Physics of organic-organic Interfaces
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Chapter 3

Effect of Supramolecular Organization on Field Effect Transistor Electrical Performance

In the first part of this chapter, we report on bottom-contact n-channel organic field effect transistors (OFETs) based on spin-coated films of N,N’-1H,1H-erfluorobutyl dicyanoperylenediimide (PDIF-CN$_2$). We found these devices to exhibit a saturation-regime mobility of 0.15 cm$^2$ V$^{-1}$ s$^{-1}$ in vacuum and good air stability, which we attribute to the high crystallinity and to the edge-on orientation promoted by the thermal treatment, as shown by confocal laser microscopy. In the second part, we compare the performance of a PDIF-CN$_2$-based transistor with a transistor based on N,N-bis(n-octyl)-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI8-CN$_2$). The fluorocarbon functionalization of the aromatic core resulted in an electron mobility one order of magnitude higher than the hydrocarbon-functionalization. Time-resolved spectroscopy allows attributing this increment to a higher degree of co-facial arrangement of the fluorinated molecules. This supramolecular arrangement enhances the π–π overlap leading to more efficient electron transport.

3.1 Introduction

OFETs have attracted considerable attention for their potential use in flexible, large area and low cost electronic devices such as radiofrequency identification tags, display drivers, smart cards and sensor arrays.\(^\text{[1-6]}\) For the realization of organic complementary metal oxide semiconductor circuits (O-CMOS),\(^\text{[7,9]}\) which are the basic elements of these devices, both p-type and n-type OFETs are required. Most studies so far have been focused on the development of p-channel semiconductors, and excellent field-effect characteristics with mobilities up to 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\) have been reported.\(^\text{[10-12]}\) However, fewer high performing n-type materials are available due to low stability and limited processability. Therefore, the development of new materials for n-channel organic transistors is crucial for the application of organic electronics in commercially relevant products.

So far there have been few reports on high performance n-type OFETs\(^\text{[13-15]}\) notable among them, the perylene alkylidimide (PDIR) family holds the distinction of having one of the highest n-type mobilities known, 0.2–0.6 cm\(^2\)V\(^{-1}\)s\(^{-1}\), uncorrected for contact resistance and 1.7 cm\(^2\)V\(^{-1}\)s\(^{-1}\) when corrected.\(^\text{[16-18]}\) In addition to these outstanding electrical properties reported for vapour deposited films, PDIR-based materials, particularly those core-functionalized with cyano groups (PDIR-CN\(_2\)), are promising materials for electronic and optoelectronic applications due to their ability to yield high performing semiconductor films from solution and to their air-stable device operation.\(^\text{[19-21]}\) Solution processability is a key factor for the realization of OFETs through inexpensive, low temperature fabrication techniques envisioned for printed electronics. Both the film forming properties and the ambient stability of these molecules arise from the cyano functionalization of the perylene core which increases the solubility by decreasing the core planarity and stabilizes the charge carriers by lowering the energies of the lowest unoccupied molecular orbital that is associated with electron transport.\(^\text{[22]}\)

3.2 Fluorocarbon functionalized pelyrene: annealed versus not-annealed

Here, we report the realization of bottom-contact bottom-gate OFETs based on spin-coated films of N,N'-1H, 1H-perfluorobutyl dicyanoperylenecarboxydiimide (PDIF-CN\(_2\)). PDIF-CN\(_2\)-based OFETs were previously fabricated by semiconductor vapour deposition, and reached mobilities of ~0.5 cm\(^2\)V\(^{-1}\)s\(^{-1}\).\(^\text{[23]}\) The corresponding N-hydrocarbon-functionalized perylene, PDIR-CN\(_2\) (R=n-octyl) exhibits high mobility, environmental stability, and solution processability.\(^\text{[17]}\)
as recently demonstrated with the fabrication of an OFET via microinjector patterning of the semiconductor.\textsuperscript{[20]} However, fluorocarbon- versus hydrocarbon-functionalization of aromatic cores usually leads to far less processable materials in conventional organic solvents.\textsuperscript{[24]} We report on the properties of PDIF-CN\textsubscript{2}, which combines solution-processability characteristics and excellent semiconductor properties with electron mobilities of up to 0.15 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} in vacuum. This high mobility value is obtained only after a thermal annealing of the spin-coated films, resulting in an enhanced highly crystalline organization of the molecules. Remarkably, PDIF-CN\textsubscript{2} devices exhibit outstanding mobilities and substantial stability in ambient conditions. Electron mobilities of ~0.08 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} are still measured after 20 days of continuous exposure to air. Furthermore, an almost complete recovery of the mobility is obtained by retesting the device under vacuum.

3.2.1 Results and discussion

The output and transfer characteristics of a bottom-contact PDIF-CN\textsubscript{2} OFETs fabricated in this study, with a channel width (W) of 10 mm and a channel length (L) of 2.5 μm, are shown in Figure 3.1(a) and (b). OFET fabrication begins with the definition of the Au source and drain contacts on top of the Si (gate)-SiO\textsubscript{2} (insulator) substrate using conventional photolithography techniques. These substrates were treated with both hexamethildisilazane (HMDS) and 3,5-bis(trifluoromethyl)thiophenol prior to semiconductor-layer deposition. The former reagent passivates the gate insulator surface, whereas the latter tunes the energy band line-up at the contact–semiconductor interface, favouring electron injection and transport. By comparing the shape of the output curves at low drain voltage (V\textsubscript{D}) for samples fabricated with and without contact thiol treatment, we observed that the current is less injection-limited when the substrates undergo this treatment. Note that the SiO\textsubscript{2} HMDS treatment provides a homogeneous hydrophobic surface on which the supramolecular organization of the semiconductor is enhanced.\textsuperscript{[25]} The semiconductor film was spin-coated on the insulator/contact surface using a chloroform solution of PDIF-CN\textsubscript{2}. The devices were then annealed at 110º C in a vacuum oven for 60 min, and finally tested. Transistors measured under vacuum exhibit a saturation-regime mobility of 0.15 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, a threshold voltage of -5.6 V (V\textsubscript{D}=50 V), and I\textsubscript{on}/I\textsubscript{off} ratio >10\textsuperscript{3}. This is one of the highest n-channel OFET mobilities reported to date for solution-processed bottom-contact devices with a sub-10 μm channel length. The pristine devices exhibit poor performances, with mobilities of ~0.002 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}. However, after annealing, both the drain current (I\textsubscript{D}) and the electron mobility increase by two orders of magnitude.
To rationalize the variation in the electrical characteristic upon annealing, the semiconductor-film morphologies were investigated by atomic force microscopy (AFM) and confocal laser microscopy (CLM). As observed recently for PDIR-CN$_2$,\textsuperscript{[26]} by using a volatile, fast-evaporating solvent such as chloroform, the semiconductor molecules do not have enough time to reorganize on the dielectric surface during film formation. Consequently, poor microstructural order and unoptimized film morphologies are achieved, as evidenced by the AFM image of Figure 3.2(a). In fact, here the pristine-semiconductor-film morphology is characterized by protruding features with an average RMS roughness of ~30 nm. In addition to eliminating residual solvent, oxygen, and moisture, the thermal treatment promotes an efficient microstructural reorganization of the film. As seen in Figure 3.2(b), after thermal annealing, the PDIF-CN$_2$ film is smooth and uniform, exhibiting small rounded protrusions with an average RMS roughness of ~1.5 nm (Figure 3.2(b)). The film roughness is comparable to that of the substrate.

The differences observed in the optical microscopy images of the PDIF-CN$_2$ film and in the photoluminescence images obtained by CLM, before and after annealing, provide further demonstration of the enhanced order of the annealed films. The wide-field microscopy image (Figure 3.3(a)) shows that the pristine film, before annealing is inhomogeneous. When excited at 514 nm (Figure 3.3(b)), the film exhibits an intense photoluminescence emission. This is due to poor film crystallinity, or small microcrystalline domains oriented randomly with respect to the substrate.
However, after annealing of the film, the wide-field image acquired under the same conditions appears completely different (Figure 3.3(c)), with the film surface becoming smooth and transparent to the impinging light. In addition, the photoluminescence emission intensity of the thermally treated sample from the region within the device channel measured under the same conditions of the non thermally treated sample is strongly reduced (Figure 3.3(d)). This is an indication of the greatly improved molecular order (Figure 3.3(d)). In fact, these data indicate an edge-on orientation of the PDIF-CN$_2$ molecules, which causes a weaker coupling between the transition dipole moment of the molecules and the electric field of the impinging laser beam. This results in a reduced absorption of the light (Figure 3.3(c)), and consequently in a weaker photoluminescence emission (Figure 3.3(d)). The edge-on molecular orientation on the dielectric surface is fundamental in order to achieve efficient OFET charge transport.\cite{27} In recent studies on vapour-deposited perylene derivatives\cite{23,17} the good charge transport properties of fluorinated compounds were attributed to an optimal orientation of the molecular long axes in respect to the substrate, and to an increased intermolecular π–π overlap. These data are in agreement with our results based on confocal laser microscopy. We conclude that in our PDIF-CN$_2$ spin-coated films, both high molecular order and minimization of surface irregularities are responsible for the increased electrical performances.
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Figure 3.3. Wide-field microscopy images of the spin-coated PDIF-CN$_2$ (a) directly after the deposition and (c) after the annealing process at 110ºC in a vacuum oven for 1 h. Confocal fluorescence images of the spin-coated PDIF-CN$_2$ (b) directly after the deposition and (d) after the annealing process at 110ºC in a vacuum oven for 1 h.

After understanding the effect of annealing, the performance and stability of PDIF-CN$_2$ transistors in ambient conditions were monitored, immediately after air exposure and as a function of the exposure time (Figure 3.4). For these devices, the electron mobility decreased from 0.15 cm$^2$V$^{-1}$s$^{-1}$ (vacuum) to 0.14 cm$^2$V$^{-1}$s$^{-1}$ (air) immediately after breaking the vacuum in the measuring chamber. After 60 h of continuous air exposure, the device mobility approached a value of ~0.08 cm$^2$V$^{-1}$s$^{-1}$ and did not decrease further even after twenty days from the initial measurement. No substantial change was recorded over time in the $I_{On}/I_{Off}$ ratio, which remained at a value $>10^3$. A similar mobility versus air-exposure-time dependence was recently reported for a series of core-cyanated perylene-based OFETs fabricated from vapour phase.$^{[21]}$ In this paper the same mobility trend is observed for every compound, regardless of the different nitrogen functionalization of the cyanated core and the degree of molecular order. These data differ from previous results on air-stable fluorinated perylenes, which attributed the air stability to the close packing of the fluoroalkyl substituents. Therefore, the exact physical and chemical mechanisms that are responsible for the organic-semiconductor degradation are still only partially understood.

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Figure 3.4. Time-dependent variation of the mobility and of the $I_{on}/I_{off}$ ratio during exposition to air. The gray square represents the mobility recovery after retesting the sample under vacuum.

A better understanding of air-stability properties of PDIF-CN$_2$ was obtained in our experiments by re-testing the same device under vacuum after ~400 h of exposure to air. In this sample, we observed an almost total recovery of the starting performance, registering a mobility of 0.135 cm$^2$V$^{-1}$s$^{-1}$. This is only slightly lower than the initial value measured under vacuum (0.15 cm$^2$V$^{-1}$s$^{-1}$). These results confirm that the mobility erosion cannot be ascribed to semiconductor chemical degradation, but instead to the physisorption of atmospheric gases at the material grain boundaries acting as electron traps.[6] In this case, the recovery effect should depend on the film morphology and on the dielectric surface treatment, as was observed for other semiconductors.[29] A mechanism based on the formation of a metastable complex between n-type semiconductors and oxygen has been proposed in order to explain similar behaviour in a perylene derivative.[30]

3.2.2 Conclusions

We have demonstrated that PDIF-CN$_2$ is a material that combines high solubility, elevated electron mobility, and good air stability. We fabricated bottom-contact n-channel OFETs that exhibited a saturation-regime mobility of ~0.15 cm$^2$V$^{-1}$s$^{-1}$ (0.08 cm$^2$V$^{-1}$s$^{-1}$ in ambient), a threshold voltage of -5.6 V, and an $I_{on}/I_{off}$ ratio greater than $10^3$ by employing a simple and inexpensive solution-deposition technique, followed by a thermal post-deposition treatment. These performances, which are among the highest ever reported for a bottom-contact configuration with a short channel length (2.5 µm), are attributed to the high crystallinity and to the
edge-on orientation promoted by the thermal treatment, as shown by CLM. Good air stability is also observed, since the devices still show a mobility value of \(-0.08 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) after 20 days of continuous exposure to air. The robustness of the solution-processed PDIF-CN\(_2\) is remarkable, considering that an almost total recovery of the initial mobility is obtained by retesting the device under vacuum.

### 3.3 Fluorocarbon- versus hydrocarbon-functionalized perylene

The N-hydrocarbon-functionalized perylene: N,N'-bis (n-octyl)-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI8-CN\(_2\)) exhibits high mobility, environmental stability and solution processability as recently demonstrated by the realization of an OFET via the micro-injector patterning of the semiconductor.\([20]\) This compound deposited by evaporation reached an electron mobility value of 0.13 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\). PDIF-CN\(_2\)-based OFETs with mobility as high as 0.64 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) were previously fabricated by semiconductor vapor deposition.\([16]\) Usually fluorocarbon- versus hydrocarbon-functionalization of the aromatic cores leads to far less processable materials in conventional organic solvents.\([24]\) However, PDIF-CN\(_2\) is unique since it combines solution processability characteristics and excellent semiconductor properties with electron mobilities up to 0.15 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) when deposited by spin-coating, as presented in paragraph 3.2. In this part of the chapter, we show that fluorocarbon functionalization of the aromatic core leads to an improvement in the electron mobilities by one order of magnitude compared to the hydrocarbon-functionalization for film processed from solution. OFETs realized by spin coating with PDI8-CN\(_2\) reached an electron mobility of 1.3x10\(^{-2}\) \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) with an \(I_{\text{on}}/I_{\text{off}}\) current ratio of 7.3x10\(^3\), while the ones realized with PDIF-CN\(_2\) exhibited electron mobilities up to 1.33x10\(^{-1}\) \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) and an \(I_{\text{on}}/I_{\text{off}}\) current ratio of 2x10\(^4\). Such a difference between the solution processed transistors is much higher than the difference reported for the vacuum processed devices. To explain this difference, we carried out both morphological and spectroscopic analyses on the spin-coated films of the two materials. By using time-resolved spectroscopy, we highlighted that the intermolecular interactions (excimer-like excitations) are more dominant in PDIF-CN\(_2\) than in PDI8-CN\(_2\). The face-to-face molecular organization responsible for the excimer formation is also the best intermolecular organization for high charge carrier mobility due to elevate \(\pi\)-\(\pi\) overlap, explaining the higher electrical performances of the fluorocarbon functionalized derivative.

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3.3.1 Results and discussion

The output and transfer characteristics of bottom-contact PDI8-CN$_2$ and PDIF-CN$_2$ OFETs with a channel width (W) of 10 mm and a channel length (L) of 3 µm are shown in Figure 3.5. Panels (a) and (b) present the transfer characteristics of the PDIF-CN$_2$-based transistor. The saturation mobility and the threshold voltage extracted from the plot of the square root of $I_D$ versus $V_G$ are $1.3 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ and 6 V, respectively. The current plotted in the semi-logarithmic scale shows that this OFET has an On/Off current ratio of $7.3 \times 10^3$, which is typical for cyanated PDI–based FETs with an unpatterned semiconductor layer.

![Figure 3.5](image)

Figure 3.5. (a) Output characteristic of 3 µm channel length PDI8-CN$_2$ OFET. Inset: chemical structure of PDI8-CN$_2$; (b) Transfer characteristic (L=3 µm, W=10000 µm) at $V_D = 80$ V, ($I_{on}/I_{off}$ ratio for $V_G = 80$ V / $V_G = -40$ V); (c) Output characteristic of 3 µm channel length PDIF-CN$_2$ OFET. Inset: chemical structure of PDIF-CN$_2$; (d) Transfer characteristic (L=3µm, W=10000 µm) at $V_D=80$. 

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When the perylene core hydrocarbon-functionalization is substituted by the fluorocarbon-functionalization there is an increment of one order of magnitude in the electron mobility. In Figure 3.5 (c) and (d), the transfer characteristics of the fluorinated compound PDIF-CN$_2$ are reported. The saturation mobility and the threshold voltage are $1.33 \times 10^{-1}$ cm$^2$V$^{-1}$s$^{-1}$ and 9.6 V, and the On/Off current ratio is $2 \times 10^4$. Further optimization of the fabrication process allowed obtaining a mobility of $1.5 \times 10^{-1}$ cm$^2$V$^{-1}$s$^{-1}$. The relative HOMO and LUMO energetic positions are crucial in determining the charge carrier stability in organic semiconductors. In the case of n-type organic materials, the lower the LUMO energy, the smaller should also be the bias required to inject the carriers, and as a consequence the electrons should be less susceptible to trapping, allowing for higher mobility values. For these two compounds, the LUMO energy positions estimated by solution cyclic voltammetry are very similar due to the identical conjugated core structure and the remote functionalization at the nitrogen atoms. Moreover, the difficulty in the conversion of the energy levels obtained by electrochemistry in solution with those of the materials in solid state, in proximity of the gold, does not allow to attribute the better FET performances of PDIF-CN$_2$ to the more favourable LUMO position.

![AFM images of the spin-coated films of (a) PDI8-CN$_2$, (b) PDIF-CN$_2$ after the annealing process at 110ºC in a vacuum oven for one hour (scan area 2.5 µm×2.5 µm with 512 points per line).](image)

To explain the difference in the electrical characteristics of the two compounds, the semiconductor film morphologies were investigated by atomic force microscopy (AFM). As reported recently for PDI8-CN$_2$ films fabricated using a volatile, fast-evaporating solvent such as chloroform, the semiconductor molecules do not have enough time to reorganize on the dielectric surface during film formation. Consequently, thermal annealing is necessary to promote an efficient microstructural reorganization of the film, as shown in the paragraph 3.2. Even after thermal treatment the PDI8-CN$_2$ film exhibits a morphology characterized by protruding features and with an average RMS roughness.
of ~10 nm, as shown in Figure 3.6(a). On the other hand, the morphology of the PDIF-CN$_2$ films shown in Figure 3.6(b) appears completely different. The AFM analysis highlights a much smoother and a more homogeneous surface with an RMS roughness of only ~1 nm and a developed connectivity between neighbouring domains. Since a smooth semiconductor film minimizes trap sites by reducing the number of grain boundaries, these data agree with the more efficient charge carrier transport. However, microscopically more precise information on the supra-molecular organization of the two compounds can be obtained by photophysical investigations.

![Figure 3.7. Time integrated photoluminescence spectra of PDIF-CN$_2$ and PDI8-CN$_2$ thin films spin-coated on a SiO$_2$ substrate. The blue dotted curves are the spectra of the two molecules in chloroform solution.](image)

The solid-state PL properties of organic molecules are extremely sensitive to the supramolecular arrangements. Figure 3.7 shows the time integrated emission spectra of PDIF-CN$_2$ and PDI8-CN$_2$ films carried out on the devices used for OFET measurements. Both materials show a strong red-shift of the thin film photoluminescence emission maxima compared to that of the isolated molecules as determined in a CHCl$_3$ solution (blue dotted trace in Figure 3.7). These data indicate strong solid-state intermolecular interactions. However, the greater red-shift emission for the PDIF-CN$_2$ film suggests that the molecular packing in the two cases is rather different as previously suggested for films grown by physical vapour deposition.

![Figure 3.8 (a) and (b) show the spectrally and time-resolved emission of PDIF-CN$_2$ and PDI8-CN$_2$ films, respectively. Both PL spectra consist of two components (centred at ~625 nm and ~700 nm) showing different time behaviour. Such a difference is highlighted by the strong red-shift of the spectrum obtained](image)
Figure 3.8. Intensity images of images of the spectrally and time-resolved photoluminescence spectra of PDIF-CN$_2$ (a) and PDI8-CN$_2$ (b) thin films (the intensity colour scale for the two image is the same). Colour rectangles delimit the temporal and spectral integration window over which the corresponding profile displayed on the right (spectra) and below (decay) are integrated. Right panels: emission spectra time integrated over the initial 0.2 ns after excitation (red) and between 1.2 ns and 4.2 ns (cyan). Bottom panels: Photoluminescence decays spectral integrated between 580 and 610 nm (green) and between 720 nm and 820 nm (orange).
integrating in time between 1.2 ns and 4.2 ns (cyan curve in the right panel of Figure 3.8 (a) and (b)) with respect to the spectrum acquired over the first 0.2 ns after excitation (red curve). The time behaviour of the shorter wavelength component (green curve in the bottom panels of Figure 3.8 (a) and (b)) shows a bi-exponential decay with similar time constants for the two materials; about ~90 ps and ~360 ps in the case of PDIF-CN$_2$, and ~150 ps and ~390 ps for PDI8-CN$_2$. The PL in this spectral range can be attributed to the radiative transition from the first singlet excited state to the ground state in the photoexcited molecular aggregate. The intermolecular interactions are responsible for the broadening and the strong red-shift of the singlet exciton transition compared to that of the isolated molecules. On the other hand, the bi-exponential and short PL decay time, compared to the ~4.7 ns long lifetime of the molecules measured in CHCl$_3$ solution (Figure 3.9), can be explained with the opening of new non-radiative decay channels in the solid state. The longer wavelength and spectrally broad emission band of PDIF-CN$_2$, centred at around 700 nm, decays exponentially with a lifetime of about ~2.6 ns (orange profile in the bottom panels of Figure 3.8 (a)). Instead, the decay integrated in the same spectral region for PDI8-CN$_2$ (orange profile in the bottom panels of Figure 3.8 (b)) is well described by a bi-exponential fitting function with amplitudes and time constant $A_1\approx0.54$, $\tau_1\approx330$ ps and $A_2\approx0.60$, $\tau_2\approx2.5$ ns.

![Figure 3.9. Photoluminescence dynamics detected at 535 nm of PDIF-CN$_2$ and PDI8-CN$_2$ in chloroform solution.](image)

The spectrally broad, featureless and slowly decaying component (similar in the two materials) can be attributed to the emission of an excimer of the molecular aggregate,[31] whereas the initial fast component (present only in the PDI8-CN$_2$ PL) can be attributed to the overlap with the singlet emission band, which is more
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dominant in this material. Excimer states are characterized by broad and featureless emissions exhibiting longer life times than singlet excitons, and are determined by the excited state delocalized over two or more molecules arranged cofacially.[32] Perylene systems are between the most notable examples of compounds showing excimer states.[32] The two semiconductors are characterized by a different contribution of the excimer state in the total photoluminescence. In fact, the longer lived component, centred at around 700 nm, is predominant in the emission spectrum of PDIF-CN₂, whereas it is less significant in PDI8-CN₂ with an amplitude of only 60%. The PL spectra of organic semiconductors are highly sensitive indicators of the intermolecular interactions,[27] as a consequence the stronger excimer emission of PDIF-CN₂ can be explained with a different supramolecular arrangement of the two materials in the spin-coated films. For PDI8-CN₂, the films fabricated by spin-coating are strongly inhomogeneous. After the thermal annealing process the molecules reorganize themselves forming relatively disordered micro-domains as testified by the rough morphology reported in Figure 3.6(a). Conversely, the fluorocarbon functionalized molecules reach a higher level of supra-molecular order after thermal annealing, testified by the stronger excimer emissions which indicate a higher degree of co-facial arrangement of the molecules in the film and by the extremely smooth morphology (Figure 3.6 (b)). The superior electrical performances of the device realized with PDIF-CN₂ are in agreement with this interpretation and underline the importance of achieving a large \( \pi-\pi \) overlap in order to maximize transport properties in organic semiconductors.

3.3.2 Conclusions

In conclusion, we report the FET performances of two perylene diimide derivatives, PDI8-CN₂ and PDIF-CN₂, and correlate them with the morphological and optical properties of the semiconductor film. Bottom contact OFETs realized with the two materials deposited by spin-coating show remarkable differences. The field effect mobility of the fluorinated compound (PDIF-CN₂) equal to \( 1.33 \times 10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) is one order of magnitude greater than the mobility obtained for the PDI8-CN₂, \( 1.3 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \). Both AFM morphological analysis and PL spectroscopic measurements confirm that the FET performance difference is due to improved packing of the fluorinated molecules which leads to an enhanced \( \pi-\pi \) overlap, and as a consequence to a higher mobility.
3.4 Experimental details

A heavily doped p-type Si substrate was used both as substrate and as gate electrode. The dielectric layer consisted of thermally grown SiO\(_2\) (200 nm) with a capacitance per unit area of 17 nF cm\(^{-2}\). Using conventional photolithography gold source and drain electrodes were defined in a bottom-contact configuration. A 10 nm layer of titanium was used as an adhesion layer for the gold (30 nm).

PDI8-CN\(_2\) and PDIF-CN\(_2\) are commercially available from Polyera Corporation under the trade name of ActivInk\textsuperscript{TM} N1200 and ActivInk\textsuperscript{TM} N1100. The solutions of PDI8-CN\(_2\) and PDIF-CN\(_2\) (5–6 mg/ml) were spin-cast from chloroform at 1500 rpm to form a 70–100 nm thick layer, on the bottom-gate bottom-contact substrates. Before use all solutions were filtered through 0.2 µm polytetrafluoroethylene (PTFE) syringe filters. After the deposition the substrates were annealed in a vacuum oven (~0 mbar) at 110 ºC for one hour.

All the substrates were first cleaned in an ultrasonic bath using acetone and isopropanol for 10 minutes each and then rinsed with deionized water. Then, they were cleaned with a UV–ozone treatment to remove organic contaminants from the surface. Prior to spin-coating the PDI8-CN\(_2\) and PDIF-CN\(_2\) solutions both hexamethyldisilazane (HDMS) and thiol treatments were performed. For the HDMS treatment a few drops of HDMS were loaded on top of the substrate. In the case of the thiol modification, the Si/SiO\(_2\) substrates were immersed in a 10 mM solution of 3,5-bis(trifluoromethyl) thiophenol in ethanol for one hour.

The transistor characteristics were measured in vacuum (~10\(^{-5}\) mbar) at room temperature using a Keithley 4200-SCS semiconductor parameter analyzer. The carrier mobility (\(\mu\)) was calculated from the drain-source current (\(I_D\)) versus the gate voltage (\(V_G\)) data in the saturation regime (\(V_D=80\) V) using the standard formula for field effect-transistors: 

\[
\mu = \frac{2L}{WC_{ox}} \left[ \frac{d(I_{DS})}{dV_{GS}} \right]^{1/2},
\]

where \(L\) is the channel length (3 µm), \(W\) is the channel width (10 mm), and \(C_{ox}\) is the gate dielectric capacitance (17 nF cm\(^{-2}\)). The \(I_{Dsh}/I_{Dth}\) ratio was calculated using \(I_D\) at \(V_G=60\) V/-40 V and \(V_D=50\) V. The values reported are the mean values obtained by testing 30 devices realized with the optimized process parameters (in total, 150 devices were tested in order to optimize the process). The average electron mobility obtained is (0.15±0.02) cm\(^2\)V\(^{-1}\)s\(^{-1}\).

Confocal microscopy measurements were performed using a Witec microscope. The sample was excited with the 514 nm line of an Ar+ laser coupled to the microscope with an optical fiber. The photoluminescence selected by a long pass filter was detected by a photomultiplier tube. For the spectrally and temporally resolved photoluminescence experiments, the samples were photoexcited in reflection geometry.
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