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High-Mobility and Low Turn-On Voltage n-Channel OTFTs Based on a Solution-Processable Derivative of Naphthalene Bisimide

Izabela Tszydel, Magdalena Kucinska, Tomasz Marszalek, Renata Rybakiewicz, Andrzej Nosal, Jaroslaw Jung, Maciej Gazicki-Lipman, Charalabos Pitsalidis, Christoforos Gravalidis, Stergios Logothetidis, Malgorzata Zagorska, and Jacek Ulanski*

This paper is dedicated to Professor Adam Pron on the occasion of his 60th birthday

In organic electronics solution-processable n-channel field-effect transistors (FETs) matching the parameters of the best p-channel FETs are needed. Progress toward the fabrication of such devices is strongly impeded by a limited number of suitable organic semiconductors as well as by the lack of processing techniques that enable strict control of the supramolecular organization in the deposited layer. Here, the use of *N,N′*-bis(4-n-butylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (NBI-4-n-BuPh) for fabrication of n-channel FETs is described. The unidirectionally oriented crystalline layers of NBI-4-n-BuPh are obtained by the zone-casting method under ambient conditions. Due to the bottom-contact, top-gate configuration used, the gate dielectric, Parylene C, also acts as a protective layer. This, together with a sufficiently low LUMO level of NBI-4-n-BuPh allows the fabrication and operation of these novel n-channel transistors under ambient conditions. The high order of the NBI-4-n-BuPh molecules in the zone-cast layer and high purity of the gate dielectric yield good performance of the transistors.

1. Introduction

The electric performance of organic thin film transistors (OTFTs) has been improved over the last years as a result of a significant progress in the organic semiconductors synthesis, their processing as well as the application of new methods of the device fabrication. The fundamental parameter used to characterize the OTFTs performance is charge carrier mobility derived from the field effect. Apart from the semiconductor molecular structure this mobility depends on the supramolecular organization of the semiconductor's molecules in the active layer and more precisely on the degree of their alignment. The last factor is especially important for low molecular weight semiconductors, since in this case the molecules often tend to form quasi-1-dimensional π–stacks resulting in a highly anisotropic charge carriers mobility. For this reason, the deposition techniques enhancing molecular ordering in the semiconductor layers are highly demanded. Among known organic layer deposition techniques the zone-casting method deserves a special attention, because it allows to produce highly oriented layers on large area in one step process without the use of preoriented substrates.[1–4] The idea of the zone-casting method is shown in **Figure 1**. The solution of an organic semiconductor is continuously supplied from the fixed flat nozzle onto a moving substrate. In the created meniscus, due to evaporation of the solvent, the concentration of the semiconductor molecules increases and when their saturation is reached, the crystallization starts. The gradient of concentration in the meniscus is a driving force of the unidirectional crystal growth.

Literature search shows that among organic semiconductors used in air operating devices the hole-transporting (p-type) materials dominate over the electron transporting (n-type) ones.

I. Tszydel, M. Kucinska, T. Marszalek, Dr. J. Jung, Prof. J. Ulanski
Department of Molecular Physics and European Centre
for Bio- and Nanotechnology
Technical University of Lodz
90-924 Lodz, Poland
E-mail: izabela.tszydel@edu.p.lodz.pl

R. Rybakiewicz, Prof. M. Zagorska
Faculty of Chemistry
Warsaw University of Technology
00-664 Warsaw, Poland

A. Nosal, Prof. M. Gazicki-Lipman
Institute of Materials Science and Engineering
Technical University of Lodz
90-924 Lodz, Poland

Dr. C. Pitsalidis, Dr. C. Gravalidis, Prof. S. Logothetidis
Laboratory for Thin Films Nanosystems
and Nanometrology
Physics Department
Aristotle University of Thessaloniki
54124, Thessaloniki, Greece

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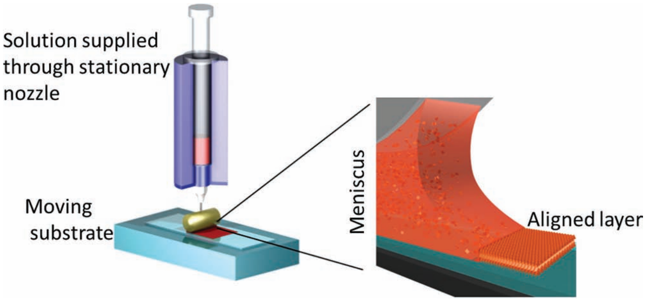

Figure 1. Schematic view of the zone-casting technique.

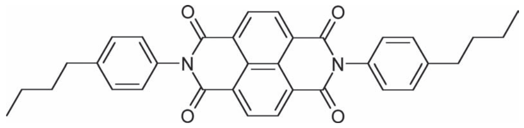

Figure 2. Chemical structure of NBI-4-n-BuPh.

This is caused by the fact that in the majority of π-conjugated molecules the lowest unoccupied molecular orbital (LUMO) level is too high to assure their air stability upon injection of extra electrons.[5–8] For these reasons reports on air operating n-channel OTFTs are rather scarce.[9–12] From the technological point of view such semiconductors are highly demanded, especially if they combine air operating stability with solution processability.

Further progress in organic electronics requires an elaboration of new semiconductors and processing techniques which yield n-channel OTFTs of electrical parameters comparable to those measured for the most advanced p-channel OTFTs. This is caused by the fact than in the majority of electronic devices both types of transistors must be used, e.g. in the construction of complementary metal oxide semiconductor (CMOS)-like circuits. Moreover, in such advanced devices as the light emitting OTFTs high values of both hole and electron mobilities are essential.

Arylene bisimides with alkyl or alkylaryl *N*-substituents are promising semiconductors for the application in the n-channel OTFTs. However, larger core bisimides, including perylene bisimides, are difficult to solution process. Moreover, their LUMO level is slightly too high to assure their air operating stability. From this point of view arylene bisimides of the smallest core i.e. naphthalene bisimides show certain advantages. In particular, their LUMO level can be downshifted by ca.70 to 110 meV, without any lowering of their solubility, via replacing alkyl *N*-substituents with alkylaryl ones.[13]

Finally in all-organic transistors, prepared by solution processing, the selection of an appropriate polymeric dielectric is also of a crucial importance. A perfluorinated polymer with a trade mark of CYTOP, commonly used in this type of devices, has some advantages as far as processing conditions are concerned, however it is not the optimum choice for n-channel OTFTs and usually yields transistors showing inferior mobility as compared to those with an inorganic dielectric layer.[14,15] In this context poly-p-xylylene and its derivatives (xylylene polymers, parylenes) seem a promising group of materials. An obvious advantage of xylylene polymers in organic electronics, is a high degree of their purity compared to conventional polymeric materials. This purity results from their polymerization method which does not require the use of an external initiator but is initiated by a monomer molecule being in its excited diradical state.[16] In the case of OTFTs an important consequence of that difference is a relatively low number of localized states on the dielectric/semiconductor interphase.[17]

In this paper we describe the use of *N*,*N'*-bis(4-n-butylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (abbreviated as NBI-4-n-BuPh, see **Figure 2**), which is one of the naphthalene bisimides described in ref. [13], for the fabrication of n-channel OTFTs. Two important changes are introduced as compared to the previous studies on this type of compounds. First, for the deposition of the active layer we apply the zone casting method under ambient conditions. Second, we replace CYTOP as the gate dielectric by Parylene C. We demonstrate that these modifications allow us to fabricate n-channel transistors which reach the field effect mobility comparable to that reported for the best p-type channel devices with organic dielectric, and show the low turn-on voltage.

2. Results and Discussion

2.1. Structural and Morphological Studies of the Semiconductor Layers

The zone-cast NBI-4-n-BuPh films are ca. 300 nm thick and are continuous on a whole deposition area (ca. 2 × 7 cm). Polarized optical microscopy (POM) images, presented in **Figure 3**, demonstrate a clear optical birefringence and unidirectional orientation of on a macroscopic scale of the films.

Polarized UV-vis spectra of the zone-cast layers are shown in **Figure 4**. They exhibit a characteristic vibronic band at 383 nm originating from the 0–0 π–π^* transition in the naphthalene bisimide core. Two other transitions are also seen: 0–1 at 367 nm and 0–2 at 347 nm.[18–21] A strong dependence of these bands on the orientation of the layer in respect to the light

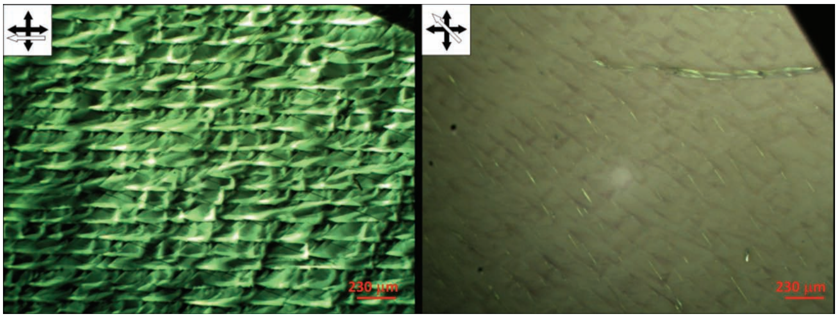

Figure 3. Polarized optical microscopy images of the NBI-4-n-BuPh layer zone-cast on a glass substrate. White arrows indicate the direction of the crystallization, black arrows show orientation of the polarization planes of the polarizer and the analyzers.

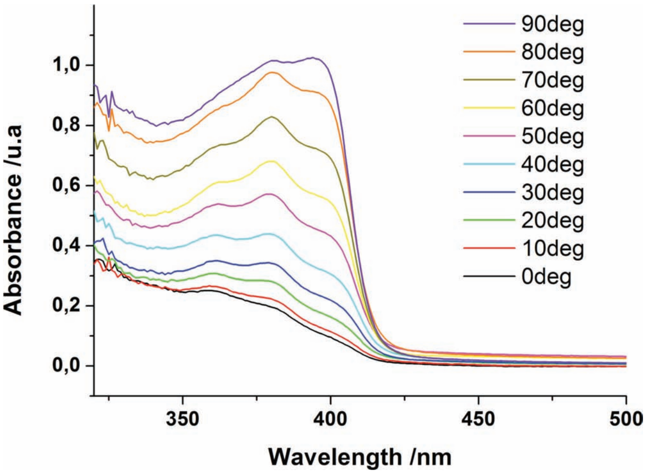

Figure 4. Polarized UV-vis spectra of the semiconductor NBI-4-n-BuPh film prepared by zone-casting technique on a glass substrate. 0° and 90° correspond, respectively, to perpendicular and parallel orientations of the polarization plane of the polarizer and the zone-casting direction.

polarization plane demonstrates that unidirectionally orientated molecules dominate in the deposited layer.

In **Figure 5** a representative X-ray diffractogram of an NBI-4-n-BuPh layer, zone-cast on glass is compared with the powder XRD pattern (inset graph) (both registered in the range 3–40°). It was determined, that in the zone-casted layer as well as in the powder sample, NBI-4-n-BuPh crystallizes in the monoclinic space group (P 1 2/m 1) with the following unit cell constants: a = 5.6550 Å, b = 3.0063 Å, c = 17.6808 Å, beta = 106.507°. From the peaks positions in the diffractogram for the zone-cast layer it can be deduced, that it exhibits a high degree of orientation: the dominating peaks belong to the same family of diffraction planes (00l) and the reflections of higher order, up to (007), are clearly visible. Additionally, taking into account the Bragg's Law ($2d\sin\theta = n\lambda$, $\lambda = 1.54$ Å) it is found, that the primary diffraction peak at $2\theta = 5.20°$ corresponds to a d-spacing of 17.0 Å, which is close to the c-axis unit cell; this indicates that the molecules are arranged almost perpendicular to the substrate surface. The very weak reflections, denoted as (001′) and (002′), which appear near the (001) and (002) reflections, respectively, correspond either to a different polymorphic form of the semiconductor studied or to a metastable orientation of the molecules, arising from a non-equilibrium state.[22]

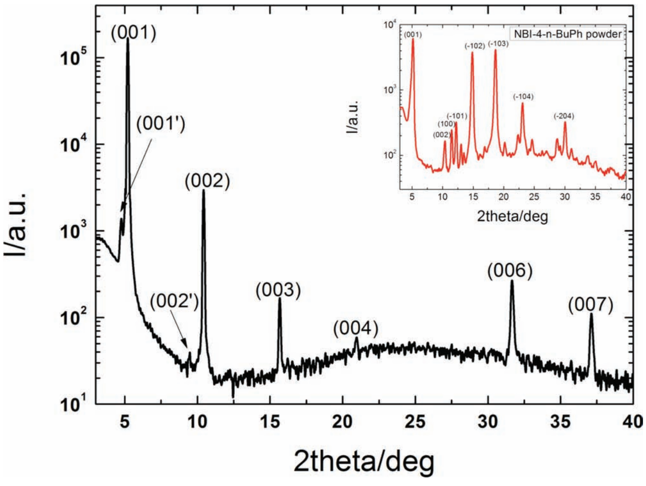

Figure 5. X-ray diffractogram of the NBI-4-n-BuPh layer zone-cast on a glass. In the inset, the X-ray diffractogram of the NBI-4-n-BuPh powder is shown for comparison.

2.2. Transistors Characteristics

Representative output and transfer characteristics of the transistors with the zone-cast NBI-4-n-BuPh layer are shown in **Figure 6**. The measurements were performed in two voltage ranges, for both gate U_{GS} and source-drain U_{DS} voltages: 0–50 V (Figure 6a,b) and 0–10 V (Figure 6c,d). The broader voltage range (up to 50 V) was tested for comparative reasons since the majority of characteristics reported in the literature for OTFTs were obtained at high voltages.[12,13] However we have found, that the devices reported in this paper can operate at much lower voltages, below 10 V, as seen in Figure 6c,d.

A pronounced increase of the drain current with increasing positive gate voltage indicates the electron-type of transport. The lack of any hysteresis in the output characteristics, measured for forward and backward sweeps, demonstrates that the electron trapping at the interface between the semiconducting layer and the Parylene C layer, if existing, is very weak. Deviations from linearity in the output characteristics are probably a consequence of a misalignment of the work function of the electrode metal and the electron affinity of the semiconductor layers.[23]

The charge carrier mobility and the on/off ratio were calculated from the saturation region, using the following equations:

$$\mu = \frac{2L}{WC}\left(\frac{\delta\sqrt{I_{DS}}}{\delta U_{GS}}\right) \tag{1}$$

$$\frac{\mathrm{ON}}{\mathrm{OFF}} = \frac{I_{DS\,\max}}{I_{DS\,\min}} \tag{2}$$

where L is the channel length, W is the channel width, C is the capacitance per unit area, I_{DS} is the drain source current, and U_{GS} is the gate voltage.

For the best device the charge carrier mobility was μ = 0.18 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$, and ON/OFF = 10^4, as determined from the characteristics measured in the range of 0–50 V (see Figure 6a,b). The characteristics measured in the range of 0–10 V (Figure 6c,d) yielded the charge carrier mobility, which was slightly (2–3 times) lower, and gave the same ON/OFF ratio. In comparison to the devices with the same NBI-4-n-BuPh semiconductor but prepared by the spin-coating method the charge carrier mobility was higher by almost three orders of magnitude.[13] Comparisons with transistors based on polycrystalline layers of NBI-4-n-BuPh, fabricated by sublimation technique, were also carried out. These devices showed a much lower mobility, below 10^{-3} $\mathrm{cm^2\ V^{-1}\ s^{-1}}$. The above outlined findings demonstrate the importance of the ordered supramolecular structure formation and the molecules orientation in the OTFT active layer for the efficient charge carrier transport. Even more impressive was the measured low turn-on-voltage, in the range

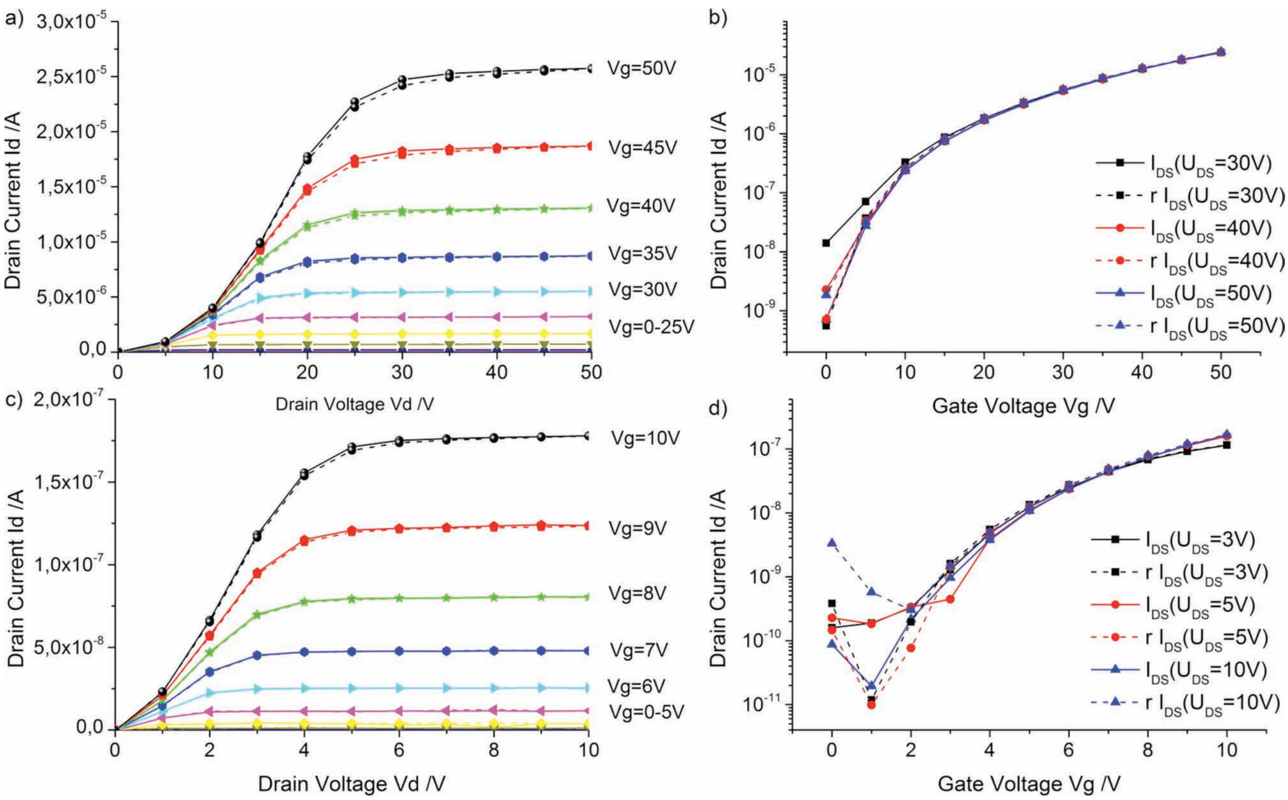

Figure 6. Output (a,c) and transfer (b,d) characteristics for a transistor with the zone-cast NBI-4-n-BuPh layer, measured in two different voltage ranges: a,b) 0–50 V; c,d) 0 –10 V. Solid lines denote characteristics measured with increasing source-drain voltage; broken lines denote characteristics measured with decreasing source-drain voltage. Channel length $L = 50$ µm, channel width $W = 4$ mm, dielectric constant of Parylene C = 3.15 and thickness of dielectric = 1 µm.

3–5 V, as seen in Figure 6c,d, which was comparable to that found for the best OTFTs with p-type channels.[24,25]

It is also worth to mention that in OTFTs with the bottom gate and top contact configuration, all measured electrical parameters were significantly worse than in the case of the top gate bottom contact device, described above. In particular, the charge carrier mobility was ca. two orders of magnitude lower, the turn-on voltage was higher (>30 V) and the ON/OFF ratio was only ca. 10.

The zone-casting technique allows to produce devices with reasonable reproducibility; the average values of main OTFT parameters for 30 transistors are: $\mu = 5 \times 10^{-2}$ cm^2 V^{-1} s^{-1}; ON/OFF = 10^3; and turn-on voltage = 4 V. From the practical point of view their remarkable long-term environmental stability is of crucial importance: the devices stored in air for over three months exhibited practically unchanged main electrical parameters. The measured changes in the charge carriers mobility and the turn-on voltage were below 10%.

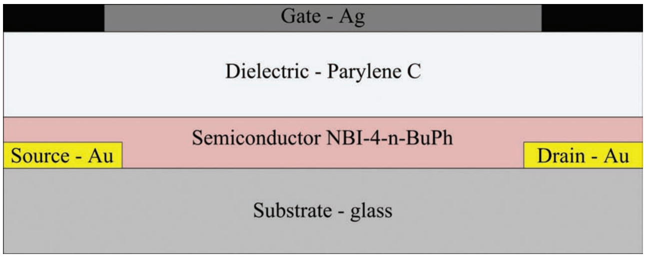

Figure 7. Schematic structure of the fabricated OTFT.

3. Conclusions

To summarize, we have demonstrated the importance of a strict control of the active layer supramolecular organization in the fabrication of high performance organic thin film transistors. Application of the zone-casting processing technique to the fabrication of n-channel transistors based on the solution processable and air stable semiconductor, namely *N,N′*-bis(4-n-butylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,4:5, 8-bisimide (NBI-4-n-BuPh), results in an improvement of the charge carriers mobility by almost three orders of magnitude and in lowering of the threshold voltage by one order of magnitude as compared to the transistors with the same semiconductor deposited by spin coating or by sublimation. This was possible through a processing induced long range alignment of the semiconductor molecules in the layer, as evidenced by UV-vis polarized spectra and by X-ray diffraction investigations. In addition, Parylene C deposited as the gate dielectric seems to be especially suitable material for the top-gate configuration because it causes no damage to the semiconductor structure, and additionally serves as a protective layer.

It should be pointed out, that the zone-casting technique is probably too slow to be implemented for a large-scale production of electronic devices. However, its main concept i.e., application of a concentration gradient in the meniscus as a driving force for unidirectional crystallisation, can be applied in the inkjet printing techniques, for example when the droplet is deposited asymmetrically on the OTFT channel. The processes occurring in such meniscus are very complex, with competing the Marangoni and convective flows influencing the nucleation process. Therefore, further investigations are needed in order to understand and control these phenomena.[27]

The basic parameters calculated for OTFTs with zone-cast NBI-4-n-BuPh layer: $\mu = 0.18$ cm^{2}V^{-1}s^{-1}, ON/OFF = 10^4 and turn-on voltage <5 V, are comparable to those reported for the best p-type channel devices with organic dielectric. In particular the low turn-on-voltage for OTFT with n-type channel gives possibility to produce the complementary CMOS-like devices which will work in voltage range of 3–10 V in ambient conditions.

4. Experimental Section

Materials: *N,N′*-bis(4-n-butylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (NBI-4-n-BuPh) was synthesized from naphthalene dianhydride and n-butylphenylamine using the procedure described in ref. [13] Its first reduction potential, as determined from cyclic voltammetry, was –1.035 V vs Fc/Fc$^+$, which corresponds to the electrochemically determined LUMO level of –3.77 eV, a promising value for its stability in ambient processing conditions.

Transistors Fabrication: **Figure 7** shows a schematic structure of a bottom contact and top gate OTFT in which the active layer was deposited by zone casting. The device was fabricated in six steps. First, 50 nm thick gold drain (D) and source (S) electrodes were evaporated on a glass substrate, yielding, after patterning, a channel width of 4 mm and a channel length of 30–100 μm. On the glass substrate with dimensions 2.5 cm × 7.5 cm usually 18 pairs of drain and source electrodes were evaporated. Then, a solution of NBI-4-n-BuPh in chlorobenzene was cast through the flat nozzle onto the moving glass substrate; the casting direction was along the channel length. In order to get a continuous, highly ordered crystalline layer of NBI-4-n-BuPh several parameters of the zone-casting procedure had to be optimized: concentration and temperature of the solution, rate of solution supply, height of the meniscus, temperature and moving speed of the substrate. The prepared layers, ca. 300 nm thick, were then dried in vacuum at 100 °C for 4 h with the goal of complete removal of the solvent. Then, as the dielectric gate material, Parylene C was deposited using the procedure described elsewhere.[26] The thickness of the dielectric layer was 1 μm. The silver gate electrode (100 μm thick) was vacuum deposited on the top of the dielectric layer.

Measurements: NBI-4-n-BuPh layers zone-cast on glass or quartz substrates, which were not covered with electrodes, were examined using polarized optical microscopy (POM) in the light transmission mode. The polarized UV-vis absorption spectra of these films were measured on a Varian Cary 5000 spectrometer. X-ray diffraction (XRD) investigations were performed for NBI-4-n-BuPh layers zone-cast on a glass substrate using a D-5000 Siemens diffractometer equipped with a conventional Cu Kα source, a reflectometry sample stage (RSS) and a Goebel mirror. The measurements were carried out at room temperature.

The electrical output and transfer characteristics of the transistors were measured in air, using needle electrodes and circuits with voltage/current sources and electrometers (Keithley 2410). The gate voltage U_{GS} was applied in two ranges: 0–10 V and 0–50 V; the source-drain voltage U_{DS} was also applied in two ranges: 0–10 V with a step $\Delta U_{DS} = 1$ V, and 0–50 V with a step $\Delta U_{DS} = 5$ V.

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