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Highlights:

- ✓ Probe the influence of alkylphosphonic acids-based SAMs on the electronic and magnetic properties of the LSMO

- ✓ Measure the modification of the Mn oxidation state of LSMO surface induced by the molecules grafting

- ✓ Evaluate the modification of the LSMO work function induced by the the alkylphosphonic acids molecules

Influence of alkylphosphonic acid grafting on the electronic and magnetic properties of La2/3Sr1/3MnO3 surfaces

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Abstract:

Self-Assembled Monolayers (SAMs) are highly promising materials for molecular engineering of electronic and spintronics devices thanks to their surface functionalization properties. In this direction, alkylphosphonic acids have been used to functionalize the most common ferromagnetic electrode in organic spintronics: $La_{2/3}Sr_{1/3}MnO_3$ (LSMO). However, a study on the influence of SAMs grafting on LSMO electronic and magnetic properties is still missing. In this letter, we probe the influence of alkylphosphonic acids-based SAMs on the electronic and magnetic properties of the LSMO surface using different spectroscopies. We observe by X-ray photoemission and X-ray absorption that the grafting of the molecules on the LSMO surface induces a reduction of the Mn oxidation state. Ultraviolet photoelectron spectroscopy measurements also show that the LSMO work function can be modified by surface dipoles opening the door to both tune the charge and spin injection efficiencies in organic devices such as organic light-emitting diodes.

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1. Introduction

Self-Assembled Monolayers (SAMs) have been considered for a long time as promising tools for building electronic devices down to the molecular scale [1,2]. Another application of SAMs is the surface modification of materials [3] to tune, for example, electrodes work functions and thus carriers injection/extraction in organic devices [4] such as organic field effect transistors and organic light-emitting diodes or solar cells. In many cases [5,6,7], phosphonic acids have been used to functionalize the extensively used transparent metal oxide electrodes in organic devices. Recently, it has been shown that alkylphosphonic acids could be grafted on magnetic oxide thin films such as $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) [8] and could be used as a tunnel barrier in magnetic tunnel junctions [9]. Whereas it could be of great importance for the fine understanding of the mechanisms governing spin injection in future hybrid devices, the influence of dodecylphosphonic acids (DPA) molecules on the LSMO's electronic and magnetic properties has not been investigated yet. LSMO is a mixed-valence manganite [10] where the electronic and magnetic properties are strongly correlated and linked to its Mn^{3+}/Mn^{4+} ratio. Hence, it is important to probe the influence on the Mn oxidation state of SAMs grafting. Moreover, spectroscopic measurements such as photoemission and absorption are powerful tools to investigate the electronic and magnetic properties of LSMO surfaces [11]. In this letter, we report that DPA molecules grafted on LSMO electrodes induce a reduction of the Mn oxidation state and a decrease of the LSMO work function as deduced from X-ray/Ultraviolet Photoemission spectroscopies (XPS/UPS) and X-ray Absorption spectroscopy (XAS) measurements.

2. Experimental

Bare LSMO reference and LSMO/DPA samples were characterized in order to study the influence of DPA molecules grafting on the electronic and magnetic properties of LSMO surfaces. LSMO thin films (20 nm thick) were grown by pulsed laser deposition using KrF excimer (λ=248 nm, 2 Hz) on $SrTiO_3$ substrates at 800°C in partial O_2 atmosphere (1.5 10^{-1} mbar). SAMs were formed by overnight immersion of LSMO in DPA ethanolic solutions. More

details on SAMs grafting protocol can be found in reference [8]. XPS measurements were performed on bare LSMO surfaces and LSMO functionalized with DPA. All spectra were collected using Al-Kα radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot with a diameter of 400μm, at 3 mA and 12 kV. The atomic concentration has been determined by using the Scofield libraries. XAS and XMCD (X-ray Magnetic Circular Dichroism) experiments were performed at the DEIMOS beamline [12] at the synchrotron SOLEIL. Measurements at the Mn $L_{2,3}$ edges were performed in total electron yield (TEY) detection mode in order to be sensitive to the surface. Spectra were recorded at 4.2K with the photon wave vector and magnetic field (3T) perpendicular to the sample surface for bare LSMO surface and LSMO/DPA. UPS measurements have been performed in order to determine the electronic structure of the LSMO/DPA interface. UPS was performed using the He-I line (21.2 eV) of an Omicron HIS 13 vacuum ultraviolet lamp and a photon incident angle of 45°. The emitted photoelectrons were energy filtered using a cylindrical sector analyser and detected by a SPLEED detector [13]. The sampling depth is at least 2.4 nm for these alkyl chain [14] and thus longer than the length (1.3nm) of the DPA SAMs [8].

3. Results and discussion

XPS measurements were performed on bare LSMO surfaces and LSMO functionalized with DPA. XPS provided the information on the composition of the samples as well as the electronic properties. As the electronic and magnetic properties of LSMO are linked to the Mn oxidation state, XPS measurements were focused on Mn. The Mn 3s splitting is generally measured to probe the Mn oxidation state [15]. We do not observe any modification of the splitting after DPA grafting (Figure 1-a). However it has been shown for LSMO [16] that the Mn 3s splitting does not change for Mn oxidation state between 3+ and 3.3+, which is very close to the Mn oxidation state (3.33+) expected in our $La_{2/3}Sr_{1/3}MnO_3$ samples. Hence we cannot extract accurate information on the evolution of manganese oxidation state from Mn 3s. We now focus on the Mn 2p spectra recorded for a bare LSMO surface and LSMO/DPA samples (Figure 1(b)). The Mn $2p_{3/2}$ and $2p_{1/2}$ peaks have been fitted by two Gaussian-Lorentzian functions, which allow reproducing well the experimental data. The Gaussian-Lorentzian curve at lower energy (about 641.5 eV) corresponds to the Mn^{3+} contribution whereas the Gaussian-Lorentzian curve at about

643 eV is associated to Mn^{4+} [17,18,19]. After DPA grafting the amplitude of the curve at 643 eV slightly decreases indicating a weaker contribution of Mn^{4+} ions whereas the Mn^{3+} contribution is almost constant. From these fits, a 17% increase of the Mn^{3+}/Mn^{4+} ratio was found after DPA molecules grafting. In order to check if the Mn^{3+}/Mn^{4+} ratio variation is linked to a modification of the La/Sr ratio we have recorded Sr 3d and La 3d spectra (figure 1(c) and 1(d)). $La3d_{5/2}$ spectra[a] were deconvoluted into three peaks [20], one main peak (dark gray curve) and two satellite peaks (gray curves). $Sr3d_{3/2}$ and $Sr3d_{5/2}$ spectra[b] can be deconvoluted into two pair of peaks corresponding to bulk (dark gray curves) and surface contributions (gray curves) [21].The average La/Sr ratio (~1.8) deviates slightly from the expected ratio (2.0) and according to literature it has been associated to a surface Sr rich phase [19,21,22,23,24,25]. We observe a decrease in the La/Sr ratio of about 5% after DPA grafting (~ 1.85 for bare LSMO and ~1.75 for LSMO/DPA samples). By comparing La and Sr peak area (Figure 1c and d) we observe a very small increase for La (2.8%) and decrease for Sr (3.3%) after DPA grafting. Nevertheless, these changes are not significative and thus the Mn^{3+}/Mn^{4+} ratio variation cannot be ascribed only to a chemical composition modification after DPA molecules grafting.

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[a] The spin-orbit splitting is about 16.8eV, the energy difference between poorly screened and unscreened peaks is about 4.1eV [20].

[b] The spin-orbit splitting is 1.7eV and the full width half-maximum is about 1.15 eV.
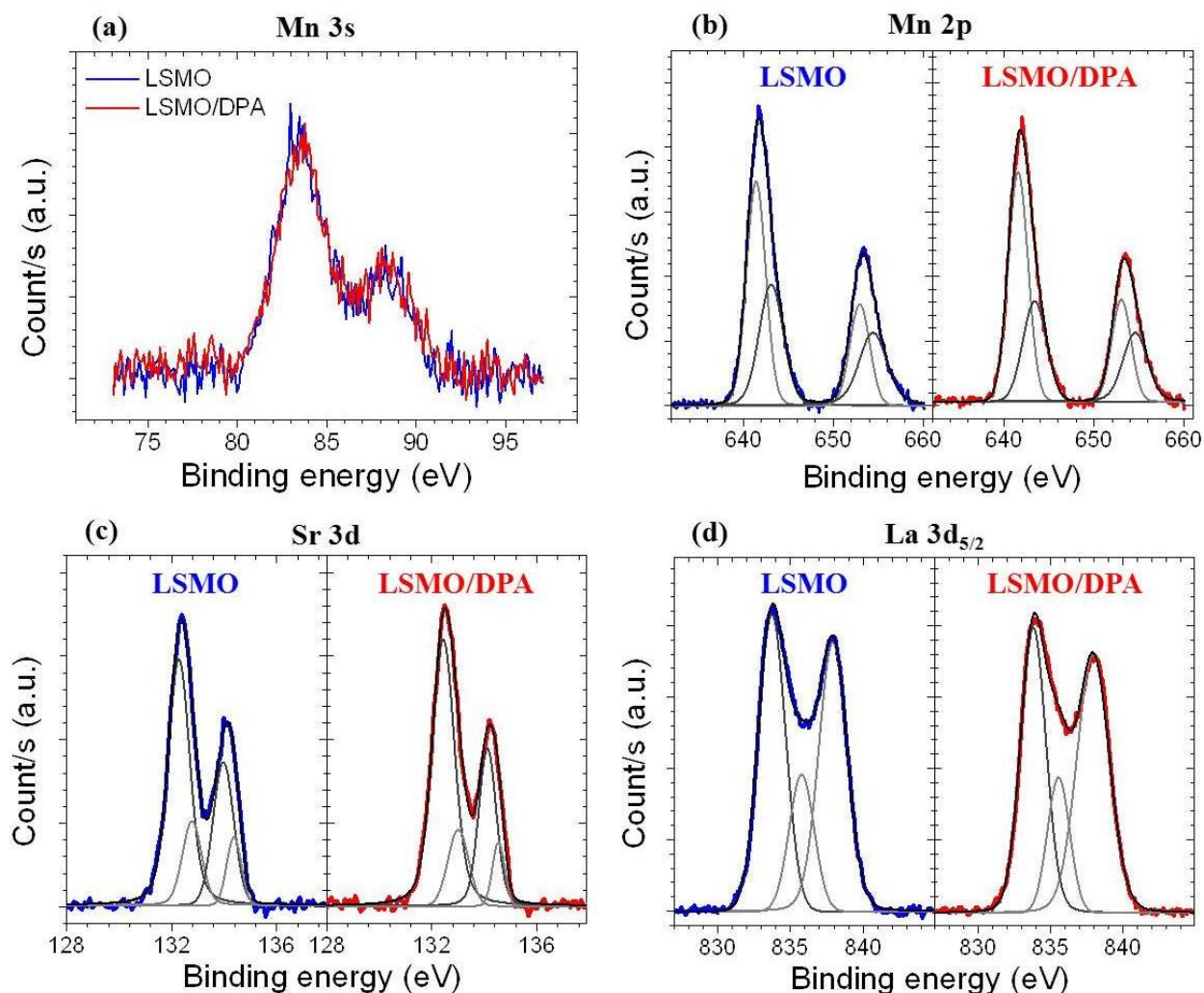
Figure 1: XPS spectra recorded at Mn 3s (a),Mn 2p (b), Sr 3d (c) and La $3d_{5/2}$ (d) edges for bare LSMO (blue curves) and LSMO functionalized with DPA SAMs (red curves). Each of the Mn 2p, Sr 3d and La $3d_{5/2}$ spectra are fitted by the sum of Gaussian-Lorentzian functions (grey and dark grey), black curves are the envelope. The lower intensity of dark gray curve at ~643 eV (Mn 2p) after DPA grafting suggests a decrease of Mn^{4+} contribution.

Although XPS reveals a reduction of the Mn oxidation state at the LSMO surface, it is difficult to associate it only to a decrease of Mn^{4+} concentration and to exclude formation of lower oxidation states. More accurate information can be obtained from x-ray absorption (XAS) measurements. The XAS spectra of LSMO at the Mn $L_{2,3}$ edges present features which can be easily attributed to different Mn valence states.

In order to gain further information on the nature of the Mn valence change observed in our samples, we thus performed XAS and XMCD experiments for bare LSMO surface and LSMO/DPA. In Figures 2-a and 2-b, we plot the XAS spectra recorded for left (red) and right (black) circular polarized light as well as XMCD spectra (blue). The superposition of the Mn L_3 normalized isotropic XAS spectra for the two samples is also shown in Figure 2-c to allow for an easier comparison. The different peaks in the XAS spectra of the Mn L_3 edge can be identified by comparison with results reported in the literature [26,27,28,29,30,31]. Peak A (~ 643.4 eV for bare LSMO) corresponds to a mixed contribution of Mn^{3+} and Mn^{4+} ions. Peak B (641.6 eV) represents the contribution of Mn^{4+} ions and peak C (640.9 eV) is principally due to Mn^{2+} ions, even if a small contribution of Mn^{3+} cannot be excluded.
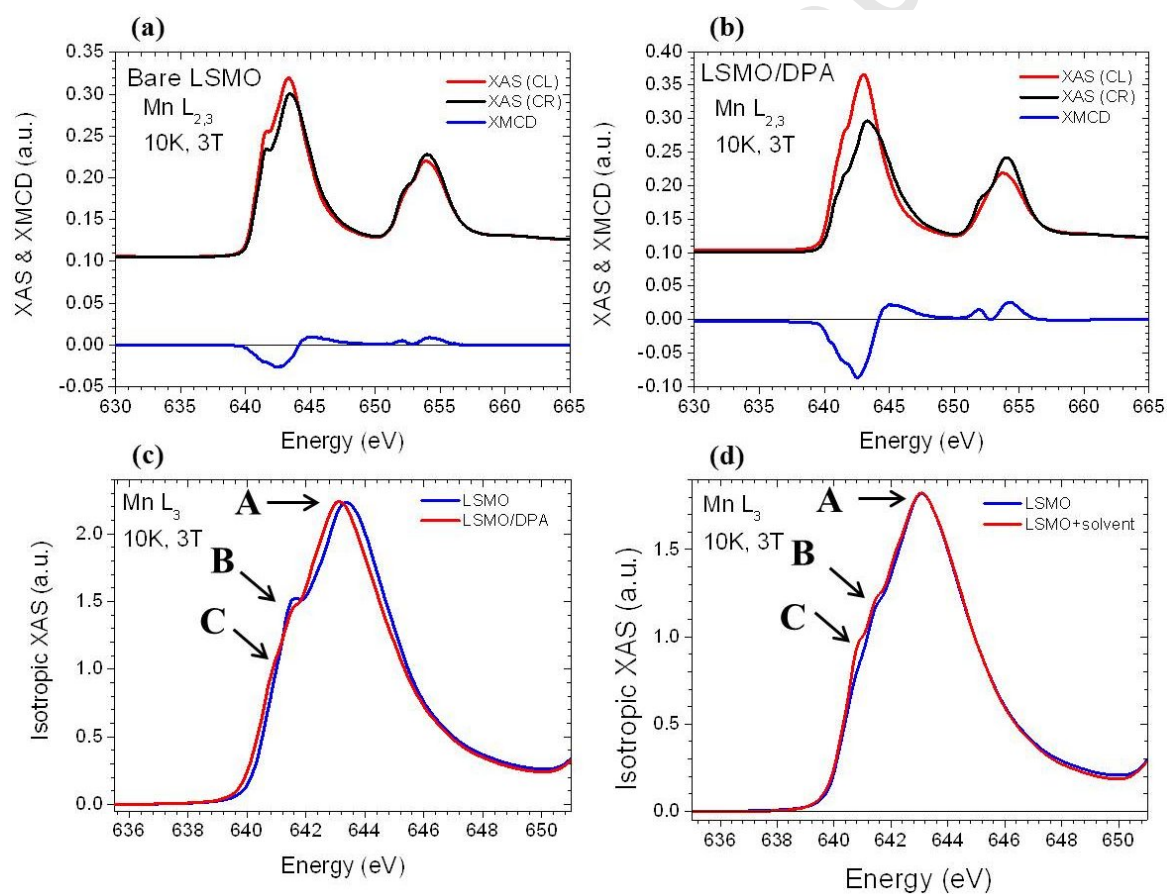

Figure 2 : XAS and XMCD spectra recorded at 4.2 K and 3 T for bare LSMO (a) and LSMO functionalized with DPA SAMs (b). Black and red curves are XAS spectra for right (CR) and left (CL) circular polarized light and blue curves are the XMCD spectra. (c) Normalized isotropic XAS spectra for the two samples. The shift towards the low energy of peak A indicates a reduction of the Mn valence states. A slight increase of intensity of peak C after grafting

indicates formation of Mn^{2+} species. d) Isotropic XAS spectra for the bare LSMO and LSMO immersed in neat ethanol samples. Energy position of peak A is unchanged which means that the Mn^{3+}/Mn^{4+} ratio is constant. A slight increase of intensity of peak C after LSMO immersed in ethanol indicates formation of Mn^{2+}.

From Figure 2-c, one can observe that in the case of the LSMO/DPA sample, peak A is shifted towards lower energies (0.3 eV) and intensity of peak B decreases. This indicates an increase of the Mn^{3+}/Mn^{4+} ratio mainly due to a decrease of the Mn^{4+} concentration [29]. Moreover, in the case of the functionalized sample, peak C slightly emerges while it is almost absent for the bare LSMO sample. This could imply an increase of Mn^{2+} ions for LSMO/DPA vs. bare LSMO. The reduction of the Mn oxidation state is also reflected on the magnetic properties of the functionalized LSMO surface. The increase of XMCD signal for the LSMO/DPA sample reflects the increase of Mn^{3+}, which has a higher magnetic moment ($4\mu_B$) compared to Mn^{4+} ($3\mu_B$). Unfortunately we cannot quantify the reduction of the Mn oxidation state because the mixed valence behavior of Mn does not permit to derive the spin and orbital moments of Mn atoms from XAS and XMCD using the sum rules [32].

In order to ensure that this modification is induced by the presence of the molecules and not from the grafting protocol itself, we also studied the effect of the solvent. In this regard, normalized isotopic XAS spectra for new bare LSMO surface and LSMO immersed in neat ethanol were recorded (Figure 2-d). As one can see, curves match except for peak C that looks more pronounced in the sample that was immersed in ethanol. This shows that the increase of Mn^{2+} ions could just be an effect produced by ethanol over the surface, while it confirms that the shift of peak A towards lower energies (with the consequent increase of the Mn^{3+}/Mn^{4+} ratio) is clearly due to the grafted molecules and not to the grafting protocol. To summarize, these results thus suggest that hybridization between molecules and LSMO magnetic oxide substrates induces a modification of the electronic structure of the interface with an increase of the Mn^{3+}/Mn^{4+} ratio and a consequent increase of the magnetic moment of the functionalized surface.

Finally, UPS measurements have been performed in order to determine the electronic structure of the LSMO/DPA interface. Figure 3(a) shows the UPS spectra measured at 120K for LSMO/DPA

and bare LSMO samples as a function of the energy E-E$_F$. The bare LSMO film shows a very low spectral weight close to the Fermi level, which is attributed to a low cross section for the given photon energy [33]. The comparison with the DPA covered sample shows a shifted low energy cut-off, which implies a reduction of the work-function of 0.5 eV [34]. This work function modification is generally attributed to interface dipole [4] which includes several contributions such as charge transfer, hybridization, pillow effect and intrinsic dipole of the molecule. This interface dipole and in particular charge transfer could be also at the origin of the Mn oxidation state modification. By fitting the spectrum for the LSMO/DPA after background subtraction (inset of figure 3(a)) we can extract two peaks. The peaks at -6.5 eV and -9.5 eV are identified as the highest occupied molecular level (HOMO) and HOMO-1 level and are in good agreement with photoemission measurements of short alkyl chain molecules [35]. Figure 3(b) summarizes the energy level alignment of the functionalized interface.
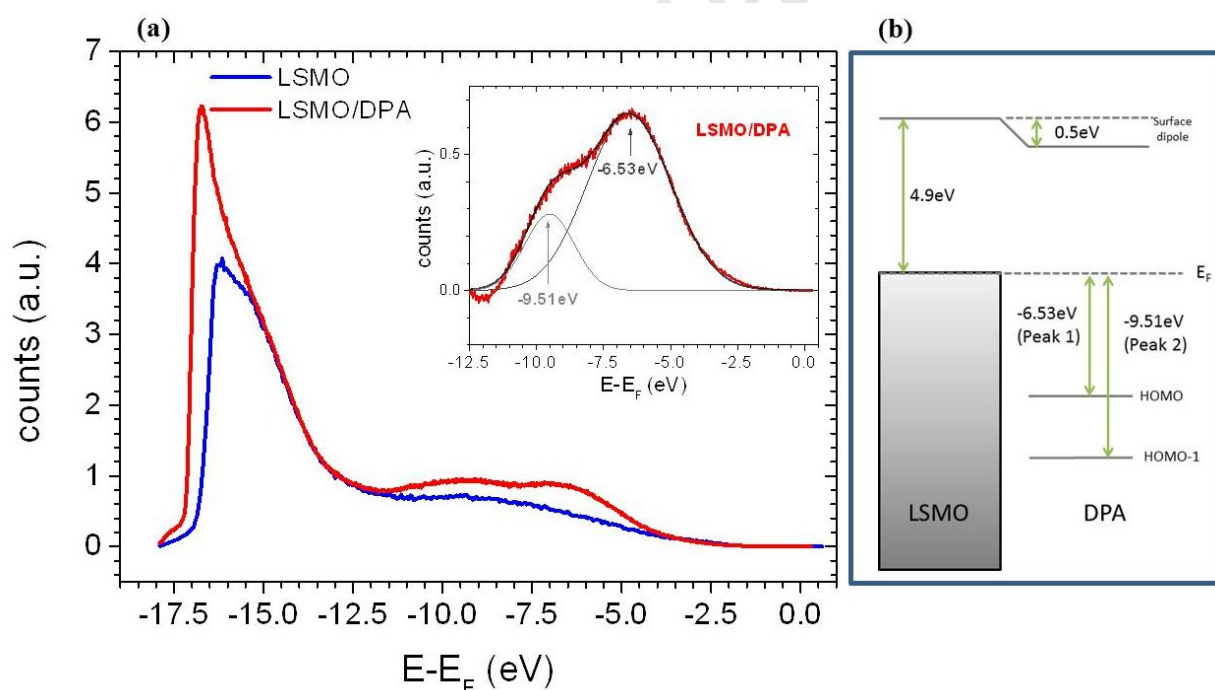

Figure 3: (a) UPS spectra recorded at 120K for bare LSMO (blue line) and LSMO/DPA samples (red line). SAMs grafting induces a decrease of 0.5 eV of the work function, as visible from the shift of the low energy cutoff of the spectra to lower energies. (b) Energy level alignment at the LSMO/DPA interface extracted from the UPS measurements. The energetic position of the HOMO and HOMO-1 levels of the DPA molecules was determined by fitting the UPS spectra with a multi-Gaussian function after background subtraction. The fit is shown in the inset of (a).

4. CONCLUSION

To conclude, we have shown that XPS, UPS and XAS measurements reveal that alkylphosphonic acids molecules grafted on LSMO affect the electronic and magnetic properties of LSMO surfaces. Molecules grafted on the surface induce an increase of the Mn^{3+}/Mn^{4+} ratio whereas the solvent used for the grafting is at the origin of the formation of Mn^{2+}. The Mn average oxidation state reduction could be ascribed to the formation of surface dipoles which induces also a modification of the LSMO work function. Although alkylphosphonic acids SAMs influence the electronic and magnetic properties of the LSMO surface, it does not seem to be crippling for spin dependent transport since tunnel magnetoresistance has been observed in LSMO/DPA/Co magnetic tunnel junctions [9]. Furthermore, as these alkylphosphonic acids SAMs allow tuning the LSMO work function, LSMO/DPA functionalized electrodes could be used for tailoring charge and spin injection efficiencies into organic devices such as OLEDs [36]. The study of SAMs influence on LSMO electric and magnetic properties thus represents an important step towards the understanding and future engineering of the mechanisms governing charge and spin injection in this kind of devices.

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