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1 Spinterface formation at α -sexithiophene/ ferromagnetic 2 conducting oxide

3

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11

12 **ABSTRACT:**

13 The inorganic/molecular spinterface is an ideal platform for generating extraordinary spin effects. Understanding and
14 controlling these spin-related effects is mandatory for the exploitation of such interfaces in devices. For this purpose,
15 we have investigated the adsorption of α -sexithiophene (α -6T) on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO), as one of the prototypical
16 material combinations used in organic spintronic devices. Atomic force microscopy, confocal photoluminescence, X-
17 ray photoelectron spectroscopy, and metastable de-excitation spectroscopy unraveled the structure and electronic
18 configuration of 6T for various surface coverages. This data set allowed the determination of characteristic features of
19 occupied states, the band diagram and the work function. Finally, density functional theory enabled us to establish
20 that the spin polarization in 6T molecular orbitals critically depends on the termination layer of LSMO. We believe that
21 this research provides important hints for a comprehensive understanding of spinterface effects in general and
22 provides key suggestions for further engineering of LSMO/6T-based devices.

23

24

25 **INTRODUCTION:**

26 Hybridization at the interface between molecular entities and ferromagnetic metals leads to drastic
27 changes of the properties of both layers [1,2]. Notably, an increase of spin polarization of states around the
28 Fermi level [2], modulation of the magnetic anisotropy [3] and spin re-orientation transitions were
29 observed in ferromagnetic layers as well as the appearance of spin polarized states in the molecular
30 material [5]. Such new hybrid interfaces with unexpected spin functionality, named after the seminal paper
31 by Sanvito as “spinterfaces” [6], act as a key element at the molecular level for engineering the properties
32 and the performance of spin-devices. Among the plethora of spinterfaces, those including half-metallic
33 ferromagnetic oxides such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) are of special interest. LSMO has been coupled to a
34 variety of organic molecules and successfully used in spintronic devices [7,8], even showing the inversion of
35 the sign of the polarization upon the deposition of an organic molecule [9]. Nonetheless, the variability of
36 the composition of the termination layer of LSMO [10–12] hindered a reliable investigation of its interface
37 with organic molecules. In this paper we focus on the coupling between a π -conjugated oligothiophene, 6T
38 (sexithiophene), and LSMO; one of the first hybrid interfaces used in spin injection devices [13]. 6T is a rod-
39 like model organic molecule [14] which contains six thiophene rings linked together; it can be easily
40 sublimated in ultrahigh vacuum (UHV), a pre-requisite for the control and reproducibility of interfacial
41 states, and it is also known to form ordered thin layers on solid surfaces. Here, the growth process of 6T on

1 LSMO has been studied by photoemission spectroscopy and metastable helium de-excitation spectroscopy
2 to follow the evolution of spectral signatures as a function of coverage. The complementary investigation of
3 morphology by atomic force microscopy (AFM) and molecule-LSMO coupling by confocal microscopy allows
4 a full description of the 6T/LSMO interaction. First principles calculations based on density functional
5 theory (DFT) help to bridge the gap between the experimental reports on molecular orientation, binding
6 energies, and heights, in addition to the electronic structure of the interface. Our results demonstrate that
7 the interface is characterized by a weak electronic coupling but that, nonetheless, spin polarization extends
8 over the 6T molecule allowing spin polarized injection.

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1 EXPERIMENTAL

2 Epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) films were grown on a single crystal SrTiO_3 (100) substrate by channel spark
3 ablation (CSA) from a stoichiometric polycrystalline target [15]. Substrate temperature was kept close to
4 $880\text{ }^\circ\text{C}$ in an oxygen pressure of $P=4\times 10^{-2}$ mbar. LSMO films were then transferred to a UHV system (base
5 pressure of $<2\times 10^{-10}$ mbar) to perform surface analysis and the deposition of organic material. To recover
6 surface quality and remove the contamination due to air exposure, LSMO films were subjected to a mild
7 anneal at $250\text{ }^\circ\text{C}$ following the procedure described in Refs. [8] and [10] with optimal surface quality
8 confirmed by ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS).
9 During the evaporation of 6T (Sigma-Aldrich), the LSMO temperature (T_{sub}) was held at $120\text{ }^\circ\text{C}$ and the
10 deposition rate was 0.02 \AA/s . The total quantity of organic material deposited on the LSMO was evaluated
11 by using a room temperature quartz microbalance. UPS experiments were conducted using a He discharge
12 source at photon energies of 21.2 eV with a monochromated Al $K\alpha$ source at 1486.6 eV (XM1000, Scienta
13 Omicron GmbH) used to perform XPS. Metastable de-excitation spectroscopy (MDS) was performed using a
14 helium 2^3S beam generated using a cold-cathode DC discharge source [16]. The cross-section for de-
15 excitation of He 2^3S atoms at a sample surface is sufficiently large to ensure there is zero penetration below
16 the topmost layer providing extreme surface sensitivity when compared to UPS and XPS which provide
17 information averaged over at least several atomic layers. All three electron spectroscopies were performed
18 in the same UHV chamber with emitted electrons detected using a hemispherical energy analyzer (Scienta
19 Omicron EA 125).

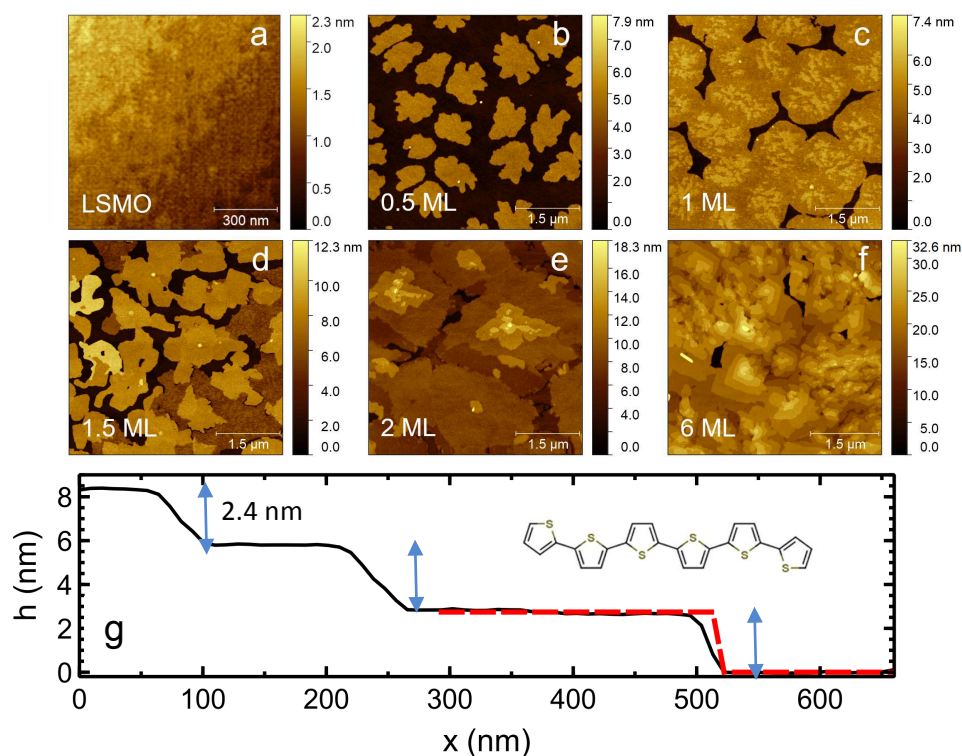
20 The topography of 6T films was investigated by using an AFM Smena microscope (NT-MDT, Moscow,
21 Russia) in Intermittent Contact Mode (ICM) under ambient conditions. The silicon cantilevers employed in
22 ICM measurements (NSG11, NT-MDT, Moscow, Russia) had nominal resonant frequency, ω_0 , of ~ 150 and
23 $\sim 240\text{ kHz}$ and spring constant, k , of ~ 5 and $\sim 12\text{ N/m}$, respectively. The 6T molecular packing was explored
24 by confocal photoluminescence (PL) microscopy with images obtained using a Nikon Eclipse TE-2000-E
25 fluorescence confocal microscope and excitation light provided by a 488 nm Ar^+ laser. A $405/488\text{ nm}$ dual
26 dichroic mirror reflected the excitation beam towards a $60\times$ air objective (N.A.=1.4).

27 All electronic structure calculations were performed using the Vienna Ab-initio Simulation Package
28 (VASP) [17–20] within the DFT framework. A plane wave basis set with the projector augmented wave
29 (PAW) method [21,22] and the GGA-PBE functional [23,24] taking into account Hubbard corrections (GGA +
30 U) [25,26] and the Grimme correction [27] for van der Waals interactions were used. Monkhorst-Pack
31 Brillouin zone k-point sampling was implemented, and the k-point mesh contained $2\times 2\times 1$ k-points for the
32 corresponding supercells. A vacuum interval of 20 \AA was set normal to the plane to avoid artificial
33 interactions between adjacent images. The cutoff energy was equal to 400 eV . A maximum force acting on
34 atoms less than 0.001 eV/\AA was used as a stopping criterion for structural optimizations. The $U = 2$ and $J =$
35 0.7 eV parameters of GGA + U approach were adopted from earlier calculations of LSMO [28–30].

36 RESULTS AND DISCUSSION

37 Adsorption of α -6T on the LSMO surface

38 Topographic AFM images in Figure 1 show the morphological evolution of 6T films grown on the surface of
39 15 nm thick LSMO films deposited on crystalline STO(100). The bare LSMO surface in Figure 1a shows the
40 typical atomic steps of the STO substrate surface (step height of $\sim 0.4\text{ nm}$) and exhibits a very flat surface
41 between steps with surface roughness of nearly 0.3 nm , close to the LSMO unit cell [15,31,32]. As shown in
42 Figure 1b – f, 6T films deposited on LSMO follow the Stranski-Krastanov growth mode (2D + 3D) as usually
43 observed for rod-like conjugated molecules deposited on oxides [33]. The first two monolayers (Figure 1b –
44 e) present the Frank – van der Merwe growth mode (2D, layer-by-layer) then for subsequent monolayers
45 up to 6 ML (Figure 1f), the Volmer – Weber growth mode (3D) dominates the film growth.



1

2 **Figure 1:** Evolution of 6T morphology for increasing coverage (b-f). Bare LSMO (a). Height profile of the 6 ML thick film
 3 (g). The inset in (g) shows the molecular structure of 6T.

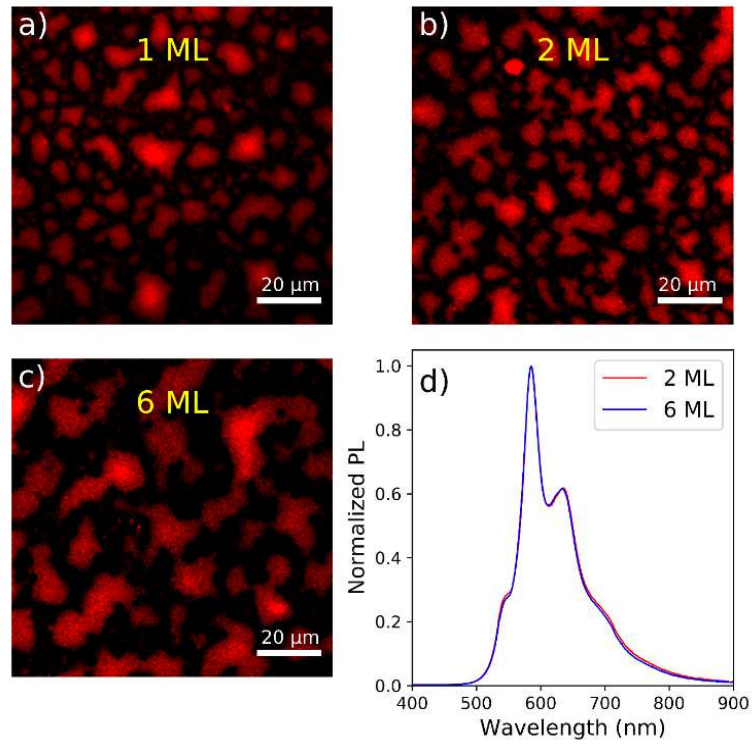
4 In the sub-monolayer regime of 6T deposition, AFM images show the formation of islands (Figure 1b)
 5 similarly to what was observed for 6T on silicon oxides [34–36] or other π -conjugated molecules on
 6 LSMO [37]. As the thickness increases, the islands expand and eventually coalesce to form an almost
 7 complete monolayer (Figure 1c). Notably, on top of 6T islands, the 1 ML-thick film clearly shows aggregates
 8 of molecules in the second layer (brighter regions in Figure 1c). By increasing the thickness, i.e. 1.5 ML
 9 (Figure 1d), 6T films experience a spontaneous molecular rearrangement (dewetting) [38,39]. Although the
 10 dewetting of the film is preserved in the following deposition steps, 2 ML-thick films show the formation of
 11 the third and even the fourth ML (Figure 1e), suggesting that the Volmer – Weber growth mode (3D) has
 12 started. The profile image (Figure 1g) suggests that the film is formed by upright molecules, with the
 13 molecular long axis almost perpendicular to the substrate ~ 2.4 nm, in analogy to 6T grown on SiO_2 [40] and
 14 TiO_2 [41].

15

16 Confocal photoluminescence (PL) microscopy

17 The conformation of molecules on LSMO is confirmed by confocal PL investigations. The PL images
 18 corresponding to 1, 2, and 6 ML coverages of 6T on LSMO films are shown in Figure 2a-c. Films are all
 19 characterized by low fluorescence quantum yields except red bright spots corresponding to emission from
 20 islands of 6T. As expected for the vertical packing of 6T molecules [40,42], the PL spectra of the samples
 21 correspond to the emission of an H-type aggregate as shown in Figure 2d. In H-type aggregates, transition
 22 moments lie along long molecular axes parallel to one another so that relaxation occurs mainly via
 23 nonradiative processes resulting in a low fluorescence quantum yield, in agreement with the low PL
 24 intensity detected in our films. Considering the full surface coverage detected by AFM, the presence of dark
 25 spots is therefore interpreted as 6T regions with poor dipole coupling resulting in a very weak PL intensity.
 26 Such PL quenching is often associated with inhomogeneity in the packing arrangement [ref]. The lack of

- 1 new absorption bands or a shift in the spectrum at different coverages indicates that the interface does not
- 2 originate new excitonic species.



3
 4 Figure 2. PL images of 1 (a), 2 (b), and 6 (c) ML of T6 on LSMO/STO ($\lambda_{\text{ex}} = 488 \text{ nm}$). The PL spectra of 2 ML and 6 ML of T6 on
 5 LSMO/STO are also shown (d) ($\lambda_{\text{ex}} = 375 \text{ nm}$).

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7 **Ultraviolet photoelectron spectroscopy**

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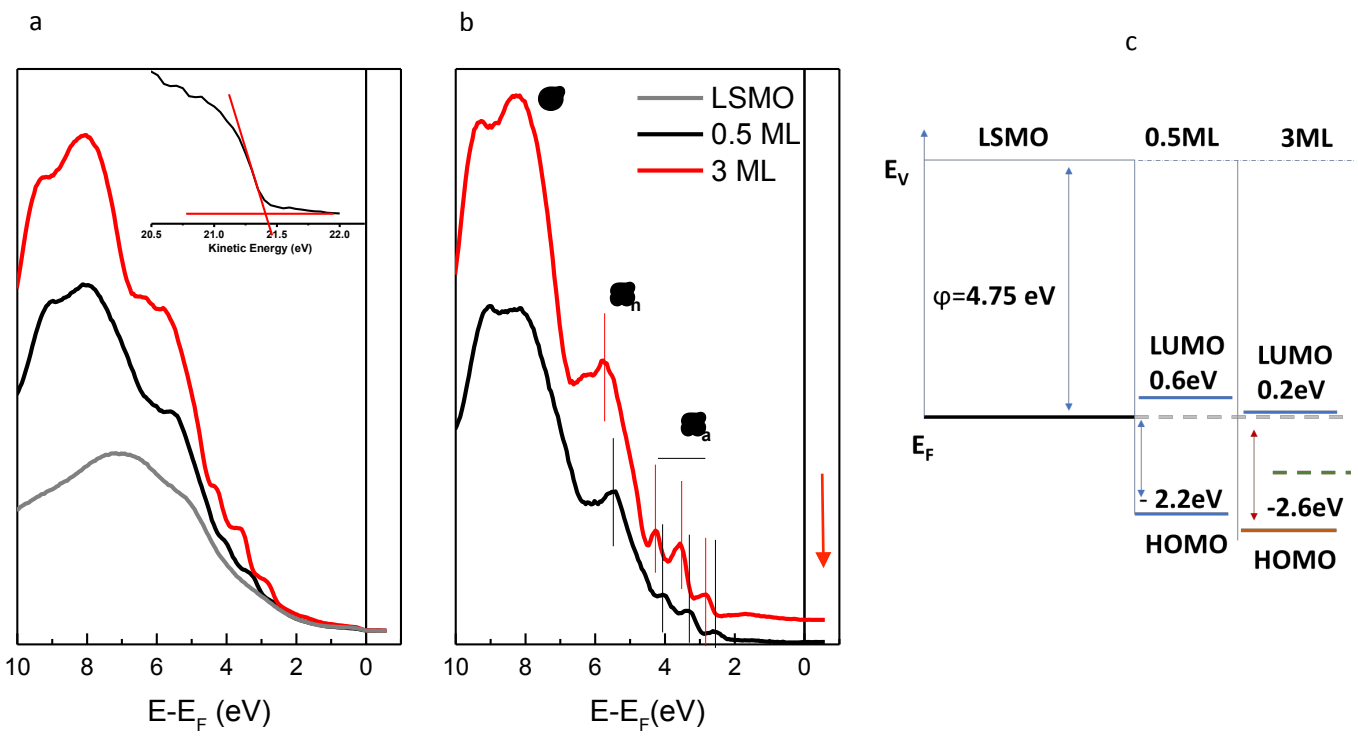
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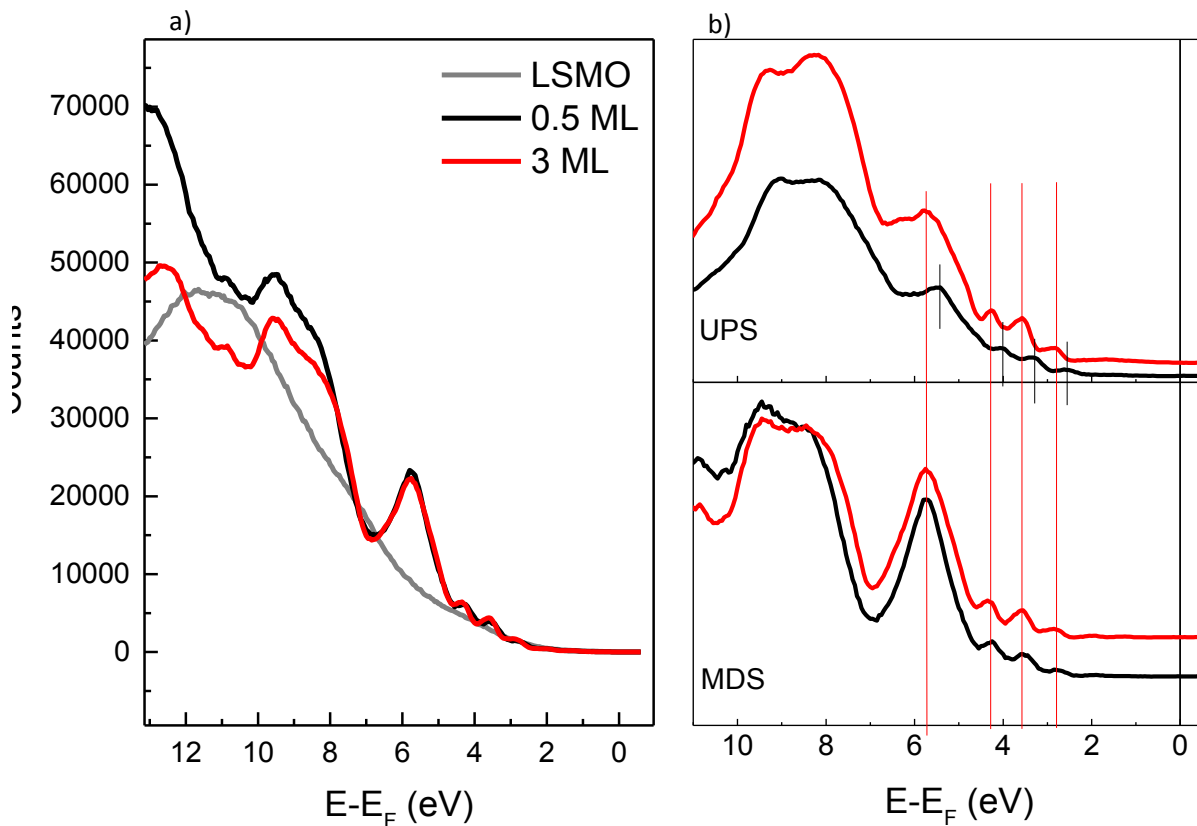
1 **Figure 3.** (a) Ultraviolet photoemission spectra of an LSMO surface following incremental growth of sexithiophene films. (b) Spectra
2 obtained by subtraction of the LSMO signal from the total photoemission intensity of the spectra with nominally 0.5 and 3 ML thick
3 6T overlayers. (c) Band diagram corresponding to the LSMO/6T interface.

4 We investigate now the energetic configuration at the 6T/LSMO interface. Fig. 3a presents ultraviolet
5 photoemission spectra, collected at normal emission, of the LSMO surface upon incremental growth of
6 sexithiophene films. The spectrum of bare LSMO shows the onset of metallicity at E_F corresponding to Mn
7 e_g states (see inset) and a prominent peak due to emission from O $2p$ and Mn t_{2g} states, in agreement with
8 previous experimental investigations [29] confirming the surface quality of our samples. For the ultrathin
9 0.5 ML organic layer considered in this study, the UPS spectra consist of contributions from both the
10 organic molecule and the bare LSMO substrate. Therefore, to reveal the contribution of the 6T alone, we
11 subtracted the spectrum of the bare LSMO from the 6T film data, as shown in Figure 3b for 6T coverages of
12 0.5 ML and 3 ML. The molecular band is already clear at 0.5 ML and both coverages show well-resolved
13 features, as expected for an ordered film and allowing a clear identification of orbital contributions to the
14 density of states (DOS). The peak assignment follows previous studies [43]. The three peaks at around 2–4
15 eV are the antibonding π_a states; these orbitals are delocalized over the carbon backbone of the molecule,
16 with negligible sulfur contribution [44]; the peak at 5-6 eV is assigned to the nonbonding π states related to
17 localized orbitals of sulphur atoms (π_n), and extended and complex spectral features at 8 eV are ascribed to
18 bonding (σ) states [45]. On increasing coverage from a single molecular layer to multilayer 6T stacks, all
19 peaks shift to a higher energy. We exclude charging effects as the cause of this shift as different features
20 move by different amounts. The onset of the HOMO level, deduced from the onset of emission of the
21 HOMO peak, is measured to be at an energy of 2.2 (2.4) eV relative to the Fermi level for 0.5 ML (3 ML).
22 The position of the lowest unoccupied molecular orbital (LUMO) with respect to the HOMO is deduced
23 from the literature [46] and is close to 2.8 eV. Since the transport gap in the solid state can be larger by
24 several hundreds of meV than the optical gap, our experimental results indicate that E_F is very close but
25 slightly below the LUMO of 6T [47], as depicted in Fig 3c. The position of the LSMO Fermi level with respect
26 to the 6T LUMO favors charge donation from the substrate to the organic molecule.

27 The shift in position of the work function (ϕ) with increasing film coverage provides further insight into the
28 strength of the interfacial interaction. The bare LSMO work function was measured to be $\phi_{\text{LSMO}}=4.75\text{eV}$, as
29 determined from the difference between the excitation energy ($E=21.2\text{ eV}$) and the secondary electron
30 emission cut-off. On increasing 6T deposition, a small ϕ change is observed: for the incomplete coverage
31 (0.5 ML), ϕ increases by approximately +0.15 eV, and for further 6T deposition (3 ML), the work function
32 decreases and leads to a stabilization of $\Delta\phi=+0.05\text{ eV}$. The adsorbed molecules are reasonably expected to
33 generate a decrease in ϕ due to the electron push-back effect [48,49]. On the other hand, the presence of
34 charge transfer can cause an increase in the sample work function due to the additional dipole moment
35 induced by the electron transfer from the metal to the molecule. These two competing effects could
36 reasonably explain the scarce change of work function in our bilayer. The small $\Delta\phi$ for the 3 ML sample can
37 be due to multilayer formation, where no further charge transfer occurs, but subtle changes in the
38 monolayer conformation may be induced by multilayer overgrowth. The strength of the interface dipole
39 depends also on the charge-carrier concentration of the substrate. It is important to note that LSMO has a
40 free carrier concentration on the order of 10^{21} cm^{-3} [50], well below the carrier concentration of a standard
41 metal. The appearance of a low intensity broad peak centered at 1.9 eV below E_F for the 3 ML-thick 6T
42 layer (red arrow in Figure 3b) supports this picture of charge transfer [47], in analogy to what has been
43 observed for molecules on doped ZnO [51] where charges from the pseudo-metallic substrate are
44 transferred into the LUMOs. The charge transfer from LSMO to 6T is facilitated by the LUMO position close
45 to E_F however exact quantification is difficult due to the compensating effect of push-back and charge
46 transfer on the work function ϕ . Note that the electron transfer is likely very small for the 0.5 ML film,
47 inhibiting its observation by UPS.

48 **Metastable de-excitation spectroscopy**

1 MDS is an extremely surface sensitive spectroscopy technique that allows the investigation of the topmost
2 frontier orbitals of the sample. In our case, taking into account the upright orientation of the molecule on
3 LSMO as deduced from AFM and PL spectroscopy, we expect that He 2^3S de-excitation takes place at the
4 terminal thiophene ring. Figure 4a shows the evolution of MDS spectra as 6T is deposited onto the clean
5 LSMO surface. As expected for the helium 2^3S de-excitation process associated with metallic surfaces
6 (resonance ionization followed by Auger neutralization) [52], the bare LSMO layer presents a relatively
7 featureless spectrum. Upon the deposition of the organic molecules, the quasi-one-electron de-excitation
8 process of Auger de-excitation becomes favorable leading to well-defined features associated with HOMO
9 levels. In order to evidence the contribution of the organic phase, the spectrum corresponding to the bare
10 substrate was subtracted due to the incomplete 6T coverage. The peak's assignment follows the
11 description for UPS (see previous section) provided that in MDS the average DOS results from the frontier
12 atoms. The first three peaks (2.8, 3.5 and 4.2 eV) correspond to the antibonding π_a states, which are
13 delocalized over the carbon backbone with negligible coefficients on the sulfur atoms, and are scarcely
14 probed by the He 2^3S beam due to the packing of the 6T island. This explains the low intensity of these
15 components in the spectra. The well-defined peak at 5.8 eV is assigned to nonbonding π_n states from sulfur
16 whose contribution as terminal atoms in the outermost thiophene ring is dominant. The difference in
17 intensity for the components corresponding to the broad peak at 8 eV is associated with an increase of
18 sigma bonds for the 3 ML sample. The direct comparison of UPS and MDS spectra shown in Figure 4b
19 clearly indicates that the position of HOMO states in MDS spectra is similar for both coverages and
20 resembles the 3 ML UPS spectrum. In MDS, the energy spectra of emitted electrons represent the density
21 of states at the very topmost surface of the sample, while UPS, with more penetrating ultraviolet radiation,
22 provides information averaged over the density of states of the entire molecule. This result indicates that
23 the external frontier orbitals of 6T probed by MDS are barely involved in the interaction with LSMO and
24 that only the atomic orbitals at the interface are affected. The calculation of the projected density of states
25 on all the thiophene rings of the molecule under the configuration described in the DFT calculation section
26 (see below) are in agreement with these findings. (see Supplementary S1).



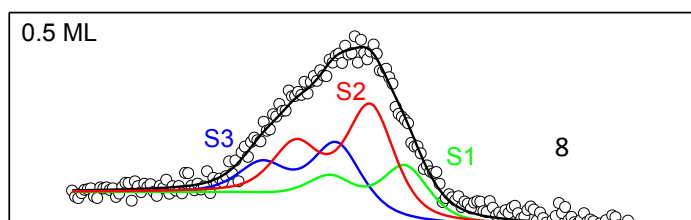
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2 **Figure 4.** (a) MDS spectra of the LSMO surface upon incremental growth of sexithiophene films. (b) The UPS and MDS spectra are
 3 obtained by subtraction of the LSMO signals from the total intensities of the spectra with nominally 0.5 and 3 ML thick 6T
 4 overlayers. Lines indicate peak positions for UPS and MDS spectra.

5 X-ray photoelectron spectroscopy

6 To understand the interactions between the sulfur headgroups in thiophene and the LSMO surface, we
 7 measured the XPS spectra in the S 2p region as a function of coverage. The S 2p XPS spectra are shown in
 8 Figure 5. After a Shirley background subtraction, spectra were decomposed into three multiple doublet
 9 components with a 1.2 eV spin-orbit splitting reflecting the nonequivalent S atom in the molecule [53].
 10 Considering that 6T adsorbs on LSMO with its long axis upright to the surface, three such S components can
 11 be assigned to the central thiol sulfur atoms from the main chain and the two sulfur atoms at the sides, the
 12 one close to the surface and the one that is free [54] [55,56]. The lower binding energy peak at 162.7 eV
 13 (S1) is typical of sulfide which is presumably S linked to the metal atoms of the LSMO surface [57,58]. This
 14 feature is also consistent with partial charge transfer, as observed for aluminum deposition on 6T [58].
 15 Higher binding-energy components (S2 and S3) can be attributed to the thiophene groups not directly
 16 interacting with the substrate because their photoemission-induced core holes are not well screened by
 17 valence electrons of the substrate [59]. The main S2 component is associated to the thiol sulfur of the
 18 chain, while the S3 component to the apical S. Additionally, no sulfur–oxygen bonding is present due to the
 19 lack of the corresponding S 2p peak typically appearing at higher binding energy (~168 eV) [60]. Coverage
 20 increase from 0.5 ML to 3 ML gives no significant change in binding energy while only a slight change of
 21 relative intensities of components is detected. This is consistent with a change in relative weight on
 22 increasing the thickness.

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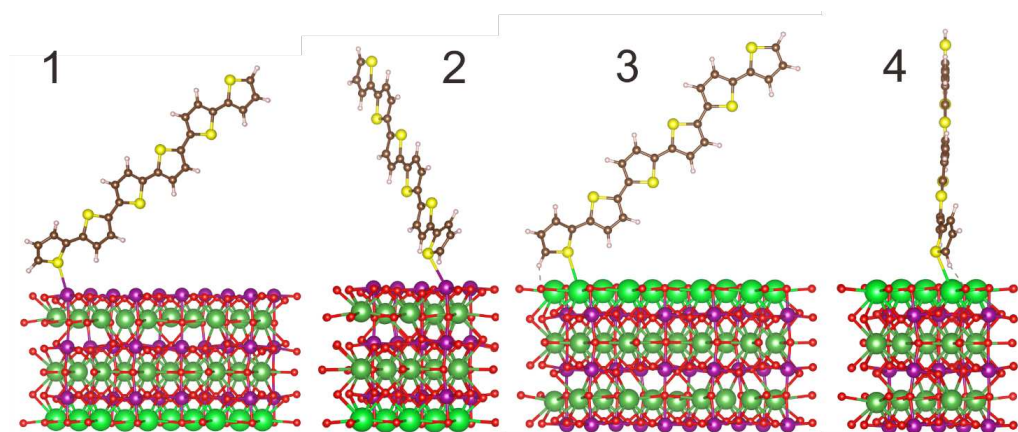
	E (eV)	0.5 ML % Area	3 ML % Area
S1	162.7	0.24	0.19
S2	163.2	0.48	0.55
S3	163.8	0.28	0.26

11 **Figure 5.** XPS spectra of the S 2p of sexithiophene films for 0.5 ML (top) and 3 ML (bottom) coverage. Three multiple doublet
12 components (S1 green, S2 red, S3 blue) with a 1.2 eV spin orbit splitting contribute to the full spectrum (data: open circles, fit: black
13 line). Table (right) indicates core level binding energies and population as a function of the coverage.

14 The effect of the organic deposition on LSMO has been checked by following evolution of Mn 2p
15 photoelectron spectra as a function of 6T coverage. The resulting spectra (see Supplementary S2) are in
16 agreement with data in the literature for LSMO; the line shape remains almost unaffected, indicating that
17 any possible interfacial effects are below the sensitivity in the sampling LSMO volume investigated by XPS.

18 DFT calculations

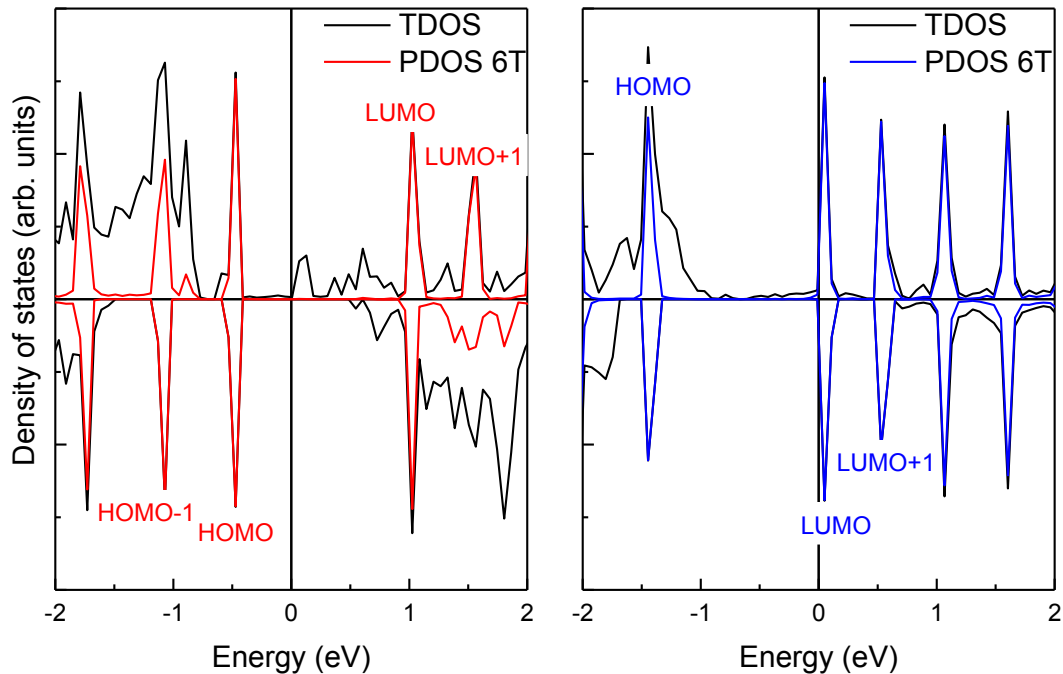
19 In agreement with experimental LSMO surface investigations [12] and following previous theoretical
20 studies [23], both Mn-O and Sr-O terminated LSMO(001) surfaces were considered in possible 6T/LSMO
21 heterostructures. LSMO slabs of six atomic layer thickness with both Mn-O and Sr-O termination layers
22 were produced by cutting the LSMO crystal along the (001) crystallographic plane as depicted in Figure 6.
23 The 4x2 supercell of the LSMO surface was used to calculate the electronic structure of the 6T/LSMO
24 interface with each supercell containing a single 6T molecule coordinated either to the MnO or the SrO
25 surface.



26 **Figure 6.** Structure of 6T/LSMO interface with MnO termination (1-2) and SrO termination (3-4). Mn, O, La, Sr, C, and S atoms are
27 depicted in purple, red, green, neon, brown, and yellow, respectively. S atoms are bonded to Mn (1,2) and Sr atoms (3,4).
28

29 After structural optimization, the orientation of 6T molecules relative to LSMO/MnO and LSMO/SrO
30 surfaces is determined as $\sim 60^\circ$ inclined with the molecular plane perpendicular to the LSMO(001) surface.
31 Such molecule orientation is consistent with the upright orientation of molecules deduced by AFM and PL
32 spectroscopy. The 6T molecule is coordinated to both MnO and SrO surfaces by a thiol atom with S-Mn and

1 S-Sr bond lengths equal to 2.85 Å and 3.15 Å which may be characterized as complex and weak dispersion
 2 types, respectively. In the case of Sr-O termination, an H-O bond (2.02 Å) can be realized due to a change in
 3 the rotational angle with the surface. The distortion of the edge pentagon of 6T is similar for both
 4 terminations, as shown in Figure 6, i.e. the contacting pentagon is twisted around a C-C bond while the
 5 entire structure remains planar.

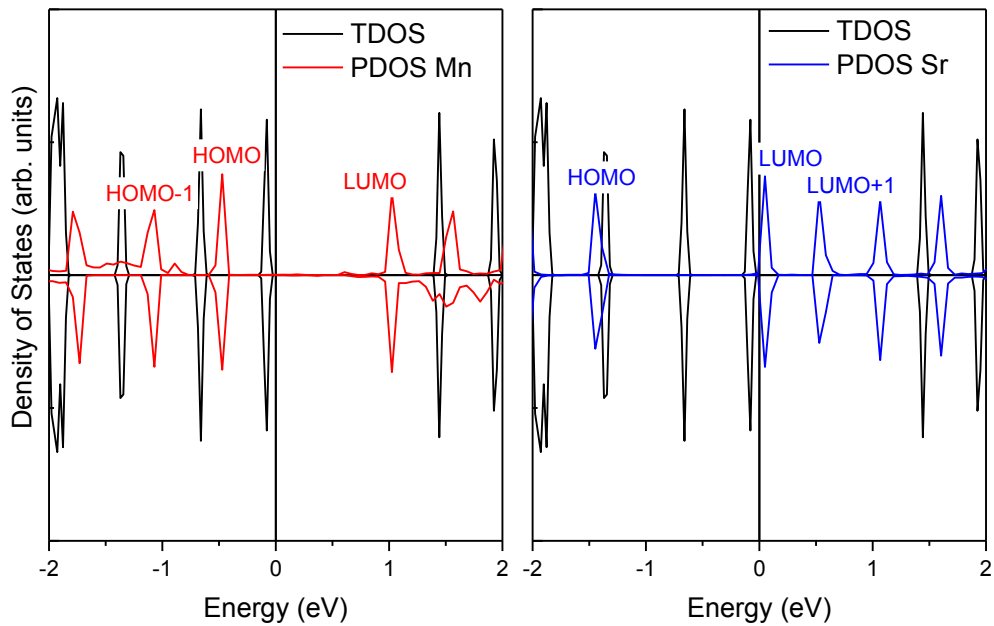


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 7 :
 8 **Figure 7** (Left) Partial density of states of a 6T molecule (red) and of 6T/LSMO(001)(MnO) with only LSMO atoms in direct contact
 9 with 6T (black). (Right) Comparison of the partial density of states of a 6T molecule (blue) and of 6T/LSMO(001)(SrO) with only
 10 LSMO atoms in direct contact with 6T (black).
 11

12 We focus first on MnO-terminated LSMO. In Figure 7 (left), we compare the spin-resolved partial density of
 13 states (PDOS) of the 6T molecule adsorbed on the MnO-terminated surface with that corresponding to the
 14 LSMO layer considering only the bonding surface atoms. The 6T molecular interaction with the LSMO
 15 surface causes a pronounced induced spin polarization of the 6T quasi-molecular LUMO+1 state. The
 16 change of 6T in conductivity band due to spin polarization may cause visible asymmetry of intensities of
 17 HOMO-LUMO+1 electron transitions for different spin channels. The 6T pseudomolecular spin-up HOMO-1
 18 state coincides in energy with the main LSMO PDOS MnO-layer peak (in the interval -1.1 - -1.3 eV) revealing
 19 electronic interactions of LSMO and 6T electronic subsystems. Some interaction of the electronic
 20 subsystems is also detected for the secondary LSMO peak at the energy -0.9 eV. Figure 7 (right) displays
 21 PDOS of a 6T molecule adsorbed on the SrO-terminated surface with that corresponding to the LSMO layer
 22 considering only the bonding surface atoms. Interface interactions of the fragments causes a significant shift
 23 in energy of pseudomolecular 6T HOMO and LUMO states making the LUMO state very close in energy to
 24 the Fermi level. The 6T pseudomolecular HOMO state coincides in energy with the most intensive LSMO
 25 peak in the spin up channel revealing direct interactions of the spin-up electronic subsystems without
 26 causing significant induced spin polarization of 6T.

27 A comparison of the total DOS for the free-standing 6T molecule with the PDOS for 6T on the MnO-
 28 terminated heterostructure is presented in Figure 8 (left). The adsorbed molecule presents a decrease of
 29 the HOMO-LUMO gap by 0.08 eV with molecular orbitals shifting down by 0.5 eV. All orbitals (except the
 30 HOMO and LUMO) possess high spin-polarisation due to high asymmetry in the distribution of the spin-up
 31 and spin-down states. The HOMO-1 state is split into two sub-peaks with a negligible gap between them.
 32 For SrO-terminated LSMO, the corresponding configuration does not lead to spin polarization of the 6T
 33 (Figure 8 right) with the general shape of the spin-up and spin-down peaks similar to the parent 6T TDOS. A

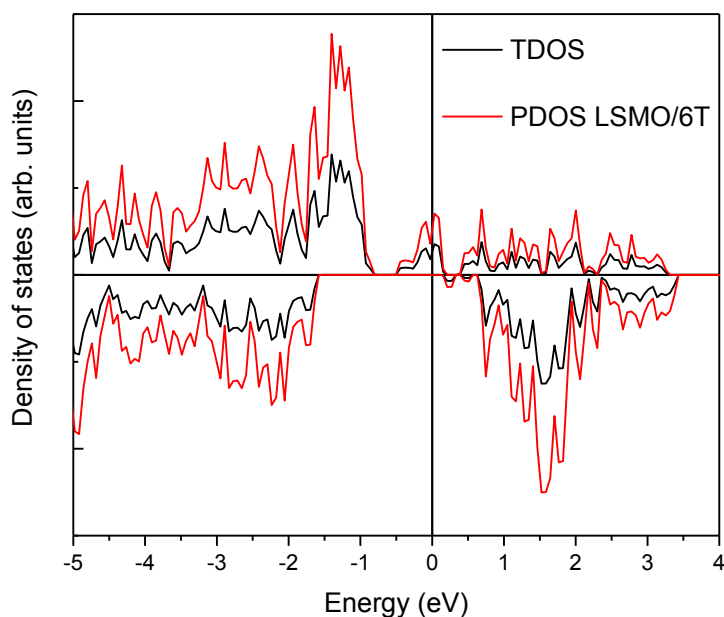
1 small decrease of the HOMO-LUMO band gap (15%) is observed but a large shift in the energy of molecular
2 orbitals by 1.4 eV takes place to position the LUMO very close to the Fermi level.



3
4 **Figure 8.** Comparison of TDOS of a free-standing 6T molecule (black) with PDOS of 6T adsorbed on a Mn-O surface (red) (left).
5 (Right) Comparison of TDOS of a free-standing 6T molecule (black) with PDOS of 6T adsorbed on a Sr-O surface (blue).

6 These results indicate that the LSMO termination layer significantly influences the spin polarization of the
7 6T molecule. In particular, an effective spin polarization is calculated for 6T adsorption on the MnO
8 termination, while on the SrO termination the electronic properties of the molecule are largely unaffected.
9 The good match of experimental and theoretical results validating the chosen theoretical model is
10 presented in Supplementary Material S3.

11 As demonstrated by detailed surface analysis [12], our LSMO sample features both SrO and MnO
12 terminations. This surface mixture could justify the LUMO position at 0.6 eV from the Fermi level as an
13 intermediate value between the two configurations. Focusing on the LSMO only, the adsorption of the 6T
14 molecule does not affect the spin polarization of the oxide as presented in Figure 9. All orbitals possess a
15 high spin polarisation due to the asymmetry between spin up and spin down states, as expected for the
16 bulk system. LSMO retains its half-metallic nature with an increase in the majority peak intensity at the
17 Fermi level.



1

2 **Figure 9.** A comparison of the TDOS of pristine LSMO (black) and the LSMO PDOS of a heterostructure with 6T (red).

3

4 **SUMMARY AND CONCLUSIONS:**

5 Data obtained in this work allow us to describe the typical features of the adsorption of 6T on a
 6 ferromagnetic LSMO surface. Importantly, we find that the molecular orbitals of 6T deposited on LSMO are
 7 spin polarized and the extent of spin polarization strongly depends on the termination layer of LSMO.
 8 Following the trend generally observed for adsorption on oxides, 6T molecules adsorb almost upright on
 9 the LSMO surface. The ML formation proceeds via the formation of 6T islands characterized by a quasi
 10 vertical stacking of adjacent molecules with π - π orbital interactions of thiophenic rings as detected by
 11 confocal PL. Looking in more detail at the interfacial configuration, the most stable geometry calculated by
 12 DFT involves the S atoms of the thiophene ring facing the LSMO surface. This is confirmed by the presence
 13 of a S 2p component in the XPS spectra associated with the sulfide contribution due to the bond between S
 14 and the metal atom of the LSMO. In terms of electronic structure and DOS, the adsorption of 6T onto
 15 stoichiometric LSMO surfaces was shown to be characterized by charge transfer from the surface LSMO
 16 states into the π -orbitals of the molecule, which is compensated by a push-back effect Pauli repulsion
 17 between the metal and molecular electrons. Importantly, no indication of the presence of new electronic
 18 states is found in UPS. The surface sensitivity of MDS also reveals that external frontier orbitals are barely
 19 involved in the interaction with LSMO and that only the atomic orbitals in close proximity to the interface
 20 are affected. Between the possible configurations and binding sites for thiophene adsorption on the two
 21 stoichiometric surfaces of LSMO, the Sr-O terminated surface does not impact the spin properties of the
 22 interface significantly while the molecular orbitals of 6T linked to the MnO-terminated LSMO surface
 23 present spin polarization on the LUMO+1 level. This result enables 6T to act as a spin filtering molecule
 24 offering different spin selectivity for majority and minority spins in combination with LSMO.

25

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