New indolo[3,2-b]carbazole derivatives for field-effect transistor applications[†]

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The synthesis, characterization, and field-effect transistor (FET) properties of new indolo[3,2b]carbazole (IC) based materials are reported. Instead of adding the long alkyl chains on the nitrogen atoms of the IC backbone like many other IC-based molecules, they were added at both ends of the molecule (octylthiophene, *p*-octylbenzene). Also, the amine groups on the IC backbone were either free or protected by methyl groups. The impact on the organization and thin-film morphology showed that the molecules stand perpendicular to the surface as demonstrated by XRD and AFM. The highest hole mobility obtained by these new *p*-type organic semiconductors was 0.22 cm² V⁻¹ s⁻¹ with an on/off ratio of about 10⁵. The best performance was obtained with 3,9-di(*p*-octylbenzene)-5,11-

dihydroxyindolo[3,2-*b*]carbazole. This performance is one of the best obtained by both IC derivatives and materials containing a secondary amine on the backbone.

Introduction

Great attention has been paid to organic semiconductors (OSCs) over the past two decades.¹ This class of materials is promising because of its great versatility and potential as organic field-effect transistors (OFETs),² photovoltaic cells (PCs),³ and organic light-emitting diodes (OLEDs).⁴ Significant progress has been made such that oligomers and polymers might be competitive with amorphous silicon (α -Si) in FET and PC applications. Organic semiconductors may be used for applications currently using α -Si transistors for integrated large area, flexible, low cost circuits such as radio frequency identification (RFID) tags, smart cards, and active matrix displays.⁵ Although there are some OSCs with charge carrier mobilities higher than those of α -Si, most of them still have stability and solubility issues. For instance, pentacene and rubrene⁶ are oxidized under ambient conditions and present a lack of solubility and photostability.

A promising pathway to afford stable and soluble OSCs is the synthesis of indolo[3,2-*b*]carbazole (IC) derivatives.⁷ It has been shown for the past few years that carbazole- and indolocarbazole-based materials combine great stability, solubility, and good performance in OFETs,⁸⁻¹¹ PCs,¹² and thermoelectric materials.¹³ Our group reported an IC derivative, *i.e.*, the 5,11-dioctyl-6,12-dimethylindolo[3,2-*b*]carbazole in an OFET application with a hole mobility of 10^{-3} cm² V⁻¹ s⁻¹.⁹ X-Ray crystallographic analysis showed that the molecules possessed strong cofacial π - π stacking, with short intermolecular distances of 3.6 Å. This kind of organization was obtained due to the planar structure of the

backbone and a favorable side chain conformation. Ong and coworkers subsequently reported that the mobility could be improved by 2 orders of magnitude if halogens were added at the 2.8-positions or if the linear alkyl chains on the amino group were replaced by 4-octylphenyl substituents.¹⁰ More recently, we reported new IC derivatives, with phenyl or thiophene groups at the 2,8- or 3,9-positions and alkyl chains on the amine groups, that show hole mobilities up to 0.20 cm² V⁻¹ s⁻¹.¹¹ Crystallographic data of the phenyl-substituted indolo[3,2-b]carbazole derivatives indicated that their aromatic backbones formed layered packing with strong bidirectional face-to-face and edgeto-face interactions within each layer. Thin-film X-ray diffraction analyses also indicated that the aromatic backbone adopted an edge-on orientation relative to the substrate with the alkyl chains pointed toward the surface. This kind of organization where the long axis of the active semiconducting core is parallel to the substrate surface is very interesting and explains the high mobility values obtained with the phenyl-substituted IC derivatives.

However, linear IC derivatives with alkyl chains at both ends of the aromatic backbone have not been reported. Therefore, it could be interesting to develop such molecules and evaluate their performance in OFETs. Moreover, the organization of these linear IC derivatives in thin-films may be completely different to those with long side chains on the amino groups.¹¹ Thus, the development of these linear IC derivatives will provide additional information about the relationships between molecular structure, solid state organization, and charge transport properties of IC derivatives.

In this article, we report the synthesis and characterization of six new linear IC derivatives with terminal alkyl side chains. We introduce phenyl and thiophene units at the 3,9-positions (as shown in Fig. 1), instead of the 2,8-positions, to allow the formation of such linear structures. Moreover, 3,9-aryl-substituted IC derivatives with alkyl chains on the amino groups have shown better thin-film organization and higher performances than their corresponding 2,8-aryl-substituted IC derivatives.¹¹ Since we used octyl side chains for the previously

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Fig. 1 Chemical structure of 3,9-disubstituted indolo[3,2-b]carbazole.

synthesized oligomers, we decided to continue with the same trend by comparing different molecules with the same chain length. For two of the IC derivatives, vinylene units were introduced into the oligomeric structures and, hopefully, they will result in coplanar molecules with low dihedral angles between the vinylene and aryl groups.¹⁴ In addition, we studied the effect of having two hydrophilic free amines on the molecule compared with the amine protected with methyl side chains. Up to now, only a few molecules containing free amines on their backbones have been synthesized with limited success for OFET applicaand coworkers15 tions. Nuckolls reported dihydrodiazapentacene with a field-effect mobility of about 0.06 cm² V^{-1} s⁻¹ in the saturation regime. Also, imidazolylquinoline derivatives were synthesized by Chen et al. with a hole mobility of 0.15 cm² V⁻¹ s⁻¹.16

Results and discussion

Synthesis of the indolo[3,2-b]carbazole derivatives

The complete synthesis of the new IC-based materials is described in Scheme 1. The starting compound for the synthesis of the new IC derivatives is 3,9-dibromo-5,11-dihydroindolo[3,2-b]carbazole, whose synthesis has been described in the literature.¹⁰ The next step is to add bulky *t*-butyloxycarbonyl (Boc) on both amines of the IC backbone. Those groups will not only act as protecting groups for further reactions but will also make the framework more readily soluble in common solvents such as dichloromethane and tetrahydrofuran (THF). Tholander and Bergman¹⁷ have described an efficient way to add the Boc units onto the amines of the IC. Using the same synthetic procedure with 3,9-dibromo-5,11-dihydroindolo[3,2-*b*]carbazole, the pure protected IC (**2**) was isolated in a 86% yield.

Afterwards, we were able to add aromatic units to both ends of compound **2**. 5-Octylthiophene units were added using Stille coupling¹⁸ to afford compound **3** in a 59% yield. On the other hand, a *p*-octylbenzyl group was introduced using the Suzuki cross-coupling reaction reported by Buchwald and coworkers¹⁹ giving compound **4** in a 73% yield. It was also possible to perform a Suzuki cross-coupling between compound **2** and compound **5**, affording compound **6** in a 76% yield. Compound **5** was obtained from vinylboronic acid pinacol ester and 1-iodo-4-octylbenzene



Scheme 1 Synthesis of new indolo[3,2-b]carbazole derivatives. DMAP = dimethylaminopyridine. SPhos = 2-dicyclohexylphosphino-2',6'-dimethoxy-biphenyl. TFA = trifluoroacetic acid. BTAC = benzyltriethylammonium chloride.

via a modified Heck coupling developed by Stewart and Whiting.²⁰ These conditions allow the Heck reaction product to be produced at the expense of the Suzuki product. A deprotection reaction was performed on compounds 3, 4, and 6 by treating them with a dichloromethane–TFA (1 : 1) mixture to give the new materials 7, 8 and 9 in good yields. Finally, compounds 10-12 were synthesized in good to moderate yields by a double alkylation of the unprotected compounds using the phase transfer condensation reaction in basic conditions.¹¹ The materials were characterized by elemental analyses and high resolution mass spectroscopy. It was very difficult to obtain NMR spectra from these molecules because of their very low solubility. We believe that the purity should be high enough to be tested in transistor devices. We hope to investigate the effect of the structural modification on the organization of the molecules when sublimated onto Si-SiO₂ substrates.

Thermal, optical, and electrochemical properties

Thermogravimetric analysis (TGA) showed that the new derivatives are all thermally stable with decomposition temperatures above 250 °C. Differential scanning calorimetry (DSC) measurements were performed on all new materials and revealed quite surprising thermal properties. With the exception of compound 10, all the other compounds did not show any thermal transition before the decomposition temperature. For compound 10, we observed two transitions during the heating process; one sharp peak at 195 °C and a second small peak at 250 °C. When cooling the sample down, a crystallisation transition can be observed at 244 °C.

Furthermore, UV-vis absorption spectra of these molecules in dichloromethane and N,N-dimethylformamide solutions and as thin-films are reported in Table 1 and shown in Fig. 1S and 2S (ESI[†]). A trend can be extracted from both sets of spectra: the longest conjugation length was obtained with ICs disubstituted with 5-octylthiophene (382 nm) and *p*-octylphenylenevinylene (380 nm). The *p*-octylbenzene moieties induced the shortest conjugation length among these 3 derivatives (364 nm). These results are not surprising considering that thiophene units usually produce more planar molecules with a more quinoid-like structure than phenyl units, increasing the conjugation with the IC unit.^{11,21}

In the case of compound 10, the UV-vis absorption properties in the thin-films were studied as a function of the substrate temperature applied during the deposition (Fig. 2). For substrate temperatures below 100 $^{\circ}$ C, the main absorption band maxima



Fig. 2 UV-vis absorption spectra of vacuum-deposited thin-films of compound 10 at different deposition temperatures.

are located at around 370 nm and the longest wavelength absorption maxima are at 460 nm. Above this deposition temperature, the absorption band at 370 nm is considerably smaller relative to the band left at around 460 nm. The same phenomenon is observed for the band at 290 nm which greatly diminishes at higher deposition temperatures leaving a relatively strong band at 260 nm. Similar behaviours were also observed for compounds 7, 8 and 11. This could be caused by a different organization on the surface at higher deposition temperatures. It will be shown later that this behaviour is in good agreement with the atomic force microscopy (AFM) images, X-ray diffraction (XRD) analyses and FET properties. Finally, the optical bandgap (E_g) of the new materials estimated from the solid state spectra range from 2.62 to 2.76 eV.

Cyclic voltammetry (CV) experiments showed irreversible oxidation processes in the case of the IC derivatives containing secondary amines (7–9) and a quasi-reversible oxidation wave for their corresponding methylated compounds (10–12). The highest occupied molecular orbital (HOMO) energy levels, estimated from the oxidation onset,²² range from 5.3 to 5.6 eV (Table 1). Surprisingly, compounds 7 and 10 with thiophene moieties have the lowest HOMO energy levels. Also, the addition of a methyl group on the secondary amine of the IC derivatives increases their HOMO energy levels. The HOMO energy levels are below the air oxidation threshold (which is around 5.27 eV), indicating good oxidation stability for all the IC derivatives.²³

Field-effect transistor performances

Top-contact field-effect transistors were made from the six new materials by high-vacuum evaporation. Bare and

Table 1 Optical absorption maxima (λ_{max}) and electrochemical properties of the new materials

Compound	λ_{max} solution/nm ^a	λ_{\max} thin-film/nm ^b	$E_{\rm g}$ thin-film/eV ^b	$E_{\rm ox}$ vs. SCE/ V^c	$E_{\rm HOMO}/{\rm eV}^d$
7	288, 382	<i>343</i> , 441	2.70	0.88	5.59
8	300, 364	<i>334</i> , 436	2.76	0.67	5.38
9	284. 380	351. 431	2.64	0.70	5.41
10	290, 385, 430	372, 438, 460	2.62	0.74	5.45
11	288, 366, 425	333. 435	2.76	0.66	5.37
12	290, 393, 450	347, 429	2.64	0.60	5.31

^{*a*} Measurements performed in DMF for 7, 8, 9 and in CH₂Cl₂ for 10, 11, 12. ^{*b*} Measurements performed on 300 Å thin-films vacuum-deposited on quartz. ^{*c*} SCE: standard calomel electrode. The values correspond to the oxidation peak onset. ^{*d*} Ionization potential (E_{HOMO} ; HOMO = highest occupied molecular orbital) measured from the cathodic onset.

octadecyltrichlorosilane (OTS)-treated Si–SiO₂ substrates, as well as different substrate deposition temperatures (T_d), were used in this study in order to increase order within the deposited thin-films and consequently to study the effect of the molecular organization on the charge transport properties. The Si–SiO₂ substrate functionalization with alkyl silanes has been proven to be very useful in obtaining high performances in OFET devices.²⁴ It decreases the number of traps located at the semiconductor– dielectric interface.²⁵ Moreover, it is interesting to compare the performances of our ICs containing hydrophilic amines on the framework with the corresponding hydrophobic ICs on both bare and OTS-treated Si–SiO₂ substrates.

As expected, all the IC derivatives behave as *p*-type organic semiconductors with well-defined linear and saturation regimes. For example, Fig. 3 shows the source–drain current (I_{DS}) versus the source–drain voltage (V_{DS}) for an OFET made with compound **8** at various gate voltages (V_G). The hole mobilities calculated in the saturation regime, the on/off current ratios and the threshold voltages obtained at different T_d are summarized in Table 2. It is worth noting that all the devices were stored and tested under ambient conditions.

The compound leading to the highest hole mobility among the new linear ICs was found to be the free amine phenyl-substituted IC 8. Indeed, compound 8 deposited at $T_d = 25$ °C on OTStreated substrates shows a hole mobility and an on/off ratio of $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 7×10^3 , respectively. As shown in Table 2, when the substrate deposition temperature was increased, both the hole mobility and the on/off ratio improved. At $T_d = 125 \text{ }^{\circ}\text{C}$, the maximum hole mobility and the on/off ratio are $0.22 \text{ cm}^2 \text{ V}^{-1}$ s^{-1} and 3 \times 10⁵, respectively. This particular film was tested in two different devices and the mobility average was 0.21 cm² V⁻¹ s^{-1} . The performances were also tested over two months and the mobility was still 0.11 cm² V⁻¹ s⁻¹ indicating a good stability of the thin-film. Higher T_{ds} were also used, but the FET performance began to decrease and the devices were difficult to reproduce probably due to the presence of voids and disconnected films as seen by optical microscopy. Interestingly, good performances were also obtained with compound 8 using bare SiO₂ substrates. For example, at $T_d = 125$ °C, the hole mobility and the on/off ratio are $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 2×10^6 , respectively.

The performances obtained with thiophene-substituted IC 7 are lower (about 3 times) than those obtained with phenylsubstituted IC 8. As shown in Table 2, a hole mobility of 0.08 cm² $V^{-1} s^{-1}$ and an on/off ratio of 10⁶ were obtained when the thinfilm was deposited at $T_d = 175$ °C. We note also that the performances obtained with compound 7 on bare or OTS-treated Si–SiO₂ substrates are very close when the substrate deposition temperature is equal to or higher than 75 °C. Compound 9 with vinylene groups shows relatively unchanged mobilities, about 4×10^{-3} cm² V⁻¹ s⁻¹, when the substrate temperature is varied between 25 and 125 °C. This mobility is at least one order lower than the one measured with compound 8 having no vinylene group.

The results obtained with the methylated ICs **10–12** are also very interesting. First, these ICs clearly have lower performances than their corresponding free amine ICs **7–9**. For example, compound **10** shows a hole mobility of 9×10^{-4} and $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $T_d = 25 \text{ °C}$ and 125 °C, respectively. These values are about one order of magnitude lower than those obtained with IC **7**. Moreover, as shown in Table 2, the hole mobility of IC **10** increased by one order of magnitude when the substrate deposition temperature was changed from 75 to 100 °C. These results are in good agreement with the UV-vis results showing a significant change in the molecular arrangement (orientation) at $T_d = 100 \text{ °C}$. As we will see later, the AFM images and XRD analysis clearly show this modification in the thin-film organization and consequently explain this improvement.

Secondly, as observed for compounds 7 and 8, the hole mobility of thiophene-substituted IC 10 is lower than the one measured for phenyl-substituted IC 11 when the substrate was heated during the deposition. This goes along with the trend reported by our group in 2007 for other indolocarbazoles.¹¹ The phenyl units on both ends of the IC unit lead to higher mobilities than the thiophene units even though the latter usually provides more planar π -conjugated molecules.¹⁴ In fact, it has recently been shown that oligomers containing phenyl functional groups can achieve high performance.²⁶ Finally, as shown in Table 2, compound 12 exhibits very low hole mobilities, no matter what substrate temperature was used during the deposition. The addition of vinylene units between the indolocarbazole and the



Fig. 3 (a) Source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) at various gate voltages (V_G) for top-contact field-effect transistors using compound 8 on OTS-treated SiO₂ ($T_d = 125 \text{ °C}$). (b) The transfer characteristics in the saturation regime at a constant source-drain voltage (-100 V) are also shown.

Table 2 B substrate d	est field-ef eposition 1	fect mobility (μ_{\max}) , on temperatures (T_d)	/off current r	atio and th	reshold voltage (V_{T}) o	f vacuum-dej	posited thir	1-films of indolo[3,2- <i>b</i>]	carbazoles 7-	-12 on diff	erently treated SiO_2 su	ubstrates at di	ifferent
Oligomer	SiO_2	$\mu_{ m max}/ m cm^2~V^{-1}~s^{-1}) T_{ m d} = 25 ~^\circ m C$	$I_{ m on}/I_{ m off}$	$V_{\rm T}/{ m V}$	$\mu_{\rm max}/{\rm cm}^2 \ {\rm V}^{-1} \ {\rm s}^{-1}$ $T_{\rm d} = 75 \ ^{\circ}{\rm C}$	$I_{\rm on}/I_{\rm off}$	$V_{\rm T} N$	$\mu_{ m max}/ m cm^2~V^{-1}~s^{-1}$ $T_{ m d}=100~ m ^{\circ}C$	$I_{ m on}/I_{ m off}$	$V_{\rm T}V$	$\mu_{\rm max}/\rm cm^2 \ V^{-1} \ s^{-1}$ $T_{\rm d} = 125 \ ^{\circ}\rm C \ ^{a}$	$I_{ m on}/I_{ m off}$	$V_{\rm T}V$
7	Bare	$4 imes 10^{-5}$	$2 imes 10^{0}$	-23	0.05	$5 imes 10^4$	-8	0.06	$3 imes 10^4$	6	0.05	$3 imes 10^4$	-8
	OTS	$8 imes 10^{-3}$	$2 imes 10^3$	-25	0.05	1×10^4	-32	0.03	$2 imes 10^4$	-30	0.08	$4 imes 10^5$	-32
8	Bare	No field-effect			$4 imes 10^{-3}$	$5 imes 10^3$	L	0.04	$3 imes 10^4$	-5	0.12	$2 imes 10^{6}$	-17
	OTS	0.03	7×10^3	-26	0.05	9×10^4	-13	0.10	$2 imes 10^4$	-24	0.22	$3 imes10^5$	-23
6	OTS	$4 imes 10^{-3}$	7×10^{10}	-50	$3 imes 10^{-3}$	9×10^2	-22	$6 imes 10^{-3}$	1×10^3	-18	$6 imes 10^{-3}$	$6 imes 10^2$	-43
10	Bare	$6 imes 10^{-6}$	$1 imes 10^3$	-44	$1 imes 10^{-3}$	1×10^3	-8	$3 imes 10^{-3}$	$7 imes 10^4$	-57	0.01	$5 imes 10^3$	-17
	OTS	$9 imes 10^{-4}$	$1 imes 10^5$	-41	$1 imes 10^{-3}$	$5 imes10^5$	-26	0.01	$1 imes 10^4$	-34	0.02	$3 imes10^4$	-34
11	Bare	$2 imes 10^{-4}$	$5 imes 10^{0}$	-19	$7 imes 10^{-3}$	$6 imes 10^3$	-28	0.02	$2 imes 10^5$	-16	0.03	$5 imes 10^4$	-25
	OTS	$9 imes 10^{-4}$	$3 imes 10^2$	-21	0.01	7×10^3	-28	0.03	$1 imes 10^4$	-25	0.05	$3 imes 10^4$	-30
12	OTS	$2 imes 10^{-4}$	$3 imes10^{0}$	-42	$4 imes 10^{-4}$	$2 imes 10^{0}$	-57						

phenyl (compounds 9 and 12) does not seem to be a good strategy to improve the IC performance in OFETs.

Morphological and structural characteristics

The morphology and structure of vacuum-deposited thin-films were studied by AFM and XRD in order to explain the OFET results, and to understand the relationship between molecular structures, thin-film properties and device performances. First, as shown in Fig. 4, the deposition of compound 8 at $T_d = 25 \text{ }^{\circ}\text{C}$ leads to thin-films with an irregular granular morphology and high roughness. By increasing the substrate deposition temperature, the grains become larger and the surface is smoother which corresponds to improved OFET performances. At $T_{\rm d} = 125$ °C a lamellar-like morphology appears with the presence of isolated grains on the top of the film. One can presume that this kind of morphology leads to fewer grain boundaries in the film and consequently the hole mobility increases. Similar behaviour was observed for compound 7; Fig. 4d shows the morphology of a thin-film deposited at $T_{\rm d} =$ 175 °C.

Amine-methylated ICs, **10** and **11**, reveal interesting features by AFM. For example, IC **10** exhibits an irregular granular morphology when deposited at $T_d = 25 \text{ °C}$ (Fig. 5). However, as shown in Fig. 5, a more crystalline morphology appears starting from $T_d = 100 \text{ °C}$ with a terrace-like layered structure. The stacked terrace layers lay parallel to the Si–SiO₂ surface with the step height of the terrace layers about 39 Å. Interestingly, the apparition of this new organization corresponds well with the increase in mobility by one order observed at $T_d = 100 \text{ °C}$. A similar trend was also observed in the case of IC **11**, where a multilevel island-like structure appeared at $T_d = 75 \text{ °C}$ (Fig. 3S, ESI†). At this substrate temperature, the mobility is one order higher than the one measured at $T_d = 25 \text{ °C}$. The



Fig. 4 AFM images of vacuum-deposited thin-films (40 nm) of compound 8 at (a) room temperature (b) 75 °C (c) 125 °C and (d) 175 °C. The size of all the images is 1 μ m².

= 175

^{*a*} Except for compound 7 where $T_{\rm d}$



Fig. 5 AFM images of vacuum-deposited thin-films (40 nm) of compound 10 (a) at room temperature (b) at 75 °C (c) at 100 °C and (d) at 125 °C. The size of all the images is 1 μ m².

crystallites become more defined at $T_d = 125$ °C, which could explain the mobility enhancement observed in OFETs. The AFM images of compounds 9 and 12 show irregular granular morphologies with a high film roughness (Fig. 4S, ESI†). The introduction of vinylene units between the IC and the phenyl groups produces amorphous films with poor organization which could be a reason for the low mobilities measured in OFETs.

The X-ray data obtained from deposited thin-films of compounds 8 and 10 provide important information about the film structures at different substrate deposition temperatures. As shown in Fig. 6, the XRD pattern of compound 10, deposited without any substrate heating, indicates the formation of an amorphous structure. When deposited at $T_d = 75$ °C, only a small diffraction peak was observed at $2\theta = 5.56^{\circ}$ (*d*-spacing = 15.9 Å)



Fig. 6 XRD patterns of an evaporated thin-film of compound 10 on OTS-treated SiO₂ at different substrate temperatures.

in the XRD spectrum. On the other hand, this oligomer deposited at $T_{\rm d} = 100$ °C exhibits a sharp primary diffraction peak at $2\theta =$ 2.36°, corresponding to a layer distance of 37.4 Å. At $T_d = 125$ °C, the primary peak moves to $2\theta = 2.23^{\circ}$ (d-spacing = 39.5 Å) and its intensity increases. Interestingly, the d-spacing of compound 10 at $T_{\rm d} = 125 \,^{\circ}{\rm C}$ corresponds exactly to the step height of the terrace layers measured by AFM at this temperature. Moreover, the length of compound 10 is estimated to be around 39 Å in an extended linear conformation. Therefore, on the basis of the XRD and AFM results, we suppose here that compound 10 adopts a vertical orientation relative to the substrate. This organization is completely different to the one observed with our previous IC derivatives with alkyl chains on the nitrogen where the IC core is quasi-parallel to the substrate and the alkyl chains are pointed towards the surface. This example shows how the position of the alkyl side chains can have a major effect on the molecular organization of these ICs. It also shows that thin-films, where the IC molecules have a parallel or vertical orientation relative to the substrate, could be obtained by simple modification of the alkyl side chain position on the IC core.

As shown in Fig. 7, the XRD patterns of compound **8** were not that clear. At $T_d = 25$ °C, the XRD spectrum did not exhibit any diffraction peaks, indicating an amorphous structure. When the film was deposited at 75 °C, a small peak could be observed at 2θ = 3.04° corresponding to a *d*-spacing of 29.1 Å. Even with this small peak, it is believed that the heating of the substrate induced some long range organization of the molecules on the OTStreated SiO₂. Furthermore, by heating the film at 125 °C, the XRD pattern is clearly different. The peak that was observed at 75 °C has completely disappeared and instead there are two new peaks. First, at $2\theta = 2.87^\circ$ corresponding to a *d*-spacing of 30.8 Å and a second peak at $2\theta = 3.19^\circ$ (*d*-spacing = 27.7 Å). This could mean that there are two different types of packing within the same film.

These data are not enough to reveal whether the molecules stand perpendicular or lay parallel to the substrate. The amine groups on the backbone of the molecule change the organization within the thin-film. The addition of new interactions between the molecules probably leads to hydrogen bonding or other intermolecular bonds that enhance the charge transport



Fig. 7 XRD patterns of an evaporated thin-film of compound 8 on OTS-treated SiO₂ at different substrate temperatures.

properties. Further work on these IC derivatives will help to understand the organization in three dimensions and the difference between the packing of the ICs containing secondary and tertiary amines.

Experimental

Instrumentation

¹H and ¹³C NMR spectra were recorded on a Varian AS400 apparatus in the appropriate deuterated solvent solution at 298 K. Chemical shifts were reported as δ values (ppm) relative to the internal tetramethylsilane standard. Differential scanning calorimetry (DSC) analyses were performed on a Mettler Toledo DSC823^e instrument, calibrated with ultrapure indium. UV-vis absorption spectra were taken using a Varian Cary 500 UV-VIS-NIR spectrophotometer. Cyclic voltammetry (CV) measurements were recorded on a Solartron 1287 potentiostat and C3 Cell Stand using platinum electrodes at a scan rate of 50 mV s⁻¹ against a Ag/Ag⁺ (0.1 M of AgNO₃ in acetonitrile) reference electrode in an anhydrous and argon saturated solution of 0.1 M tetrabutylammonium perchlorate (TBAP) in CH2Cl2. Under these conditions, the oxidation potential (E_{Ox}) of ferrocene was 0.053 V versus Ag/Ag⁺, whereas the E_{Ox} of ferrocene was 0.343 V versus SCE. Top-contact devices were made according to a literature procedure.²⁷ The Philips PANalytical X'Pert diffractometer with a PreFIX X-ray mirror at the incident beam, and a parallel plate collimator at the diffracted beam was used on the thin-films of the evaporated molecules. $\Omega/2\theta$ scans were performed with Cu Kal radiation at a power of 45 mV and 40 mA, with a step size of 0.02, and a step time of 1.0 s. A Digital Instruments MMAFM-2 scanning probe microscope was used to perform tapping mode AFM on the samples with a silicon tip of 300 kHz frequency.

Material synthesis and characterization

2-Octyl-5-(tributyltin)thiophene,²⁸ 1-iodo-4-octylbenzene,²⁹ 4octylbenzeneboronic acid³⁰ and 3,9-dibromo-5,11-dihydroxyindolo[3,2-*b*]carbazole¹⁰ were synthesized according to already published procedures. All starting organic compounds were purchased from Aldrich, Alfa Aesar and TCI America and used without further purification. All reactions were carried out under argon at 1 atm unless mentioned otherwise. Some reaction solvents were distilled before use (THF from potassium–benzophenone; acetonitrile from CaH₂). Column chromatography was carried out on silica gel (size 40–63 μ m, pore size 60 Å, Silicycle). All the other compounds have been synthesized following procedures described in the ESI†.

Device fabrication

Highly doped n-type (100) Si wafers (<0.004 Ω cm) were used as substrates for the devices. SiO₂ layers (unit area capacitance, C = 10 nF cm⁻²), as gate dielectric, were thermally grown to 3000 Å thickness onto the Si substrates. The Si–SiO₂ substrates were then cleaned with acetone and isopropyl alcohol. The wafers were then treated with a 3 mM octadecyl trimethoxysilane (C₁₈H₃₇Si(OCH₃)₃, OTS) solution in trichloroethylene, which was spin-coated onto the substrates before treating with a saturated atmosphere of NH₄OH overnight. 40 nm organic films were vacuum-deposited on the treated Si–SiO₂substrates at room temperature and elevated temperatures, as described in the text, at a deposition rate of 0.4–0.5 Å s⁻¹ and 10⁻⁶ Torr. The thinfilm thickness of each derivative was determined *in situ* using a quartz-crystal microbalance (QCM). A top-contact thin-film transistor was used for measuring the charge mobility of the indolo[3,2-*b*]carbazole derivatives: gold source and drain electrodes (channel length (*L*) and width/length (*W*/*L*) of 50 µm and *ca.* 20 respectively) were vacuum-deposited through a shadow mask. The electrical characteristics of the organic field-effect transistor (OFET) devices were measured under an accumulation mode using a Keithley 4200-SCS semiconductor parameter analyzer.

Conclusion

We reported in this study the synthesis, characterization and FET performance of new indolo[3,2-b]carbazole derivatives. 3,9-Di(p-octylbenzene)-5,11-dihydroindolocarbazole (8) exhibits a good hole mobility ($0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Compound 7 also led to a mobility close to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. It was demonstrated that the new materials organized quite differently depending on the substrate temperature using UV-vis spectroscopy, AFM and X-ray diffraction. We were also able to show that the alkylation on both ends of the molecule leads to a clearly different film morphology. The molecules tended to stand perpendicular to the surface instead of laying down parallel to it. Furthermore, the performances for the free amine compounds were almost the same with and without surface modification. The new methylated compounds did not demonstrate good performances compared to their unprotected amine counterparts. This may be due to the steric hinderance created by the methyl groups on each side of the IC framework. Future work will focus on synthesizing new polymers and oligomers based on the indolo[3,2-b]carbazole backbone that can be solution processed. This could lead to very promising materials if the crystallinity observed in previous compounds can be maintained.

Moreover, the application of these molecules in sensing devices is under way. It is believed that they may be efficient in detecting different kinds of analytes because of the reactive amines on the IC. By comparing compounds 8 and 11 in sensor devices, we have already found that ICs containing secondary amines were 20-30 times more sensitive in the vapour sensing of solvents such as acetone than the tertiary amines. This highlights the versatility and the potential of indolocarbazole derivatives for applications in electronic devices.

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