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Two-dimensional supramolecular electron spin arrays

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In the pursuit of future spintronic applications, investigations of addressable atomic and molecular arrangements of spin systems on surfaces have received increasing attention in recent years.[1–3] Common to this work is that spin-bearing ad-surface atoms are probed individually by scanning tunneling microscopy/spectroscopy (STM/STS) and that they are arranged by atomic repositioning techniques. This piece by piece assembly technique is very time-consuming and therefore impractical for technological applications. Further, the limited resolution of lithography does not yet allow for the production of spin-systems with atomic precision. In the present work, we demonstrate that spontaneous molecular self-assembly[4,5]

is able to provide an interesting alternative. A well-defined supramolecular spin-array on a ferromagnetic substrate is obtained by the self-assembly of appropriately functionalized square-planar molecular building-blocks.[6–16] In these unique bi-molecular arrays the electron spin state can be reversibly controlled by a chemical stimulus[17,18] acting specifically on one of the two metal centers. Our approach involves a combination of supramolecular chemistry for *engineering* the spin arrays and coordination chemistry for *manipulating* them. A selective magnetic control over specific sublattices in large area spin arrays has therefore been achieved.

The on-surface self-assembly of spin-bearing molecules is obtained by decorating the substrate with oxygen atoms[11] and by supramolecular arrangement being directed by functional groups incorporated into the building blocks. The incorporation of fluorine-substituents into the Fe-phthalocyanine enables the formation of intermolecular C–F···H hydrogen-bonds with the Mn-phthalocyanine.[19,20] The generated bimolecular chessboard pattern is thermodynamically the most stable arrangement as the number of hydrogen-bond interactions is maximized (**Figure 1**). Specifically, we use a perfluorinated iron(II) phthalocyanine ($FeF_{16}Pc$)[21] and a manganese(II) phthalocyanine (MnPc) as the molecular building blocks. Thereby a 2D *spin array* of alternating Fe—Mn—Fe spins (Fe—Mn pitch: ~1.65 nm) is produced by mere co-evaporation of the molecules. Here, we have assembled the molecules on a c(2×2) oxygen-reconstructed Co(001) surface[11], but we show that the chessboard-like assembly also takes place on other surfaces, e.g. on Ag(111) (Supporting Information). Note that, in absence of fluorine-functionalization, the molecules occupy random sites in the self-assembled layer (Supporting Information).

The electronic configuration and the corresponding magnetization of the transition metal centers in the $FeF_{16}Pc$ and MnPc molecular building blocks and in the ferromagnetic Co substrate are probed by X-ray absorption (XA) spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD).[22] XMCD, the difference between XA spectra obtained with

circular plus and minus (circ+/circ-) polarized X-rays, provides a measure of the magnetization for each element. The dichroism measured at the $L_{3,2}$ absorption edges allows for the element-specific detection of the magnetic moments in the Fe and Mn ions of the supramolecular array and in the Co atoms of the substrate (Figure 1). The presence of a negative XMCD signal (the direction of the substrate XMCD signal is defined as positive) at the L_3 edge denotes an antiferromagnetic (AFM) spin alignment of the Fe and Mn ions in the molecules with respect to the oxygen-reconstructed substrate.[23,11] We call the initial state of the supramolecular spin array, in which both Fe- and Mn-lattices bear an AFM-coupled spin, the spin ON/ON state (**Figure 2a&e**). The oxidation states can be identified from the XA spectra. Specifically, the Mn L_3 XA peak-shape and position (maximum at ~641.7 eV) of MnPc on the oxygen-reconstructed cobalt surface identify it as Mn(III)Pc, in contrast to the molecule in bulk.[24] In the case of $FeF_{16}Pc$, the L_3 XA peak-shape and position (maxima at ~710.0 eV) can be assigned to $Fe(II)F_{16}Pc$.[25]

We selectively control the electron spin states in the self-assembled array by the metal center's specific response towards exposure to a chemical stimulus.[17,18] This approach is inspired by the biochemical oxygen transport and storage through O_2 coordination to the metal-organic heme group. The coordination and desorption of NH_3, the chemical stimuli chosen in this study, switch the spin states of the self-assembled supramolecular array (Figure 2). The axial NH_3-ligation is imposed by dosage of 100 Langmuir while the sample has been kept at ~70 K. The electronic structures of *both* the Fe and Mn are consequently modified, as reflected in the characteristically different peak shapes observed in both XA spectra (Figure 2b&f). The coordination with NH_3 via its lone-pair results in an increased energy of the $3d_{z^2}$ orbital, consequently yielding a low-spin (S=0) configuration in NH_3-ligated $Fe(II)F_{16}Pc$ which corresponds to a vanished Fe-XMCD signal as seen in Figure 2b. Note that NH_3-ligation is distinctly different from the axial coordination with nitric oxide (NO, S=1/2) where the observed annihilation of the spin has been attributed to the unpaired electron in the NO

ligand.[26] In the case of NH$_3$-ligated Mn(III)Pc, the coordination *does not* quench the spin

(Figure 2f) but merely modifies it, as evidenced by the modified XMCD peak-shape, cf. ref.

[16]. Since the Fe spin is quenched, whereas the Mn spin remains in a modified spin ON'

state, this results in a spin OFF/ON' state of the supramolecular checkerboard. The relatively

weak binding between NH$_3$ and the ad-complexes allows desorption of the NH$_3$ ligand and

restoration of the original spin "ON state by annealing to 300 K (Figure 2c&g). Repeated

exposure to NH$_3$ again leads to the spin OFF/ON' state of the supramolecular spin array,

demonstrating reversibility of the switching process (Figure 2d&h). Importantly, the substrate

is not affected by the adsorption/desorption cycles (Figure 2i-l).

Besides the selective spin switching we observe a site specific bonding strength of the NH$_3$ by

direct STM experiments. The native spin array (**Figure 3a-b**) appears with distinct imaging

contrast at a bias-voltage of +1.9 V. Under these conditions, the FeF$_{16}$Pc macrocycle appears

larger than the MnPc macrocycle and an eight-lobed feature is observed. The feature

corresponds well to the macrocycle's lowest unoccupied molecular orbital as also depicted in

Figure 1. Upon exposure to NH$_3$ at a sample temperature of 78 K, we observe the ligands on

both FeF$_{16}$Pc and MnPc molecules at a bias voltage of +0.4 V (Supporting Information).

Upon increasing the sample temperature to ~130 K, the NH$_3$ ligands are only found on the

MnPc molecules, where they are seen as shaky, streak-like features which appear and

disappear between individual scan lines (Figure 3c). Note that at both temperatures a low

current set-point is important to minimize the interaction with the STM tip and to avoid NH$_3$

desorption. These data directly reveal a higher affinity of NH$_3$ to Mn(III)Pc over Fe(II)F$_{16}$Pc.

This selectivity constitutes an additional parameter to control the spin in the self-assembled

bi-molecular array. We may note here, that the formation constants of NH$_3$ complexes with

metal ions are not yet well known, since aqueous phase coordination chemistry of NH$_3$ is

limited as most metal ions do not form stable ammonia complexes, but react with hydroxide.

Nevertheless, the estimation of the formation constants of NH$_3$ complexes for a large

selection of metal ions also demonstrates a considerably higher affinity for Mn(III) over Fe(II) ions.[27,28] In vacuum, the coordination of NH_3 with FePc[29] is consistent with our observations.

The interaction with the oxygen-reconstructed substrate results in the formation of two mirror-domains of the self-assembled 2D lattices.[11] These mirror domains of self-assembled molecules not only differ in their orientation with respect to the substrate but also in the relative orientation of the molecular building blocks. The $FeF_{16}Pc$ and MnPc molecules are found to be rotated by +/- 14° with respect to the <110> directions of the substrate, leading to organizational chirality.[30] (Figure 3 and Supporting Information). Thereby a 2D magnetic lattice without an inversion symmetry is obtained, as currently discussed in the context of magneto-chiral effects.[31]

The combination of on-surface *supramolecular chemistry* with *coordination chemistry* provides a facile and unique approach to manufacture extended supramolecular arrays with switchable spin states. This methodology works irrespective of the lateral extent of the 2D spin array. The observation of Mn(III)Pc as the on-surface species, also demonstrates that it is important to further explore the influence of the surface *trans* effect on the electronic[32] as well as on the spin states[16,17] of coordination complexes. Together with the ability to chemically turn "OFF" the spin states of one species in the supramolecular array leading to spin ON/ON and OFF/ON' states, the present approach opens the possibility to gain selective magnetic control over large area spin arrays.

The spin array can be fabricated on other, non-magnetic, superconducting[33] or anti-ferromagnetic[34] substrates since self-assembly is governed by intermolecular interactions between the molecular building-blocks.[19,20] Particularly interesting for future spintronics applications might be antiferromagnetic substrates since they promise to obtain exchange-coupled spin arrays at room temperature, which can be manipulated with external fields independent of the substrate.[35]

Experimental
Sample preparation and STM experiments. Cu(001) single crystals were cleaned by cycles of sputtering with Ar^+ ions and annealing. The preparation of the oxygen-reconstructed Co thin films is described in ref. [11]. MnPc (Sigma-Aldrich, Switzerland) and $FeF_{16}Pc$ (synthesized according to ref. [21]) were co-evaporated on the substrate at room temperature. To obtain a ~50:50 molar ratio of two building blocks, the deposition rates were controlled independently for both molecules. The cleanliness, the Co film thickness, the oxygen induced surface reconstruction, the molecular coverage and the stoichiometry of the surface layers were checked by XPS and STM. The STM experiments were performed using electrochemically etched W tips and cut Pt-Ir tips which were treated *in-situ* by sputtering. Positive bias voltages result in tunneling from the tip into unoccupied states of the samples. The tunneling parameters used in the STM experiments are summarized in the Supporting Information.

XAS/XMCD measurements and NH₃ dosage. XAS/XMCD measurements were carried out at the Surfaces/Interfaces Microscopy (SIM) beamline of the Swiss Light Source, Paul Scherrer Institute, Switzerland.[36] A portable vacuum chamber with a base pressure in the order of ~10^{-10} mbar, as established in previous experiments by our group[11,13,16,17], has been used for sample transfer without breaking the vacuum. NH_3 (99.98%, water-free, Air Liquide, Germany) was introduced with the sample kept at ~70 K for XMCD (100 Langmuir) and at 130 K (100 Langmuir) resp. 78 K (20 Langmuir) for STM. NH_3 was desorbed by annealing to 300 K. The gas-line was cleaned by repeated filling/pumping cycles. The gas-line was pumped by an oil-free pump, the obtained base-pressure of the line was < 10^{-1} mbar, i.e. less than 10^{-4} of the NH_3 pressure in the line (~1 bar).

Supporting Information
Supporting Information is available online from Wiley InterScience or from the author.

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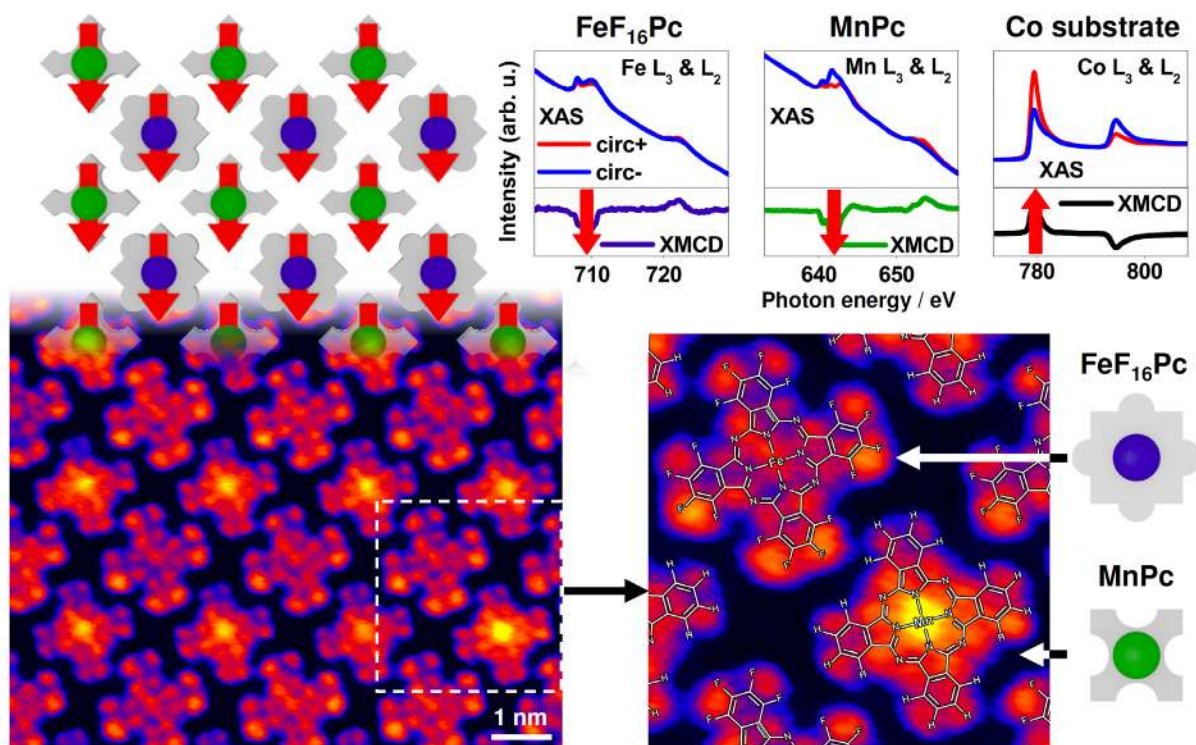
Figure 1. Bottom-up assembly of the supramolecular spin array. Chemical structures of $FeF_{16}Pc$ and MnPc are superimposed on the scanning tunneling microscopy (STM) image which directly visualizes the supramolecular chessboard-like 2D lattice and the intramolecular electronic structure. Thus, the resulting molecular array consists of two superimposed spin-bearing lattices: Fe (dark-blue spheres in jigsaw pieces) and Mn (green spheres in jigsaw pieces). X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) on the respective $L_{3,2}$ edges indentify the antiparallel orientation of the Fe or Mn magnetic moments in the self-assembled 2D array with respect to the magnetization of the ferromagnetic Co substrate. This antiparallel alignment stems from the super-exchange interaction via the oxygen-reconstruction. The data shown here are obtained at 70 K, but the spin-alignment as well as the supramolecular arrangement is strong enough to be observed up to room temperature.
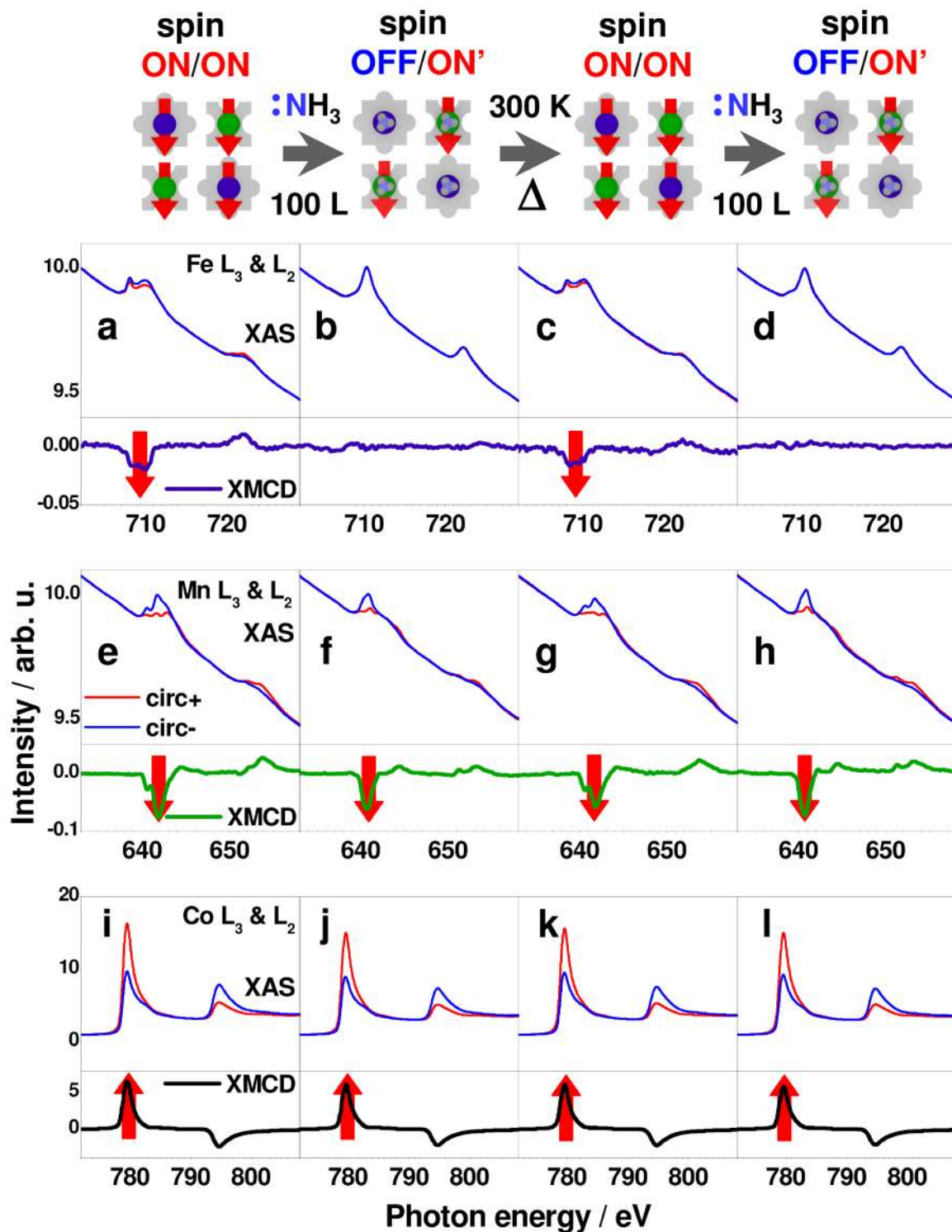
Figure 2. Reversible and selective manipulation of the electron spin states in the Fe and Mn lattices on the oxygen covered Co substrates. X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) of the Fe (a-d), Mn (e-h) and Co (i-l) $L_{3,2}$ edges of the respective $Fe(II)F_{16}Pc$ (with dark-blue centers) and $Mn(III)Pc$ (with green centers) molecules and the oxygen-reconstructed Co substrate. The complex electronic structure of the transition metal ions is reflected in the XAS (red and blue for circ+ and circ- XAS respectively). XMCD is a measure for the magnetic moment induced by the ferromagnetic substrate. The spins in the bimolecular array (a,e) are controlled by consecutive ammonia (NH_3)-ligation to both complexes (b,f), thermal NH_3 desorption (c,g) and subsequent NH_3-ligation (d,h). As a result, the spin of $FeF_{16}Pc$ is selectively switched between the spin ON and OFF states (a-d), while

the electronic structure of MnPc is modified but the molecules remain spin ON respective spin ON' (a slightly modified state with close to identical magnetization after forming the NH_3-complex) during the whole process (e-h). The magnetic moment in the substrate remains unchanged during the cycles (i-l).
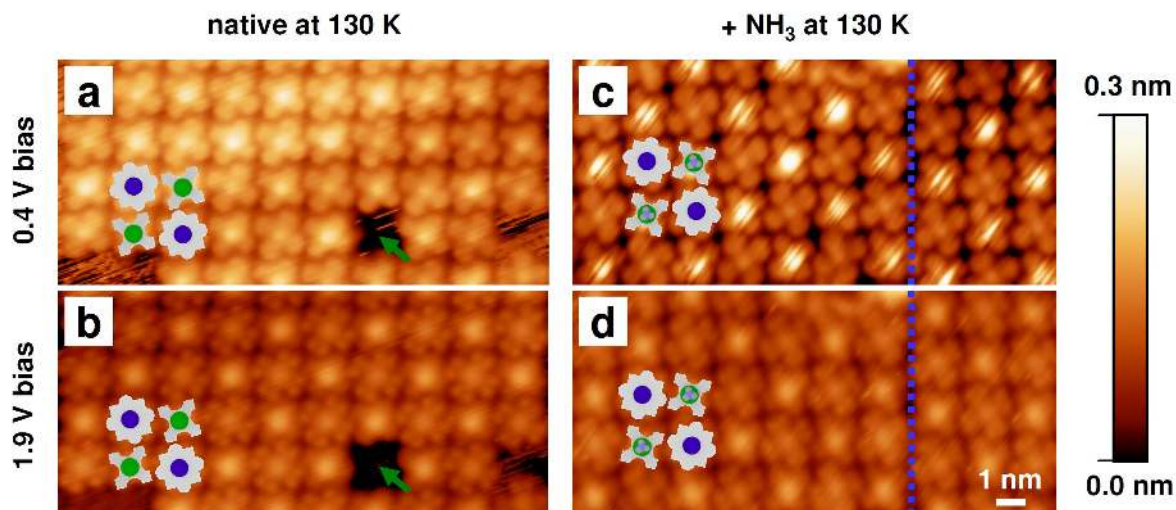

Figure 3. Direct observation of the coordinated NH_3 ligands by STM. The bi-molecular lattice is imaged at different bias voltages before (native, a-b) and after NH_3 exposure (c-d). The $FeF_{16}Pc$ and MnPc molecules are represented by jigsaw pieces with dark-blue and green centers, respectively. The coordinating NH_3 can be observed at ~0.4 V bias voltage as elevated streaks (c). At ~130 K, NH_3 is only observed on the MnPc molecules. The green arrows and the blue dotted lines denote a vacancy defect where one molecule is missing (a-b) and a phase-shift domain boundary in the supramolecular lattice (c-d), respectively.