Supplementary Materials To:

Spin State of a Molecular Adsorbate driven by the ferroelectric substrate polarization

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1. Experimental: preparation of the poled P(VDF-TrFE 70:30)

2. X-ray absorption spectroscopy

3. Magnetic measurements

1. Experimental: preparation of the poled P(VDF-TrFE 70:30)

Ultrathin ferroelectric films of the copolymer 70% vinylidene fluoride with 30% trifluoroethylene, P(VDF-TrFE 70:30) were fabricated by Langmuir-Blodgett (LB) deposition techniques on graphite substrates from the water subphase and dimethylsulphoxide (DMSO). [1-19] The films were nominally 9 molecular layers thick, roughly equivalent to 30 Å thick, as determined by atomic force microscopy studies. The films were annealed in ultrahigh vacuum at 110º C, which has proven to be an effective recipe in prior studies for preparing a clean and ordered surface[1-18] and has been demonstrated to result in a surface free from impurities (including water).

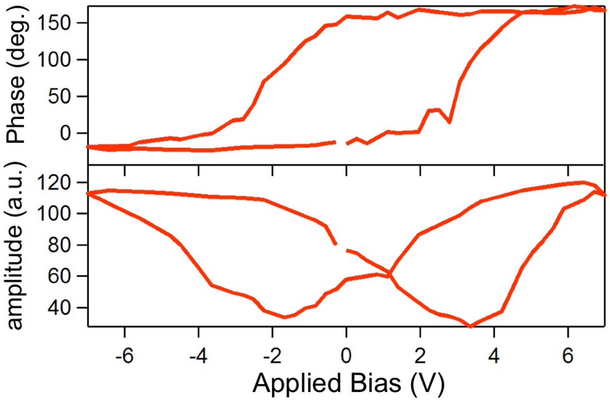

Figure S1. *The piezoresponse force microscopy (PFM) phase and amplitude hysteresis loops measured in a 30 Å thick P(VDF-TrFE, 70:30) film, as a function of applied voltage.*[2]

The ferroelectric behavior and polarization orientation were determined by means of piezoresponse force microscopy (PFM) measurements in ambient environment.[2,20] Figure S1 shows the PFM hysteresis loops (phase and amplitude PFM signals as a function of applied dc bias) typical for these ferroelectric films (and indeed of ferroelectrics in general). As grown films are weakly polarized with the dipoles generally oriented up (away from the substrate). Macroscopic poling of the P(VDF-TrFE, 70:30) films was carried out by scanning over the entire film area (of the order of square cm) with an electrically biased external probe (applied voltage was in the range from -900 V to 900 V) held at 100 µm above the surface (non-contact poling), as diagramed in Figure S2. This non-contacting poling technique is a large scale poling of the sample similar to that used with a more local scale by using various scanning probe microscopy techniques on P(VDF-TrFE, 70:30) films,[16,17,21-32] and is seen to produce stable ferroelectric poling in our samples. The results of the poling process were confirmed by PFM testing as in many of these prior studies of P(VDF-TrFE, 70:30) films.[2]

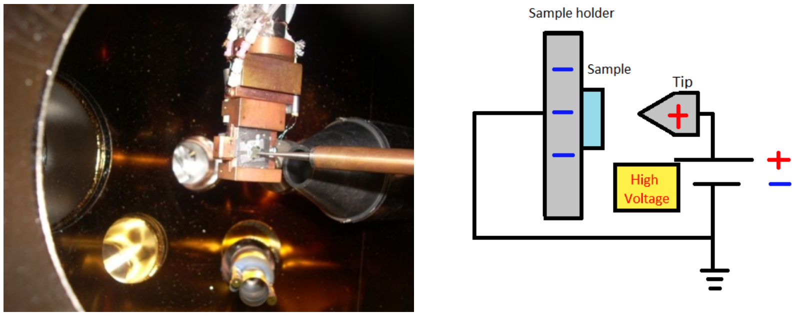

Figure S2. *The schematic (right) and actual apparatus (left) for successfully reversing the direction of a PVDF-TrFE ferroelectric ultrathin film in ultra high vacuum.*[2]

2. X-ray absorption spectroscopy

To illustrate that the changes in the inverse photoemission spectra reflect changes in the unoccupied density of states, as seen in X-ray absorption spectroscopy, as reported elsewhere,[33] we performed X-ray absorption at the Fe L2 and L3 edges of the $[Fe(H_2B(pz)_2)_2(bipy)]$ complex, where pz=(pyrazol-1-yl)borate and bipy = 2,2'-bipyridine, thin films. As seen in Figure S3, the unoccupied density of states is much weaker in the vicinity of the Fe L3 edge (706.8 eV) at low temperature (corresponding to the low spin state) than at higher temperatures (corresponding to the high spin state). These changes in the unoccupied density of states are reflected in the inverse photoemission.

The XAS spectra, like the inverse photoemnission, also show the signature of the effect of the ferroelectric substrate polyvinylidene fluoride with trifluoroethylene (PVDF-TrFE: 70-30) polarization. To illustrate the effect of substrate polarization, we have plotted the XAS spectra of the $[Fe(H_2B(pz)_2)_2(bipy)]$ complex, where pz=(pyrazol-1-yl)borate and bipy = 2,2'-bipyridine, thin films deposited on the organic ferroelectric PVDF-TrFE 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). Here the XAS are plotted in Figure S4 with the spectrum for polarization "up" substracted from the spectrum for polarization down, to highlight the change at the L3 leading edge.

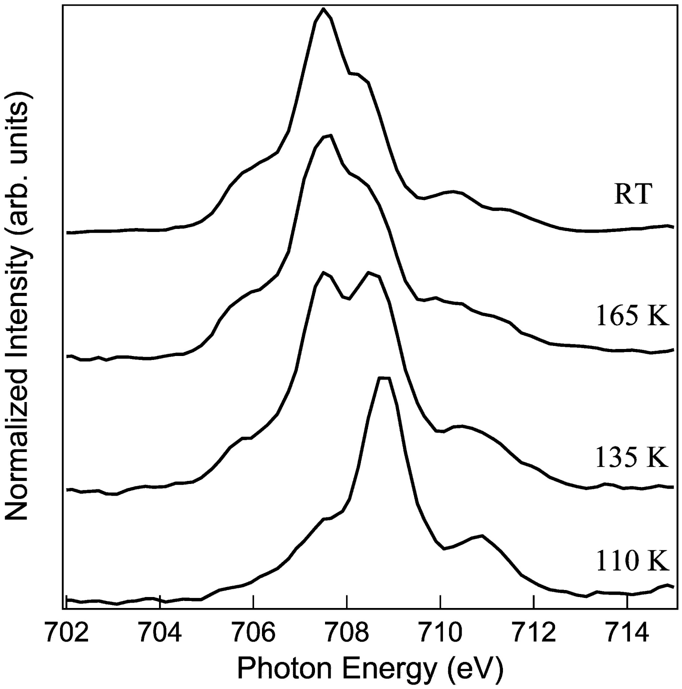

Figure S3. *The XAS spectra of the Fe L3 edge shows distinct change with temperature change track the changes in magnetic susceptibility across the spin cross-over transition as reported elsewhere.*[34-36]

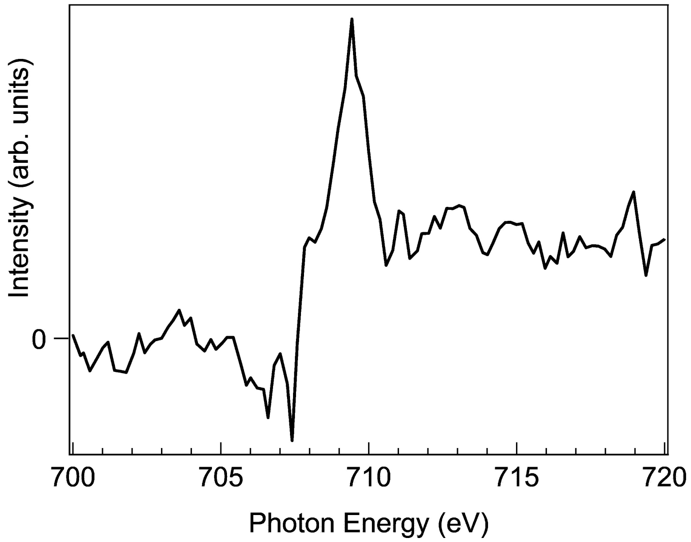

Figure S4. *The difference XAS spectra of the [Fe($H_2B(pz)_2)_2$(bipy)] complex thin films on PVDF-TrFE, with the spectrum for ferroelectric polarization "up" subtracted from the spectrum for ferroelectric polarization "down" of the Fe L3 edge. Data taken at 165 K shows distinct change with polarization, with a deacrease in density of states at L3 edge, follwed by a increase 4 eV above the L3 edge, as also seen in the inverse photoemission..*

3. Magnetic measurements

Determination of the magnetic susceptibility of our thin films is delicate, owing to the unfavorable film-to-substrate signal ratio, The graphite plus PVDF-TrFE substrate (1 mm × 5 mm × 8 mm) creates a diamagnetic background of the order of $5\mathrm{x}10^{-4}$ emu = 10^{-7} A m^2 in an applied magnetic field of $\mu_0H = 0.9$ T. This is about two orders of magnitude larger than the signal for $[\mathrm{Fe}(\mathrm{H_2B}(\mathrm{pz})_2)_2(\mathrm{bipy})]$ complex thin films in the diamagnetic state. Different strategies were used to circumvent this problem dependent on measurements with a reference substrate, with and without without the SCO films, identical to the measured sample, but then subtracted from one another. Alternatively, we made samples with various amounts of SCO or no SCO. The necessity of breaking samples for the magnetometer, and matching samples to better than 1%, as well as uncertainties in the measurements. We present by purpose data with measured magnetic moment as a function of applied field in the main text, for showing without ambiguity that the claims of paramagnetism/diamagnetism hold for a significant applied field range, and these conclusion hold regardless of the background subtraction and methodology of background subtraction.

In cases where the ratio of film-to-substrate signal is 10^{-2} at most, measurements in two orthogonal directions of the sample, and then applying known rules to differentiate between the diamagnetic substrate susceptibility and the paramagnetic one coming from the SCO film can still be considered. This more sophisticated subtraction technique is described in details in [37], but does not work for diamagnets, and thus is ill suited to ascertaining the diamagnetic response.

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