

Engineering On-Surface Spin Crossover: Spin-State Switching in a Self-Assembled Film of Vacuum-Sublimable Functional Molecule

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The realization of spin-crossover (SCO)-based applications requires study of the spin-state switching characteristics of SCO complex molecules within nanostructured environments, especially on surfaces. Except for a very few cases, the SCO of a surface-bound thin molecular film is either quenched or heavily altered due to: (i) molecule–surface interactions and (ii) differing intermolecular interactions in films relative to the bulk. By fabricating SCO complexes on a weakly interacting surface, the interfacial quenching problem is tackled. However, engineering intermolecular interactions in thin SCO active films is rather difficult. Here, a molecular self-assembly strategy is proposed to fabricate thin spin-switchable surface-bound films with programmable intermolecular interactions. Molecular engineering of the parent complex system $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$ (pz = pyrazole, bpy = 2,2'-bipyridine) with a dodecyl (C_{12}) alkyl chain yields a classical amphiphile-like functional and vacuum-sublimable charge-neutral Fe^{II} complex, $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ ($\text{C}_{12}\text{-bpy}$ = dodecyl[2,2'-bipyridine]-5-carboxylate). Both the bulk powder and 10 nm thin films sublimed onto either quartz glass or SiO_x surfaces of the complex show comparable spin-state switching characteristics mediated by similar lamellar bilayer like self-assembly/molecular interactions. This unprecedented observation augurs well for the development of SCO-based applications, especially in molecular spintronics.

Metal–organic spin-crossover (SCO) complexes^[1–4] that are capable of undergoing switching between low-spin (LS) and high-spin (HS) states as a function of temperature, light, pressure, and electric field are suitable candidates to fabricate room-temperature-operable molecular electronic/spintronics architectures.^[5–10] Relentless efforts have been made to study spin-state switching characteristics of SCO complexes on different surfaces^[11–19] to harness the device utility of SCO entities. Several interesting results, e.g., the spin-state dependence of electrical conductance,^[6,20] memristance behavior,^[21] electric field or electron-induced SCO,^[22,23] and locking and unlocking of SCO around room temperature,^[24] have been reported. Vacuum sublimation of the complexes onto a suitable surface is the preferred method to obtain high-quality surface layers of SCO complexes.^[20,25–30] Despite continuing efforts, only a few families of sublimable SCO complexes have been realized. These include charge-neutral $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ (phen = 1,10-phenanthroline),^[31] $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{L})]$ (pz =

pyrazole, L = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen)),^[32,33] and $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ ^[34] systems. Among them, the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{L})]$ complexes have been studied in detail on metallic $\text{Au}(111)$,^[18,35–37] nonmetallic $\text{Bi}(111)$,^[13] and highly oriented pyrolytic graphite (HOPG) surfaces.^[17] The switching is reported to be coverage dependent on metallic $\text{Au}(111)$ substrate on which the first layer of the complex undergoes fragmentation and loss of SCO,^[38] whereas switching is retained on $\text{Bi}(111)$ and HOPG surfaces even at sub-monolayer level due to the weak molecule–surface interfacial interactions.^[13,17]

While the role of the surface in affecting spin-state switching of SCO thin film architectures is well established, control of the intermolecular interactions, a governing factor in dictating SCO in the bulk phase, is a rather difficult problem to tackle within nanostructured environments. This is especially the case regarding surface-bound thin films due to a lack of control associated with the film fabrication processes in engineering intermolecular interactions, thereby warranting systematic

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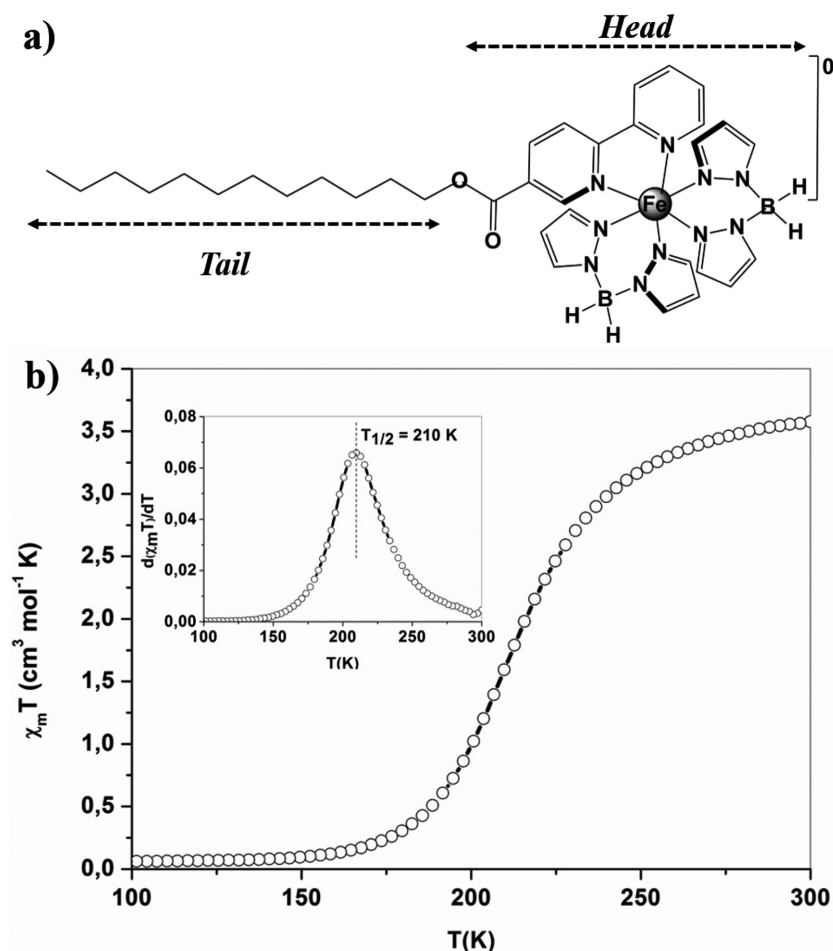


Figure 1. a) Molecular structure of the pseudo amphiphile-like SCO complex [Fe(H₂B(pz)₂)₂(C₁₂-bpy)] and b) $\chi_m T$ versus T plot of bulk powder form of [Fe(H₂B(pz)₂)₂(C₁₂-bpy)], inset shows $d(\chi_m T)/dT$ versus T curve indicating $T_{1/2} = 210$ K.

experimentation in this direction. Toward this end, a self-organization strategy using tailored intermolecular interactions could be employed. One approach is to synthesize a functional SCO complex with a propensity to self-assemble via intermolecular interactions, which could be copied “as such” when translating from bulk to thin film state. This would enable the realization of similar, if not identical, SCO characteristics between bulk and thin film phases.

To start anew in this direction, a functional [Fe(H₂B(pz)₂)₂(C₁₂-bpy)] (C₁₂-bpy = dodecyl [2,2′-bipyridine]-5-carboxylate) SCO complex (cf. **Figure 1a**), whose structure is reminiscent of a classical amphiphilic molecule, featuring SCO active pseudohydrophilic head and hydrophobic dodecyl (C₁₂) tail groups, and which is capable of self-assembly via intermolecular hydrophobic interactions, has been designed and synthesized (cf. Scheme S1, Supporting Information). Note that the tailoring of the dodecyl (C₁₂) tail with the parent SCO system [Fe(H₂B(pz)₂)₂(bpy)] yielded the [Fe(H₂B(pz)₂)₂(C₁₂-bpy)] SCO complex with self-assembly propensity. This is why we call it a “functional SCO complex,” so as to differentiate it from the related functionalized SCO complex systems studied on surface.^[39] The spin-state switching characteristics of the

[Fe(H₂B(pz)₂)₂(C₁₂-bpy)] complex in bulk and thin film state have been probed to elucidate the role of intermolecular interactions in mediating SCO characteristics upon moving from the bulk to the thin film environment.

The magnetic susceptibility measurement of the [Fe(H₂B(pz)₂)₂(C₁₂-bpy)] complex powder showed gradual SCO with $T_{1/2} = 210$ K (160 K for the parent complex) without any noticeable hysteresis upon repeated cycling (cf. Figure 1b). The obtained $\chi_m T$ product of 3.55 and 0.05 cm³ K mol⁻¹ at 300 and 100 K, respectively, indicate the presence of pure high- and low-spin species at those temperatures and a genuine temperature-induced SCO behavior. To get insights into the SCO characteristics and self-assembly of the [Fe(H₂B(pz)₂)₂(C₁₂-bpy)] in the thin film state, the complex was sublimed on quartz glass and SiO_x surfaces from a crucible held at a temperature of 150 °C, i.e., below the onset of degradation inferred from thermogravimetric analysis (cf. Figure S1, Supporting Information). Electronic spectral analysis of the thin film sample sublimed on quartz glass showed that the ligand-centred and metal-to-ligand charge transfer ¹(MLCT) bands are analogous to the electronic absorption spectrum of the chloroform solution of the complex (cf. Figure S2a,b, Supporting Information), thereby confirming the structural integrity of [Fe(H₂B(pz)₂)₂(C₁₂-bpy)] on the quartz substrate after sublimation.

The SCO characteristics of a 10 nm thick film of [Fe(H₂B(pz)₂)₂(C₁₂-bpy)] on a SiO_x surface have been probed using X-ray absorption spectroscopy (XAS) at the Fe L_{2,3} edges.

Comparable XAS spectra recorded at room temperature for both the 10 nm thick film on SiO_x and the powder sample further confirm the conserved electronic structure of the complex in the film (cf. **Figure 2**). Upon cooling the bulk powder and the thin film of [Fe(H₂B(pz)₂)₂(C₁₂-bpy)] from 300 to 100 K, a spectral intensity ratio change of the Fe L₃ edge multiplet features at ≈706.8 and ≈708.1 eV, which respectively originate from the HS $t_{2g}^4 e_g^2$ ($S = 2$) and LS $t_{2g}^6 e_g^0$ ($S = 0$) configurations, has been observed in line with previous studies.^[18]

A decrease in the branching ratio,^[18,40] defined as $b = I_3/(I_3 + I_2)$, I_x = integrated intensity at the corresponding L_x edge, from $b = 0.7$ at 300 K to $b = 0.61$ at 100 K, indicates reduced spin-orbit coupling due to the diamagnetic nature of the LS state. This further confirms the occurrence of SCO in the thin film sample. Variable temperature XAS measurements have been performed in order to get insights into the thermal SCO characteristics of bulk powder and 10 nm film of [Fe(H₂B(pz)₂)₂(C₁₂-bpy)]. By using the peak intensity ratios from the HS (LS) reference curve recorded at 300 K (100 K), the HS proportion of the complexes within the probed region at a given temperature has been assessed (cf. Figure S3c, Supporting Information). The analysis establishes $T_{1/2} = 197$ K

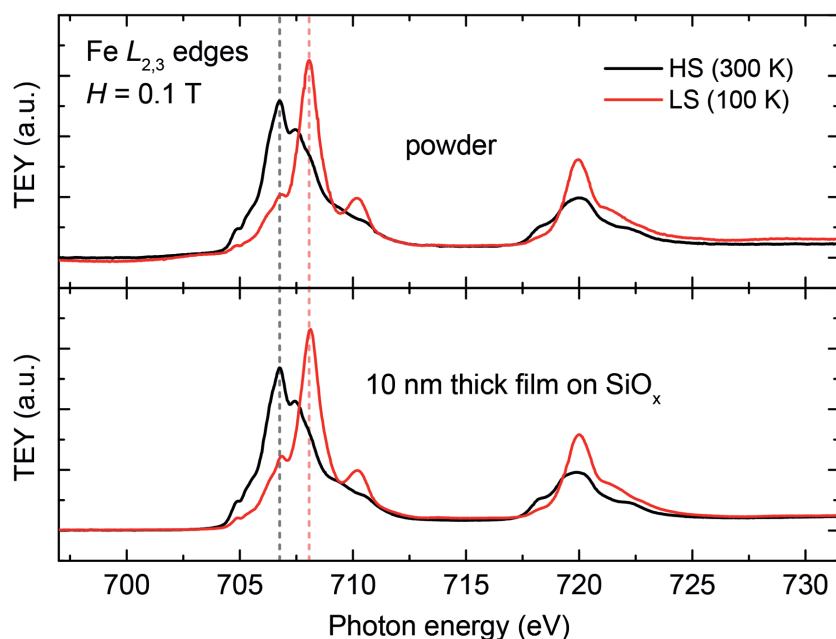


Figure 2. XAS at the Fe $L_{2,3}$ edges of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$. XAS spectra acquired for powder (top) and sublimed 10 nm thick film on SiO_x (bottom) at 300 and 100 K. The vertical dotted lines are guides for the eyes indicating multiplet features at ≈ 706.8 and ≈ 708.1 eV characteristic for HS and LS state molecules, respectively, of bulk and thin film samples. The curves were recorded in total electron yield mode at normal X-ray incidence and normalized to the sum of integrals over the Fe L_3 and L_2 edges.

for the bulk sample, which is ≈ 13 K lower than the $T_{1/2}$ recorded for the powder sample using SQUID magnetometry, and is most probably due to temperature calibration issues. The transition curve of the 10 nm film is clearly more gradual in character, with a transition temperature shifted by ≈ 20 K toward lower values with respect to the bulk sample. This could be attributed to a weak effect of the interface, or to the slightly different intermolecular interactions among the molecules in sublimed film in comparison with the powder form (vide infra).^[41] Apart from the thermal SCO, the light-induced excited spin-state trapping (LIESST) effect at the nanoscale is of great importance, especially from applications perspective.^[17,42] Since our detection method of SCO in the film sample is XAS, which results in soft X-ray-induced excited spin-state trapping (SOXIESST)^[11,43] at low temperature, the XAS measurements were performed at an intermediate temperature of 100 K to avoid mixing of thermally activated SCO with SOXIESST. Attempts have not been made to observe the visible-light-induced LIESST effect in the thin film sample of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$. Nevertheless, we strongly believe that the studied film should exhibit LIESST similar to other surface-bound SCO complexes.^[17,42,44] However, these investigations are beyond the scope of the present study.

X-ray diffraction (XRD) measurements have been performed to investigate the nature of the self-organization of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ in the bulk and the thin film states. The powder pattern of the bulk sample is characteristic of a lamellar crystal phase. It is composed of a series of strong and sharp fundamental and higher-order reflections of the layer sequence (reflections (00*l*), periodicity $d = 25.4$ Å), and of some weak, unresolved crossed reflections of the 3D crystalline cell

(cf. Figure 3a). This arrangement directly follows the “amphiphile-reminiscent” design of the molecules, as they bind covalently two antagonistic segments, namely the alkyl chains and the metal complex counterpart. These incompatible moieties spontaneously phase separate in juxtaposed domains and most often form multilayered lamellae as in this case.^[45–47]

A side effect of intercalating layers of a different nature is the loss of positional correlation between molecular segments within subsequent lamellae. This results in a blurring of the 3D superstructure, as revealed by the weak crossed reflections. Indeed, the pattern of the thin film sublimed on quartz glass only displays the (00*l*) reflections, presumably because the film grew with the lamellar system oriented parallel to substrate. In this case, all the reflections other than (00*l*) lie out of the specular plane and thus beyond the measured reciprocal space zone. Remarkably, film and powder patterns exhibit identical lamellar periodicity and same intensity ratios in the reflection series. The lamellar structure of the bulk sample was therefore maintained in the film, which fulfills the experimental realization of an SCO complex maintaining the same phase in bulk powder

and thin film states. Some differences might nevertheless exist in the in-plane arrangements and in the related 3D structure, which could explain the small switching behavior differences, in particular the gradual and lower $T_{1/2}$ temperature observed for the thin film of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ complex.

Beyond the information directly extracted from the XRD patterns, the common lamellar structure of bulk sample and film can be scrutinized using a geometrical analysis.^[48–50] To do so, the geometrical features of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ complex have been modeled by extracting the density and crystallographic data of the constituent molecular entities, the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$ SCO head and the dodecyl carboxylate tail, and compared with the molecular area A_{mol} of the layer sequence, defined as the ratio of molecular volume V_{mol} to lamellar thickness d .^[51–53] The volume contribution of the SCO head V_{head} was found to range between 620 and 660 Å³, on the basis of the single crystal structure of the parent $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$ SCO complex without the dodecyl carboxylate tail^[32] and of reference partial volume data. The volume contribution of the alkyl tail V_{tail} is either of 280–300 Å³ for crystallized chains or ≈ 320 Å³ for molten chains.^[54,55] Hence, for the entire $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ complex molecule, V_{mol} ($V_{\text{mol}} = V_{\text{head}} + V_{\text{tail}}$) ranges between 900 and 1000 Å³ (cf. Figure 3b), and thus A_{mol} ($A_{\text{mol}} = V_{\text{mol}}/d$), between 37 and 41 Å². This is about half of the transverse section of the SCO head ($\sigma_{\text{head}} \approx 80$ Å², also determined from the single-crystal data of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$) and about twice the section of the stretched tail ($\sigma_{\text{tail}} = 18.5\text{--}20$ Å² if crystallized, and $\sigma_{\text{tail}} \approx 21$ Å², if molten). The compactness of the whole multilayered structure is imposed by the requirement of the bulkiest segments, thus

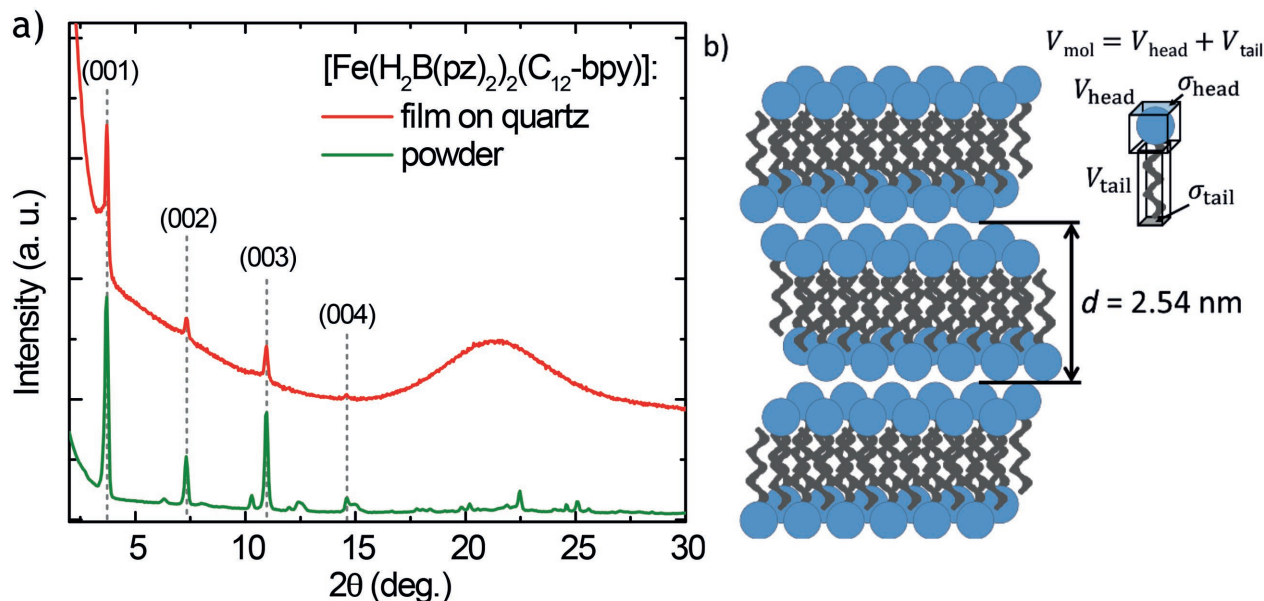


Figure 3. Self-organization of an $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ thin film. a) X-ray diffraction pattern of a 10 nm thick sublimed $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ film on a quartz substrate compared to the powder reference. The equidistant reflections (001)–(004) reveal the lamellar structure of 2.54 nm periodicity in powder and film. The broad feature at 17° – 25° is the scattering signal from the quartz glass substrate. b) Schematic view of the internal structure of lamellae of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ consisting of double layers of the complex heads (blue spheres) alternating with aliphatic tails arranged in double layers, according to the deduced bilayer crystalline arrangement.

here the SCO heads, which arrange in double-layer configuration to minimize A_{mol} (cf. Figure 3b).^[56] To realize compact space-filling with aliphatic chains between successive SCO double layers, the residual discrepancy with σ_{tail} is compensated through various mechanisms, depending on the crystallized or molten state of the chains, in particular tilting, folding, and interdigitation.^[57]

In any case, the amphiphile-like molecular organization of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ into double layers spaced by tails is clearly established from XRD, as well as the identity of the lamellar structure between powder and thin film, and the spontaneous surface alignment of the lamellar system in the film. The morphology of the thin film was further investigated by tapping mode atomic force microscopy (AFM) experiments (cf. Figure 4) performed on 10 nm thick film of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ on SiO_x . The large-scale AFM image on Figure 4a clearly reveals the formation of flat terraces by the molecules. A relative height of the steps either in the range $d = 1.1$ – 1.3 nm or $d = 2.2$ – 2.6 nm was found, in good agreement with the lamellar spacing deduced from XRD, and corresponds to half or entire double-layer structures as deduced from the structural model in Figure 3b. The observation of half double-layer structures stems from the fact that the film can end with a layer of either strongly folded/tilted aliphatic tails or of side-by-side arranged complexes. Remarkably, the stepwise terrace-like growth of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ on SiO_x compares well with previous XRD and AFM studies for other lamellar systems,^[58,59] and highlights the role of the lateral intermolecular interactions inside layers in mediating the oriented growth on the surface.

The above results clearly indicate the role of intermolecular interactions in successfully preserving SCO in nanostructured thin films, and underscore the role of chemical structure

alterations leading to desired material properties. Importantly, functionalization of the parent system with the dodecyl chain also resulted in a 50 K increase in the $T_{1/2}$ value relative to its parent complex. This clearly elucidates the role of the chemical substituent in tuning SCO, in line with the literature reports detailing alkyl chain tuning of SCO characteristics.^[60–62] The parent $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$ complex was reported to grow on amorphous surfaces in a Volmer–Weber mode (i.e., the atoms of the film are more strongly coupled with each other than with the substrate) by crystallites formation, whereas functionalization of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$ head with the C_{12} chain imposed a preferential stacking direction and facilitated vertically ordered growth on the surface beneficial in terms of fabricating multilayer vertical SCO junctions.^[63] The alignment of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ lamellae into large terraces parallel to substrate is the consequence of the strong internal cohesion of the layer sequence, overcoming the potential effects of molecule–surface interfacial interactions. This enables systematic distance scaling between the SCO head and surface via synthetic modification of alkyl chain length and could be considered as a novel strategy to decouple SCO heads from the surface, via insulating alkyl chains. This is akin to adding an insulating layer between the strongly interacting metallic surface and the SCO complex. Note also a recent report by Zhang et al.,^[24] detailing quenching of SCO in a 5 nm film of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$ on SiO_2 and Al_2O_3 ; the preservation of SCO in 10 nm films observed in the present work is also important in this context and in terms of realizing large area spintronics junctions based on SCO complexes.

To summarize, the present study demonstrated a functionalization strategy of the parent $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$ complex system that alters the material properties by modifying

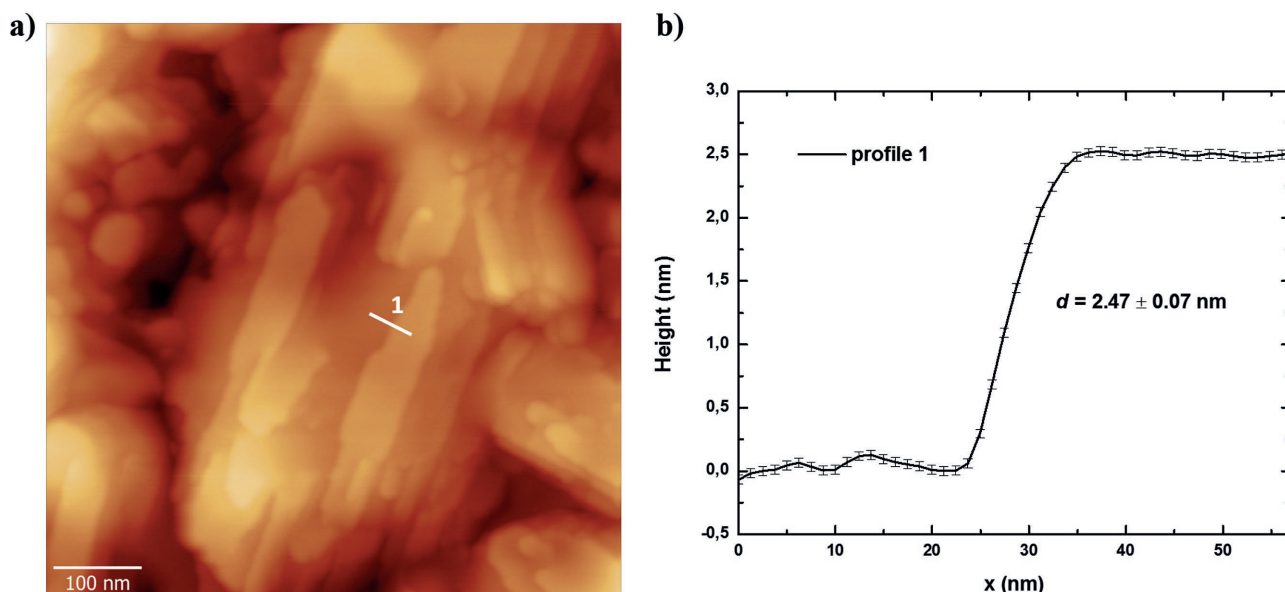


Figure 4. Surface morphology of a sublimed $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ film on SiO_x substrate. a) Surface topography measurement performed by room temperature ambient pressure AFM in tapping mode of $\text{Si}/\text{SiO}_x(400 \text{ nm})/[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})](10 \text{ nm})$ highlighting bilayers of the lamellar molecular stacking. b) Height profile of the step along the profile 1 shown in (a) of height $d = 2.47 \pm 0.07 \text{ nm}$ consistent with lamellar spacing extracted from XRD.

the molecular stacking arrangement while preserving its spin transition and sublimation propensity. The functional $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{C}_{12}\text{-bpy})]$ complex could be sublimed at relatively low temperatures in comparison with its parent counterpart, and was found to self-assemble in the same amphiphile-like lamellar structure in the bulk and the thin film state, leading to near-identical switching characteristics of the complex in both states. To the best of our knowledge, this is the first successful attempt at sublimating an amphiphilic SCO complex and observing similar SCO temperatures in bulk and thin film states. The results presented in this study are expected to open a way for a more molecular-engineering-oriented approach in the SCO materials research direction and studying of on-surface switching characteristics of vacuum-sublimable functional SCO complexes with strict control of the nanostructure morphology. Furthermore, several functional addends featuring advantageous physical properties, such as luminescence and chirality, could be coupled with the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bpy})]$ skeleton and the resultant functional SCO complexes may be sublimed on surfaces. This would galvanize SCO-based research toward realistic SCO-based applications.

Experimental Section

Synthesis and characterization of the ligand and complex were detailed in the Supporting Information.

The 10 nm thick film was sublimed from a molybdenum boat heated up by electric current to 120 °C under pressure of 10^{-8} mbar using a Plassys deposition machine. The thickness of the film was established based on the quartz balance used during the process and calibrated with X-ray reflectivity performed on a test sample.

The XAS measurements were performed at the X-Treme beam line at the Swiss Light Source, Paul Scherrer Institute, Switzerland.^[64] The

powder sample was pressed into an indium foil. The XAS spectra were recorded at normal X-ray incidence in total electron yield mode and normalized to the sum of integrals over the L_3 and L_2 edges of Fe.

Ultraviolet-visible absorption measurements were performed with a Varian Cary 5000 double-beam UV-vis-NIR spectrometer, with referential complex dissolved in chloroform (CHCl_3).

Magnetic susceptibility measurements were performed on MPMS-XL5 SQUID magnetometers (Quantum Design) at $B_{\text{DC}} = 0.1 \text{ T}$ field and sweep rate 2 K min^{-1} . Gelatine capsules were used as sample holders in the temperature range $100 \leftrightarrow 300 \text{ K}$. The diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constants.

The crystalline phase of the powder and the films were determined using a Bruker D8 Advance diffractometer equipped with a LynxEye detector in the θ - 2θ mode with a monochromatic wavelength $\lambda_{\text{Cu K}\alpha 1} = 1.54056 \text{ \AA}$, $0.2^\circ \text{ min}^{-1}$ over a 2θ range from 2 to 30° and at room temperature.

Atomic force microscopy measurements of the complex sublimed onto SiO_x surface were performed with Bruker Ikon microscope in tapping mode at ambient pressure and room temperature. The error bars of the height along the profile were established as a standard deviation of the points in flat regions above and below the step.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

functional spin crossover complexes, molecular electronics/spintronics, on-surface switching, self-assembly, thin films

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