

Decacyclene-tri-anhydride (DTA) at Functional Interfaces: an Ideal Electron Acceptor Material for Organic Electronics.

Dimas G. de Oteyza,^{a,b,c,} Juan M. Garcia-Lastra,^d Francesca M. Toma,^{e,f,*} Patrizia Borghetti,^a Luca Floreano,^g Alberto Verdini,^g Albano Cossaro,^g Toan V. Pho,^e Fred Wudl,^e J. Enrique Ortega^{a,b,h}*

^a Donostia International Physics Center, Paseo Manuel Lardizabal 4, 20018 San Sebastián, Spain

^b Centro de Física de Materiales (CSIC-UPV/EHU) - Materials Physics Center (MPC), Paseo Manuel Lardizabal 5, 20018 San Sebastián, Spain

^c Ikerbasque, Basque Foundation for Science, 48011 Bilbao, Spain

^d Department of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark

^e Department of Chemistry and Biochemistry, Department of Materials, Center for Polymers and Organic Solids, University of California, Santa Barbara, CA 93106 (USA)

^f Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

^g CNR-IOM, Laboratorio Nazionale TASC, Basovizza SS-14 Km. 163.5, Trieste, Italy.

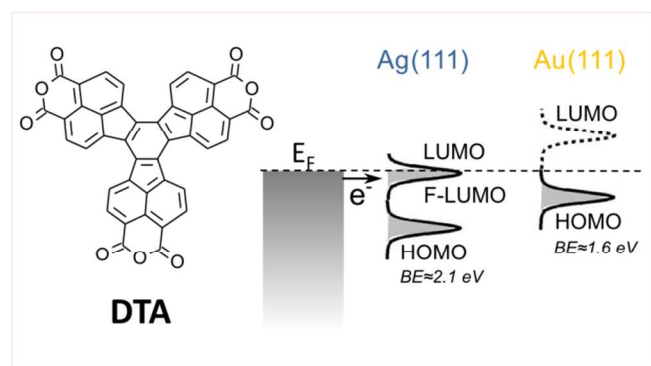
^h Departamento de Física Aplicada I, Universidad del País Vasco, Paseo Manuel Lardizabal 5, 20018 San Sebastián, Spain

* d_g_oteyza@ehu.es, Tel.: +34 943018820 * fmtoma@lbl.gov Tel: +1 5104952342

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT. We report the interface energetics of decacycene-tri-anhydride (DTA) monolayers on top of two distinct model surfaces, namely Au(111) and Ag(111). On the latter, combined valence band photoemission and X-ray absorption measurements that access the occupied and unoccupied molecular orbitals, respectively, reveal that electron transfer from substrate to surface sets in. Density functional theory calculations confirm our experimental findings and provide an understanding, not only of the photoemission and X-ray absorption spectral features of this promising organic semiconductor, but also of the fingerprints associated with the interface charge transfer.

TOC Graphic



KEYWORDS. Energy level alignment, charge transfer, metal-organic interfaces, photoemission, NEXAFS, DFT.

Organic semiconducting materials hold great promise in several applications relying both on electron accepting (n-type) and electron donating (p-type) components, such as organic light-emitting diodes,¹ photovoltaics² or complementary logic circuits³. However, in spite of intensive research, n-type organic materials typically show susceptibility to air,⁴ which affects their transport properties. Consequently they normally have significantly worse performance as compared to their p-type counterparts. The search for novel electron acceptors that prevent oxidation and improve electron transport in the material has brought to the development of novel synthetic approaches that enable addition of electron-deficient groups to a π -conjugated core, thereby increasing its electron affinity.⁴ Examples of such π -conjugated cores are rylene, such as perylene, which can amenably form perylene tetracarboxylic dianhydride (PTCDA). PTCDA is, along with few other molecules, amongst the most popular n-type organic semiconductors for fundamental metal-organic interfacial studies.⁵ The success of this acceptor molecule featuring two electron-deficient anhydride groups calls for the synthesis and characterization of molecules with an increased number of anhydrides as promising candidates for n-type organic semiconductors.⁶

Recently, we have demonstrated a facile and efficient pathway towards the synthesis of a decacyclene molecule bearing three anhydride functional groups, decacyclene trianhydride (DTA, Figure 1a), which holds great promise in the field of organic electronics.^{7,8} While metal/organic interfaces define the charge carrier injection in organic optoelectronic devices, which is a key parameter for their efficiency,⁹ no studies have been performed yet on the electronic properties of the interfaces between DTA and metal surfaces. Because gold is amongst the most common electrode materials in devices, we focus this work on the characterization of the interfacial electronic properties between DTA and the Au(111) surface. On the other hand, minimized charge carrier injection barriers from n-type semiconductors are expected for low work function electrodes. For this reason, the same experiments have been performed on Ag(111) and compared to those on Au(111) in order to learn about the substrate effect on the interfacial properties and energy level alignment.

DTA molecular layers were prepared on Au(111) and Ag(111) by sublimation, and C and O core levels were analyzed by x-ray photoelectron spectroscopy. Core levels are sensitive to the atom's chemical environment and have been further shown to allow following energy level alignment changes from their energy shifts.^{10,11} The core level spectra of DTA monolayers on Au reveal two main lines for the C1s levels (Fig. 1b), in line with previous findings on PTCDA.¹² These features comprise, on the one hand, the C atoms bonded to O, displaying a higher binding energy (288.5 eV) due to their loss of electrons to the more electronegative O atoms. On the other hand we find the signal of the decacycene core C atoms grouped (within our experimental resolution) into a single and more intense peak at 284.4 eV. The O1s spectra also display two lines, corresponding to the two chemically different O atoms (Fig. 1b), namely O1 and O2. The peak assignment is done by analogy to the core levels of PTCDA¹² and NTCDA.¹³ An unexpectedly large O1/O2 intensity ratio is derived from a simple two-peak fitting. Note, however, that the O1 line sits on the inelastic background of the O2 peak and is largely affected by satellites.¹³ Because our deconvolution attempts did not provide unambiguous results, a precise analysis of the O1 peak energy and intensity is hampered and the values provided henceforth correspond to those of a single line including the contribution of the main O1 peak convolved with the O2 satellites.

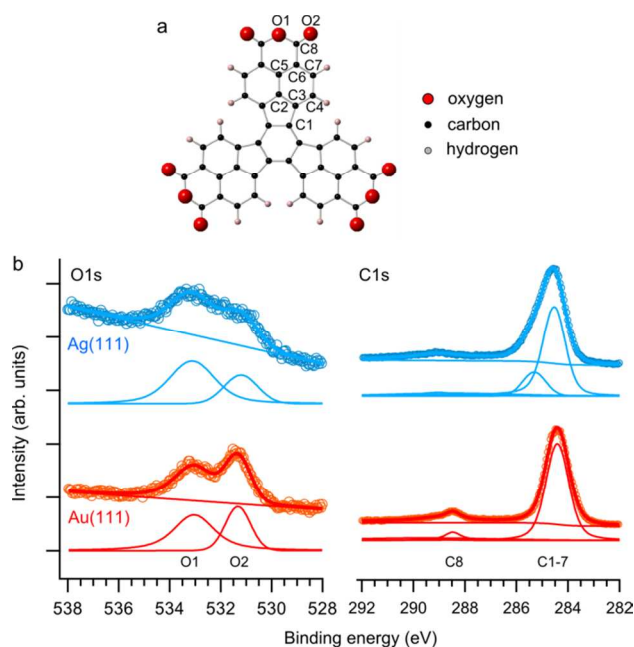


Fig. 1. a) Molecular structure of DTA, displaying its 8 chemically non-equivalent C sites and 2 non-equivalent O sites. b) O 1s and C 1s core-level photoemission spectra (symbols) and fits (solid lines) of DTA monolayers on Ag(111) and Au(111) surfaces (top and bottom, respectively). The assignment of the core-level fit components to the various atomic species in DTA is displayed at the bottom of the graph.

On the more interactive Ag(111) surface, the C1s and O1s spectra both show broader and less defined peaks. Indeed, the strongest line in the C1s spectrum presents an increased, asymmetric width and directly requires an additional component in the fit (Fig. 1b). The O1s spectrum also shows a remarkable increase in the peak widths (Fig. 1b), related to the shorter photo-hole lifetime upon stronger hybridization of the molecule with the substrate. It is worth noting that in spite of the significantly different work function of Ag(111) and Au(111) (close to 1 eV different),¹⁴ the core level binding energies do not shift accordingly. Instead, except for the signal from C8 atoms and the new C 1s component, the peak's binding energies remain relatively unchanged (see Table 1 summarizing the binding energies of all fitted components). In the case of O2 there is even a slight shift in the opposite direction, all of it hinting toward a counterbalancing charge transfer effect as the work function decreases.^{11,15,16}

Table 1. Core level binding energies of DTA on Au(111) and Ag(111) and energy level shift (δ) between substrates.

Binding energies in eV		Au(111)	Ag(111)	δ
C1s	C1,C3,C4,C6,C7	284.41	284.52	0.11
	C2, C5		285.31	0.9
	C8	288.47	289.08	0.61
O1s	O2	531.33	531.21	-0.12
	O1	533.05	533.12	0.07

The charge transfer is indeed corroborated by combined valence band photoemission and near edge X-ray absorption spectroscopy (NEXAFS), used to access the occupied and unoccupied molecular

1 orbitals, respectively. Valence band photoemission spectra are shown in Fig. 2a after subtraction of the
2 signal measured on the clean substrates. On Au(111) no signal is observed at energies above the highest
3 occupied molecular orbital (HOMO, centered at about 1.5 eV). On Ag(111), the HOMO level is
4
5 observed at about 0.4 higher binding energies. The concomitant reduction in electron injection barrier
6
7 aligns the lowest unoccupied molecular orbital (LUMO) with the Fermi level, an ideal situation for the
8
9 use of DTA as electron acceptor material. This is concluded from an unambiguous additional signal
10
11 appearing at low binding energies, truncated at the Fermi level. This signal is a clear signature of a
12
13 partial filling of the LUMO, as previously observed on Ag(111) also for the closely related PTCDA
14
15
16
17
18
19^{12,17,18} as well as for other molecules.^{14,19,20}

21 The models describing weakly interacting interfaces fail to account for this LUMO filling.^{11,15} Even
22
23 under Fermi level pinning conditions, only very small charge transfer amounts are needed to create the
24
25 associated interface dipoles that keep the LUMO close to, but above, the Fermi level upon work
26
27 function reductions.^{11,15} Instead, a scenario must be invoked beyond Fermi level pinning, in which a
28
29 significant chemical interaction with the substrate accounts for this substantial charge transfer. In the
30
31 case of its “sister molecule” PTCDA, the following interaction was proposed: a strong molecule-
32
33 substrate bonding by the O2 atoms causes a lengthening of their C=O double bonds towards a C-O
34
35 single bond. This change is accompanied by a rehybridization of the backbone structure that increases
36
37 the aromaticity of the adsorbate. In turn, this surface-induced aromatic stabilization allows the LUMO to
38
39 lower its energy below the Fermi level in spite of competing phenomena that tend to keep the LUMO
40
41 above it.²¹ Based on the similarity of PTCDA and DTA, we assume a comparable scenario. This is
42
43 indeed supported by density functional theory calculations (DFT) revealing the O2 atoms to be about
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
0.5 Å closer to the surface than the other atoms in the adsorbed molecule (see supplementary
information).

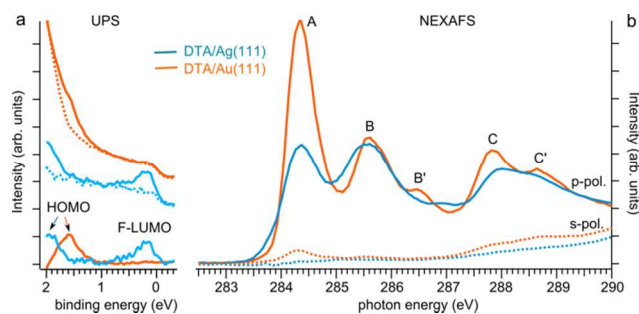


Fig. 2. a) Valence band photoemission signal of DTA monolayers (solid lines) on Ag(111) and Au(111) surfaces together with the respective clean substrate reference signal (dashed lines). The substrate spectra have been rescaled to account for the overlayer attenuation and allow their subtraction from the spectra of molecular layers. At the bottom, the differential intensity after subtraction of the respective contribution of either substrate is displayed for comparison. b) Associated NEXAFS C K-edge spectra on the same samples measured under p-polarization (solid lines) and s-polarization (dotted lines) conditions.

The filling of the LUMO level is observed also in the NEXAFS spectra, measured both at the C and O K-edges. We first focus on the C K-edge spectrum on Au(111), displayed in Fig. 2b for s- and p-polarization, that is, with the electric field vector parallel and nearly perpendicular to the surface, respectively. Three main peaks are observed under p-polarization, namely A, B, and C. For the two latter, side peaks are observed (labelled B' and C') separated 0.9 eV from the main lines. The absence of an A' side peak may be real or the signal may be hidden due to its superposition with peak B. However, the origin of these side peaks remains unknown. When comparing with the spectra on Ag, we observe various changes: (i) the resonances appear broader and worse resolved, (ii) the side peaks are not observed any more (whether their origin disappears or they are no longer observed because of the overall broadening, is unclear), (iii) resonance A is significantly quenched, and to a lesser extent also resonance C. The lowest energy transition, resonance A, is expected to represent excitations into the LUMO level. Its quenching implies a reduced availability of the empty states for transitions and thus confirms the partial filling of the LUMO, as previously concluded from photoemission experiments. Alternatively, changes in intensity may arise also from changes in molecular orientations. In that case,

1 however, the resonance's intensity should increase under s-polarization, while it remains absent for that
2 polarization on both Ag and Au substrates alike. A similar lying down molecular configuration is thus
3 concluded for both substrates and the possibility that the reduced intensity of A is due to changes in the
4 molecular orientation amongst substrates can be discarded.
5
6
7
8

9
10 Similar deductions can be drawn from the O K-edge spectra (Fig. S1). On Ag(111) the spectra also
11 show a significant quenching of the first resonance as compared to the spectrum on Au(111), again
12 without any intensity increase under s-polarization. In addition to the partial LUMO filling, this hints to
13 a LUMO distribution across both C and O atoms in the molecule.
14
15
16
17

18
19 The above conclusions are further supported with DFT calculations. Figure 3a and 3b show,
20 respectively, the energy and spatial distribution of low energy molecular orbitals in free standing
21 molecules, including the HOMO and the lowest unoccupied molecular orbitals. These calculations serve
22 our need to visualize the molecular orbitals and confirm, as expected, that the doubly degenerate LUMO
23 orbitals distribute across most of the molecule's C and O atoms. However, to get further insight into the
24 effect of the substrate, additional calculations for DTA adsorbed on Au(111) and Ag(111) have also
25 been performed.²² The projected density of states on the low energy molecular orbitals of the adsorbed
26 molecules is depicted in Fig. 3c. It reveals a shift to higher binding energies of the molecular orbitals
27 when changing from Au(111) to Ag(111). In addition, the orbitals broaden on Ag(111). This is observed
28 strongest on the originally unoccupied orbitals and is indicative of a stronger molecule-substrate
29 hybridization on Ag(111). As a result of the molecular shift and the broadening, the LUMO and
30 LUMO+1 orbitals cross the Fermi level and become partially filled. Thus, the appearance of an
31 occupied electronic state truncated at the Fermi level in the photoemission spectra, as well as the
32 broadening of the unoccupied orbitals and the decrease in the first NEXAFS resonance, are excellently
33 explained by our calculations.
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

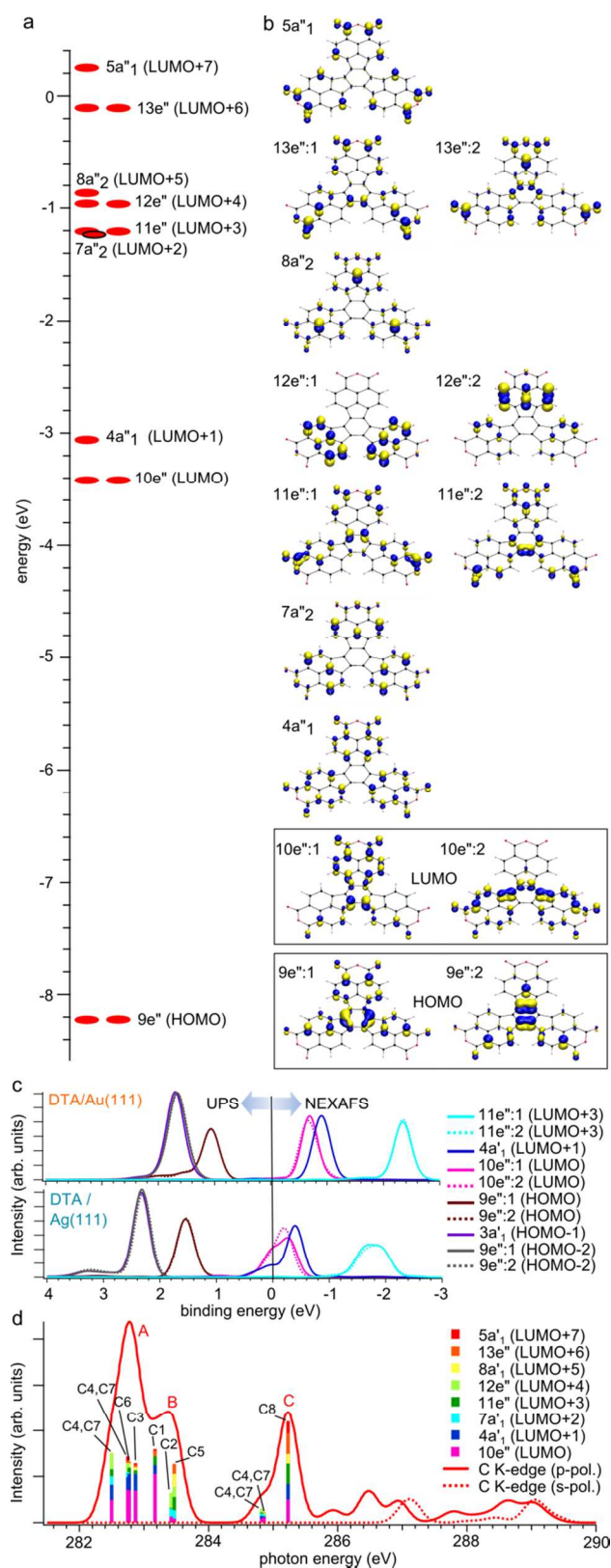


Figure 3. a) Calculated energies of the low energy molecular orbitals of DTA in gas phase. b) Spatial distribution of the molecular orbitals outlined in (a). c) Calculated projected density of states (pDOS) of low energy molecular orbitals evidencing the energy level alignment associated with DTA molecules at the interface to Au(111) and Ag(111). d) Calculated C K-edge NEXAFS spectra of DTA in gas phase for p-polarization (solid lines) and s-polarization (dashed lines).

1 The three main spectral features have been labelled A, B, and C in analogy to the experimental data. The colored bars mark
2 the discrete transitions at low energies (those contributing to A, B and C), with their heights denoting the transition intensity
3 and the colors denoting the contribution of each molecular orbital to the final excited state. The originating C atom is
4 additionally given for each of the transitions.
5
6
7
8
9
10

11 Also the disparate response of the different core levels to charge transfer can be understood from our
12 calculations. Core levels are known to be particularly sensitive to the chemical state of the atomic
13 species and thus to hybridization or charge transfer across the metal-organic interface. The associated
14 chemical shifts of the different core-levels depend on the degree to which they are affected by the
15 hybridization or charge transfer, which in turn depend on the spatial distribution of the orbital(s)
16 involved.¹¹ This has been nicely observed for example with the various core levels of CuPc as it is
17 gradually doped with Na.²³ Core levels of atoms with low contribution to the electron-accepting orbitals
18 show shifts close to that of the vacuum level. Instead, core levels of atoms with strong contribution to
19 the electron-accepting orbitals significantly depart from the vacuum level shift and even shift in the
20 opposite direction due to the additional charge.²³ The same occurs with DTA on Ag(111): The atoms
21 with largest contribution to the electron-accepting orbitals LUMO and LUMO+1 are C1,C3,C4,C6,C7
22 and O2. Their core level energies thus remain unchanged with respect to the Fermi level and do not
23 follow the vacuum level shift associated with the change from Au(111) to Ag(111). Instead, the signal
24 from C8 partially follows the vacuum level and thus shows a significant shift when comparing both
25 substrates. The same applies to the signal of C2 and C5, which therefore separates from the main peak
26 and appears as a new independent component in the XPS spectra on Ag(111).¹⁵
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48

49 However, because of the presence of so many chemically different carbon atoms, all acting as initial
50 states for X-ray absorption, the NEXAFS spectra are not as straightforward to understand. To clarify
51 why also resonance C in Fig. 2b decreases in intensity on Ag(111) as compared to Au(111) we have
52 performed additional calculations. Figure 3d displays simulated NEXAFS C K-edge spectra of free-
53 standing DTA molecules, evidencing under p-polarization three first resonances clearly reminiscent of
54
55
56
57
58
59
60

the resonances A, B and C in Fig. 2b. Below the calculated spectrum, the various transitions contributing to the calculated intensity of resonances A, B and C are displayed as bars. And within each bar, the contribution of the various unoccupied orbitals to the excited state is provided by the corresponding color code. We can thus observe that while the orbitals contributing the most to the transitions included in resonance A are LUMO and LUMO+1, the orbitals contributing most to the transitions included in B are higher energy orbitals. Coming to resonance C we see that, although to a lesser extent than in A, the transitions involved include again excited states with a significant contribution of LUMO and LUMO+1. Here, however, the initial state is the C1s level of C8, which features a higher binding energy and therefore results in a higher excitation energy in the NEXAFS spectrum. Because LUMO and LUMO+1 are the orbitals affected by charge transfer on Ag(111), this is all in excellent agreement with a decrease in the C K-edge NEXAFS spectra of resonance A, a lower decrease in resonance C, and a hardly unchanged intensity in resonance B.

Altogether, we have performed a synchrotron-based spectroscopic analysis of DTA's electronic properties at the interface to metallic surfaces of significantly different work function and reactivity, namely Au(111) and Ag(111). When changing from Au to Ag, the molecular levels distinctly lower their energies. The hole injection barrier increases by 0.4 eV and the concomitant reduction in the electron injection barrier causes charge transfer into DTA's empty molecular states to set in on Ag(111). DFT calculations reveal the charge transfer to involve the LUMO and LUMO+1 levels and provide an excellent understanding of the spectroscopic fingerprints observed both in the photoemission and X-ray absorption measurements. This understanding is expected to be of great use for future research on this new and highly promising n-type organic semiconductor.

METHODS

The Au(111) and Ag(111) surfaces were prepared by standard Ar⁺ ion sputtering and annealing cycles, and their cleanliness checked by XPS prior to molecular deposition. The molecular layers were prepared by DTA sublimation from a resistively heated Knudsen cell onto single crystal surfaces held at room temperature. The sample coverage was monitored by means of a quartz crystal microbalance.

All measurements were performed at room temperature under ultrahigh vacuum (UHV) conditions at the ALOISA beamline of the synchrotron light source ELETTRA in Trieste (Italy). The photoemission data were collected by means of a hemispherical electron energy analyzer in normal emission (for XPS) and at 45° off-normal emission (for the valence band) while keeping the sample at grazing incidence ($\sim 4^\circ$), with excitation energies of 140 eV (valence band) 500 eV (C1s) and 610 eV (O 1s). The binding energy of core-level spectra is carefully calibrated taking the substrate core-level energies as absolute references. NEXAFS spectra were taken in partial electron yield by means of a channeltron detector. Spectra measured at the C and O K-edges were calibrated by acquisition of the C1s- π^* and O1s- π^* gas phase transitions of CO at $h\nu=287.4$ eV and 534.21 eV, respectively.²⁴ The manipulator is coaxial to the photon beam, which allows to change the orientation of the surface with respect to linear polarization of the beam while keeping constant the grazing angle, i.e., without changing the beam footprint on the sample. For more details about the scattering geometry, see Ref. 25.

DFT calculations were carried out by means of the Amsterdam Density Functional (ADF) code.²⁶ All atoms were described through basis sets of TZP quality (triple- ζ Slater-type orbital plus one polarization function) given in the program database, including all of the core electrons in the calculation (i.e., with no frozen-core approximation). The exchange-correlation energy was computed according to the BHandHLYP hybrid functional.²⁶ The results were checked using the local density approximation (LDA) by means of the Vosko–Wilk–Nussair (VWN) functional²⁷ and generalized gradient approximation (GGA) by means of the Perdew–Burke–Ernzerhof (PBE) functional.²⁸ The first step of the calculations consisted of obtaining the structure of the DTA in its ground state. The structure was relaxed until a maximum force below 0.04 eV/Å was obtained. In a second step, the NEXAFS transitions were modeled. Taking as starting point a DFT calculation, there are several strategies to calculate and to analyze NEXAFS spectra. Some of these methods allow calculating individual peaks of the spectra assigning each peak to a single transition (i.e. a transition of an electron from one single core level to a single unoccupied level). These approaches, e.g. Δ -SCF methodology²⁹ or the transition

potential approximation (TPA),³⁰ make possible to analyze the NEXAFS spectra in a simple and intuitive way, providing also, in general, accurate results. However, these approaches, although very useful in practice, lack a fully rigorous theoretical basis. On the other hand it is possible to employ the Time-Dependent DFT (TDDFT) method to study NEXAF spectra,³¹ which has a solid theoretical ground. The price to pay by using TDDFT is that the analysis of the single peaks becomes more complex, involving in general more than a single transition. This happens because upon an electron excitation, the created hole makes the electrostatic potential more attractive close to it and thus the excited level will not be anymore the one of the molecule in its ground state, but will be polarized. In order to describe this polarization is necessary to express the transition as combination of several unoccupied levels. In the present work we have used the TDDFT method. As was expected, there was a shift between the TDDFT-calculated and experimental spectra. The smallest shift (a 2 eV blueshift) was obtained with the BHandHLYP functional and also the relative positions of the different peaks in the spectra were better reproduced with the BHandHLYP functional. For this reason, we used the BHandHLYP results for the peak assignment and analysis of the C 1s and O 1s edges experimental spectra.

ACKNOWLEDGMENT. This work was supported by the Spanish Grants No. MAT2013-46593-C6-4-P, and the Basque Government Grant No. IT-621-13. The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 312284. JMGL acknowledges support from the Spanish Ministry of Economy and Competitiveness under Projects FIS2012-30996 and FIS2013-46159-C3-1-P and from the Villum Foundation's Young Investigator Programme (4th round, project: *In silico design of efficient materials for next generation batteries*. Grant number: 10096) F.M.T. acknowledges financial support from the Area Science Park of Trieste and EU (TALENTS Fellowship Programme, PCOFUND-GA-2009-245574). F.M.T. and F.W. thank the Center for Energy Efficient Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy under award number DE-SC0001009 for the DTA

1 synthesis and characterizations. T.V.P. and F.W. acknowledge the ConvEne IGERT Program (NSF-
2 DGE0801627) for financial support.
3

4
5 SUPPORTING INFORMATION. Oxygen K-edge NEXAFS spectra of DTA monolayers on Au(111)
6 and Ag(111) (Fig. S1), details on the DFT calculations, including description and comparison of the
7 various functionals used, the geometry and unit cell used in the calculations of the adsorbed molecule
8 (Fig. S2), and distance to substrate for each molecular atom (Table 1). Full references including the
9 complete author list for references with more than 10 authors. This material is available free of charge
10 via the Internet at <http://pubs.acs.org>.
11
12
13
14
15
16
17
18
19

20 REFERENCES

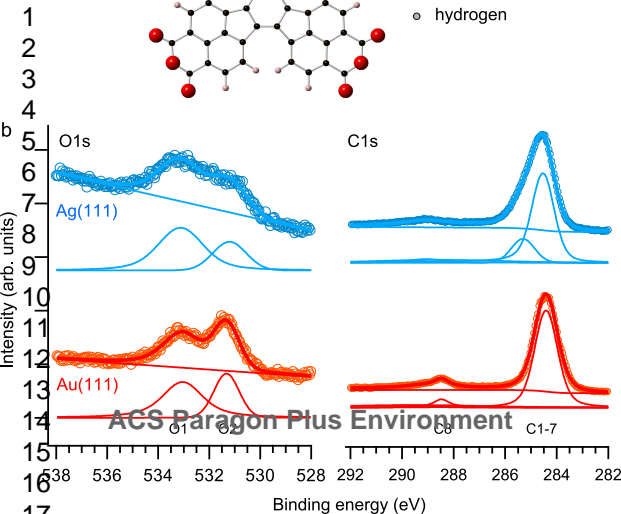
- 21
22
23
24
25 (1) Chen, S.; Deng, L.; Xie, J.; Peng, L.; Xie, L.; Fan, Q.; Huang, W. Recent Developments in Top-
26 Emitting Organic Light-Emitting Diodes. *Adv. Mater.* **2010**, *22*, 5227–5239
27
28
29 (2) Peumans, P.; Uchida, S.; Forrest, S. R. Efficient Bulk Heterojunction Photovoltaic Cells Using
30 Small Molecular-Weight Organic Thin Films. *Nature* **2003**, *425*, 158-162
31
32
33 (3) Klauk, H.; Zschieschang, U.; Pflaum, J.; Halik, M. Ultralow-Power Organic Complementary
34 Circuits. *Nature* **2007**, *445*, 745-748
35
36
37 (4) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Bredas, J.-L.; Ewbank, P. C.; Mann, K. R.
38 Introduction to Organic Thin Film Transistors and Design of n-Channel Organic Semiconductors.
39 *Chem. Mater.* **2004**, *16*, 4436
40
41
42 (5) F. S. Tautz, Structure and Bonding of Large Aromatic Molecules on Noble Metal Surfaces: The
43 Example of PTCDA. *Prog. Surf. Sci.* **2007**, *82*, 479-520
44
45
46 (6) Pho, T. V.; Toma, F. M.; Chabinye, M. L.; Wudl, F. Self-Assembling Decacyclene Triimides
47 Prepared Through a Regioselective Hextuple Friedel–Crafts Carbamylation. *Angew. Chem. Int. Ed.*
48
49
50
51
52
53
54
55
56
57
58
59
60

- (7) Pho, T. V.; Toma, F. M.; Tremolet de Villers, B. J.; Wang, S.; Treat, N. D.; Eisenmenger, N. D.; Su, G. M.; Coffin, R. C.; Douglas, J. D.; Fréchet, et al. Decacyclene Triimides: Paving the Road to Universal Non-Fullerene Acceptors for Organic Photovoltaics. *Adv. Energy Mater.* **2014**, *4*, 1301007-1-7
- (8) Toma F. M.; Puntoriero, F.; Pho, T. V.; La Rosa, M.; Jun, Y.-S.; Tremolet de Villers, B. J.; Pavlovich, J.; Stucky, G. D.; Campagna, S.; Wudl, F. Polyimide Dendrimers Containing Multiple Electron Donor–Acceptor Units and Their Unique Photophysical Properties. *Angew. Chem. Int. Ed.* **2015**, *54*, 6775-6779
- (9) Koch, N. Organic Electronic Devices and Their Functional Interfaces. *ChemPhysChem* **2007**, *8*, 1438-1455
- (10) El-Sayed, A.; Borghetti, P.; Goiri, E.; Rogero, C.; Floreano, L.; Lovat, G.; Mowbray, D. J.; Cabellos, J. L.; Wakayama, Y.; Rubio, A.; et al. Understanding Energy-Level Alignment in Donor–Acceptor/Metal Interfaces from Core-Level Shifts. *ACS Nano* **2013**, *7*, 6914-6920
- (11) Goiri, E.; Borghetti, P.; El-Sayed, A.; Ortega, J.E.; de Oteyza, D. G. Multi-component Organic Layers on Metal Substrates. *Adv. Mater.* doi:10.1002/adma.201503570
- (12) Zou, Y.; Kilian, L.; Scholl, A.; Schmidt, Th.; Fink, R.; Umbach, E. Chemical Bonding of PTCDA on Ag Surfaces and the Formation of Interface States. *Surf. Sci.* **2006**, *600*, 1240-1251
- (13) Schöll, A.; Zou, Y.; Schmidt, T.; Fink, R.; Umbach, E. High-Resolution Photoemission Study of Different NTCDA Monolayers on Ag(111): Bonding and Screening Influences on the Line Shapes. *J. Phys. Chem. B* **2004**, *108*, 14741-14748
- (14) Borghetti, P.; El-Sayed, A.; Goiri, E.; Rogero, C.; Lobo-Checa, J.; Floreano, L.; Ortega, J. E.; de Oteyza, D. G. Spectroscopic Fingerprints of Work-Function-Controlled Phthalocyanine Charging on Metal Surfaces. *ACS Nano* **2014**, *12*, 12786-12795
- (15) Flores, F.; Ortega, J.; Vazquez, H. Modelling Energy Level Alignment at Organic Interfaces and Density Functional Theory. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8658-8675

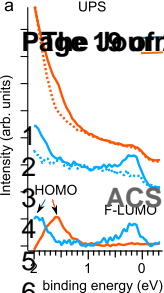
- (16) Because our deconvolution attempts of peak O1 from the satellites of O2 did not provide unambiguous results, a detailed analysis of the O1 intensity and energy variation from Au to Ag is hampered.
- (17) Duhm, S.; Gerlach, A.; Salzmann, I.; Broker, B.; Johnson, R.; Schreiber, F.; Koch, N. PTCDA on Au(111), Ag(111) and Cu(111): Correlation of Interface Charge Transfer to Bonding Distance. *Org. Electron.* **2008**, *9*, 111-118
- (18) Ziroff, J.; Forster, F.; Scholl, A.; Puschnig, P.; Reinert, F. Hybridization of Organic Molecular Orbitals with Substrate States at Interfaces: PTCDA on Silver. *Phys. Rev. Lett.* **2010**, *104*, 233004-1-4
- (19) Kroger, I.; Stadtmüller, B.; Stadler, C.; Ziroff, J.; Kochler, M.; Stahl, A.; Pollinger, F.; Lee, T.-L.; Zegenhagen, J.; Reinert, F.; et al. Submonolayer Growth of Copper-phthalocyanine on Ag(111). *New J. Phys.* **2010**, *12*, 083038-1-23
- (20) Schöll, A.; Kilian, L.; Zou, Y.; Ziroff, J.; Hame, S.; Reinert, F.; Umbach, E.; Fink, R. H. Disordering of an Organic Overlayer on a Metal Surface Upon Cooling. *Science* **2010**, *329*, 303-305
- (21) Heimel, G.; Duhm, S.; Salzmann, I.; Gerlach, A.; Strozecka, A.; Niederhausen, J.; Burkner, C.; Hosokai, T.; Fernandez-Torrente, I.; Schulze, et al. Charged and metallic molecular monolayers through surface-induced aromatic stabilization. *Nat. Chem.* **2013**, *5*, 187-194
- (22) It should be noticed that the HOMO-LUMO gap calculated for DTA in gas phase using the BHandHLYP hybrid functional (Fig. 3a) is considerably larger than the gap calculated for DTA on top of the substrates using the PBE functional (Fig. 3c). As explained in more detail in the supplementary information, this substantial difference can be ascribed to a large extent to the different functional used in those calculations, each chosen so as to be optimized for our particular aims.
- (23) Ding, H.; Park, K.; Green, K.; Gao, Y. Electronic Structure Modification of Copper Phthalocyanine (CuPc) Induced by Intensive Na Doping. *Chem. Phys. Lett.* **2008**, *454*, 229-232

- (24) Floreano, L.; Naletto, G.; Gvetko, D.; Gotter, R.; Malvezzi, M.; Marassi, L.; Morgante, A.; Santaniello, A.; Verdini, A.; Tommasini, F.; et al. Performance of the Grating-Crystal Monochromator of the ALOISA Beamline at the Elettra Synchrotron. *Rev. Sci. Instrum.* **1999**, *70*, 3855-3864
- (25) Floreano, L.; Cossaro, A.; Gotter, R.; Verdini, A.; Bavdek, G.; Evangelista, F.; Ruocco, A.; Morgante, A.; Cvetko, D. Periodic Arrays of Cu-Phthalocyanine Chains on Au(110). *J. Phys. Chem. C* **2008**, *112*, 10794-10802
- (26) Velde, G. T.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S.J. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22*, 931-967
- (27) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: a Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200-1211
- (28) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868
- (29) Garcia-Lastra, J. M.; Bass, J. D.; Thygesen, K. S. Strong Excitonic and Vibronic Effects Determine the Optical Properties of Li₂O₂. *J. Chem. Phys.* **2011**, *135*, 121101-1-4
- (30) Triguero, L.; Peterson, L.G.M.; Ågren, H. Calculations of Near-edge X-ray-absorption Spectra of Gas-phase and Chemisorbed Molecules by Means of Density-functional and Transition-potential Theory. *Phys. Rev. B* **1998**, *58*, 8097-8110
- (31) Schmidt, N.; Fink, R.; Hieringer, W. Assignment of Near-edge X-ray Absorption Fine Structure Spectra of Metalloporphyrins by Means of Time-dependent Density-functional Calculations. *J. Chem. Phys.* **2010**, *133*, 054703-1-13

- oxygen
- carbon
- hydrogen



a



NEXAFS

b

