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The spin state of a molecular adsorbate driven by the ferroelectric substrate polarization†

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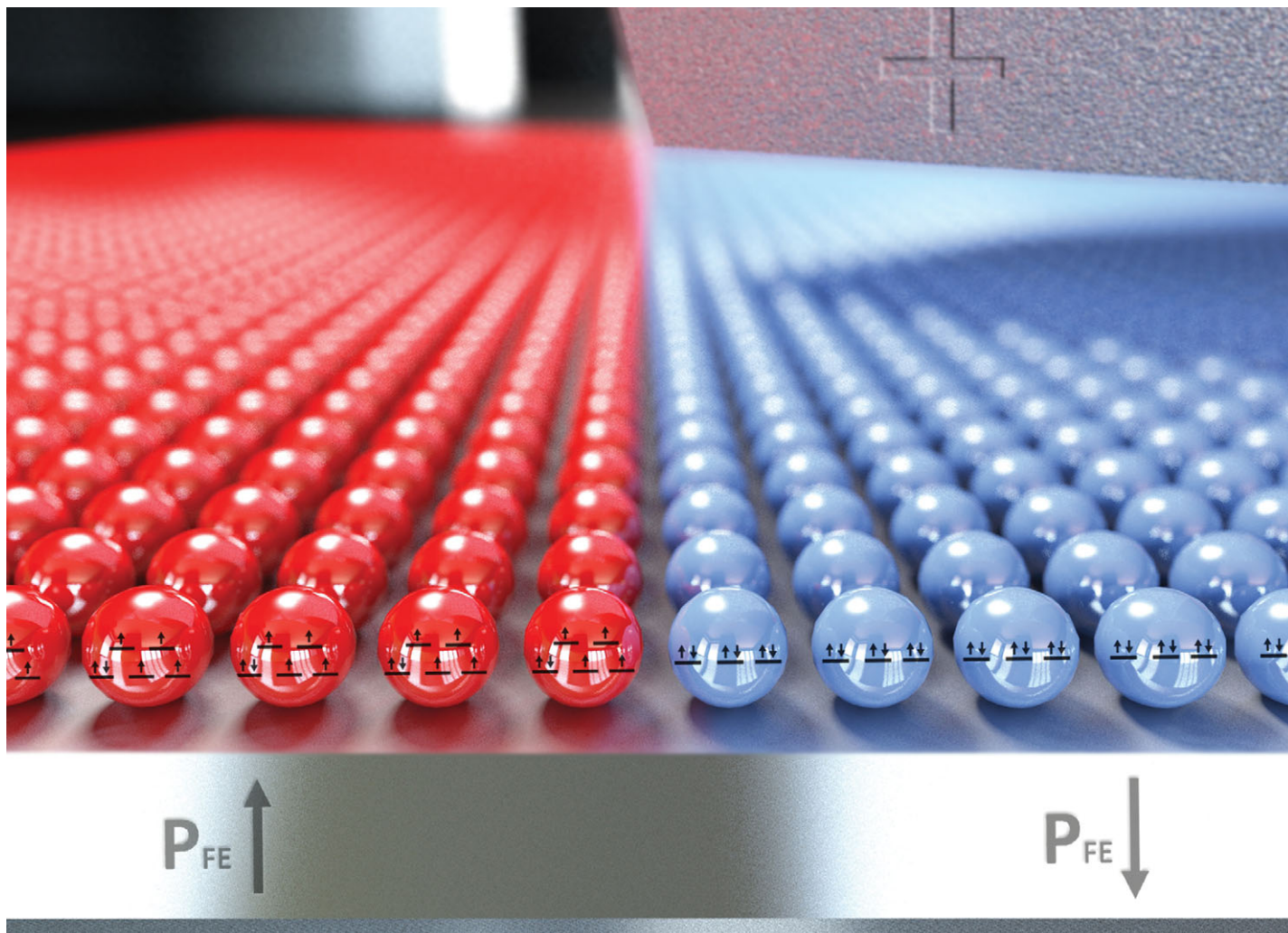
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Showcasing research from the Dowben Laboratory, Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, Nebraska, USA made in collaboration with the Molecular Sciences Group ICMCB, Bordeaux University, France

The spin state of a molecular adsorbate driven by the ferroelectric substrate polarization

The ferroelectric polarization of the organic polyvinylidene fluoride with trifluoroethylene (PVDF-TrFE) substrate mediates the spin state of adsorbed $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ spin cross-over molecular thin films. The change from a diamagnetic low spin to a paramagnetic high spin state is evident not only from magnetic properties, but also from changes in the unoccupied density of states. This influence of the polarization state of an organic ferroelectric substrate, and the subsequent effect on a molecular adsorbate spin state may pave the way to molecular magneto-electrics.

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The spin state of [Fe(H₂B(pz)₂)₂(bipy)] thin films is mediated by changes in the electric field at the interface of organic ferroelectric polyvinylidene fluoride with trifluoroethylene (PVDF–TrFE). Signatures of the molecular crossover transition are evident in changes in the unoccupied states and the related shift from diamagnetic to paramagnetic characteristics. This may point the way to the molecular magneto-electric effect on devices.

Spin cross-over (SCO) molecules form a significant class of materials for which the magnetic structure can be altered at the atomic level by an external stimulus. Low spin (LS) diamagnetic to paramagnetic high spin (HS) transitions can be induced by pressure, temperature, illumination, or magnetic pulses.¹ The possibility of inducing a SCO transition by an electric field^{2–5} could lead to molecular magnetic state transition altered by an applied electric field either in the ground state or the excited state. This is attractive because molecular systems are among the very few systems where nonvolatile magnetic state switching at GHz and coercive voltages less than 2 V (ESI,† SR1) may in fact be possible.

The SCO transition is associated with changes to the molecular electronic structure, as a consequence of the splitting of the energy of the transition metal d orbitals into the t_{2g} and e_g sets in the ligand field of the whole molecule.^{1,6,7} This has important consequences, in particular for electronic transport properties.^{3–5,8,9}

The modification of the conductivity induced by the spin transition remains difficult to characterize,^{3–5} possibly hindered by transition-induced changes of crystallinity⁷ or complexities at the molecule–electrode interfaces.¹⁰ The characterization of the electronic structure is therefore essential, and the spectroscopic signature, particularly of the unoccupied electronic structure, has been shown to be a powerful indication of electronic changes between high and low spin states.^{11–13} In this communication, we use the changes in inverse photoemission to show that the stable SCO phase at intermediate temperature values can be modified by the ferroelectric polarization of the substrate. The signature of a voltage-controlled spin crossover transition in inverse photoemission is validated using magnetometry.

The [Fe(H₂B(pz)₂)₂(bipy)] complex, where pz = (pyrazol-1-yl)-borate and bipy = 2,2'-bipyridine, was synthesized as previously described.^{12,14} The 3 nm thick organic copolymer ferroelectric polyvinylidene fluoride with trifluoroethylene (PVDF–TrFE: 70–30) substrates were prepared by a Langmuir–Blodgett technique on graphite (see ESI†), sufficient to create a pin-hole free ferroelectric organic film, while preserving a low coercive voltage.¹⁵ The ferroelectric polarization state was imposed by scanning a probe over the substrate surface, contact free (see ESI,† SR2), with an applied voltage of +900 V or –900 V, more than sufficient to obtain the up or down ferroelectric polarizations,¹⁶ prior to adsorbate deposition. The [Fe(H₂B(pz)₂)₂(bipy)] complex was deposited on both gold and PVDF–TrFE substrates, in an ultra high vacuum system equipped with both photoemission and inverse photoemission (IPES).

Thin films of the complex [Fe(H₂B(pz)₂)₂(bipy)] are known to display a rather abrupt SCO transition (in the temperature range of 130 to 200 K), as occurs in the powder,^{12,14,17,18} and this complex meets the stringent requisites for sublimation under ultra-high vacuum conditions. We showed previously that thin films made by sublimation do preserve molecular integrity,^{12,14,19} a result confirmed independently by other authors.^{2–4,9} Indeed temperature-dependent magnetic properties of vacuum evaporated thin film samples measured using a superconducting quantum interference device (SQUID) magnetometer

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indicate a thermal SCO transition in agreement with earlier reports.^{12,14,18}

The unoccupied molecular orbitals of the iron complex $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films were characterized by inverse photoemission spectroscopies (IPES), as described elsewhere.¹² The spectra were obtained by using variable kinetic energy incident electrons while detecting the emitted photons at a fixed energy (9.7 eV) using a Geiger–Müller detector,¹² with an instrumental linewidth of approximately 400 meV.

IPES was used to identify the spin state of the spin crossover molecular complex. The molecular orbitals show a shift in the unoccupied density of states when the spin state changes. The most significant change with decreasing temperature is the loss of density of states just above the Fermi energy in the high spin (HS) state upon transition to the low spin (LS) state (Fig. 1). The thin films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on both gold (Fig. 1, left) and polyvinylidene difluoride 70:30 (PVDF–TrFE) (Fig. 1, right) substrates also show similar changes in the unoccupied density of states, consistent with previous results indicating a change in the unoccupied density of states across the spin cross-over (SCO) transition in both inverse photoemission¹² and X-ray absorption¹⁹ (see ESI,† SR3).

Our key finding is that this inverse photoemission fingerprint of the spin state also occurs on the dipole polarized ferroelectric substrate PVDF–TrFE when the polarization of the organic ferroelectric is reversed from having the interface dipoles pointing “up” (*i.e.* hydrogen at the PVDF–TrFE interface and polarization towards the vacuum) to “down” (*i.e.* fluorine at the PVDF–TrFE interface and polarization towards the PVDF–TrFE). When $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ is deposited on PVDF–TrFE substrates poled “up” and “down”, the IPES at 170 K revealed changes in the density of states, as seen in Fig. 2, and in X-ray absorption at the Fe L3 edge (see ESI,† SR4),

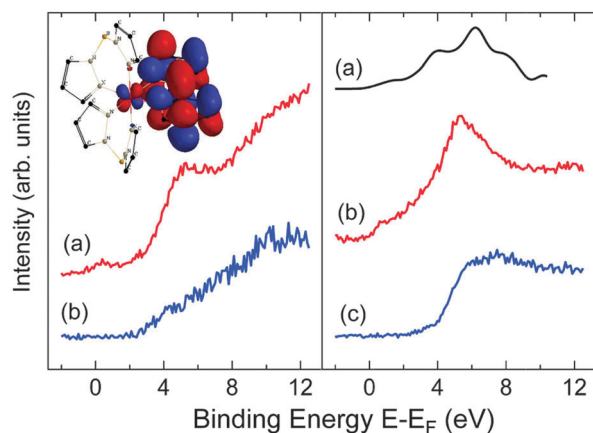


Fig. 1 The inverse photoemission results for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ films, 40 molecular layers thick, on gold (left panel) and PVDF–TrFE (right panel) showing similar changes in the unoccupied electronic structure with temperature. The density of states (a) from a semiempirical molecular orbital parametric method model calculation (PM3), calculated for the high spin state, resemble the measured unoccupied density of states at 300 K, in the high spin state (red) (b) but do not resemble the density of states in the low spin state (blue) as measured at 170 K (c). The lowest unoccupied state, showing a profound shift across the SCO transition, is shown as an inset.

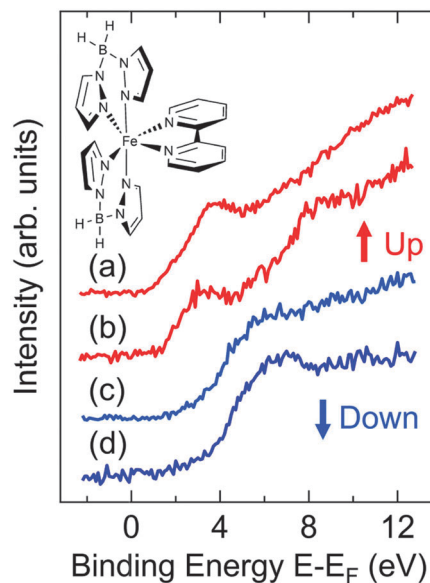


Fig. 2 Inverse photoemission at 170 K of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ (schematically shown in the inset) 25 (a) and 10 (b) molecules thick on polarized ferroelectric PVDF–TrFE, with the dipole “up”, compared to a SCO molecular film 10 (c) and 25 (d) molecules thick on PVDF with the polarization “down”.

similar to those observed with temperature for thicker films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on both gold and PVDF–TrFE in the naturally poled “up” state (Fig. 1). This established thermal SCO transition, evident in thicker (40 molecular layers) $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on both gold and PVDF–TrFE, is modified significantly in thinner molecular films (10–25 molecular layers thick) in the presence of a substrate with a large permanent interface electric field. This may be compared to results of theoretical calculations supporting that the Madelung field produced by the molecule dipoles contributes to the occurrence of thermal hysteresis in SCO compounds.²⁰

More compelling evidence of voltage control of the SCO spin state comes from magnetometry studies. Transition from the HS state to the LS state for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ is characterized by a transition from paramagnetism (temperatures above the transition) to diamagnetism (temperatures below the transition), as illustrated in Fig. 3a, and is evident both before and after the diamagnetic background of the substrate is subtracted.

Magnetometry performed on thin films on a ferroelectric substrate reveals however that the spin state at low temperatures depends on the ferroelectric polarization of the substrate (Fig. 3b), confirming the IPES and XAS results. The paramagnetic properties of 25 molecular layer thick films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on ferroelectric PVDF–TrFE poled “up” persist down to 100 K, well below the thermal crossover transition to diamagnetism observed for powder samples. The $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films on the ferroelectric PVDF–TrFE poled “down”, on the other hand, exhibit robust diamagnetic properties from the same temperature of 100 K up to 300 K, well into the normal temperature region for paramagnetic behavior in the bulk. These results are consistent with the changes seen with IPES with ferroelectric poling. We are aware that the magnetic moment of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on

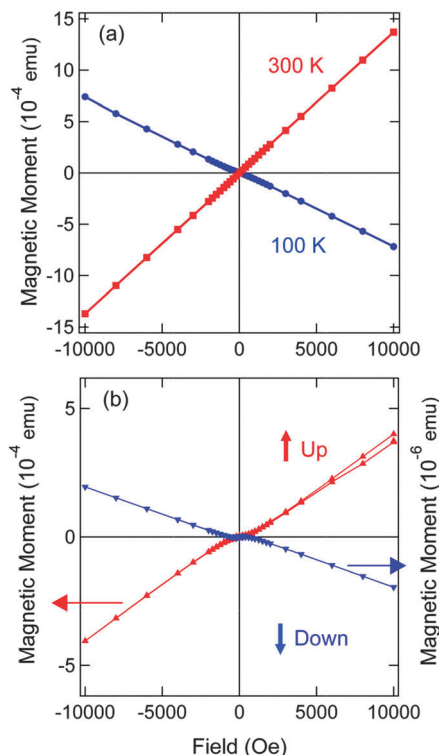


Fig. 3 Magnetic properties of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ powder and thin films on the ferroelectric PVDF-TrFE. The molecular powder shows (a) paramagnetism and diamagnetism at 300 K (red) and 100 K (blue) respectively. 25 molecule thick thin films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on ferroelectric PVDF-TrFE (b) are robustly paramagnetic (red curve, measured at 170° K) even down to 100 K, when the ferroelectric is polarized “up”. Diamagnetic behavior is evident with PVDF-TrFE polarized down (blue curve, measured at 100 K). Deviations from paramagnetic and diamagnetic behavior seen at low field may be gratuitous instrumental contributions (artifacts) that appear significant because of the low signals resulting from the very small amount of SCO molecules.

ferroelectric PVDF-TrFE poled “up” is surprisingly large, but without an accurate assessment of the packing density, no value per molecule can be assigned. The SQUID measurements and substrate/sample holder diamagnetic contributions were carefully checked to exclude experimental errors. More importantly, ferromagnetic impurities are inconsistent with the observed diamagnetic state seen when switching the substrate polarization. Deformation of the coordination sphere of the iron is considered to affect the separation of the iron d orbitals, possibly resulting in a larger moment than measured in the bulk. We would expect molecular deformation to stabilize the high (or low) spin Fe(II) complex configuration. These latter issues demand further investigation.

Thin films of the molecular spin crossover complex $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, grown on a poled ferroelectric PVDF-TrFE in a saturated ‘up’ state, exhibit a high spin state that persists down to 100 K, well below the SCO transition temperature. Our results show that electric fields can be used to manipulate spin states in molecular systems, as suggested by the voltage-controlled conductance experiments.⁵ The use of a spectroscopic signature (IPES) of the SCO thin films to reveal the magnetic phase allows

us to identify the materials and the necessary electric field conditions that control the spin state.

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