a nitrogen flow. They were then washed according to the SC1 and SC2 cleaning procedures. Films of D3ANT were deposited by spin coating-from 0.05 wt% solutions in anhydrous CHCl₃ at 2000 rpm for 30 s. Drain and source electrodes were fabricated on the organic semiconducting layer by thermal evaporation through a shadow mask at various channel width and length (Table 1). Some of the films were subjected to an annealing procedure consisting of a treatment at 100 °C for 30 min under a nitrogen atmosphere. The devices were measured with an Agilent 4155 C semiconductor parameter analyzer kept in a glove box at room temperature. The mobilities in saturation regimes were extracted using the equation:

$$I_{\rm ds} = C_{\rm i} \mu (W/2L) (V_{\rm g} - V_{\rm t})^2$$
 at $V_{\rm ds} > V_{\rm g}$

where I_{ds} is the drain-source current, C_i is the capacitance per unit area of the gate dielectric layer, V_g is the gate voltage and V_t is the threshold voltage. V_t was extrapolated from the $(I_{ds})^{1/2}$ vs. V_g plot. Fig. 1 shows the current–voltage characteristics $(I_{ds} vs. V_{ds})$ for top contact devices (W/L = 500/150) (µm/µm)



Fig. 1 FET characteristics (top contact device): substrate deposited by spin coating from a 0.05 wt% solution. Output characteristics (left) and transfer characteristics (right) at $V_{ds} = -30$ V.



Scheme 1 Synthesis of D3ANT.

with **D3ANT** film spin coated from 0.05 wt% chloroform solution and annealed as previously described. Fig. 1 also shows $I_{\rm ds}$ and $I_{\rm ds}^{1/2}$ vs. $V_{\rm g}$ plots at $V_{\rm ds} = -30$ V.

Results and discussion

The synthetic approach followed to obtain 9,10-bis[(10-decylanthracen-9-yl)ethynyl]anthracene **D3ANT** is shown in Scheme 1. 9,10-Dibromoanthracene **1** was mono-metallated with phenyllithium and subsequently reacted with decyl bromide to afford 9-bromo-10-decylanthracene **2**. The use of BuLi as the metallating agent was avoided due to the formation of butyl bromide as byproduct. A Negishi coupling of **2** with [(trimethylsilyl)ethynyl]zinc chloride yielded the trimethylsilyl-ethynyl derivative **3**. Deprotection of **3** with tetrabutylammonium fluoride gave 9-ethynyl-10-decylanthracene **4**, which was subsequently reacted with **1** in a Sonogashira coupling for the obtainment of **D3ANT**.

Product **D3ANT** was obtained in good yield (60%) as a purplered powder slightly soluble (1.0 mg ml⁻¹) at room temperature in CHCl₃. The proposed structure is fully supported by its molecular mass (APCI-MS), as well as by the ¹H-NMR spectrum recorded in toluene at 80 °C. The thermal properties of **D3ANT** were evaluated by means of thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC). A good thermal stability was revealed, the decomposition temperature being 375.9 °C at 5% weight loss. For DSC, the sample was subjected to a heating scan to 300 °C, a cooling scan and a re-heating scan, all carried out at 10 °C min⁻¹ under inert atmosphere. The only recorded thermal event in both heating scans was the **D3ANT** fusion at 247.1 °C with the same fusion enthalpy. No thermal event ascribable to decomposition could be identified in the explored temperature range.

The UV–vis spectrum of **D3ANT** recorded in CHCl₃ (Fig. 2) showed a structureless absorption band with a maximum at 504 nm. In the solid state, the spectrum exhibited two bands with maxima at 535 nm and 603 nm, the latter one due to intermolecular interactions. The fluorescence spectrum of **D3ANT** in



Fig. 2 Top: absorption spectra of D3ANT in CHCl₃ (7.5×10^{-6} M) and in the solid state (drop casting from 0.05 wt% chloroform solution). Bottom: emission spectra of D3ANT in CHCl₃ ($\sim 10^{-6}$ M, $\lambda_{ex} = 504$ nm) and in the solid state (drop casting from 0.05 wt% chloroform solution, $\lambda_{ex} = 532$ nm).

CHCl₃ ($\lambda_{ex} = 504$ nm) showed a band at 568 nm. In the solid state, by exciting the sample at 532 or 603 nm, a red-shifted emission band at 677 nm was recorded owing to the above mentioned aggregate formation.

The electrochemical behavior of **D3ANT** was studied in CH_2Cl_2 using Ag/Ag⁺ as the reference electrode (calibrated with respect to the Fc/Fc⁺ couple). The cyclic voltammogram showed two quasi-reversible oxidation peaks at 1.05 V and 1.20 V and an irreversible oxidation peak at 1.49 V. This behavior is likely due to the sequential abstraction of three electrons from the three anthracene moieties. Two irreversible reduction peaks at -1.26 V and -1.53 V were also observed. The HOMO and LUMO energy levels, estimated from the onset of the first oxidation and reduction, are -5.23 eV and -3.15 eV respectively, resulting in an energy gap of 2.1 eV, in reasonable agreement with the optical gap in CHCl₃ (2.2 eV) and the HOMO–LUMO gap calculated at the DFT/B3LYP/6-31G(d) level (2.3 eV).

OTFT devices were fabricated both in bottom and top contact configurations. A thin film of **D3ANT** (10 nm) was deposited onto the SiO₂ (100nm)/n-doped Si substrate by spin coating from a 0.05 wt% chloroform solution. Gold was evaporated as the source–drain contact material. The results obtained on 15 representative devices are reported in Table 1. An average mobility of 1.3×10^{-3} cm² V⁻¹ s⁻¹ with on–off ratios of most



Fig. 3 AFM micrograph of D3ANT as deposited on Si/SiO₂. $1 \times 1 \mu m^2$.

devices higher than 10⁴ were reached with a "bottom" contact geometry. These figures were improved by annealing the substrate film for 30 min at 100 °C resulting in an average mobility of 2.5×10^{-3} cm² V⁻¹ s⁻¹. A consistent mobility improvement was achieved in a "top" contact geometry comprising a spin coated and subsequently annealed film of **D3ANT**. The average mobility reached the value of 1.2×10^{-2} cm² V⁻¹ s⁻¹, although a highest mobility of 0.055 cm² V⁻¹ s⁻¹ was achieved in few cases. Data reported in Fig. 1 are relevant to one of these devices.

An investigation of the **D3ANT** film surface morphology was carried out by means of atomic force microscopy (AFM). The micrograph, reported in figure 3, shows a good substrate coverage despite the moderate solubility. A granular morphology is observed and the grain width of about 0.04 μ m is clearly evident.

Preliminary structural characterization of D3ANT films deposited on Si/SiO₂ and Au(111) substrates was carried out by means of out-of-plane grazing incidence X-ray diffraction (GIXRD). A thin film was deposited by spin coating from CHCl₃ solution on both substrates and analysed. In both cases, the diffractograms are featureless, thus indicating the absence of long range structural order in the bulk active layer and in the out-of-plane direction. Similarly to D3ANT, thin films of molecules of the same family, *i.e.* possessing two (trimethoxyphenyl) ethynyl substituents at the 9,10-positions of anthracene, are also inherently disordered although they do not show any field-effect modulation.¹⁷ It is reasonable to suppose that the introduction of two 10-decylanthr-9-yl-ethynyl groups at the 9,10-positions of anthracene extends the π -interactions allowing for improved charge mobility independently of the structural arrangement of the D3ANT systems in the active layer. However, GIXRD data provide structural information on the bulk organization of D3ANT films but cannot access the molecular arrangement of the first monolayer in direct contact with the α -SiO₂ surface where the channel of the field-effect transistor presumably forms.

In order to shed more light on the two-dimensional selforganization of **D3ANT**, we investigated monolayers on highly organized pyrolitic graphite (HOPG) and Au(111) by scanning tunnelling microscopy (STM) in a liquid environment of *n*-tetradecane.¹⁸ The STM study allows disclosing of the highly ordered



a

b

Fig. 4 Typical constant current STM images of self-organized monolayers of **D3ANT** adsorbed (a) at the *n*-tetradecane–HOPG interface (16 × 16 nm²; $V_t = -333$ mV; $I_t = 27$ pA) and (b) at the *n*-tetradecane–Au(111) interface (16 × 16 nm²; $V_t = 62$ mV, $I_t = 83$ pA).

2D organization of the monolayers when adsorbed on conducting and atomically flat substrates When adsorbed on HOPG, monolayers of D3ANT self-organize into highly-ordered monodomains extending over distances of 100-400 nm. Each domain consists of a closed-packed arrangement of linear and parallel rows of molecules (Fig. 4a). Adjacent rows are separated by a distance of ~ 1.3 nm (in dark contrast) corresponding to the decyl chains in a slightly tilted position. The bright contrast areas correspond to the π -conjugated cores of **D3ANT** with a length of ~ 2.0 nm, in good agreement with the calculated core length (1.9 nm) and the profile of frontier wave functions which is mainly defined by three anthracene sub-units. The 2D unit cell parameters as measured by STM are a = 3.1 nm; b = 1.2 nm; $\alpha = 94^{\circ}$. Finally, the three anthracene sub-units of each individual molecule are clearly visible on the high-resolution STM image thus reflecting a nearly planar adsorption of the entire molecule on HOPG, that is with no twist angle and full conjugation between the anthracene sub-units.

When adsorbed on reconstructed Au(111) (Fig. 4b), **D3ANT** also forms self-organized domains whose 2D structure in linear and parallel rows resembles that on HOPG. However, these domains do not extend over distances as large as on HOPG.

Another noticeable difference between both substrates is that the distance between adjacent **D3ANT** rows on Au(111) (\sim 0.3 nm) is markedly smaller than that on HOPG and therefore cannot accommodate decyl chains which are probably folded below or above the anthracene sub-units. This results in a more densely packed 2D structure on Au(111) as compared to HOPG. Again, the individual anthracene sub-units of each molecule are clearly visible.

Conclusions

We conceived and synthesised a new solution-processable ter(anthrylene-ethynylene) based architecture exhibiting a fieldeffect mobility as high as 0.055 cm² V⁻¹ s⁻¹. This result is the best one obtained so far for solution-processed anthracene based OTFTs. The ter-anthrylene-ethynylene molecules self-organize into well-ordered monolayers both on the HOPG and Au(111) surfaces when deposited at the interface with an *n*-tetradecane solution. However, GIXRD carried out on **D3ANT** films spincoated onto Si/SiO₂ and Au(111) seem to indicate a disordered nature of the thin film. Work is in progress to further investigate the organic semiconductor–dielectric interface properties and optimize the device performances by tuning of the molecular structure.

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