

Supplementary Materials

Modulation of the Organic Heterojunction Behavior, from Electrografting to Enhanced Sensing Properties

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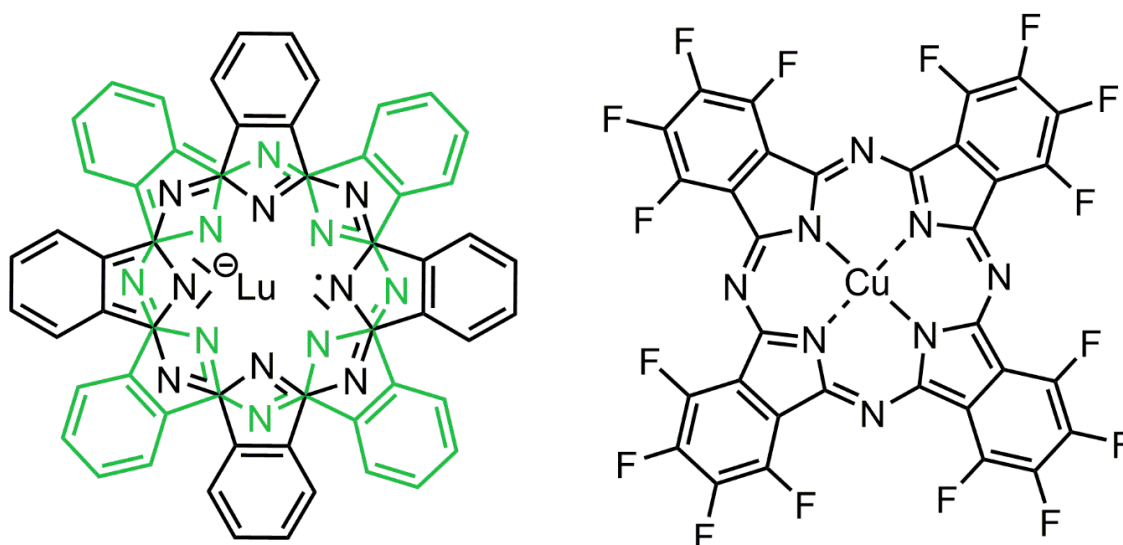


Figure S1. Schematic view of the lutetium bisphthalocyanine LuPc₂ and the perfluorinated copper phthalocyanine Cu(F₁₆Pc) complexes, from left to right.

S2. Electrochemical methods

All electrochemical experiments were performed with a PGSTAT302 N (Metrohm) potentiostat and the collected data were analyzed using Nova® 2.1 software. Cyclic voltammetry (CV) was carried out by means of a three-electrode setup consisting of ITO interdigitated electrodes (IDE, deposited onto a 1 x 1 cm² floated glass substrate and separated by 75 μm with 50 nm thickness and an active area of 0.176 cm²) as working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) plugged in a guard with HClO₄ 2 M as reference electrode. Potentials were reported versus SCE. ITO plate electrodes and IDE were sonicated during 10 minutes in CH₂Cl₂ then in acetone, EtOH and water. Next, the electrodes were dried under air flow.

Electrochemical Quartz Crystal Microbalance (EQCM) measurements were performed with a QCA922A system (Seiko-EG&G, Princeton Applied Research) in a microelectrochemical cell (Biologic 092-QCA-FC model), equipped with an ITO coated quartz crystal (Biologic SE-9C-M, resonance frequency of 9 MHz with an active surface of 0.2 cm²), a platinum wire as counter electrode and an Ag/AgCl reference electrode. Considering that the deposited layer is rigid (no viscoelastic changes occur at the electrode interface) the relationship between the frequency change and the mass change was calculated from the chronocoulometry of a solution of CuSO₄ 5 mM in H₂SO₄ 1 M, at -0.4 V. The surface coverages were calculated from the mass increase using a proportionality constant of 182.3x10⁶ Hz cm² g⁻¹. The ITO coated quartz crystal was cleaned by sonication during 5 min, in CH₂Cl₂, then in EtOH. The cleanliness of the surface was verified by CV in HClO₄ 0.1 M from -0.5 to 1.2 V, then in a solution of K₃[Fe(CN)₆] 1 mM + K₄[Fe(CN)₆] 1 mM in KCl 0.1 M from -0.1 to 0.6 V at a scan rate of 0.1 V s⁻¹. A solution of aniline derivative 2 mM and NaNO₂ 4 mM was kept under argon for 5 min. Just after its injection into the cell, the EQCM experiment was started and the variations of the frequency and of the consumed charge were recorded during 50 cyclic voltammograms from 0 to -0.65 V at 40 mV s⁻¹.

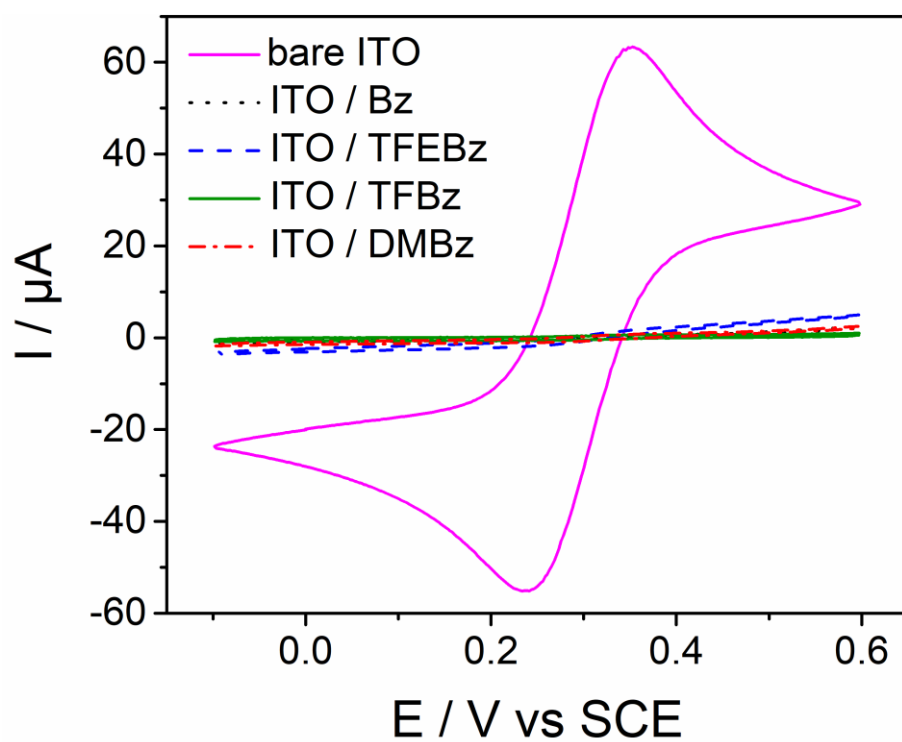


Figure S3. CV of $\text{K}_3[\text{Fe}(\text{CN})_6]$ 1 mM + $\text{K}_4[\text{Fe}(\text{CN})_6]$ 1 mM in 0.1 M KCl on bare IDE (pink), after grafting of DMBz (red), TFBz (green), TFEBz (blue) and Bz (black).

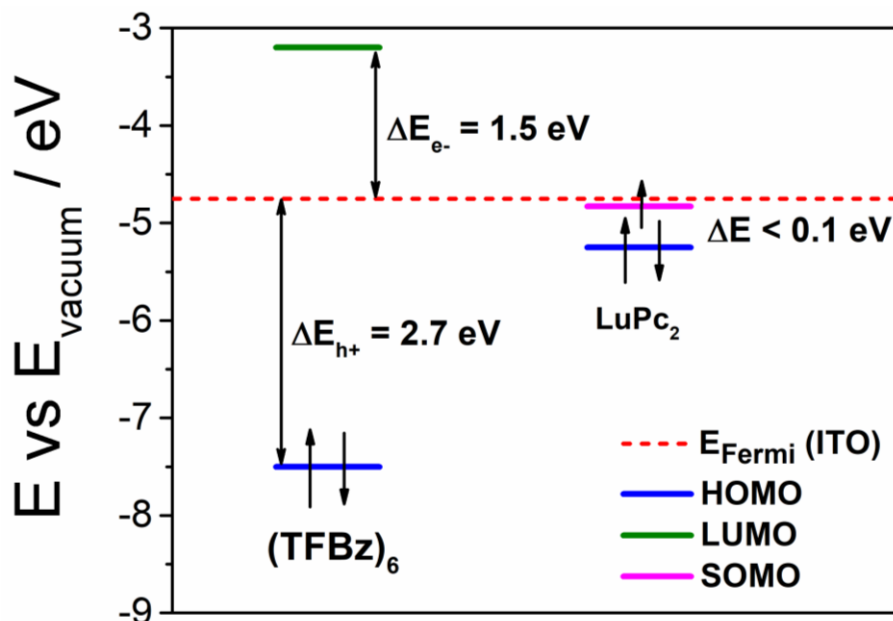


Figure S4. Diagram of frontier orbitals of (TFBz)₆ and LuPc₂ compared to the Fermi level of ITO. ^[1-3]

The grafting of a layer with a large HOMO/LUMO gap with frontier orbitals far from the Fermi level of ITO is not in favor of charge injection. Indeed, according to the HOMO (-7.5 eV) and LUMO (-3.2 eV) level of poly(p-tetrafluorobenzene) oligomer[2] compared to the Fermi level of ITO (-4.8 eV),[1] the hole and electron injection barriers of 2.7 eV and 1.5 eV, respectively, were deduced for the ITO – TFBz interface (Fig. 4). These values are very high compared to the injection barriers between ITO and LuPc₂, which are less than 0.1 eV as deduced from the energy of the frontier electronic states of LuPc₂.^[4]

Impedance spectroscopy of n-MSDI.

The detailed analysis of the parameters of the equivalent circuit for the DMBz grafted device showed that i) α_1 fluctuated between 0.92 and 0.96 while $C_{\text{eff}1}$ was stable at 6 pF (Fig. 5a) and R_1 at $215 \pm 15 \text{ k}\Omega$ (Fig. 5b) and ii) α_2 fluctuated between 0.84 and 0.91 while $C_{\text{eff}2}$ was stable at 1.7 nF (Fig. 5a) and R_2 decreased from 11.4 M Ω to 84 k Ω (Fig. 5b) when the bias increased from 0 to 10 V, and a large part of the decrease occurred before 3 V. It results that the LF semicircle represents the contribution of the interfaces, preponderant at low bias ($< 3\text{V}$), in accordance with the U_{th} voltage of 3.3 V (Fig. 3c), and negligible at high bias. This assumption was supported by the fact that $C_{\text{eff}2}$ was a thousand times larger than $C_{\text{eff}1}$, the latter corresponding to the overall capacity of the device. The R_1 -CPE $_1$ block represents the resistive and dielectric properties of the bulk materials, preponderant at high bias. The grafting of TFBz gave results quite similar to those obtained with DMBz. The major difference lied in the behavior of R_2 that varies from 80 M Ω to 460 k Ω . Most of the drop of R_2 appeared for a voltage lower than 7 V, still remaining higher than R_1 (Fig. 5c).

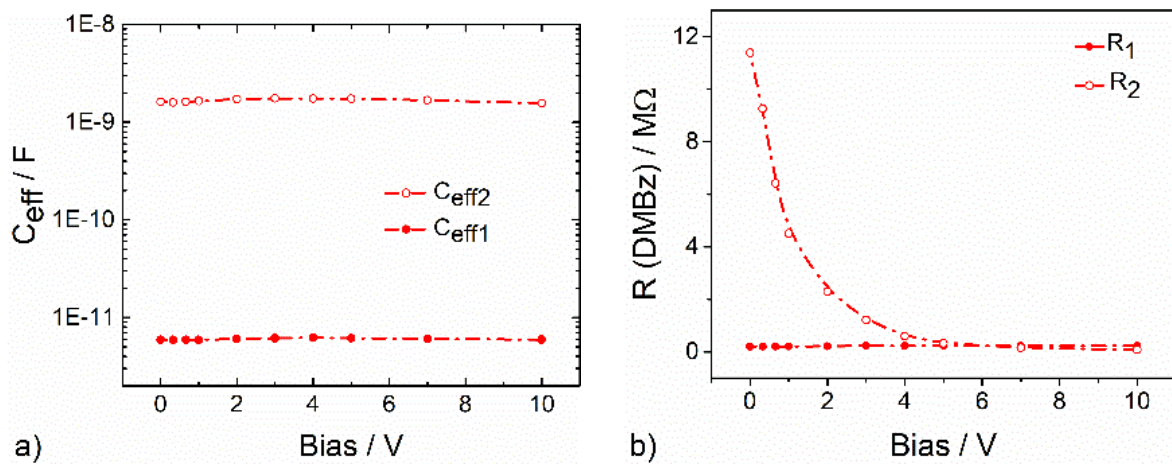


Figure S5. Evolution as a function of the bias of: a) the effective capacitances of an n-MSDI with DMBz grafting; b) the resistances R_1 and R_2 of n-MSDI with DMBz grafting; c)

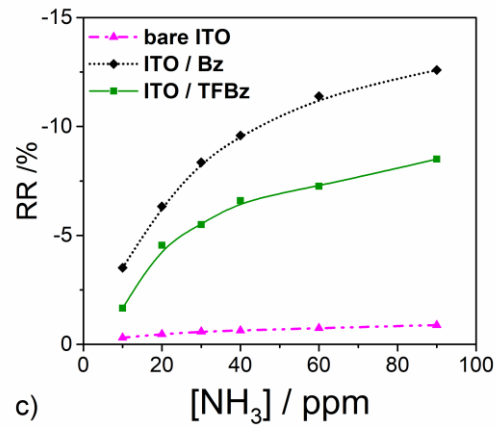


Figure S6 Relative responses in the range 10-90 ppm NH₃ of the different LuPc₂ resistors, at 50% relative humidity. Polarization of 1 V for the bare ITO and ITO/TFBz curves and 0.5 V for the ITO/Bz curve.

Table S1. Values of the linear regressions of the curves $RR = f([NH_3])$ (Fig. 6c) of the different n-MSDIs at 50% rh determined in the region 1–9 ppm NH_3 , the “a” parameter gives the sensitivity of the device.

$Y = a*x + b$	Bare ITO	ITO / DMBz	ITO / TFBz
b	0.2 ± 0.4	1.1 ± 0.6	1.39 ± 0.02
a	1.52 ± 0.08	3.04 ± 0.11	1.10 ± 0.01
R²	0.99248	0.99444	0.99195

Table S2. Fitting according to the Langmuir isotherm, of the curves $RR = f([NH_3])$ (Fig. 6c) of the different n-MSDI at 50% rh determined in the region 1 – 90 ppm.

$Y = c*x / (1 + d*x)$	Bare ITO	ITO / DMBz
c	2.1 ± 0.1	3.6 ± 0.1
d	0.020 ± 0.001	0.015 ± 0.001
R²	0.99686	0.99951

References

- [1] R. Schlaf, H. Murata, Z.H. Kafafi, Work function measurements on indium tin oxide films, *Journal of Electron Spectroscopy and Related Phenomena*. 120 (2001) 149–154. doi:10.1016/S0368-2048(01)00310-3.
- [2] Q.V. Nguyen, P. Martin, D. Frath, M.L. Della Rocca, F. Lafalet, C. Barraud, et al., Control of Rectification in Molecular Junctions: Contact Effects and Molecular Signature, *J. Am. Chem. Soc.* 139 (2017) 11913–11922. doi:10.1021/jacs.7b05732.
- [3] M. l'Her, Y. Cozien, J. Courtot-Coupez, Electrochemical behaviour of lutetium diphthalocyanine in methylene chloride, *J. Electroanal. Chem.* 157 (1983) 183–187. doi:10.1016/S0022-0728(83)80390-8.
- [4] R. Murdey, M. Bouvet, M. Sumimoto, S. Sakaki, N. Sato, Direct observation of the energy gap in lutetium bisphthalocyanine thin films, *Synth. Met.* 159 (2009) 1677–1681. doi:10.1016/j.synthmet.2009.05.002.