

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/277980111>

Looking Inside the Perchlorinated Trityl Radical/Metal Spinterface through Spectroscopy

ARTICLE in JOURNAL OF PHYSICAL CHEMISTRY LETTERS · MAY 2015

Impact Factor: 7.46 · DOI: 10.1021/acs.jpclett.5b00848

READS

76

8 AUTHORS, INCLUDING:



Veronica Mugnaini

International Iberian Nanotechnology Laborat...

44 PUBLICATIONS 937 CITATIONS

SEE PROFILE



Arrigo Calzolari

Italian National Research Council

108 PUBLICATIONS 1,901 CITATIONS

SEE PROFILE



Jaume Veciana

Spanish National Research Council

983 PUBLICATIONS 12,373 CITATIONS

SEE PROFILE



M. Pedio

Italian National Research Council

112 PUBLICATIONS 1,301 CITATIONS

SEE PROFILE

Looking Inside the Perchlorinated Trityl Radical/Metal Spinterface through Spectroscopy

Veronica Mugnaini,[†] Arrigo Calzolari,[‡] Ruslan Ovsyannikov,[§] Antje Vollmer,[§] Mathieu Gonidec,[†] Isaac Alcon,[†] Jaume Veciana,^{*,†} and Maddalena Pedio^{*,||}

[†]Department of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC/CIBER-BBN), Cerdanyola del Valles, 08193 Barcelona, Spain

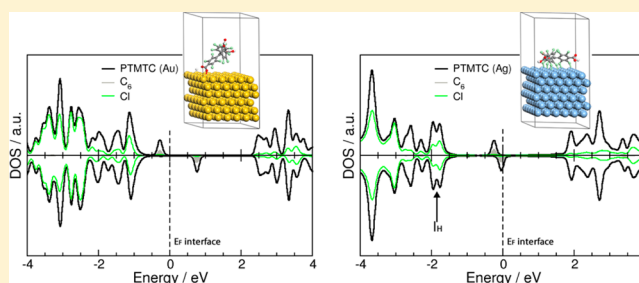
[‡]CNR-NANO Istituto Nanoscienze, Centro S3, I-41125 Modena, Italy

[§]Helmholtz Zentrum Berlin für Materialien und Energie GmbH, D-12489 Berlin, Germany

^{||}CNR IOM TASC National Lab, I-34149 Trieste, Italy

S Supporting Information

ABSTRACT: We report on a spectroscopic multitechnique approach to study the metal/radical spinterface formed by a perchlorinated trityl radical derivative and either gold or silver. The spectroscopic fingerprint of their paramagnetic properties could be determined by comparison with their diamagnetic precursor and by DFT calculations. Thanks to the presented approach, we could gain unprecedented insight into the radical–metal interaction and how this latter perturbs the spin polarization and consequently the magnetoelectronic properties of the radical adlayer. Knowledge of the factors influencing the spinterface is an essential tool toward the tailoring of the properties of spin-based electronic devices.



Organic radical derivatives,¹ that is, metal-free molecular derivatives with an unpaired electron spin, traditionally known as key players in protein chemistry² and as tectons of multifunctional materials,³ have been recently shown as suitable components of spin-based molecular electronic (molecular spintronics) devices.^{4–8} Indeed, their chemical synthetic flexibility, absent in inorganic materials traditionally used in spintronics,^{9,10} allows one to engineer specific network structures¹¹ and their magnetoelectronic properties by tuning the strength of the interaction with the surface.^{12–14} This latter is indeed a crucial point for the actual implementation of molecular spintronics in devices because realistic large-scale applications require the fabrication of supported architectures, which ensure well-ordered, reproducible, and easy-grown structures. Nevertheless, the formation of chemical bonds between the deposited radical molecular derivative and the anchoring metal may change the electronic structure of the molecule and thus the spin polarization (i.e., the magnetic properties). Additionally, the nature of the chemical bonds at the interface governs the spin injection mechanism into the molecule. Consequently, understanding of the electronic and magnetic properties of the organic radical–metal interface is mandatory toward the realization of operating spintronic devices. Organic radical–metal interfaces can be considered as spinterfaces, a term initially coined for interfaces with a spin dependence DOS,¹⁵ because such a property can be attained in these interfaces under a very large magnetic field or at moderate

magnetic fields but very low temperatures. Standard microscopy techniques, even though important to visualize the supramolecular arrangements of nano-objects on metal substrates, may not be sufficient to characterize the modifications of the electronic structure induced at the spinterface. Therefore, we herein present a multitechnique spectroscopic approach, based on synchrotron and laboratory emission and absorption techniques (e.g valence band and core level photoemission spectroscopies, VB PES and PES; inverse photoemission spectroscopy, IPS; angle-resolved near-edge X-ray absorption spectroscopy, NEXAFS), supported by ab initio simulations to investigate the spinterfaces formed by a perchlorinated trityl radical derivative (tri-*p*-carboxy polychlorotriphenylmethyl radical, PTMTC, Figure 1a) and two noble metals, Au(111) and Ag(111). As it will be discussed, we have been able to elucidate the effects of the strength of the molecule–substrate interaction on the electronic properties and on the preservation of the paramagnetism of the first molecular layer. The molecular orbitals and the structure of PTMTC appear differently perturbed on the two substrates. The strong electronegativity of the chlorine substituents on the PTMTC plays a major role on Ag(111), leading to a strong interaction and hybridization of the molecular orbitals with formation of an

Received: April 24, 2015

Accepted: May 18, 2015

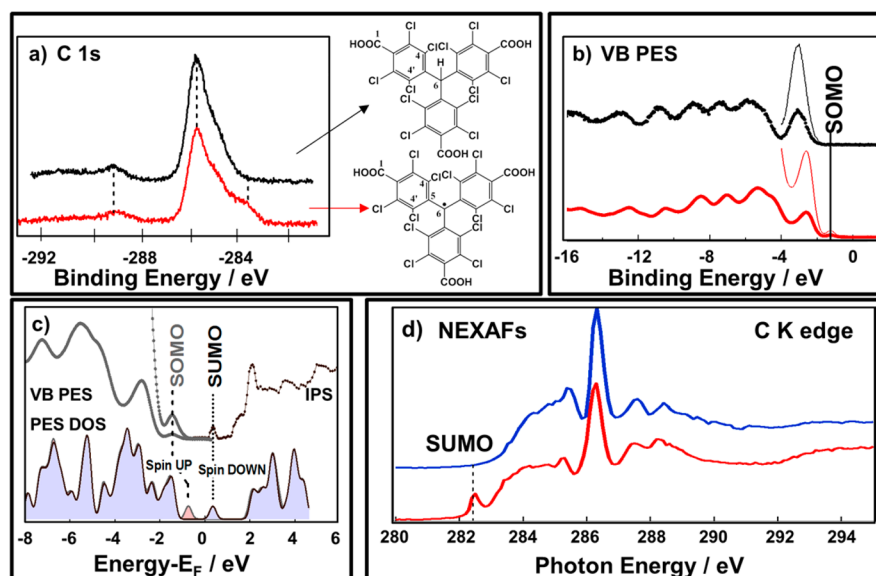


Figure 1. (a) (Left) C 1s PE spectra of thin films of PTMTC radical (red) and its diamagnetic precursor (α H-PTMTC, black). The molecular structures of both compounds with the carbon numbering are on the right. (b) Extended VB PE spectra of PTMTC (red) and its nonradical precursor (black). (c) Combined PES (gray) and IPS (black) spectra of thin films of PTMTC. The SOMO and its empty counterpart SUMO are clearly seen and show an energy distance of 2.3 ± 0.2 eV. The spectra are compared with the calculated density of states (DOS) of the spin up (red shadow) and spin down (blue shadow) of an isolated molecule. (d) NEXAFS C K edge of the nonradical α -PTMTC thin film (blue) and PTMTC thin film (red).

interface molecular state with quenching of the paramagnetic character of the layer, while on Au(111), the weaker radical–metal interaction has no effect neither on the electronic nor on the paramagnetic properties, in agreement with what was hypothesized in a previous work.¹⁶ Our results reveal that the chemical composition of the organic radical layer and hence the type of interface bonding between the molecule and the metal substrate plays a crucial role in the fine tuning of the interfacial electronic and paramagnetic properties.^{13,17–21}

The PTMTC (Figure 1a) is a stable and persistent molecule with an open-shell electronic configuration. Its stability comes from the bulky chlorine atoms in the six ortho positions (C_4 and C_4' , Figure 1a) that protect the central radical carbon atom (C_6 , Figure 1a) from unwanted reactions that could lead to the loss of the radical character. Additionally, the PTMTC shows a high thermal stability that allows sublimation under ultrahigh vacuum (UHV) conditions, as we demonstrated in a previous work¹⁶ where thin films of PTMTC were prepared on Au(111) and studied by scanning tunneling microscopy (STM). Herein, we instead used a multitechnique approach to identify the radical spectroscopic fingerprint of multilayered films prepared by UHV sublimation by comparison with the PTMTC diamagnetic precursor (α H-PTMTC, Figure 1a). As shown in Figure 1a, the C 1s core level PE spectra of the thin films of PTMTC¹⁶ (in red, Figure 1a) and of its diamagnetic precursor (in black, Figure 1a) show several components related to the different C atoms. The band at a binding energy (BE) of -283.7 eV can be attributed to the central C_6 atom (Figure 1a) on the basis of the comparison with the C 1s spectra of the nonradical derivative, where it is absent (Supporting Information Figure 1). DFT calculations confirmed the assignments of the BE of the other carbon atoms (Supporting Information Table 1). The Cl 2p and O 1s PE spectra (Supporting Information Figure 2) are, as expected, similar for both PTMTC and α H-PTMTC. VB PE spectra of PTMTC (Figure 1b, red) and α H-PTMTC (Figure 1b, black),

instead, show a striking difference. A molecular state at -1.6 eV is present in the case of the radical derivative and not in the case of the diamagnetic precursor. Its absence in this latter case, together with the paramagnetic character of the radical film found by electron spin resonance (ESR),¹⁶ confirms that this state is attributable to the single occupied molecular orbital (SOMO). The empty counterpart of this molecular state (the single unoccupied molecular orbital, SUMO) is indeed observed in IPS (Figure 1c) and C K edge NEXAFS spectra (Figure 1d) of thin films of PTMTC. This result is valuable because the final state in the two techniques is different due to the presence of the core hole in absorption.²²

All the assignments of the molecular orbitals are confirmed by the DOS of DFT-PBE calculations (Figure 1c) that find a magnetic moment of 1 Bohr magneton per molecule. This framework provides only a partial description of the magnetic properties of paramagnetic complexes due to the difficulty of modeling exchange and electron correlation phenomena using effective one-electron potentials. IPS (PES) represents a negative (positive) ion state, while absorption spectroscopy represents an excited neutral state containing an electron–hole pair. Special care must be taken in comparing PES and IPS with the DFT DOS due to the different final state effects.²³ Taking that into account, it is possible to extract a coherent description and to rationalize important information. Interestingly, on the basis of the comparison of IPS spectra and of the C K and Cl L 2,3 edges NEXAFS (Supporting Information Figure 3), the SUMO is mainly formed by C contribution with a faint contribution from Cl detectable at the Cl L 2,3 edge. This indication, confirmed also by partial DOS curves, implies that the spin does not reside only on the central C_6 atom but is delocalized on the whole molecule, as it was already suggested as a consequence of the out-of-plane torsion of the three phenyl rings caused by the bulky chlorine atoms in C_4 and C_4' .²⁴

In order to address the PTMTC–metal interface and understand how the electronic structure of the PTMTC is

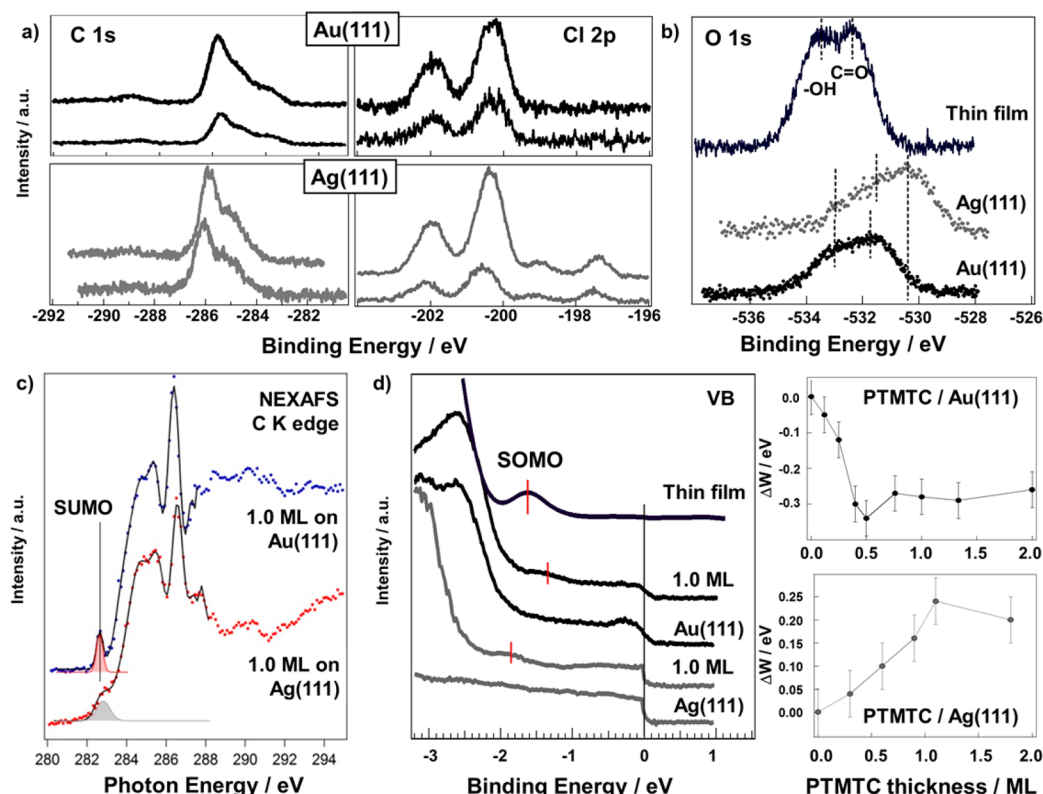


Figure 2. (a) C 1s (left) and Cl 2p (right) PE spectra of PTMTC on Au(111) (black) and Ag(111) (gray) at 1 ML coverage (top) and 0.5 ML coverage (bottom). The intensity of the lower BE in the Cl 2p spectra is about 30%, and taking into account the photoelectron signal attenuation of the interface Cl atoms due to the electron mean free path, it is indeed compatible with the suggested DFT-optimized geometry. (b) O 1s PE spectra of the PTMTC thin film (continuous dark blue line) and as 1 ML on Au(111) (black) and on Ag(111) (gray). (c) C K edge NEXAFS of 1 ML of PTMTC on Au(111) and Ag(111). The SUMO is clearly indicated. (d) (Left) VB maximum of the PTMTC thin film and as 1 ML on Au(111) and on Ag(111). Clean Au(111) and clean Ag(111) are reported for the sake of comparison. (Right) Evolution of the work function (WF) with the coverage for PTMTC on Au(111) (top) and Ag(111) (bottom). PE spectra at different coverages on Au(111) and Ag(111) are shown in Supporting Information Figure 5.

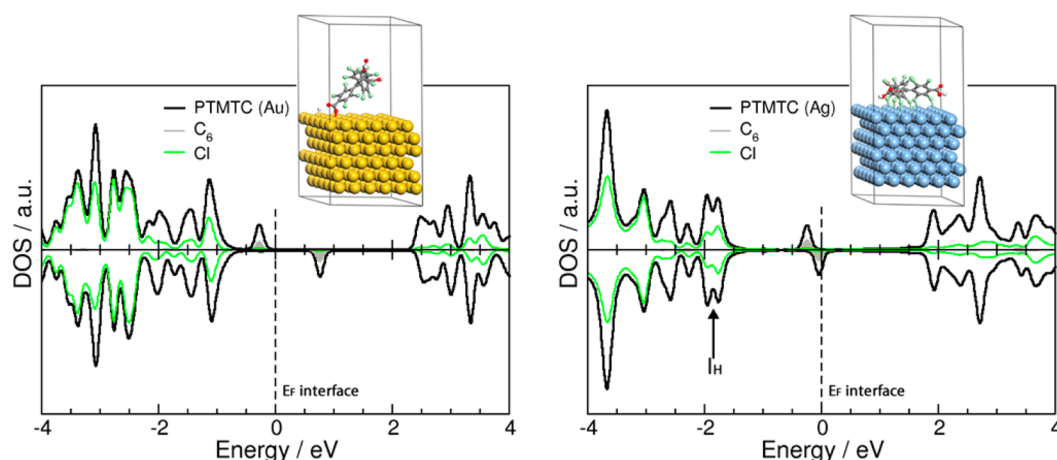


Figure 3. Partial DOS for PTMTC adsorbed on Au(111) (left) and on Ag(111) (right) with the side views of the structure of PTMTC on Au(111) (yellow) and on Ag(111) (light blue) substrates and the electronic charge profile in the two cases. For Au(111), a depletion (pillow effect) is obtained, while in the Ag interface, an increase of charge takes place at interfaces. Positive curves and negative curves indicate the spin-up and spin-down contributions. The Au/Ag contributions to the DOS are not shown for clarity. The zero-energy reference is set to the Fermi level of each hybrid interface.

affected by the interaction with the surface, we deposited the PTMTC as a submonolayer (subML) and monolayer (ML) on Au(111) and Ag(111). On Au(111), the C 1s and Cl 2p core level PES do not show significant changes (Figure 2a, black), while the O 1s PES suggests a partial deprotonation of the

carboxylic groups (Figure 2b, black). By recording the Au 4f core level PE in surface-sensitive mode, we can indeed discard a strong interaction of the PTMTC with the gold substrate (Supporting Information Figure 4). NEXAFS spectra (Figure 2c) show the transition to the SUMO orbital at 282.5 eV, and

VB PES (Figure 2d) shows a feature attributable to the SOMO at all the investigated coverages, with a BE that decreases with the increase from the subML to ML regime, approaching the value of the SOMO in thin films.

The change in the SOMO position is accompanied by the change in the work function (WF, Figure 2d, on the top right) with the coverage.²⁵ The WF decreases until a minimum at -0.34 eV in correspondence of 0.5 ML, and then, it undergoes a slight and continuous increase for higher coverages. The WF trend is compatible with a noncovalent interaction of the PTMTC islands on Au(111) until 0.5 ML with the prevalence of the pillow effect,²⁶ hence supporting the recently suggested hypothesis.¹⁶ The slight increase observed for coverages higher than 0.5 ML implies that additional intermolecular interactions take place at higher coverages. The observed changes in WF are in qualitative agreement with DFT results that show a slight but not negligible reduction of WF (-20 meV) in the case of the Au substrate. Therefore, the collected data suggest a scenario so far not reported for radicals on Au(111). We can discard the presence of any hybridization and hence of any change in the electronic and paramagnetic structure at the spinterface. Interestingly enough, not even at coverages lower than 0.5 ML, there is an effect on the electronic and paramagnetic structure.

Confirmation of the given interpretation of the experimental data comes from DFT-PBE calculations extended to 1 ML PTMTC on Au(111). For the study of the molecule–substrate interfaces, two configurations have been examined, one with PTMTC standing almost vertical (small tilted angle) and one where the molecule lies horizontally flat. According to the optimized geometry (Figure 3, left panel), the PTMTC is at a small tilting angle with the surface and loses a $-H$ atom on the COOH moiety, in agreement with the O 1s core level spectra. The results of electronic structure calculations show that on Au(111), PTMTC maintains all the features of the isolated molecule (Supporting Information Figure 6). In particular, both the SOMO and SUMO survive (as confirmed by NEXAFS) as result of a weak interaction with the metal, and the calculated magnetic moment maintains the molecular value (1 Bohr magneton). The central atom C_6 adsorbed on Au maintains the same Löwdin charge (3.95e) and atomic spin polarization (charge up–charge down = 0.65) as the pristine molecule. Therefore, on Au(111), a weak interaction mainly drawn by dipole interaction (and possibly by redistribution of the charge in the molecules) takes place with a slight SOMO–SUMO energy separation shift.¹⁶ The screening, excitonic, and polarization effects can result in a shift of the frontier orbital features. These contributions have been evaluated for a plethora of organic layers, including paramagnetic copper phthalocyanine derivatives, resulting in a shift in the range of 0.1–0.4 eV in the combined PES–IPS spectra.^{23a}

When using Ag(111) as a substrate, a different scenario appears. Both C 1s and Cl 2p PES (Figure 2a) indicate a strong interaction of the PTMTC with the metal; in C 1s core level spectra at both 0.5 and 1 ML, the band at a BE of -283.7 eV, attributed to the central C_6 atom, is unambiguously suppressed. This cannot be attributed to fragmentation of the molecule because in both NEXAFS (Figure 2c) and VB PES (Figure 2d), occupied and empty molecular orbitals, respectively, remain clearly distinguishable. From the Cl 2p spectra, another striking difference arises. Two doublets are observed, with the one at a lower BE being about 30% of the other one. The presence of two doublets is compatible with the presence of two sets of

chlorine, one facing the vacuum and one, at a lower BE, facing the metal and hence interacting strongly with it. A strong interaction with the metal finds confirmation in C K edge NEXAFS (Figure 2c) taken on 1 ML where the transition to the SUMO orbital at 282.5 eV appears quenched and broadened. Accordingly, VB PES spectra (Figure 2d) show that the peak below the Fermi level (at 1.8 eV) is detected for all the investigated coverages, but its BE remains unchanged, differently from what happens on Au(111), thus remarking that it is an interface state. In agreement with this finding, we observe a continuous increase in the WF as result of a strong interaction with the metal. The changes in WF (Figure 2d, on the bottom right) are again in qualitative agreement with DFT results that show a WF increase of about $+0.02$ eV in the case of Ag. Therefore, our results indicate a strong interaction between the metal surface and the molecule and a charge transfer from the Ag(111) to the radical that leads to the filling of the SUMO and hence to the appearance at the interface of a new hybridized state whose energy does not change with the coverage. The hybridization at the interface has been reported in the case of 1,3,5-phenyl verdazyl radical derivatives on Au(111), where a Kondo resonance could be seen by scanning tunneling spectroscopy.¹³ In the present case, we suggest that the chlorine atoms strengthen the interaction with the Ag(111) substrate, leading to a quenching of the SUMO as well as the suppression of the C_6 component in the C 1s spectra. DFT-PBE calculations performed for 1 ML of PTMTC on Ag(111) are in full agreement with the spectroscopic data. Analogously to what was done on Au(111), two configurations—with PTMTC standing almost vertical (small tilted angle) and horizontally flat—were examined. In the case of Ag (Figure 3, right panel), the molecule adsorbs almost parallel to the surface, maximizing the number of Cl–Ag interactions, as it could also be inferred from the relative intensity of the two doublets in the Cl 2p spectra (Supporting Information Figure 7). The results of electronic structure calculations show an overall modification of the molecular-projected DOS over the entire energy range, with respect to the gas-phase reference. The most evident change involves the molecular sharp SUMO peak, which is now largely broadened across the Fermi level becoming partially occupied, with a calculated magnetic moment quenched to 0.3 Bohr magneton. The Löwdin charge of C_6 increases its atomic value (4.12e), and the spin polarization is reduced to 0.14, this being a clear signature of a metal-to-molecule charge transfer and the formation of direct chemical bonds mediated by the chlorine. The quenching of the SUMO is calculated also for higher-energy geometry, that is, with the molecule tilted with respect to the surface, like in the configuration on Au(111), and with a lower number of Cl atoms in contact with the Ag substrate, supporting the existence of a stronger interaction in the case of silver. The calculations confirm an overall charge transfer from the metal to the molecule, as also proposed on the basis of PES and NEXAFS; the interface state detected in the VB PES is indeed well reproduced by our calculations at about -1.9 eV. This state derives from the hybridization of the Ag s band with the pristine π -like spin-unpolarized HOMO–1 state of PTMTC, which has a relevant contribution from Cl atoms (see Supporting Information Figure 5). We can thus conclude that on Ag(111) the molecular orbitals are deformed and shifted, and the relevant features are broadened, emerging as new hybrid interface states.¹⁶ We note however that, even though the formation of chemical bonds at the interface may reduce the energy barrier for electron injection, this is not

necessarily an advantage for spin injection; the electronic structure redistribution induced by the presence of the Ag substrate washes out the magnetic polarization of PTMTC, vanishing its application in spintronic devices.

The spinterface between a trityl radical derivative and either gold or silver has been investigated by means of a multi-technique spectroscopic approach to gain insight in the perturbation caused by the metal substrate to the spin polarization. While on Au(111) the radical/metal interaction is weak and no loss in the spin polarization takes place,²⁷ on Ag(111), the Cl atoms are responsible for the formation of Ag–Cl bonds that lead to a charge redistribution with broadening of the SUMO that becomes an interfacial state whose energy coincides with the one of the Fermi level. The experimental evidence is confirmed by calculations that clearly indicate that the SOMO–SUMO energy difference decreases, that the SUMO lies across the Fermi Level and that the paramagnetism of the radical results strongly quenched. The reported results shed light on the charge redistribution at the metal–organic interfaces on the molecular scale toward the understanding of the energy level alignment and the transport processes at the spinterface, with huge implication on the nanomagnetism and the knowledge of the parameters to be taken into account toward the actual implementation of organic radicals in spintronic devices.

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis of the PTMTC radical.²⁸ Experimental conditions used in spectroscopic studies. Procedures for theoretical calculations. C 1s core level spectra (C 1s, Cl 2p, and O 1s) of PTMTC and its no-radical precursor α H-PTMTC and assignments of the C 1s core level based on DFT calculations. Comparison between IPS and element-sensitive NEXAFS data (C K edge and Cl L_{2,3} edge) of PTMTC films. PES Au 4f core level for clean and subML coverages of PTMTC on Au(111) taken at 350 eV of photon energy. PE spectra at different coverages on Au(111) and Ag(111). Spin-unrestricted DOS of the PTMTC isolated molecule and isosurface plot of representative molecular orbitals. Description of the Cl 2p core level spectra for PTMTC on Ag(111) and coverage dependence. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00848.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: vecianaj@icmab.es (J.V.).

*E-mail: pedio@iom.cnr.it (M.P.).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. V.M., M.P., and J.V. conceived and designed the experiments; M.G., I.A., R.O., A.V., V.M., and M.P. performed the experiments; V.M. and M.P. analyzed the data; V.M., A.C., M. P., and J.V. cowrote the paper.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the Helmholtz-Zentrum Berlin for provision of synchrotron radiation beamtime at SURICAT apparatus of

BESSY II, receiving funding from the FP7/2007-2013 grant agreement no. 312284. The authors acknowledge financial support from the Instituto de Salud Carlos III, through “Acciones CIBER”. The Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN) is an initiative funded by the VI National R&D&I Plan 2008-2011, Iniciativa Ingenio 2010, Consolider Program, CIBER Actions and financed by the Instituto de Salud Carlos III with assistance from the European Regional Development Fund. The authors also appreciate the financial support through the projects BE-WELL (CTQ2013-40480-R), granted by DGI (Spain), and GenCat (2014-SGR-17), financed by DGR (Catalunya). This work is partially supported by the Italian Ministero dell’Istruzione dell’ Università e della Ricerca through the PRIN “GRAF” (Contract 2010SZZTSE) and Progetto Premiale ABNANOTECH.

■ ABBREVIATIONS

VB PES, valence band photoemission; PES, core level photoemission; IPS, inverse photoemission; NEXAFS, angle-resolved near-edge X-ray absorption spectroscopy; UHV, ultra high vacuum; PTMTC, tri-*p*-carboxy polychlorotriphenylmethyl radical

■ REFERENCES

- (1) Hicks, R. E. *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*; Wiley: Chichester, U.K., 2010.
- (2) Stubbe, J.; van der Donk, W. Protein Radicals in Enzyme Catalysis. *Chem. Rev.* **1998**, *98*, 705–762.
- (3) Ratera, I.; Veciana, J. Playing with Organic Radicals as Building Blocks for Functional Molecular Materials. *Chem. Soc. Rev.* **2012**, *41*, 303–349.
- (4) Raman, K. V.; Kamerbeek, A. M.; Mukherjee, A.; Atodiresi, N.; Sen, T. K.; Lazic, P.; Caciuc, V.; Michel, R.; Stalke, D.; Mandal, S. K.; et al. Interface-Engineered Templates for Molecular Spin Memory Devices. *Nature* **2013**, *493*, 509–513.
- (5) Sanvito, S. Molecular Spintronics. *Chem. Soc. Rev.* **2011**, *40*, 3336–3355.
- (6) Affronte, M. Molecular Nanomagnets for Information Technologies. *J. Mater. Chem.* **2009**, *19*, 1731–1737.
- (7) Rocha, A. R.; García-Suárez, V. M.; Bailey, S. W.; Lambert, C. J.; Ferrer, J.; Sanvito, S. Towards Molecular Spintronics. *Nat. Mater.* **2005**, *4*, 335–339.
- (8) Wolf, S. S.; Awschalom, D. D.; Buhrman, R. A.; Daughton, J. M.; von Molnár, S.; Roukes, M. L.; Chtchelkanova, A. Y.; Treger, D. M. Spintronics: A Spin-Based Electronics Vision for the Future. *Science* **2001**, *294*, 1488–1495.
- (9) Chappert, C.; Fert, A.; van Dau, F. N. The Emergence of Spin Electronics in Data Storage. *Nat. Mater.* **2007**, *6*, 813–823.
- (10) Awschalom, D. D.; Flatté, M. E. Challenges for Semiconductor Spintronics. *Nat. Phys.* **2007**, *3*, 153–159.
- (11) Mas-Torrent, M.; Crivillers, N.; Veciana, J. Attaching Persistent Organic Free Radicals to Surfaces: How and Why. *Chem. Rev.* **2012**, *112*, 2506–2527.
- (12) Requist, R.; Modesti, S.; Baruselli, P. P.; Smogunov, A.; Fabrizio, M.; Tosatti, E. Kondo Conductance across the Smallest Spin 1/2 Radical Molecule. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 69–74.
- (13) Mugarza, A.; Krull, C.; Robles, R.; Stepanow, S.; Ceballos, G.; Gambardella, P. Spin Coupling and Relaxation inside Molecule–Metal Contacts. *Nat. Commun.* **2011**, *2*, 490.
- (14) Liu, J.; Isshiki, H.; Katoh, K.; Morita, T.; Breedlove, B. K.; Yamashita, M.; Komeda, T. First Observation of a Kondo Resonance for a Stable Neutral Pure Organic Radical, 1,3,5-Triphenyl-6-oxoverdazyl, Adsorbed on the Au(111) Surface. *J. Am. Chem. Soc.* **2013**, *135*, 651–658.

- (15) Sanvito, S. Molecular Spintronics: The Rise of Spininterface Science. *Nat. Phys.* **2010**, *6*, 562–564.
- (16) Grillo, F.; Mugnaini, V.; Oliveros, M.; Francis, S. M.; Choi, D.-J.; Rastei, M. V.; Limot, L.; Cepek, C.; Pedio, M.; Bromley, S. T.; et al. Chiral Conformation at a Molecular Level of a Propeller-Like Open-Shell Molecule on Au(111). *J. Phys. Chem. Lett.* **2012**, *3*, 1559–1564.
- (17) Grillo, F.; Fruchtl, H.; Francis, S. M.; Mugnaini, V.; Oliveros, M.; Veciana, J.; Richardson, N. V. An Ordered Organic Radical Adsorbed on a Cu-Doped Au(111) Surface. *Nanoscale* **2012**, *4*, 6718–6721.
- (18) Kakavandi, R.; Savu, S.-A.; Sorace, L.; Rovai, D.; Mannini, M.; Casu, M. B. Core–Hole Screening, Electronic Structure, and Paramagnetic Character in Thin Films of Organic Radicals Deposited on SiO₂/Si(111). *J. Phys. Chem. C* **2014**, *118*, 8044–8049.
- (19) Steil, S.; Grossmann, N.; Laux, M.; Ruffling, A.; Steil, D.; Wiesenmayer, M.; Mathias, S.; Monti, O. L. A.; Cinchetti, M.; Aeschlimann, M. Spin-Dependent Trapping of Electrons at Spininterfaces. *Nat. Phys.* **2013**, *9*, 242–247.
- (20) Barraud, C.; Seneor, P.; Mattana, R.; Fusil, S.; Bouzehouane, K.; Deranlot, C.; Graziosi, P.; Hueso, L.; Bergenti, L.; Dediu, V.; et al. *Nat. Phys.* **2010**, *6*, 615–620.
- (21) Djeghloul, F.; Ibrahim, F.; Cantoni, M.; Bowen, M.; Joly, L.; Boukari, S.; Ohresser, P.; Bertran, F.; Le Fèvre, P.; Thakur, P.; et al. Direct Observation of a Highly Spin-Polarized Organic Spininterface at Room Temperature. *Sci. Rep.* **2013**, *3*, 1272.
- (22) Cook, P. L.; Yang, W.; Liu, X.; García-Lastra, J. M.; Rubio, A.; Himpsel, F. J. Unoccupied States in Cu and Zn Octaethyl-Porphyrin and Phthalocyanine. *J. Chem. Phys.* **2011**, *134*, 204707.
- (23) (a) Krause, S.; Casu, M. B.; Schöll, A.; Umbach, E. Determination of Transport Levels of Organic Semiconductors by UPS and IPS. *New J. Phys.* **2008**, *10*, 085001. (b) Hesper, R.; Tjeng, L. H.; Sawatzky, G. A. Strongly Reduced Band Gap in a Correlated Insulator in Close Proximity to a Metal. *Europhys. Lett.* **1997**, *40*, 177–180.
- (24) Paniagua, J. C.; Mugnaini, V.; Gabellieri, C.; Feliz, M.; Roques, N.; Veciana, J.; Pons, M. Polychlorinated Trityl Radicals for Dynamic Nuclear Polarization: The Role of Chlorine Nuclei. *Phys. Chem. Chem. Phys.* **2010**, *12*, 5824–5829; the out-of-plane torsion of the three phenyl rings caused by the bulky chlorine atoms in C₄ and C₄' decreases the conjugation of the π -electron system and causes a substantial coupling of the unpaired electron density with the chlorine atoms..
- (25) Koch, R. J. The Intrinsic Stress of Polycrystalline and Epitaxial Thin Metal Films. *Phys.: Condens. Matter* **1994**, *6*, 9519–9550.
- (26) Bagus, P. S.; Wieckowski, A.; Wöll, C. Ionic Adsorbates on Metal Surfaces. *Int. J. Quantum Chem.* **2010**, *110*, 2844–2859.
- (27) Mugnaini, V.; Fabrizioli, M.; Ratera, I.; Mannini, M.; Caneschi, A.; Gatteschi, D.; Manassen, Y.; Veciana, J. Towards the Detection of Single Polychlorotriphenylmethyl Radical Derivatives by Means of Electron Spin Noise STM. *Solid State Sci.* **2009**, *11*, 956–960.
- (28) Maspoch, D.; Domingo, N.; Ruiz-Molina, D.; Wurst, K.; Tejada, J.; Rovira, C.; Veciana, J. A Robust Nanocontainer Based on a Pure Organic Free Radical. *J. Am. Chem. Soc.* **2004**, *126*, 730–731.