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C: Surfaces, Interfaces, Porous Materials, and Catalysis

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18 Franck Ngassam,[†] Etienne Urbain,[†] Loic Joly,[†] Samy Boukari,[†] Jacek Arabski,[†]
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20 François Bertran,[‡] Patrick Le Fèvre,[‡] Guillaume Garreau,[¶] Patrick Wetzel,[¶]
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22 Mebarek Alouani,[†] Martin Bowen,[†] and Wolfgang Weber^{*,†}
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26 *Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS), Université de*
27 *Strasbourg, CNRS UMR 7504, 23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France,*
28 *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France,*
29 *and Institut de Science des Matériaux de Mulhouse, CNRS-UMR 7361, Université de*
30 *Haute-Alsace, 68057 Mulhouse, France*
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^{*}To whom correspondence should be addressed

52 [†]Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS), Université de Strasbourg, CNRS UMR
53 7504, 23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France

54 [‡]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France

55 [¶]Institut de Science des Matériaux de Mulhouse, CNRS-UMR 7361, Université de Haute-Alsace, 68057 Mulhouse,
56 France
57

Abstract

Spin-resolved photoemission spectroscopy experiments are performed on perfluorinated Co-phthalocyanine ($F_{16}CoPc$) deposited onto ferromagnetic Co(001) to examine how doping (here with fluorine) of an organic semiconductor influences the interfacial electronic properties, and whether the formation of highly spin-polarized interface states is possible. It is found that this later property, initially reported for the non-fluorinated Pc, is also present for the fluorinated system Co/ $F_{16}CoPc$. This result shows that doping an organic semiconductor, which is an important and effective method to tailor the electronic transport properties of the molecules, does not inhibit the presence of a highly polarized spinterface.

Introduction

Organic spintronics, which blends spin electronics with organic/molecular electronics,¹ has recently received considerable attention (e.g.²⁻¹¹) because of the prospect of developing a new generation of spin devices toward information technology. In contrast to the class of inorganic semiconductors, where only relatively few semiconductors are employable, hundreds of new semiconducting molecules produced and screened out so far suggest a large number of applicable materials. A very attractive aspect of organic semiconductors (OS) is the ability to tune the semiconductive behavior via a simple chemical substitution, e.g. by replacing the H atoms by halogen atoms such as fluorine (F). In this way, the energy position of molecular orbital levels across metal-organic semiconductor (MO) and organic-organic semiconductor (OO) interfaces can be tuned. Since molecular orbital offsets define energy barriers that control carrier injection into, and transport between, layers, their control is thus of key importance for organic thin film devices such as OLEDs and photovoltaic cells.¹²

The interfaces between molecular films and contacting materials are crucial, such that interface engineering, i.e. the control of interfacial electronic properties, is a necessary prerequisite toward further progress in organic electronics. In this vein, numerous studies have investigated the electronic band structure of ferromagnetic (FM) MO-interfaces, the so-called spinterfaces,

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3 and identified spin-polarized interface states (IS) within the band gap region of the OS.^{13–18} The
4 high spin polarization of these states at room temperature (RT) was observed by spin-resolved
5 photoemission spectroscopy, for a number of systems (Co(001)/Pc,¹⁹ Co(001)/amorphous C,²⁰
6 Co(001)/phenanthroline,²¹ Co(001)/pentacontane,²¹ Fe(001)/Pc,²¹ Fe(001)/C₆₀²¹). The spinter-
7 face magnetism may be controlled electrically using either an adjacent artificial magnetoelectric,²²
8 or using ferroelectric molecules.²³ The spinterface magnetism and spin polarization may also be
9 established across noble metal spacers.^{24,25} Finally, the high transport spin polarization at RT of
10 the Co/C spinterface was also experimentally demonstrated.²⁶ At low temperatures spin-polarized
11 scanning tunneling microscopy on a single CoPc molecule adsorbed on a FM Fe film showed a
12 significant spin dependence of tunneling current flow.²⁷

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23 The electronic character of the OS studied in the above investigations is mainly determined
24 by C-C, C-H and a few C-N bonds. The Pauling electronegativity of H (2.1) and N (3) are rela-
25 tively close to that of C (2.5),²⁸ such that the charge transfer within the C-H and the C-N bonds is
26 supposed to be small. In fluorinated OS, however, the high electronegativity of F (4) leads to elec-
27 trically highly polarized C-F bonds, with the electron density substantially on F.²⁸ Of particular
28 interest is the lowering of the molecular orbitals energies close to the Fermi level upon fluorina-
29 tion, leading to an increase in the molecule's ionization potential and electron affinity.^{29,30} For
30 example, fluorinated Cu-phthalocyanine (F₁₆CuPc) exhibits a preferred acceptor behavior and has
31 been widely used as an n-type semiconductor in organic electronics.^{31–34} While a series of (spin-
32 integrated) photoemission studies of fluorinated OS on coinage metals (Cu, Ag, Au) exist (see³⁵
33 and references therein), no such studies are reported for fluorinated molecules on FM transition
34 metals such as Co. The goal of the present study is to show how doping an OS by substituting
35 H by fluorine influences the interfacial electronic properties, and whether the formation of highly
36 spin-polarized IS is still possible.

Methods

Spin-resolved photoemission experiments at room temperature were undertaken on the Cassiopée beamline at Synchrotron Soleil using p-polarized photons of 20 eV energy impinging on the sample at 45° . We emphasize that no significant photon-induced beam damage to the molecules could be evidenced. The spin polarization of the photoelectrons, which were collected in normal emission geometry, was measured using a Mott detector with an effective Sherman factor S of 0.12. The Mott detector exploits the left-right asymmetry A of electron scattering due to spin-orbit coupling to measure the polarization of an electron beam.³⁶ The energy and the angular resolution of the energy analyzer was 130 meV and 7° , respectively. In order to eliminate experimental asymmetries due to a misalignment of the electron beam with respect to the Mott detector, photoemission spectra for opposite magnetization directions were measured. The spin polarization component P_n perpendicular to the scattering plane is given by $P_n = A/S$. The spin-up and spin-down intensity spectra were obtained as follows: $I_{up} = \frac{I}{2}(1 + P_n)$ and $I_{down} = \frac{I}{2}(1 - P_n)$ with I the spin-integrated photoemission signal.

To extract the spin-resolved photoemission signal (difference spectrum) that comes from the ISs and from the molecular layers atop the interface, we used a subtraction procedure that takes into account the molecule-induced attenuation of the Co substrate photoemission signal. This procedure and its justification are presented in detail in Refs.^{19–21}

The density functional theory (DFT) calculations were carried out by means of the Vienna ab-initio simulation package (VASP)³⁷ and the generalized gradient approximation for exchange-correlation potential as parametrized by Perdew, Burke, and Ernzerhof.³⁸ We used the projector augmented wave (PAW) pseudopotentials as provided by VASP.³⁹ The van der Waals (vdW) weak interactions were computed within the so called GGA-D2 approach developed by Grimme⁴⁰ and later implemented in the VASP package.⁴¹ A kinetic energy cutoff of 450 eV has been used for the plane-wave basis set. To take into account the correlation effects of transition-metal 3d electrons, the DFT-GGA+U method⁴² is adopted and in which the Hubbard U-term was chosen to be 3 eV in all cases. Charge transfer and local magnetic moments were calculated using a Bader charge analy-

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3 sis.^{43,44} For the calculations one molecule was placed on a Co(100) slab simulated by three atomic
4 layers of a 8x8 lateral super-cell intercalated by seven vacuum layers in the vertical direction.
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7 All experiments were performed in-situ in ultrahigh vacuum systems with a base pressure in
8 the low 10^{-10} mbar range. In the first step of the sample preparation ferromagnetic Co films of
9 15 ML thickness have been deposited on a Cu(001) single crystal at room temperature from a rod
10 heated by electron beam bombardment at a deposition rate of about 1 ML/min. Prior to deposition,
11 the Cu surface was cleaned by several cycles of Ar-ion sputtering and annealing at 800 K. The film
12 system Cu(001)/Co has been extensively investigated in the past (see for instance Refs.⁴⁵⁻⁴⁸). Co
13 films on Cu(001) are magnetized remanently in-plane along the [110]-direction.
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21 In the second step of the sample preparation we deposited a thin film of CoPc or F₁₆CoPc
22 (both purchased from Aldrich) onto the ferromagnetic film at room temperature. The organic
23 molecules are evaporated by radiative heating and the evaporation rate is controlled by a quartz
24 microbalance. The evaporation rate of the organic films was determined to be around 1 ML/10
25 min. For the measurements of the work function change the effective rate was much slower as
26 the deposition steps were interrupted by the measurements. The thicknesses of the molecular
27 layers were determined by Auger electron spectroscopy as well as by studying the reflectivity
28 of electrons as a function of molecular coverage in electron reflection experiments (not shown;
29 similar to experiments in ref.⁴⁹). The similar molecular stability of CoPc and F₁₆CoPc suggests
30 that the successful adsorption of intact CoPc molecules onto Co surfaces⁵⁰ is also straightforwardly
31 expected for F₁₆CoPc.
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45 **Results and discussion**

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48 The high electronegativity of the F atoms in the fluorinated Pc molecules is supposed to have
49 a significant impact on the strength of the interfacial dipole that is created at the Co/F₁₆CoPc
50 interface. The presence of an interface dipole is signaled, using electron reflection spectroscopy,
51 by an energy shift of the secondary electron cut-off. Figure 1 shows the work function change $\Delta\phi$
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as a function of organic layer thickness for fluorinated ($F_{16}CoPc$) and non-fluorinated Pc ($CoPc$).

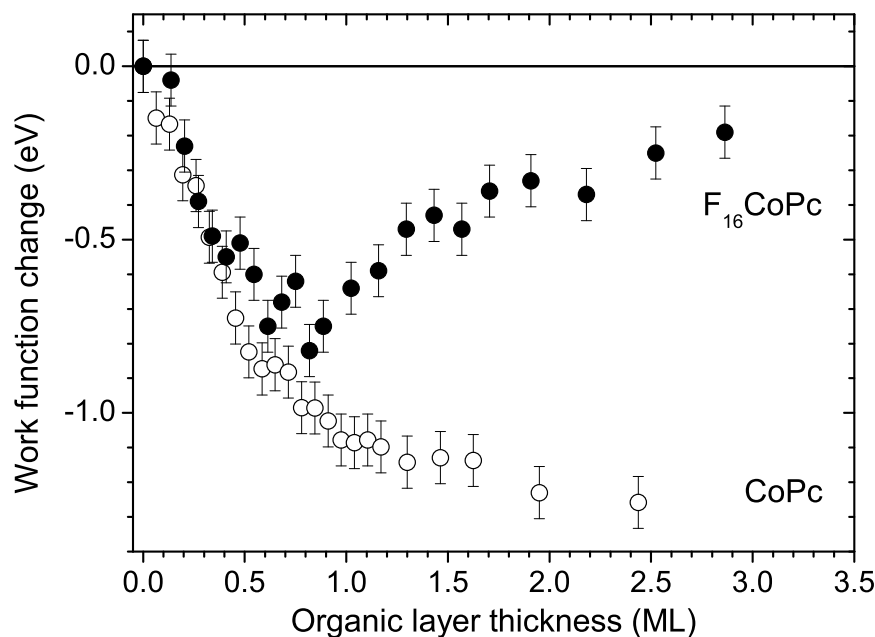


Figure 1: Change of the work function of $CoPc$ (open symbols) and $F_{16}CoPc$ (filled symbols) on $Co(001)$ for different Pc coverage.

The behavior of $\Delta\phi$ for the non-fluorinated Pc is similar to what was already observed in the past for the same system $Co(001)/CoPc$ ⁴⁹ as well as for a similar system, namely $Cu(001)/MnPc$.⁴⁹ In all cases a monotonous decrease of $\Delta\phi$ down to values of about -1.2 eV for $Co/CoPc$ and -0.9 eV for $Cu/MnPc$ is found.

It is emphasized that within a simple picture we would expect that the value of $\Delta\phi$, in particular its sign, reflects the total charge transfer (CT) at the molecule-substrate interface. Our DFT calculations show that electronic charge is transferred from the Co substrate to the molecule for both the non-fluorinated and the fluorinated molecules (3.7 electrons (e^-) for $CoPc$; 5.3 e^- for $F_{16}CoPc$; see table) such that we would expect in both cases rather an increase of the work function, i.e. $\Delta\phi > 0$. However, whether the work function decreases or increases does not only depend on the direction of the overall charge transfer. The situation is in general more complicated. This problem has been already discussed by Javaid *et al.*⁵¹ In fact, one has to go beyond the standard dipole model and to examine how the charge is spatially distributed across the interface. The es-

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sential point is that, rather than having a rigid shift in molecular orbitals, the interface dipole in fact consists of Friedel-like oscillations that more realistically reflect how the metal is screening the interface charge due to molecular adsorption.

Table 1: Site-specific charge transfer in units of the elementary charge for the systems Co/CoPc and Co/F₁₆CoPc

| | CoPc | F ₁₆ CoPc |
|--------------|-------|----------------------|
| Co (1) | -0.31 | -0.3 |
| C (32) | -3.97 | -5.29 |
| N (8) | -0.04 | +0.34 |
| H (16) | +0.61 | - |
| F (16) | - | +0.03 |
| total charge | -3.71 | -5.22 |

The behavior of $\Delta\phi$ for the fluorinated Pc, on the other hand, is quite different as it exhibits a non-monotonous behavior. While $\Delta\phi$ exhibits a decrease similar to that of CoPc up to a thickness of about one ML, $\Delta\phi$ increases for higher F₁₆CoPc coverage. In fact, the contribution of the F atoms in F₁₆CoPc is not so important. While the 16 H atoms in the CoPc lead to a CT from the molecule to the substrate of 0.61 e⁻ (see table) the 16 F atoms in F₁₆CoPc are at the origin of a CT in the same direction of only 0.03 e⁻ (see table). We thus expect the difference in $\Delta\phi$ not to be too dramatic between the two molecules. This is what we observe in the low-coverage regime. For larger coverage, however, we observe an increase of $\Delta\phi$ in the case of F₁₆CoPc.

We emphasize that a similar difference in the behavior of $\Delta\phi$ was observed for the same organic molecules but deposited onto polycrystalline Au.⁵² While $\Delta\phi$ of CoPc continues decreasing for thicknesses above 1 ML (corresponds to about 0.4 nm), an increase is found for F₁₆CoPc. A careful analysis of this problem leads to the conclusion that the work function changes for larger thicknesses are driven by the adjustment of the chemical potentials to equilibrium at the interface between the metal substrate and the formed Pc film.⁵²

To study the spin-resolved electronic structure at the interface between F₁₆CoPc and the FM Co substrate, we performed spin-resolved photoemission spectroscopy experiments. We present in Fig. 2 the spin-resolved electron distribution curves as a function of the binding energy for

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3 the uncovered Co film (top), the Co film covered by 1.3 ML F₁₆CoPc (middle), and the Co film
4 covered by 2 ML F₁₆CoPc (bottom). When studying only the Co(001) (top) surface, we observe
5 a strong imbalance of the spin-up and spin-down channels resulting from the FM Co layer, which
6 corresponds to a strong negative spin polarization close to the Fermi level. When Co is covered by
7 F₁₆CoPc (middle and bottom), the photoemission signal is attenuated in both spin channels. Apart
8 from this we observe the appearance of two new structures: one at around -0.25 eV in the spin-up
9 channel, and another at around -0.8 eV in the spin-down channel (both indicated by arrows in Fig.
10 2). These structures are similar to those that were already observed in recent experiments on non-
11 fluorinated Pc, on other organic molecules as well as on amorphous carbon and were identified as
12 highly polarized IS.^{19–21}

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14 To more directly evidence the additional features in the spectra, we examine spin-polarized
15 difference spectra so as to focus on the spin-resolved photoemission signal that arises from the
16 interface and the molecular layers atop the interface.^{19–21} Figure 3 shows the energy dependence
17 of spin-polarized difference spectra at room temperature for 1.3 ML (top) and 2 ML F₁₆CoPc on
18 Co (middle) as well as of the spin polarization of the difference spectra for 2 ML F₁₆CoPc on
19 Co (bottom). The intensity close to the Fermi level is dominated by a spin-up structure whose
20 maximum is at -0.25 eV energy. The spin-down channel, on the other hand, exhibits a small gap.
21 Consequently, the spin polarization of the interfacial electronic band structure is strongly positive
22 close to the Fermi level. At higher binding energy, around -0.8 eV, we observe a strongly negatively
23 polarized state.

24
25 By comparing the difference spectra obtained with the fluorinated Pc molecules (Fig. 3) with
26 those of non-fluorinated ones (MnPc and H₂Pc¹⁹) we find good agreement: For F₁₆CoPc on Co the
27 binding energy positions of the IS are -0.3 and -0.8 eV compared to -0.3 and -1 eV for MnPc and
28 H₂Pc. The energy position of the IS at higher binding energy may be influenced by the position of
29 the HOMO, which lies in this energy range and can slightly change its position upon fluorination⁵³
30 and depends as well on the choice of the central metal ion.⁵⁴ Concerning the -0.25 eV peak, the
31 line widths (FWHM) are for fluorinated and non-fluorinated Pc around 0.5 eV. We emphasize
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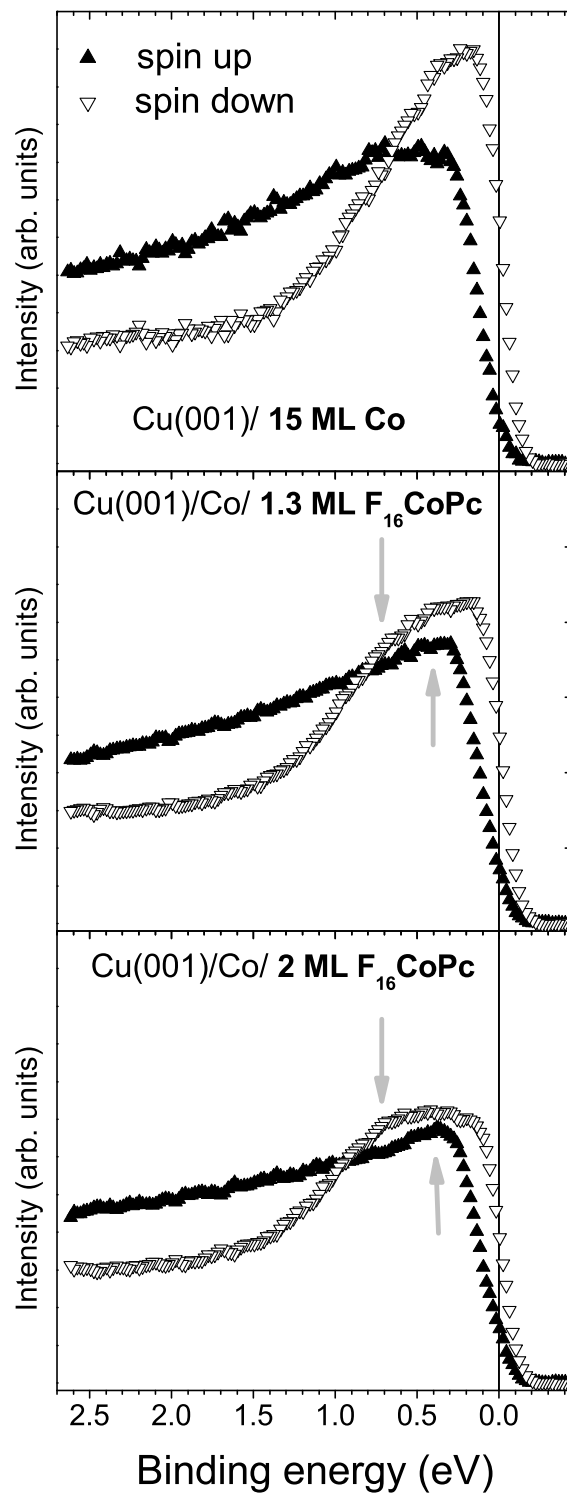


Figure 2: Spin-resolved photoemission spectra as a function of the binding energy for 15 ML Co on Cu(001) (top), 1.3 ML F₁₆CoPc on Cu(001)/Co (middle), and 2 ML F₁₆CoPc on Cu(001)/Co (bottom). The photon energy is 20 eV. The arrows in the middle and bottom panel indicate the appearance of spin-polarized IS.

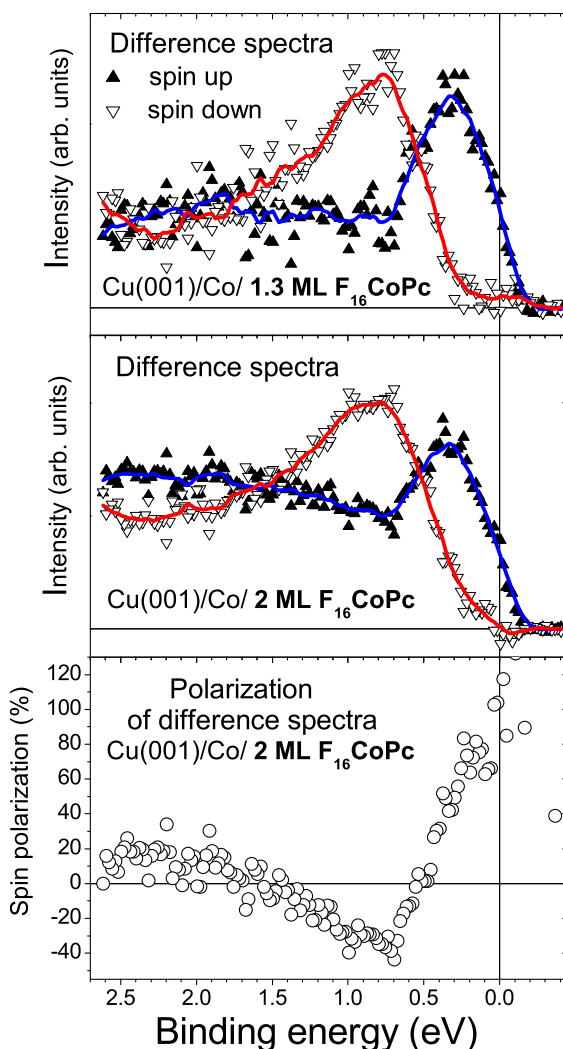


Figure 3: Spin-resolved photoemission spectra as a function of the binding energy after subtraction of a suitably normalized pure Co spectrum for 1.3 ML F₁₆CoPc on Cu(001)/Co (top) and for 2 ML F₁₆CoPc on Cu(001)/Co (middle). (bottom) The spin polarization of the difference spectra for 2 ML F₁₆CoPc on Cu(001)/Co as a function of binding energy. The photon energy is 20 eV. The lines through the data points are obtained after averaging the difference spectra.

that similar energy positions and line widths were also observed for other non-fluorinated organic molecules on Co(001).²¹

We corroborate the above experimental finding that the interface between a FM metal and fluorinated and non-fluorinated Pc molecules exhibits a very similar density-of-states structure thanks to DFT calculations. Figure 4 shows the calculated spin-polarized density of the molecules'

p-states for Co(3 ML)/CoPc(1 ML) (black line) and for Co(3 ML)/F₁₆CoPc(1 ML) (green line). While the differences between CoPc and F₁₆CoPc become more important for binding energies below -1.5 eV, no significant differences are found in the energy region closer to the Fermi level. This is thus in line with the experimental fact that both molecules on top of Co(001) possess very similar interfacial spectral features. We emphasize in this context that claims exist in the literature (see³⁵ and references therein) that the charge transfer, which occurs at a different interface, namely F₁₆CoPc on Au, is limited to the Co center of the molecule and therefore hardly affects the ligand orbitals of the molecule. If the same were happening in the case of the systems Co/CoPc and Co/F₁₆CoPc, it would not be surprising to see only little differences between these two systems for the *p*-states in an energy region close to the Fermi level. However, our calculations (not shown) in which we determined the charge transfer between Co(001) as substrate and three organic molecules (CoPc, F₁₆CoPc, and H₂F₁₆Pc) show that this is not the case. For all three molecules the dominant contribution to the charge transfer, in which electrons are transferred from the Co substrate to the molecules, comes from the 32 C atoms (3.97 e⁻ for CoPc, 5.29 e⁻ for F₁₆CoPc, and 3.97 e⁻ for H₂F₁₆Pc). The contribution from the single central Co ion in CoPc and F₁₆CoPc is only 0.3 e⁻. The charge transfer is thus distributed over the entire molecule, including the central metal ion if any is present.

Within the DFT calculations, we also studied the magnetization of the ligand and the central Co ion in both molecules. While the net magnetization of the ligand is antiparallel oriented with respect to the magnetization of the Co substrate with a magnetic moment of 0.39 μ_B for CoPc and 0.57 μ_B for F₁₆CoPc), the magnetization of the central Co ion is parallel oriented with respect to the substrate magnetization (0.43 μ_B for CoPc, 0.79 μ_B for F₁₆CoPc).

Conclusion

In conclusion, we performed spin-resolved photoemission spectroscopy experiments on F₁₆CoPc deposited onto FM Co(001) to test whether altering the electronic properties of the molecule im-

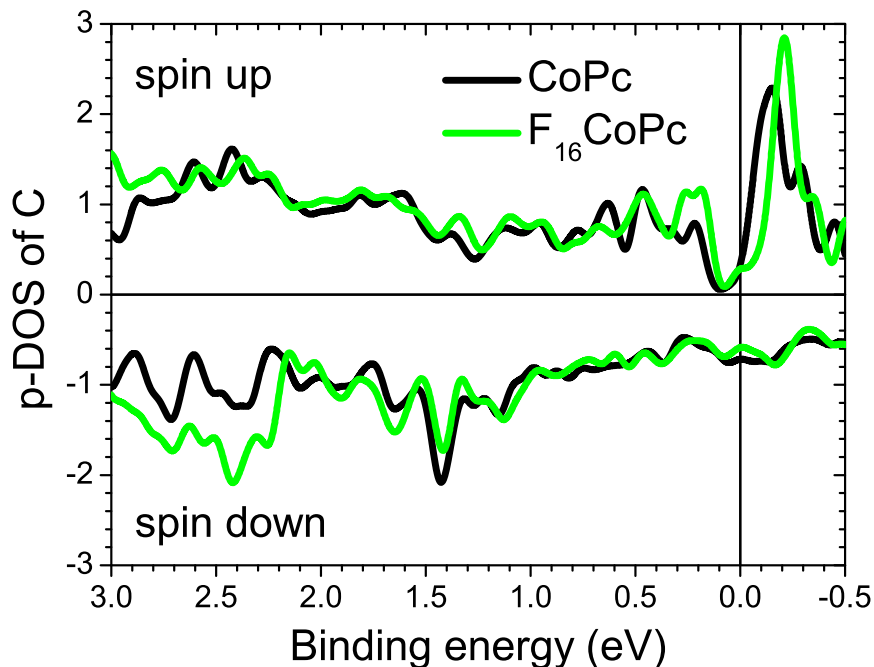


Figure 4: Calculated spin-polarized density of the molecules C *p*-states for Co(3 ML)/CoPc(1 ML) (black line) and for Co(3 ML)/F₁₆CoPc(1 ML) (green line). All DOS data have been averaged over an energy interval of 50 meV.

pacts the formation of highly spin-polarized IS close to the Fermi level. We find that this property, initially reported for the non-fluorinated Pc, also appears for the fluorinated system F₁₆CoPc on Co. This result is particularly interesting from the application point of view since it shows that doping (here with fluorine), which is an important and effective method to tailor the electronic transport properties of a system, does not inhibit the presence of a highly polarized spinterface.

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Note: The authors declare no competing financial interest.

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