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Towards understanding the behavior of indigo thin films in organic field-effect transistors: a template effect of the aliphatic hydrocarbon dielectric on the crystal structure and electrical performance of the semiconductor†

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Here we report a systematic investigation of indigo thin films grown on different dielectric underlayers. It has been revealed that aliphatic hydrocarbon chains serve as templates inducing the formation of a new crystal modification of indigo which possesses advanced charge transport properties and affords a dramatic improvement in the electrical performance of organic field-effect transistors.

Organic electronics is one of the most rapidly progressing fields in materials science. Many organic semiconductors showed reproducible charge carrier mobilities of 1–30 $cm^2\ V^{-1}\ s^{-1}$ in organic field-effect transistors (OFETs) which is interesting for industrial applications.[1] However, massive production and use of plastic electronics, in particular, various disposable devices, might cause severe pollution effects in the environment.[2] This problem might be solved *via* design and implementation of biodegradable electronics which is based entirely on environmentally-friendly non-toxic materials. This approach was pursued by M. Irimia-Vladu in collaboration with our group.[3–5] The ancient organic dye indigo was shown to be one of the most promising semiconductor materials exhibiting balanced ambipolar transport in OFETs and good performance in inverter circuits.[3,6] It was noticed that the performance of indigo-based OFETs strongly depends on the selection of the dielectric material. Hydrocarbon-based tetratetracontane ($C_{44}H_{90}$) and polyethylene dielectrics provided the best performances.[6] Low-mobility n-type transistors were demonstrated with a cross-linked benzocyclobutene derivative BCB as a dielectric.[3] At the same time, indigo did not show any semiconductor behavior on other investigated dielectrics such as poly(vinyl alcohol), shellac, melamine, adenine, and guanine as well as plain aluminum oxide.[6] After the original report, indigo and two halogenated indigo derivatives have been investigated in details as semiconductor materials for OFETs and diodes.[7–10] However, no experimental explanations were found for the observed unusual behavior of indigo thin films grown on different surfaces.

In the present study we show that the importance of the hydrogen bonding effects in the indigo-based semiconductors seems to be overestimated in previous studies.[7–10] Wide angle grazing incidence X-ray scattering (GIWAXS) experiments revealed that aliphatic hydrocarbon chains play a role of a template which induces the formation of a novel epitaxially grown crystal structure of indigo which is responsible for its advanced performance in OFETs. Therefore, the nature of the dielectric is the most crucial factor affecting the device performance rather than the hydrogen bonding effects in indigo itself.

At the initial stage of this work we reconfirmed the influence of the dielectrics on the performance of indigo-based OFETs. Polyvinyl alcohol (PVA), cross-linked benzocyclobutene derivative (BCB), tetracontane ($C_{40}H_{82}$, TC) and paraffin wax (mixture of C_{15}–C_{40} normal chain hydrocarbons, PF) were studied as underlayer materials deposited between the AlO_x dielectric and indigo semiconductor layers in a top-contact OFET geometry (Fig. 1).

Using silver for source and drain electrodes enabled fabrication of n-type OFETs (Fig. 1), while ambipolar devices were fabricated using gold electrodes (Fig. S1, ESI†).

Transfer characteristics obtained for n-type OFETs comprising four different organic dielectric materials are intentionally given in the same scale in Fig. 1 for comparison purpose. It is seen clearly that devices with linear chain aliphatic hydrocarbons (TC and PF) significantly outperform OFETs with PVA and BCB used as organic dielectrics. Very similar results were also obtained for ambipolar OFETs with gold top electrodes (Fig. S1, ESI,† Table 1).

There are few possible reasons for the observed strong influence of the dielectric material on the transistor performance. For example, the high roughness of the used dielectric coatings might potentially

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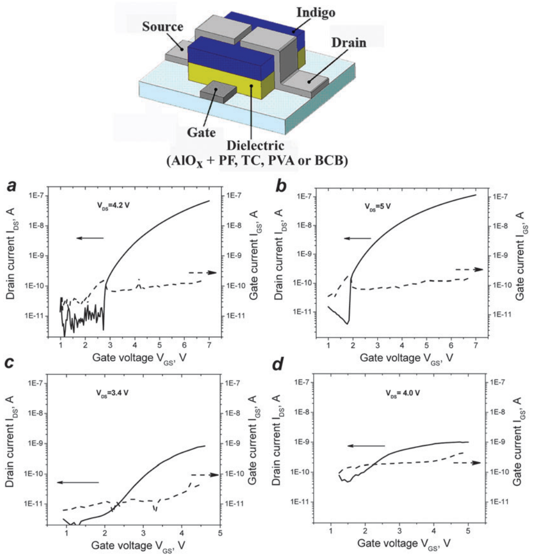

Fig. 1 Transfer characteristics of indigo-based OFETs fabricated using TC (a), PF (b), BCB (c) and PVA (d) as underlayer dielectrics.

Table 1 Characteristics of OFETs based on indigo films grown on different dielectrics

Dielectric	Electrodes	Type	Vth (V)	I_{on}/I_{off}	μ (cm^2 V^{-1} s^{-1})
PF	Ag	N	2.5	2×10^4	2.0×10^{-3}
	Au	N	4.4	3×10^3	2.0×10^{-3}
	Au	P	−3.4	1×10^3	7.0×10^{-4}
TC	Ag	N	3.0	10^4	3.0×10^{-3}
	Au	N	4.8	4×10^3	1.3×10^{-3}
	Au	P	−5.1	2×10^2	3.0×10^{-4}
BCB	Ag	N	1.5	1×10^2	1.8×10^{-4}
	Au	N	2.9	3×10^2	1.5×10^{-4}
	Au	P	—[a]	—	—
PVA	Ag	N	2	10	$<10^{-4}$
	Au	N/P	—	—	—

[a] Symbol "—" indicates that no transistor behaviour was observed.

cause some significant effects. However, the AFM images (Fig. S2, ESI†) revealed that solution-processed (spin-coated) PVA and BCB films are even smoother compared to the PF and TC films. It is known that smoother dielectric layers typically give better OFET performances.[11] However, all films showed roughness on the order of ~10 nm, which cannot account for the observed differences in the electrical performance of the devices.

The different morphology of the semiconductor films deposited on different dielectrics has to be considered as a possible factor influencing the performance of OFETs.[12] Indeed, the AFM images revealed that the dielectric materials have a strong impact on the topography of the indigo films grown above (Fig. 2).

Very similar results were also obtained using scanning electron microscopy (SEM) images (Fig. S3, ESI†). It is seen from Fig. 2 that indigo forms a very rough and noncontinuous coating on PVA which might explain its poor performance in OFETs. At the same time, the most ordered indigo films formed on BCB are expected to show better charge transport properties compared to the randomly

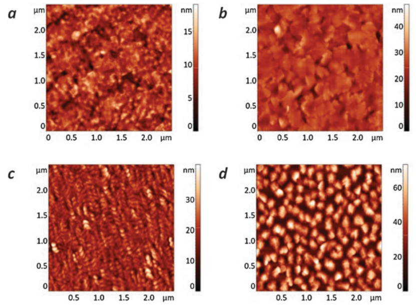

Fig. 2 AFM images of indigo thin films thermally evaporated on TC (a), PF (b), BCB (c) and PVA (d) underlayer dielectrics.

distributed flakes grown on TC and PF. However, this expectation falls in contradiction to the OFET characteristics presented above (Table 1). Therefore, a superior performance of the indigo–TC and indigo–PF systems can hardly be explained only by the film morphology issues.

In order to gain a deeper understanding of the effects occurring in the indigo films grown on different dielectrics we applied GIWAXS for their characterization. It has been revealed that indigo thin films grown on PF give considerably different GIWAXS patterns compared to the films grown on BCB and PVA (Fig. 3). The films grown on BCB exhibited excellent crystallinity. The 2D GIWAXS pattern shows a uniaxially oriented texture with an intense peak with a *d*-spacing of 8.27 Å corresponding to the 100 reflection of a classical $P2_1/c$ crystal structure[13] with the *a*-axis oriented normally to the substrate. A similar GIWAXS pattern is observed for the indigo film grown on PVA (Fig. 3e and f).

In contrast, indigo films grown on paraffin exhibited two peaks on the meridian with d = 8.27 Å (100) and d = 10.78 Å (100*) (Fig. 3a). Moreover, the relative intensity of the new peak decreases with increasing thickness of the deposited indigo films. The observed behavior of the meridional reflection evidences the formation of a new crystal modification of indigo with elongated *a*-parameters on the interface with the PF dielectric.

We emphasize that the 100* peak was reproducibly observed for all indigo films deposited on PF and solution-processed TC.

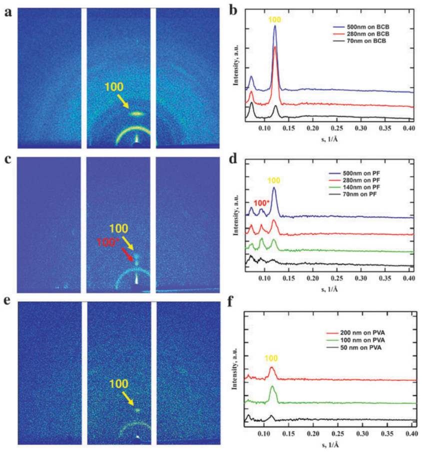

Fig. 3 GIWAXS patterns of indigo films deposited on BCB (70 nm) (a), PF (70 nm) (c) and PVA (50 nm) (e). The evolution of the scattering profiles with increase in the thickness of indigo films deposited on BCB (b), PF (d) and PVA (f).

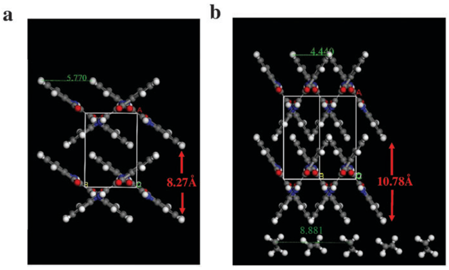

Fig. 4 The *a*–*b* projections of the conventional (a) and new (b) crystal lattices of indigo on the PF sub-layer.

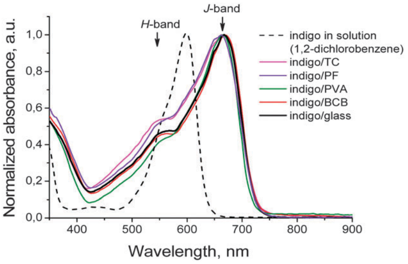

Fig. 5 Normalized absorption spectra of indigo thin films grown on different dielectric substrates compared to the spectrum of solution.

Indigo films deposited on the evaporated TC underlayer showed very weak 100* signals. No meridional 100* peaks were detected in GIWAXS patterns of indigo films grown on BCB, PVA (Fig. 3c and e), glass and silicon (SiO_2-passivated) (Fig. S4, ESI†). These findings fully correlate with the electrical characteristics of the indigo OFETs fabricated using PF, TC, BCB and PVA as dielectrics. The revealed correlation strongly suggests that superior semiconductor performance of indigo deposited on aliphatic dielectrics is related to the formation of a new crystal modification. Simple geometric modelling allowed us to reveal some details of the new crystal modification of indigo. Fig. 4 shows that a *d*-spacing of 10.78 Å arises from a distortion of a monoclinic cell of indigo along the crystallographic *a*-axis. At the same time, the *d*-spacing along the *b*-axis should be reduced from 5.77 Å to 4.45 ± 0.01 Å to compensate the crystal density mismatch.

The latter corresponds perfectly to the distance between the neighboring linear aliphatic $CH_3(CH_2)_nCH_3$ chains known, for example, from the studies of the orthorhombic phase of polyethylene.[14] Thus, elongated and ordered aliphatic hydrocarbon chains play a role of the template which orders indigo molecules in a new distorted monoclinic structure with $d = 10.78$ Å (100*) and $d = 4.45$ Å (110*). In addition, indigo molecules in a new arrangement are much less tilted with respect to the plane of the dielectric substrate (tilt angle is reduced from 54° to 40°) which should favor the lateral charge transport through the channel of OFET. The reduced tilt angle and intermolecular distance (*d*-spacing along the *b*-axis) enhance the electronic coupling between the neighboring indigo molecules thus facilitating charge transport along the stack. We believe that these effects are responsible for the improved OFET performance observed for the new crystal modification of indigo.

Another important peculiarity of the revealed new crystal modification of indigo is a smaller shift of the molecules with respect to each other in the π–π stack. The stacks of planar molecules with a large displacement of the neighbours (staircase fashion) are called J-aggregates.[15] Indigo exhibits bathochromic shift of the absorption band going from solution to the solid state which is very typical for J-aggregates. However, a new modification of indigo is characterized by a much smaller displacement of molecules with respect to each other in the stack which is more characteristic for H-aggregates. H-aggregates show hypsochromic shifts of the absorption bands going from solution to the solid state.[15] Comparison of the indigo absorption spectra revealed the pronounced H-band contribution for the films deposited on aliphatic hydrocarbons (PF and TC, Fig. 5) which agrees well with the GIWAXS data and OFET characteristics.

In conclusion, we have revealed that hydrocarbon dielectrics might serve as templates modifying the crystal structure, optical and electronic properties of the adjacent layers of the semiconductor. These findings open a new route for supramolecular engineering of the semiconductor/dielectric interface which might be very beneficial for designing highly efficient OFETs and electronic circuits.

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