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

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OFETs based on new solution-processed ester functionalized 9,10ter-anthrylene-ethynylenes show a mobility increase of four orders of magnitude, leading to mobilities as high as 4.9×10^{-2} cm² V⁻¹ s⁻¹ if the deposited film is annealed before contact deposition. The behavior is ascribed to an increase in film order at the dielectric/ semiconductor interface as revealed by X-ray studies.

Focused efforts are still required for deepening our knowledge on the structure-property relations in materials for organic field-effect transistors (OFETs)¹ and especially for solution processable semiconductors, which are particularly interesting in this respect.² Such studies can be beneficial also for very promising applications employing OFETs as biological and environmental sensors, (chemor bio-OFETs).3 In this framework, the presence of ad hoc chosen polar functional groups covalently bound to the semiconductor structure might allow for an improved degree of selectivity towards chemically homologous species.⁴ Moreover, the functionalization of an organic semiconductor with polar groups can increase its solubility and processability.5 Concerning acene-based organic semiconductors,6,7 much interest has been focused on molecular materials based on anthracene due to its high single-crystal mobility.8 Among the strategies aimed at extending the anthracene π -system,⁷ conjugation extension through the 9,10-positions has recently emerged.9 In this framework we have described the synthesis and properties of the ter-anthrylene-ethynylene chromophore, constituted by a monodispersed architecture in which three neighbouring anthracenes are linked by two ethynylene groups. The 9,10-bis[(10decylanthracen-9-yl)ethynyl]anthracene showed an average fieldeffect mobility (μ_{FET}) of 1.2 \times 10⁻² cm² V⁻¹ s⁻¹ with on/off ratios higher than 10^4 , and was also used in chem-OFETs for NO_x detection.^{10,11} Subsequently, we have investigated other alkyl functionalized ter-anthrylene-ethynylenes confirming the good semiconducting performances of the chromophore.¹²

Aiming at further exploring the semiconducting potentials of our molecular architecture and at obtaining polar materials for potential applications in chem-OFET, we embarked on the preparation of teranthrylene-ethynylenes functionalised in their terminal position with ester groups bearing ethyl (E1), *n*-butyl (E2), and *n*-octyl (E3) chains (Fig. 1). These materials show a dramatic improvement in their OFET performances upon a straightforward thermal annealing process, a behavior that we deemed worthwhile to further investigate.

The desired target molecules **E1–E3** are red powders and were obtained in 67%, 55%, and 57% yield, respectively, by optimizing our synthetic approach,^{10,12} described in Scheme S1 (ESI[†]). The oligomer **E1** was markedly less soluble with respect to **E2** and **E3** in common organic solvents. The structure and purity of **E1–E3** were fully confirmed by ¹H, ¹³C-APT NMR, FT-IR spectroscopy, HRMS spectrometry, as well as elemental analysis (ESI[†]). A very high thermal stability was revealed by the TGA analysis of **E1–E3** that indicates (Fig. S1[†]) 5% weight loss temperatures higher than 360 °C.

The spectroscopic properties of **E1–E3** were investigated by UV-Vis and photoluminescence spectroscopy (Fig. S2 and Table S1[†]) both in chloroform solution and in the solid state. In solution, the absorption and emission spectra of the three compounds are almost superimposable and show a structureless absorption band with a maximum at 500 nm, ascribed to the π – π * transition of the



Fig. 1 Structure of the ester functionalised ter-anthrylene-ethynylenes E1, E2 and E3.

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conjugated backbone. The emission spectra in solution show a λ_{em} of 561 nm along with a shoulder at longer wavelengths. The Stokes shift of E1-E3 is of 61 nm, comparable to that observed for the alkyl functionalised ter-anthrylene-ethynylenes.^{10,12} The solid state optical properties of E1 could not be recorded due to the low quality of the obtained film. The solid state UV-Vis spectra of E2 and E3 show that the main absorption peak at 512 nm (E2) and 492 nm (E3) is accompanied by a shoulder at \sim 550 nm. The solid state photoluminescence spectra are characterised by a broad emission at $\lambda_{em} =$ 650 nm for E2 and at 653 nm for E3. These optical features are symptomatic of strong intermolecular interactions between the chromophores in the film. The very similar optical behavior observed for the three molecules suggests analogous electronic structures for E1-E3. This was further confirmed by the electrochemical investigations carried out by cyclic voltammetry. In the oxidation scans, the voltammograms of thin films of E1-E3 (Fig. S3[†]) are characterized by the presence of an irreversible event; after calibration with Fc/ Fc⁺,¹³ the HOMO levels were derived by the onset of oxidation as -5.6 eV for all three compounds.¹⁴ This value warrants a good environmental stability of the structures. On the other hand the onset of the reduction scans (Fig. S4[†]) allowed the estimate of the LUMO of E1–E3 as -3.2 eV, leading to an electrochemical gap of $\sim 2.4 \text{ eV}$, slightly higher than the optical band gap value (2.1 eV) extracted from the absorption band edge (Table S1[†]).

Next, **E1–E3** were used as active layers in OFET devices fabricated in top-contact bottom-gate configuration. The active layer was a thin film of **E1–E3** deposited onto a SiO₂(300 nm)/n-doped Si substrate by spin coating from a 0.05/0.1% w/w chloroform solution. The study of the device features revealed a very intriguing behavior of these materials.

Two sets of devices were tested: in the first, the gold ohmic contacts were deposited onto the semiconductor film after the spin coating steps, without any thermal pretreatment. For the second set of devices, a thermal treatment at 100 °C for 30 min in vacuum preceded the gold contact evaporation. This treatment is usually employed to eliminate traces of volatile impurities and induce an increase of the grain dimension in the active layer. In some instances, it leads to an increase in the structural order of the organic films, eventually improving electronic performances. Usually, the thermal annealing treatment is carried out on materials already showing quite good OFET performances and it leads, in the best cases, to non-dramatic improvements of their field-effect mobility and on/off ratios.¹⁵

In our case, the current-voltage characteristics of the **E1–E3** based OFET that were not subjected to any thermal treatment were all of extremely poor quality, and did not show any appreciable current modulation (Fig. S5†). On the other hand, while the device based on **E1** showed a very low μ_{FET} ($\sim 10^{-6}$ cm² V⁻¹ s⁻¹) even after the annealing, a completely different behavior was observed for the devices bearing the thermally annealed films of **E2** (Fig. S6†) and **E3** (Fig. 2), which showed well-shaped transistor characteristics exhibiting clear linear and saturation regions along with a dramatic increase of mobility ($\mu_{\text{FET}} \approx 10^{-2}$ cm² V⁻¹ s⁻¹, Table 1) extracted following standard data treatment.¹⁶

Similar to what was observed for alkyl functionalised ter-anthrylene-ethynylenes,¹² a marked effect of the alkyl chain length was also observed on the OFET figures of merit. For **E2**, bearing *n*-butyl chains, an average μ_{FET} of $2.8 \pm 0.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an on/ off ratio of 10⁴ was obtained. The devices exhibited very low threshold voltages (V_{th}) between -5 V and -8 V. Better mobilities were obtained for the octyl functionalised E3: the average μ_{FET} was $4.4 \pm 0.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with on/off ratios of $\sim 10^4$ and V_{th} between -2 V and -10 V. The best μ_{FET} was $4.9 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

To the best of our knowledge, this is the first time that such a dramatic performance improvement is seen on OFET upon annealing.¹⁵ This remarkable behavior prompted us to study the structural features of the semiconducting thin films before and after annealing by complementing X-ray specular reflectivity (XSR) and X-ray diffraction (XRD) techniques. To this purpose, thin-films of **E1–E3** were deposited on SiO₂/Si substrates using the conditions previously described for OFET device fabrication.

In Fig. 3 the XSR experimental patterns, together with the corresponding simulations for thin **E1–E3** films both not-annealed (A) and annealed at 100 °C (B) for 30 min in vacuum, as a function of the incidence angle θ are reported.

XSR is a widely used technique to probe the variation of the electron density in thin films in the direction perpendicular to substrate plane.¹⁷ Interference fringes in reflectivity curves arise from beam reflection at the top and at the bottom film interfaces (Kiessig fringes) as well as at any inner interface (parallel to substrate plane) between regions with different electron density. The d-spacing between interfaces defining a periodically repeated structure in the film thickness can be calculated as $d = 1/\Delta Q$, where $Q = 2\sin \theta/\lambda$ is the length of the scattering vector, λ is the X-ray wavelength, and ΔQ is the distance between the O values of two consecutive maxima in the reflectivity curve, for a given modulation frequency. If molecules are oriented and ordered along a given direction, they can form alternating high and low electron density layers (bi-layers) giving rise to interference fringes that can be detected by XSR. The higher the interface sharpness, the electron density difference at interfaces, and sample in-plane homogeneity, the larger the amplitude of reflectivity fringes. From the first inspection of XSR curves in Fig. 3A and B, the presence of flatter interfaces and/or higher lateral homogeneity in the E2-E3 films, with respect to the E1 ones can be deduced. Moreover, the reflectivity curves of the annealed E2-E3 films show two distinct frequency modulations, associated to the film thickness and to bilayers stacked throughout the film, respectively. The two frequency modulations are also evident in the not-annealed E3 film, while they can barely be recognized in the analogous E2 sample, suggesting a higher degree of molecular ordering in the as-deposited E3 film with respect to the E2 one. The two modulation frequencies become markedly visible for E2 after the annealing. Also for E3 the annealing leads to more pronounced reflectivity fringes, indicating an improvement in the degree of molecular layers ordering.

In contrast, in the case of the **E1** samples the annealing process is not sufficient to induce a significant improvement of molecular ordering. The XSR scan of the not-annealed **E1** film shows a single modulation frequency, corresponding to a bi-layer thickness of 2.9 nm. Based on the simulation of the reflectivity curve, only one bilayer can be recognized close to the SiO₂ surface. The annealed **E1** sample shows similar features, with even less visible fringes, which indicates lower film homogeneity and/or molecular ordering after the annealing.

Table 2 reports the values of the overall layer thickness, the mean values of bi-layer thicknesses obtained from simulations of the XSR curves, and the derived number of stacked bi-layers for E1–E3 films.

From these values, it is apparent that all samples are characterized by a similar thickness of the overall film and of the bi-layers. In the E3 thin films the number of stacked bi-layers is the highest, both before



Fig. 2 Output characteristics (left) and transfer characteristics (right) at $V_{ds} = -100$ V for the annealed top contact OFET embodying E3 as active layer, resulting in a μ_{FET} of 4.9 × 10⁻² cm² V⁻¹ s⁻¹, an on/off of 10⁴ and a threshold value of -7.6 V.

Table 1 Figures of merit for the OFET based on E1-E3 (active layer annealed at 100 °C for 30 min under vacuum)

Molecule	$\mu_{\rm FET}$ /cm ² V ⁻¹ s ^{-1a}	$I_{\rm on}/I_{\rm off}$	V _{th} /V (min/max)
E1	${\sim}10^{-6}\ 2.8\pm0.3 imes10^{-2}\ 4.4\pm0.1 imes10^{-2}$	10^{2}	-10
E2		10^{4}	-5/-8
E3		10^{4}	-2/-10

^a Statistics carried out on 5 individual devices.



Fig. 3 XSR (experimental and simulated) for not-annealed (A) and annealed (B) E1–E3 films. The low frequency modulation fringes are clearly visible and marked by square symbols for the E3 films.

Table 2Multilayer structure of pristine and annealed thin films of E1-E3 on SiO2, derived by simulation of the XSR curves

Sample	Film thickness/nm	Average bi-layer thickness/nm	Number of stacked bi-layers
E1	11.8	2.9	1
$\mathbf{E1}^{a}$	10.6		1
E2	8.1	2.9	2
$\mathbf{E2}^{a}$	9.2	3.1	3
E3	9.9	3.3	3
$\mathbf{E3}^{a}$	10.4	3.4	3

^a After annealing at 100 °C for 30 min under vacuum.

and after the annealing; moreover, the bi-layers are repeated throughout the whole film thickness, indicating that the E3 films are endowed with the highest degree of order in the lamellar stacking. On the other hand, an improvement in the degree of order is observed in the annealed E2 sample with respect to the not-annealed E2 one, as testified by the increase in the number of stacked bi-layers. In contrast, no significant changes are detected for E1, for which a single ordered bi-layer is evaluated at most.

In order to gain insight into the nature of the low frequency fringes observed in reflectivity curves we performed XRD experiments on much thicker **E2–E3** spin coated films obtained from 0.2/0.4% w/w solutions.

Fig. 4 shows the XRD and XSR patterns as a function of the scattering angle 2θ , for the thicker **E3** and **E2** films. XSR curves of the corresponding thin films are also reported for comparison.

Inspection of the XSR part of Fig. 4A reveals that thicker films show fewer reflectivity features, however the low frequency fringes, associated with the bi-layer thickness, are still observable (and high-lighted by square symbols) for the **E3** sample. On the other hand equally spaced diffraction peaks are observed in the XRD patterns of all thicker samples, regardless of the thermal treatment, which indicates a lamellar ordering of molecules in the film bulk. The peaks related to the stacking periodicity (*d*-spacing) of the lamellae are indicated in Fig. 4 by dotted or continuous line bars, together with the calculated *d*-spacing $d = 1/\Delta Q$, where ΔQ is the difference in scattering vector length between two consecutive diffraction peaks.¹⁷

In Fig. 4A dotted line bars are relevant to the main stacking period in the **E3** film, which is 3.0 nm; a slightly smaller periodicity (2.9 nm) can also be recognized and marked by continuous line bars.





Fig. 4 XSR (log scale) experimental curves for thin and thick **E3** (A) and **E2** (B) films, and XRD (linear scale) experimental curves for **E3** (A) and **E2** (B) films before and after annealing.

Concerning E2 (Fig. 4B), the stacking period derived from the XRD data is 2.5 nm. The average bi-layer thicknesses estimated from the simulation of XSR curves are therefore consistent with the d-spacings derived from XRD analyses. Interestingly, similar trends in stacking periodicity of the E2-E3 samples are observed for the d-spacings derived by XSR and XRD analysis, which are in agreement with the difference in molecular length of E2 with respect to E3. Moreover, the simultaneous presence of both sharp diffraction peaks and reflectivity fringes in the XSR curve of the not-annealed E3 thick sample (hardly visible in the analogous E2 sample) suggests that thick crystalline domains are present in the E3 film bulk, while a thin laterally homogeneous bi-layered structure is formed close to the interface with SiO2. The thickness of such a bi-layered structure seems to be only slightly affected by the thickness of the deposited film, as shown by the barely visible fringes in the reflectivity curves of the thicker films.

The fact that this interface thin layer becomes more ordered after thermal annealing in the case of the **E3** and **E2** samples, as testified by the more intense observed reflectivity fringes (Fig. 3B), can be taken as the direct cause of the dramatic mobility enhancement recorded for OFET devices and provides further evidence of the fact that in OFET two dimensional transport occurs at the interface between the organic layer and the gate dielectric.¹⁸ In conclusion, we have reported on the intriguing OFET behavior of new solution processable 9,10-ter-anthrylene-ethynylenes functionalised with carboethoxy (E1), carbobutoxy (E2), and carboctoxy (E3) groups. The new compounds were investigated as organic semiconductors in solution processed OFET devices, which showed an intriguing activation by thermal annealing. In fact, very low fieldeffect mobility was recorded for the as-spun films, while a very good modulation and a 4 orders of magnitude higher field-effect mobility crops up for E2 and E3-based devices after a mild annealing of the active layer. The devices based on E3 showed the best figures of merit (average μ_{FET} : 4.4×10^{-2} cm² V⁻¹ s⁻¹ and on/off ratios of 10⁴). The observed behavior was attributed to an increase in molecular order at the interface between the annealed films and the gate dielectric, as revealed by XSR characterization.

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