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Improved Performance of Organic Light-Emitting Transistors Enabled by Polyurethane Gate Dielectric

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ABSTRACT

Organic light-emitting transistors (OLETs) are multifunctional optoelectronic devices that

combine in a single structure the advantages of organic light emitting diodes (OLEDs) and organic

field-effect transistors (OFETs). However, low charge mobility and high threshold voltage are

critical hurdles to practical OLETs implementation. This work reports on the improvements

obtained by using polyurethane films as dielectric layer material in place of the standard

poly(methylmethacrylate) (PMMA) in OLET devices. It was found that polyurethane drastically

reduces the number of traps in the device thereby improving electrical and optoelectronic device

parameters. In addition, a model was developed to rationalize an anomalous behavior at the pinch-

off voltage. Our findings represent a step forward to overcome the limiting factors of OLETs that

prevent their use in commercial electronics by providing a simple route for low-bias device

operation.

KEYWORDS: OLETs, OLEDs, OFETs, Organic electronics, Organic Semiconductor,

Polyurethane.

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I. INTRODUCTION

Organic light-emitting transistors (OLETs) are multifunctional optoelectronic devices that combine in a single device the advantages of light emission of an organic light emitting diode (OLED) and the electrical switching characteristics of an organic field-effect transistor (OFET)^{1,2}. Due to these functionalities, OLETs offer the opportunity to simplify circuit design and considerably increase the number of new applications of organic semiconductor-based devices, including the highly desirable flexible integrated optoelectronics, fully organic active matrix displays, electrically driven lasers, nanoscaled light-sources etc^{3,4,5,6,7}. In a simplified picture, the work and operation of a unipolar OLET can be viewed as a traditional OFET in its electrical characteristics, with a conduction channel formed by majority charge carriers. In addition, depending on the applied bias, the injection of the minority charge carrier can occur, promoting radiative recombination at the proximity of the drain electrode, resulting in a controlled emission of light.

Two of the greatest challenges in the development of all organic-based integrated circuits are the relatively low mobility and the high threshold voltage characteristics of OFETs and OLETs when compared to traditional silicon-based electronics. In the last years, considerable efforts have been made to increase charge-carrier mobility and decrease operating voltages aiming at decreasing power consumption and improving operational stability. In OFETs, and consequently in OLETs, charge mobility greatly depends on the degree of molecular (structural) and energetic order, the latter being critically affected by semiconductor/dielectric interface morphology. In order to minimize potential energy barriers and facilitate charge carrier transport low levels of molecular and energetic disorder are required^{8,9,10}.

Several dielectric materials were thoroughly characterized in OLET devices^{11,12,13}, resulting in both SiO₂ and poly(methyl methacrylate) (PMMA) as benchmark dielectrics, with k = 3.9 and k = 3.0 to 4.5, respectively^{14,15,16}. The use of these dielectric materials results in high operating voltages, *i.e.*, more than 20 V threshold voltage and operating voltage in the range of 80 to 100 V. Several approaches have been explored to allow for low-voltage operation, from vertical geometry OLETs¹⁷ which, unfortunately, present unstable OFF state and high leakage current density, to passivation techniques¹⁸, through employment of high-k dielectric layers¹⁹. In fact, the most common approach to this problem has been to use high-k metal oxides with a large

capacitance density such as Al₂O₃, HfO₂, TiO₂, and ZrO₂^{20,21,22,23}. However, the interface between organic semiconductors and high-k dielectrics is difficult to be controlled and optimized. Indeed, it typically contains deep traps due to dipolar chemical groups and hydroxyl groups (-OH) at the interface. They both act as localized defects that trap charge carrier, lower their mobility and hinder the formation of the charge transport channel, thereby degrading the electrical behavior of the device in terms of operational stability, low mobility and undesired hysteresis^{24,25,26}.

The detrimental high polarization at the dielectric/organic semiconductor interface can be avoided by using low-k dielectrics, as shown by previous works¹⁶ and recently by our group²⁷ in which polyurethane (PU) was used as gate dielectrics (k = 3.0) combined with regioregular poly(3-hexylthiophene) (rrP3HT) in a bottom-contact top-gate OFET. As these works demonstrate, depending on the chemical nature of the dielectric, it can induce a different behavior from that seen in the benchmark (PMMA). In addition, PU has also been used as dielectric layer in OFETs ^{15,28,29} and as substrates for OFETs³⁰, AMOLED display panels³¹ and several stretchable devices³².

In this work, we report the fabrication of an OLET using PU (PU-based OLET) as dielectric layer and 2,7-dioctyl[1]benzothienol[3,2-b][1]benzothiophene (C8-BTBT) as small molecule organic semiconductor combined with an emission layer of tris(4-carbazoyl-9-ylphenyl)amine (TCTA) doped with fac-tris[2-phenylpyridinato-C2,N]iridium(III) (Ir(ppy)₃). Our results show that the PU dielectric layer enhances the device's performance and decreases operating voltages in comparison to the benchmark device based on PMMA. The measured electrical and optical properties of PU-based OLET shows great improvement when compared to PMMA-based OLET, with lower threshold voltage and subthreshold swing together with higher mobility and optical power output. Also, our analysis shows that changing the dielectric layer greatly decreases the number of traps at the semiconductor/dielectric interface. A model is also presented to better understand an anomalous behavior (lump) that is observed in the output characteristic curves near the pinch-off voltage.

II. MATERIALS AND METHODS

Polyurethane was used as dielectric layers to make bottom-gate/top-contact devices (Figure 1A). Both were spin-coated on clean patterned glass/ITO substrates (Lumtec, 15Ω /sq). PU (Ellastolan® PU 85A10 from BASF) (Figure 1D) is made up of block copolymers with alternating hard segment (based on 4,4 methylene diphenyl diisocyanate) and soft segment (based on and 1,4

butane diol) without the addition of plasticizers. PU was dissolved in 1,4-dioxane and spin-coated to have 700 nm as final thickness, following the procedure in²⁷. PMMA was used as reference dielectric and all comparison data are consistent with the literature³³.

The semiconducting layers and Ag electrodes were deposited via thermal evaporation (base pressure 10^{-6} torr). The rigid-band energy diagram is shown in Figure 1B. First, a 35 nm-thick C8-BTBT (Sigma-Aldrich) layer was deposited at 0.1 Å/s rate, then the 7% wt doped 60 nm-thick host-guest emissive layer was deposited using $Ir(ppy)_3$ (Sigma Aldrich) as guest and TCTA (Sigma Aldrich) as host. Finally, 70 nm-thick Ag electrodes were deposited (0.5 Å/s) using interdigitated shadow masks (L = 70 μ m and W = 84 mm) (Figure 1C). The molecular structures of the different materials are shown in Figure 1D.

The devices were encapsulated inside a nitrogen-filled glove-box with glass lids and epoxy glue. Once encapsulated, the electrical measurements were performed in ambient conditions using a probe station from Cascade Microtech model EPS150X together with a Keysight B2912A semiconductor analyzer using its own software for data acquisition. The light output was obtained using a Newport 818-UV photodiode in direct contact with the glass substrate.

The EQE was measured by collecting the emitted photons using the same calibrated silicon photodiode (Newport 818-UV) together with its known responsivity. Although this measurement could underestimate the total power³⁴, it accurately measures the relative efficiency between devices. EQE was then calculated by the photodiode current combined with photodiode spectral responsivity, source-drain currents and emission spectra of the devices as per standard literature methods³⁵.

The photoluminescence (PL) and the electroluminescence (EL) spectra were obtained using a spectrofluorometer from Photon Technology International (PTI) Quanta Master model 40. The thickness of each layer was measured by profilometer Veeco Dektak 150 and Atomic Force Microscopy (AFM) measurements were performed using a NT-MDT Old Smena. Images were taken in semi-contact mode with a 10 nm radius tip at a resonance of 330 MHz.

Density functional theory (DFT) was used to investigate the molecular properties of the organic compounds at atomic level, such as dipole moment. Calculations were performed using the hybrid functional B3LYP (Becke three-parameter Lee-Yang- Parr)³⁶ along with a split-valence double-zeta polarized based in Gaussian type orbitals (6-31G (d, p))^{37,38} present in Gaussian 03 package.

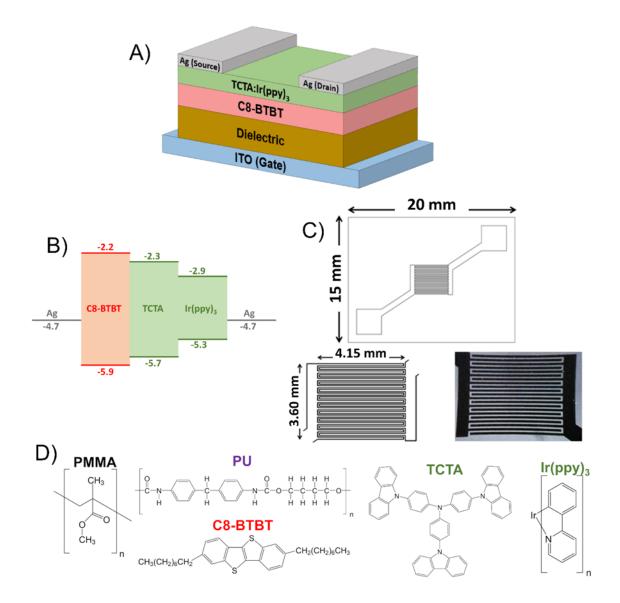


Figure 1. A) Schematic illustration of OLET architecture used, B) energy level diagram, C) interdigitated mask and D) molecular structure of PMMA, PU, C8-BTBT, TCTA and Ir(ppy)₃.

III. RESULTS AND DISCUSSION

a. Morphological Analysis

For the development of high quality OLETs, the solid-state organization and the surface quality of each layer of the device are of pivotal importance to ensure an efficient OLET operation providing state-of-the art performance. Accordingly, morphological analyses were carried out to

investigate the surface of the PU dielectric layer and its influence on the solid-state organization of the overlying layers.

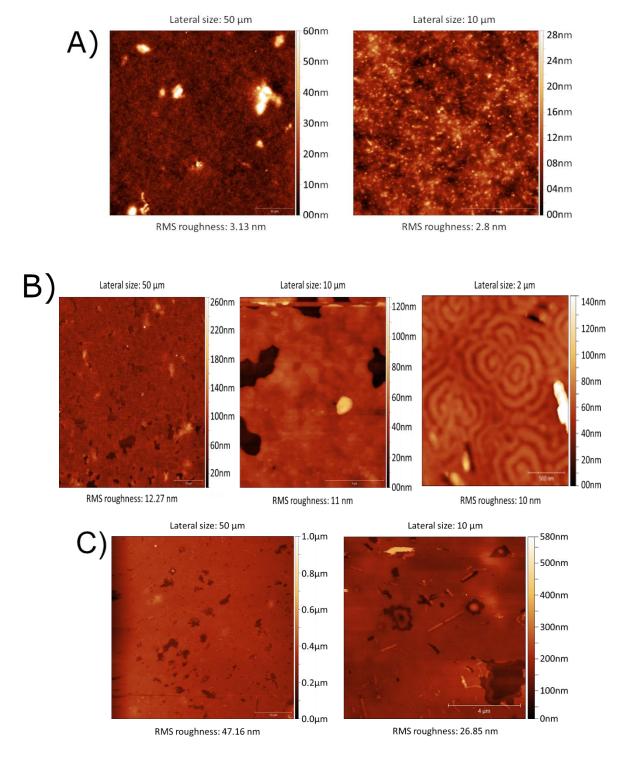


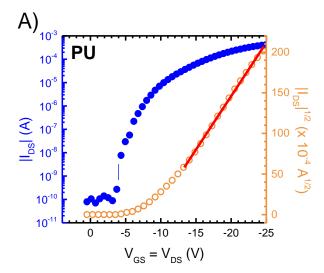
Figure 2. AFM images for A) PU, grown on glass, B) C8-BTBT, grown on PU and C) TCTA:Ir(ppy)₃, grown on C8-BTBT.

PU's surface was analyzed through AFM and the morphology is shown in Figure 2A. The AFM images do not show significant cracks or pin-holes over different areas, in agreement with the literature¹⁵. The surface morphology for the semiconducting layer C8-BTBT and for the emission layer TCTA:Ir(ppy)₃ were also analyzed, and the morphologies are shown in Figure 2B and Figure 2C, respectively.

In particular, C8-BTBT shows the expected layer-by-layer growth modality^{19,39} when deposited on top of PU. Although an increase in surface roughness and surface defects can be observed after the deposition of C8-BTBT and TCTA:Ir(ppy)₃ onto the PU layer, negligible influences on the quality of both semiconductor and emissive layers are expected, as highlighted by the state-of-the-art characteristics of the corresponding OLETs (vide infra).

b. Device's characterization

Figure 3A shows the behavior of drain-source current (I_{DS}) in locus mode for the PU-based OLETs, where both drain-source voltage (V_{DS}) and gate-source voltage (V_{GS}) are swept at the same time, keeping $V_{DS} = V_{GS}$. This type of characterization ensures saturation regime throughout the entire sweep, maintaining the pinch-off near the drain electrode⁴⁰.



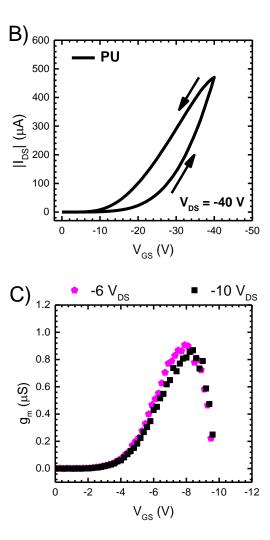


Figure 3. A) Locus characteristics (filled symbols) and linear fit (open symbols) for PU-based OLETs. B) Cyclic transfer characteristics curve for PU-based OLETs, black arrows indicate the sweep voltage direction. C) Transconductance curve for PU-based OLET.

Experimental parameters and the results of this analysis are summarized in Table 1. If compared to PMMA-based devices, the use of PU as a dielectric material shows a significant improvement of the OLET characteristics.

Specifically, a five-times decrease of threshold voltage is observed. Moreover, the emitted optical power and ON/OFF ratio are increased while the subthreshold swing (SS) value is reduced more than four times with a consequent reduction over three times in the density of interfacial traps (see electrical characterization). Interestingly, mobility and external quantum efficiency (EQE%) are doubled.

Table 1. Optoelectronic parameters of PU-based OLETS and PMMA-based OLETs. All electrical measurements represent an average over ten performing devices. *Values taken from³³.

	PU	PMMA
$C_D \left(\mu F/m^2\right)$	51±2 ²⁷	40 ± 2^{27}
m (D/Å)	0.178	0.442
$V_{th}\left(V\right)$	-6.5 ± 0.3	- 34*
SS (V/dec)	-0.84 ± 0.02	-3.90 ± 0.05 *
N^1 trap (x10 ¹¹ cm ⁻²)	2.55	8.50*
N^2 trap (x10 ¹¹ cm ⁻²)	4.21	16.20*
μ (cm ² /Vs)	0.4 ± 0.2	0.19*
Optical power at -70V (µW)	5 ± 1	0.15*
ON/OFF	>106	>106*
EQE (%)	$0.04 \text{ (V}_{DS} = \text{V}_{GS} = -60\text{V})$	$0.02 (V_{DS} = V_{GS} = -100V) *$

The optimization of the threshold voltage parameter is extremely important for a device to work at low voltages, since it provides the minimum V_{GS} needed to create a conducting channel between the source and drain terminal. Another important parameter that must be optimized for the device to have better performance at low working voltages is subthreshold swing (SS). The SS parameter measures how fast the device change from OFF to ON state and it can be extracted from locus electrical curve using the relation $SS = dV_{GS}/d(log|I_{DS}|)$. In literature, the significant improvements in V_{th} and SS measured can be attributed to a decrease in charge density at the dielectric/semiconductor interface⁴¹. In this work, two methods were used to estimate the density of traps in the devices. 1) In the first method, it is assumed that the charges are accumulated and trapped close the dielectric/semiconductor interface of the OLET, thus the value of V_{th} is equivalent to trapped charge on one side of an equivalent capacitor^{42,43}. 2) In the second method, it is estimated via Subthreshold Swing. These two methods can be written as below.

Method 1
$$N_{\rm trap}^1 \approx \frac{C_D}{q} V_{\rm th} \tag{1}$$

Method 2
$$N_{\text{trap}}^2 \approx \frac{C_D}{q} \left[\frac{qSS}{k_b T \ln 10} - 1 \right]$$
 (2)

where q is the elementary electronic charge, k_b is the Boltzmann's constant and T is the room temperature. Using methods 1 and 2, it was estimated for PU-based OLETs an interfacial trap density equal to $N_{trap}^1 \approx 2.6 \text{ x } 10^{11} \text{ cm}^{-2}$ and $N_{trap}^2 \approx 4.2 \text{ x } 10^{11} \text{ cm}^{-2}$. Comparing these values with their equivalents for the PMMA-based OLET ($N_{trap}^1 \approx 8.5 \text{ x } 10^{11} \text{ cm}^{-2}$ and $N_{trap}^2 \approx 16.2 \text{ x } 10^{11} \text{ cm}^{-2}$) from³³, the interfacial traps density in PU-based OLET is more than three times smaller than PMMA-based OLET.

Looking at the cyclic transfer characteristics curves for PU-based (Figure 3B) and PMMA-based OLETs (Figure 2a from³³), in both cases it is observed a reversible hysteresis during the sweep voltage. The presence of hysteresis in the characteristic curves of organic devices is usually attributed to charge traps in the system, as shown by Hwang *et al.*⁴⁰. The hysteresis exhibited by PU and PMMA-based devices can origin from different sources. PU-based device shows an anticlockwise hysteresis, where the forward sweep current is lower than backward sweep current. This behavior is observed in organic devices with relatively thick gate dielectrics in which there are chemical species that are capable of slow polarization (*e.g.* polar functionalities, ionic impurities and water molecules)⁴⁴. Diversely, the PMMA-based device shows a clockwise hysteresis, where the forward sweep current is higher than backward sweep current. This behavior is characterized by structural defects of semiconductor films, dielectric surface functionalities and adsorbed small molecules (*e.g.*, oxygen) at the interface. These factors are able to generate long-lived charge traps present at the dielectric/semiconductor interface, where trapping and detrapping of holes and electrons take place⁴⁴.

The determination of OLET/OFET's parameters derived from anticlockwise hysteresis curves can be influenced by the effect of slow polarization dielectrics. This polarization can cause an increase in the accumulated charge in the semiconductor channel and, consequently, resulting in overestimated parameters. Therefore, the parameters were extracted from the very first forward sweep, in order to minimize the time exposure of the devices to the applied voltages and thus minimize the effects of polarization. This approach ensures that all parameters are a lower bound

for these devices, *i.e.*, the accumulated charges due to polarization effects has the least possible influence on the parameters reported in this work.

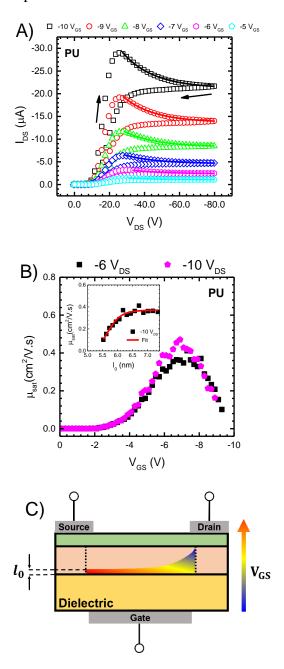


Figure 4. A) Output characteristic curves for PU-based OLETs with black arrows indicating the sweep voltage direction. Open symbols represent experimental data and solid lines represent the fitting using Eq. 8. B) Mobility curves as a function of V_{GS} for PU. The inset shows the behavior

of μ_{sat} as a function of the channel bottleneck thickness l_0 . C) Schematic representation for l_0 as a function of V_{GS} .

Some applications that mainly require amplification of small signals can benefit from the maximization of parameters like the transconductance $g_m = dI_{DS}/dV_{GS}$ and the output resistance $R_0 = g_m^{-1}$. Figure 3C shows the behavior of g_m in different V_{DS} for PU OLETs. As expected, the transconductance is independent of V_{DS} . Comparing the cases, it is observed that the maximum $g_m \sim 0.8 \ \mu S$ for the PU-based OLET is obtained around $V_{GS} \sim -8 \ V$, while the same g_m for PMMA devices is obtained under a much higher V_{GS} , around -47 V^{33} . Thus, showing a considerable improvement in g_m due to the use of PU as gate dielectric.

Figure 4A shows output characteristic curves for PU-based OLETs. Linear and saturation regimes are fully achieved as early as $V_{GS} \sim -3~V$. It is observed that PU-based OLET reaches saturation currents above 20 μ A under $V_{GS} = -10~V$ condition, while PMMA-based OLETs are not expected to show typical output curve behavior, since the conduction channel is not formed yet ($V_{th} = -34~V$). PMMA-based OLET only reaches the same magnitude of current over $V_{GS} = -40V$. Thus, the use of PU as a dielectric layer shows a relevant improvement in the reduction of OLET's working voltages.

Additionally, analyzing the output characteristic curves (I_{DS} vs V_{DS}) for PU-based OLETs (Figure 4A), two distinct behaviors are observed: 1) the output characteristics shows a high I_{DS} response for low values of V_{GS} and 2) it shows a lump when approaching the pinch-off voltage. Such overall increase in I_{DS} is associated with the reduction in threshold voltage and the increase in charge carrier's mobility in the system, *i.e.*, in the C8-BTBT/PU (semiconductor/dielectric) interface.

As saturation mobility (μ_{sat}) plays a key role in OLET performance, its understanding is crucial⁴⁵. In our study we determine saturation mobility μ_{sat} via linear best-fit using⁴³:

$$I_{DS} = \frac{W}{2L} C_{I} \mu_{sat} (V_{GS} - V_{Th})^{2},$$
 3

and over the entire gate bias range using

$$\mu_{\text{sat}} = \left(\frac{d|I_{\text{DS}}|^{\frac{1}{2}}}{dV_{\text{GS}}}\right)^{2} \frac{2L}{WC_{\text{I}}},$$

where W and L correspond to the channel width and length of the OLETs, respectively. Figure 4B report the μ_{sat} for PU-based OLETs as a function of V_{GS} . This result shows that μ_{sat} is independent on V_{DS} and the maximum $\mu_{sat} \sim 0.4$ cm²/Vs is obtained for a V_{GS} value around -7.5 V. On the contrary, the reference PMMA devices show a $\mu_{sat} \sim 0.2$ cm²/Vs, that is two times lower.

The high mobility obtained for PU-based OLETs at low working V_{GS} is associated with two factors: 1) the hydrophobic soft segment (CH₂) in the PU molecular structure is responsible for enabling strong molecule-molecule interaction, thus improving molecular ordering significantly at dielectric/semiconductor interface^{7,15}. 2) The low dipole moment per unit length (m/L ~ 0.178 D/Å) of PU, as shown in^{2,17} is responsible of the decrease of the random oriented dipoles at the dielectric/semiconductor interface and, as a consequence, of the surface energy decrease. The two factors mentioned above are frequently reported in the literature^{7,17,18,19} as crucial to obtain higher mobility and V_{th} stability.

Though, the presence of a lump in PU-based OLET output characteristic is a common feature especially observed in devices that have dipolar centers ^{32,46,47,48,49,50,51,52}. This behavior has been modeled considering a charge carrier mobility gradient in the direction perpendicular to the semiconductor/dielectric interface by Sworakowski *et al.*^{45,53}. According to the Sworakowski model, charge traps at the semiconductor/dielectric interface can cause spatially inhomogeneous charge distribution in the organic semiconductor and a variation of charge mobility as a function of the distance normal to the semiconductor/dielectric interface. In this way, the mobility will depend on the electrostatic interaction energy, E(l₀), generated by the charge traps in the conduction channel as a function of channel bottleneck thickness (l₀).

$$\mu(l_0) = \mu_0 \left(1 + \zeta \exp\left(\frac{E(l_0)}{k_b T}\right) \right)^{-1},$$

where μ_0 is the mobility in a trap-free sample, ζ is a parameter that indicates the fraction of molecules that form local states. According to Sworakowski, for dipolar interactions, $E(l_0)$ scales as:

$$E(l_0) = \frac{A}{l_0^2},$$

where A is proportional to the average dipole moment at the interface. The minimum effective channel thickness used in Sworakowski model can be independently estimated through the drift-diffusion equation, as shown by Seidel *et al.*⁵⁴:

$$l_0 = \frac{4\epsilon_s k_b T}{qC_I (V_{GS} - V_{th})'}$$

where ε_s is the semiconductor's permittivity.

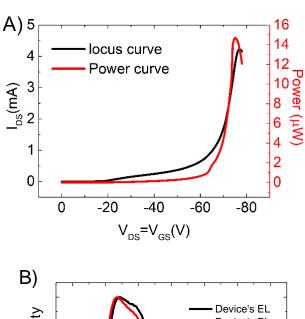
Equation 7 shows that the effective channel thickness where charge carriers cross the device is inversely proportional to V_{GS} , so large values of V_{GS} implies a reduction of the effective transport space in the semiconductor (bottleneck shown in Figure 4C) and, therefore, charge carriers will pass closer to the dielectric/semiconductor interface. This hinders the charge transport in the device, causing an increase in the channel resistance with a consequent decrease in g_m . The inset in Figure 4C shows the behavior of μ_{sat} as a function of l_0 , where Eqs. (5-7) are used to fit the data (red line). A small value of l_0 means that the charge carries will cross the device close to the dielectric/semiconductor interface. The decrease in mobility observed when $l_0 \rightarrow 0$ is associated with an increase in the dipolar interaction (Eq. 6) that can be interpreted as the increase in the cross section between charge carrier and dipolar groups at the interface ⁴⁵. According to Veres *et al.* ¹⁶, the increase in interaction energy close to the interface is a determining factor for the mobility reduction observed in the Figure 4B. Thus, the increase in interaction energy can be interpreted as the emergence of a hindering current formed by scattering centers ⁵⁵.

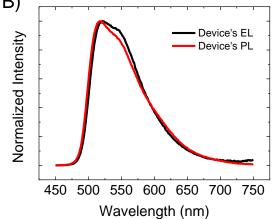
Therefore, our results allow us to conclude that the formation of lumps near the pinch-off regime is associated with the presence of slow polarization centers in gate dielectrics. Hence, while the linear regime maintains its well-known behavior, the presence of charge traps together with the bottleneck effect reduces the mobility in the device, so the current after the pinch-off regime can be written as

$$I_{DS,sat} = I_{pinch} \left[1 - \exp\left(-\frac{qV_{DS}}{\gamma E(l_0)}\right) \right],$$
8

where $I_{DS,sat}$ is the current in saturation regime and I_{pinch} is the maximum current after linear regime. The γ parameter is a proportionality factor between the electrostatic energy of interaction and the average transport barrier (randomly oriented surface dipoles lead to a rough energy landscape for charge carriers).

Using Eq. 8 and the calculated interaction energy $E(l_0)$, it is possible to describe the output characteristics for PU-based OLET as a function of V_{DS} for various V_{GS} , as shown in Figure 4A solid lines. We found a very good agreement between the experimental data (empty symbols) and the results obtained from Eq. 8 (solid lines), which once again leads us to conclude that the lump behavior is indeed associated to slow polarization centers present in the system.





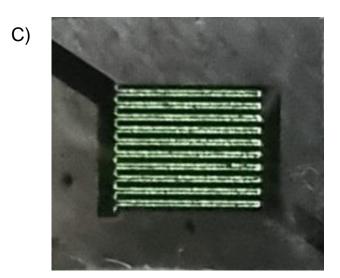


Figure 5. A) PU-based OLET's optical power output curves. B) photoluminescence and electroluminescence spectra comparison and C) PU-based OLET under -40V locus mode optical images.

Finally, the optical power associated with the locus sweep is shown in Figure 5. When comparing optical power output, PU-based OLETs also clearly outperforms PMMA-based OLETs. This becomes more evident around -50 V bias condition, where PU surpasses PMMA output under -100 V bias³³. Also, the maximum EQE% for PU-based devices doubles the EQE% for PMMA-based devices at much lower biases, -60 V and -100 V, respectively. Finally, from Figure 5B it is possible to compare both photoluminescence (PL) and electroluminescence (EL) and conclude that the emission occurs effectively through recombination within the emissive layer. Figure 5C is a device's picture taken in locus mode operation.

IV. CONCLUSIONS

PU-based OLETs, besides preserving the possibility of flexible organic electronics via flexible substrates compatibility, exhibit electrical low operating voltages from 0 to -10 V, with threshold voltage of -6.5 V, indeed one of the lowest values reported in literature to date. Such low bias causes less stress to devices by avoiding high electric fields when compared to standard PMMA-based OLETs^{43,56}.

The high performance obtained by the PU-based OLET results from the low number of traps in the semiconductor/dielectric interface generated by PU's hydrophobic tail. These results

suggest that the use of a PU with a larger portion of the flexible and non-polar -CH₂- segment can further improve the performance of PU-based OLET.

We demonstrate that the non-monotonic behavior (lumps) in the I_{DS} vs. V_{DS} curve near the pinch-off regime result from the forced interaction with polarization centers, which increases the interaction energy and consequently reduces mobility. Furthermore, the model used to describe the current in the pinch-off regime is in agreement with the experimental data obtained for PU-based OLETs.

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CONFLICT OF INTEREST

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

AUTHOR CONTRIBUTIONS

A.R.J.B. fabricated the devices, carried out electrical and optical characterization, discussed results and wrote the manuscript. G.C. performed data evaluation and ab initio calculation, discussed results, wrote and revised the manuscript. H.J.C.A. and R.S.C. discussed results and experimental procedure. A.M.S. helped with the fabrication of the devices and the experiments. M.P. performed AFM experiments and discussed results. S.M. performed additional

AFM experiments. E.B. and S.T. suggested OLET's architecture. R.B.C. supervised data evaluation and discussed results. M.M. discussed results and revised the manuscript. M.C conceived the original idea for the manuscript, discussed results, revised the manuscript and led the work.

ABBREVIATIONS

OLETs, Organic Light-Emitting Transistors; OLEDs, Organic Light-Emitting Diodes; OFETs, Organic Field-Effect Transistors; PMMA, poly(methylmethacrylate); rrP3HT, regioregular poly(3-hexylthiophene); PU, polyurethane; C8-BTBT, 2,7dioctyl[1]benzothienol[3,2-b][1]benzothiophene; TCTA, tris(4-carbazoyl-9-ylphenyl)amine; fac-tris[2-phenylpyridinato-C2,N]iridium(III); PL, photoluminescence; $Ir(ppy)_3$, EL, electroluminescence; AFM, Atomic Force Microscopy; DFT, Density functional theory; SS, subthreshold swing; W, channel width; L, channel length;

REFERENCES

⁽¹⁾ Capelli, R., Toffanin, S., Generali, G., Usta, H., Facchetti, A., Muccini, M. Organic Light-Emitting Transistors with an Efficiency That Outperforms the Equivalent Light-Emitting Diodes. *Nature materials* **2010**, 9(6), 496-503.

⁽²⁾ Muccini, M. A Bright Future for Organic Field-Effect Transistors. *Nature materials* **2006**, 5(8), 605-613.

⁽³⁾ Ullah, M., Tandy, K., Li, J., Shi, Z., Burn, P. L., Meredith, P., Namdas, E. B. High-Mobility, Heterostructure Light-Emitting Transistors and Complementary Inverters. *ACS Photonics* **2014**, 1(10), 954-959.

⁽⁴⁾ Maasoumi, F., Ullah, M., Shaw, P. E., Li, J., Burn, P. L., Meredith, P., Namdas, E. B. Charge Transport and Recombination in Heterostructure Organic Light Emitting Transistors. *Organic Electronics* **2015**, 25, 37-43.

- (5) Kim, D. K., Oh, J. D., Kim, J. W., Lee, H. Y., Choi, J. H. Effects of Doping and Electrode Contacts on Performance of Organic Light-Emitting Transistors Based on Pentacene and Tris (8-Hydroxyquinoline) Aluminum. *The Journal of Physical Chemistry C* **2016**, 120(25), 13716-13724.
- (6) Prosa, M., Benvenuti, E., Kallweit, D., Pellacani, P., Toerker, M., Bolognesi, M., Lopez-Sanchez L., Ragona V., Marabelli, F., Toffanin, S. Organic Light-Emitting Transistors in A Smart-Integrated System for Plasmonic-Based Sensing. *Advanced Functional Materials* **2021**, 31(50), 2104927.
- (7) Bansal, A. K., Sajjad, M. T., Antolini, F., Stroea, L., Gečys, P., Raciukaitis, G., André P., Hirzer A., Schmidt V., Ortolani L., Toffanin S., Allard, S., Scherf, U., Samuel, I. D. In Situ Formation and Photo Patterning of Emissive Quantum Dots in Small Organic Molecules. *Nanoscale* **2015**, 7(25), 11163-11172.
- (8) Cho, S., Lee, K., Yuen, J., Wang, G., Moses, D., Heeger, A. J., Surin, M., Lazzaroni, R. Thermal Annealing-Induced Enhancement of The Field-Effect Mobility of Regioregular Poly (3-Hexylthiophene) Films. *Journal of applied physics* **2006**, 100(11), 114503.
- (9) Chang, J. F., Sun, B., Breiby, D. W., Nielsen, M. M., Sölling, T. I., Giles, M., McCulloch, I., Sirringhaus, H. Enhanced Mobility of Poly (3-Hexylthiophene) Transistors by Spin-Coating from High-Boiling-Point Solvents. *Chemistry of Materials* **2004**, 16(23), 4772-4776.
- (10) Candiotto, G., Torres, A., Mazon, K. T., Rego, L. G. Charge Generation in Organic Solar Cells: Interplay of Quantum Dynamics, Decoherence, And Recombination. *The Journal of Physical Chemistry C* **2017**, 121(42), 23276-23286.
- (11) Zhang, C., Chen, P., Hu, W. Organic Light-Emitting Transistors: Materials, Device Configurations, And Operations. *Small* **2016**, 12(10), 1252-1294.
- (12) Muccini, M., Toffanin, S. Organic Light-Emitting Transistors: Towards the Next Generation Display Technology. *John Wiley & Sons* **2016**.
- (13) Yoo, S., Kim, D. G., Park, H., Ha, J., Kim, J., Won, J. C., Kim, Y. H. Solution-Processable and Photocurable Aromatic Polyurea Gate Dielectrics for High-Performance Organic Thin-Film Transistors. *Materials Research Bulletin* **2023**, 157, 112005.

- (14) Kato, Y., Iba, S., Teramoto, R., Sekitani, T., Someya, T., Kawaguchi, H., Sakurai, T. High Mobility of Pentacene Field-Effect Transistors with Polyimide Gate Dielectric Layers. *Applied physics letters* **2004**, 84(19), 3789-3791.
- (15) Li, Y., Wang, H., Zhang, X., Zhang, Q., Wang, X., Cao, D., Shi, Z., Yan, D., Cui, Z. Organic Thin Film Transistors with Novel Photosensitive Polyurethane as Dielectric Layer. *RSC advances* **2016**, 6(7), 5377-5383.
- (16) Veres, J., Ogier, S. D., Leeming, S. W., Cupertino, D. C., Mohialdin Khaffaf, S. Low-K Insulators as The Choice of Dielectrics in Organic Field-Effect Transistors. *Advanced Functional Materials* **2003**, 13(3), 199-204.
- (17) Yang, S., Du, W., Qi, J., Lou, Z. Vertical Organic Light-Emitting Transistors with An Evaporated Al Gate Inserted Between Hole-Transporting Layers. *Journal of luminescence* **2009**, 129(12), 1973-1977.
- (18) Kim, D. K., Choi, J. H. Low-Voltage Organic Light-Emitting Field-Effect Transistors Using N-Dodecylphosphonic Acid-Passivated HfOx Dielectrics. *Organic Electronics* **2017**, 51, 287-294.
- (19) Soldano, C., D'Alpaos, R., Generali, G. Highly Efficient Red Organic Light-Emitting Transistors (OLETs) On High-K Dielectric. *ACS Photonics* **2017**, 4(4), 800-805.
- (20) Lee, J., Kim, J. H., Im, S. Pentacene Thin-Film Transistors with Al₂O_{3+x} Gate Dielectric Films Deposited on Indium-Tin-Oxide Glass. *Applied physics letters* **2003**, 83(13), 2689-2691.
- (21) Oh, J. D., Kim, D. K., Kim, J. W., Ha, Y. G., Choi, J. H. Low-Voltage Pentacene Thin-Film Transistors Using Hf-Based Blend Gate Dielectrics. *Journal of Materials Chemistry C* **2016**, 4(4), 807-814.
- (22) Wang, G., Moses, D., Heeger, A. J., Zhang, H. M., Narasimhan, M., Demaray, R. E. Poly (3-Hexylthiophene) Field-Effect Transistors with High Dielectric Constant Gate Insulator. *Journal of Applied Physics* **2004**, 95(1), 316-322.
- (23) Oh, J. D., Seo, H. S., Shin, E. S., Kim, D. K., Ha, Y. G., Choi, J. H. ZrO₂ Dielectric-Based Low-Voltage Organic Thin-Film Inverters. *Applied Physics Letters* **2013**, 103(6), 148 1.

- (24) Acton, B. O., Ting, G. G., Shamberger, P. J., Ohuchi, F. S., Ma, H., Jen, A. K. Y. Dielectric Surface-Controlled Low-Voltage Organic Transistors Via N-Alkyl Phosphonic Acid Self-Assembled Monolayers on High-K Metal Oxide. *ACS Applied Materials and Interfaces* **2010**, 2(2), 511-520.
- (25) Ha, Y. G., Emery, J. D., Bedzyk, M. J., Usta, H., Facchetti, A., Marks, T. J. Solution-Deposited Organic–Inorganic Hybrid Multilayer Gate Dielectrics. Design, Synthesis, Microstructures, and Electrical Properties with Thin-Film Transistors. *Journal of the American Chemical Society* **2011**, 133(26), 10239-10250.
- (26) Zaumseil, J., Donley, C. L., Kim, J. S., Friend, R. H., Sirringhaus, H. Efficient Top-Gate, Ambipolar, Light-Emitting Field-Effect Transistors Based on a Green-Light-Emitting Polyfluorene. *Advanced Materials* **2006**, 18(20), 2708-2712.
- (27) Avila, H. C., Serrano, P., Barreto, A. R., Ahmed, Z., Gouvea, C. D. P., Vilani, C., Capaz, R. B., Marchiori, C. F. N., Cremona, M. High Hole-Mobility of Rrp3ht in Organic Field-Effect Transistors Using Low-Polarity Polyurethane Gate Dielectric. *Organic Electronics* **2018**, 58, 33-37.
- (28) Zhang, C., Cui, Z., Wang, H., Yan, D., Li, Y., Shi, Z., Wu, A., Zhao, Z., Luan, S. Crystallization of Sexiphenyl Induced by Polyurethane Containing Terphenyl Groups Affording High-Mobility Organic Thin-Film Transistor. *Organic Electronics* **2014**, 15(10), 2295-2301.
- (29) Tabi, G. D., Nketia-Yawson, B., Jo, J. W., Noh, Y. Y. Improved Electron Transport in Ambipolar Organic Field-Effect Transistors with PMMA/Polyurethane Blend Dielectrics. *Macromolecular Research* **2020**, 28(1), 1248-1252.
- (30) Chai, Z., Jeong, H., Abbasi, S. A., Busnaina, A. A. Fabrication of Organic Field Effect Transistors Using Directed Assembled and Transfer Printed Carbon Nanotube Source/Drain Electrodes. *Applied Physics Letters* **2019**, 114(10), 103301.
- (31) Kim, J. S., Song, C. K. AMOLED Panel Driven by OTFTs on Polyethylene Fabric Substrate. *Organic Electronics* **2016**, 30, 45-51.

- (32) Ma, R., Chou, S. Y., Xie, Y., Pei, Q. Morphological/Nanostructural Control Toward Intrinsically Stretchable Organic Electronics. *Chemical Society Reviews* **2019**, 48(6), 1741-1786.
- (33) Prosa, M., Benvenuti, E., Pasini, M., Giovanella, U., Bolognesi, M., Meazza, L., Galeotti, F., Muccini, M., Toffanin, S. Organic Light-Emitting Transistors With Simultaneous Enhancement of Optical Power and External Quantum Efficiency Via Conjugated Polar Polymer Interlayers. *ACS applied materials and interfaces* **2018**, 10(30), 25580-25588.
- (34) Cusumano, P., Garraffa, G., Stivala, S. A Simple Method for The Photometric Characterization of Organic Light-Emitting Diodes. *Solid-State Electronics* **2022**, 195, 108394.
- (35) Forrest, S. R., Bradley, D. D., Thompson, M. E. Measuring the Efficiency of Organic Light-Emitting Devices. *Advanced Materials* **2003**, 15(13), 1043-1048.
- (36) Candiotto, G., Giro, R., Horta, B. A., Rosselli, F. P., De Cicco, M., Achete, C. A., Cremona, M., Capaz, R. B. Emission Redshift In DCM2-Doped Alq 3 Caused by Nonlinear Stark Shifts and Förster-Mediated Exciton Diffusion. *Physical Review B* **2020**, 102(23), 235401.
- (37) Merces, L., Candiotto, G., Ferro, L. M. M., de Barros, A., Batista, C. V. S., Nawaz, A., Júnior A. R., Capaz, R. B., Bufon, C. C. B. Reorganization Energy Upon Controlled Intermolecular Charge-Transfer Reactions in Monolithically Integrated Nanodevices. *Small* **2021**, 17(45), 2103897.
- (38) Benatto, L., Mesquita, O., Rosa, J. L., Roman, L. S., Koehler, M., Capaz, R. B., Candiotto, G. FRET-Calc: A Free Software and Web Server for Förster Resonance Energy Transfer Calculation. *Computer Physics Communications* **2023**, 108715.
- (39) Generali, G., Soldano, C., Facchetti, A., Muccini, M. P-176: Innovative Trilayer Organic Light Emitting Transistor (OLET) Structure for Blue Emission. *In SID Symposium Digest of Technical Papers* **2016**, 47, 1, 1779-1782.
- (40) Hwang, D. K., Oh, M. S., Hwang, J. M., Kim, J. H., Im, S. Hysteresis Mechanisms of Pentacene Thin-Film Transistors with Polymer/Oxide Bilayer Gate Dielectrics. *Applied Physics Letters* **2008**, 92(1), 4.

- (41) McDowell, M., Hill, I. G., McDermott, J. E., Bernasek, S. L., Schwartz, J. Improved Organic Thin-Film Transistor Performance Using Novel Self-Assembled Monolayers. *Applied Physics Letters* **2006**, 88(7), 073505.
- (42) Siol, C., Melzer, C., von Seggern, H. Electron Trapping in Pentacene Based P- and N-Type Organic Field-Effect Transistors. *Applied Physics Letters* **2008**, 93(13), 357.
- (43) Padma, N., Sawant, S. N., Sudarsan, V., Sen, S., Gupta, S. K. Comparison of The Role of Holes and Electrons in Hysteresis and Threshold Voltage Stability of Organic Field Effect Transistors. *Physica Status Solidi* (A) **2013**, 210(10), 2111-2120.
- (44) Kim, S. H., Yun, W. M., Kwon, O. K., Hong, K., Yang, C., Choi, W. S., Park, C. E. Hysteresis Behaviour Of Low-Voltage Organic Field-Effect Transistors Employing High Dielectric Constant Polymer Gate Dielectrics. *Journal of Physics D: Applied Physics* **2010**, 43(46), 465102.
- (45) Sworakowski, J., Bielecka, U., Lutsyk, P., Janus, K. Effect of Spatial Inhomogeneity of Charge Carrier Mobility on Current-Voltage Characteristics in Organic Field-Effect Transistors. *Thin Solid Films* **2014**, 571, 56-61.
- (46) Nawaz, A., Meruvia, M. S., Tarange, D. L., Gopinathan, S. P., Kumar, A., Kumar, A., Bhunia, H., Pal, A, J., Hümmelgen, I. A. High Mobility Organic Field-Effect Transistors Based on Defect-Free Regioregular Poly (3-hexylthiophene-2, 5-diyl). *Organic Electronics* **2016**, 38, 89-96.
- (47) Nawaz, A., de Col, C., Cruz-Cruz, I., Kumar, A., Kumar, A., Hümmelgen, I. A. Gate Dielectric Surface Treatments for Performance Improvement of Poly (3-Hexylthiophene-2, 5-Diyl) Based Organic Field-Effect Transistors. *In Organic Field-Effect Transistors XIV; and Organic Sensors and Bioelectronics VIII* **2015**, 9568, 71-78.
- (48) de Col, C., Nawaz, A., Cruz-Cruz, I., Kumar, A., Kumar, A., Hümmelgen, I. A. Poly (Vinyl Alcohol) Gate Dielectric Surface Treatment with Vitamin C For Poly (3-Hexylthiophene-2, 5-Diyl) Based Field Effect Transistors Performance Improvement. *Organic Electronics* **2015**, 17, 22-27.

- (49) Nawaz, A., Hümmelgen, I. A. Poly (Vinyl Alcohol) Gate Dielectric in Organic Field-Effect Transistors. *Journal of Materials Science: Materials in Electronics* **2019**, 30(6), 5299-5326.
- (50) Nawaz, A., de Col, C., Hümmelgen, I. A. Poly (Vinyl Alcohol) Gate Dielectric Treated with Anionic Surfactant in C 60 Fullerene-Based n-Channel Organic Field Effect Transistors. *Materials Research* **2016**, 19, 1201-1206.
- (51) Mao, L. K., Hwang, J. C., Chang, T. H., Hsieh, C. Y., Tsai, L. S., Chueh, Y. L., Hsu, S. S. H., Lyu, P. C., Liu, T. J. Pentacene Organic Thin-Film Transistors with Solution-Based Gelatin Dielectric. *Organic Electronics* **2013**, 14(4), 1170-1176.
- (52) Hsieh, C. Y., Hwang, J. C., Chang, T. H., Li, J. Y., Chen, S. H., Mao, L. K., Tsai, L. S., Chueh, Y. L., Lyu, P. C., Hsu, S. S. H. Enhanced Mobility of Organic Thin Film Transistors by Water Absorption of Collagen Hydrolysate Gate Dielectric. *Applied Physics Letters* **2013**, 103(2), 118 1.
- (53) Sworakowski, J. Current-Voltage Characteristics in Organic Field-Effect Transistors. Effect of Interface Dipoles. *Chemical Physics* **2015**, 456, 106-110.
- (54) Seidel, K. F., Koehler, M. Modified Lampert Triangle in An Organic Field Effect Transistor with Traps. *Physical Review B* **2008**, 78(23), 235308.
- (55) Nawaz, A., Kumar, A., Hümmelgen, I. A. Ultra-High Mobility in Defect-Free Poly (3-Hexylthiophene-2, 5-Diyl) Field-Effect Transistors Through Supra-Molecular Alignment. *Organic Electronics* **2017**, 51, 94-102.
- (56) Hsieh, H. H., Chen, W. C., Generali, G., Soldano, C., D'Alpaos, R., Turatti, G., Biondo, V., Muccini, M., Huitema, E., Facchetti, A. Invited Paper: Flexible Active-Matrix OLET Display on a Plastic Substrate. *In SID Symposium Digest of Technical Papers* **2016** 47, 1, 739-742).