Supporting Information for

Controlling the Spin States of FeTBrPP on Au(111)

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1. STM Topographs of FeTBrPP vs. Sample Voltage



Figure S1. (a) top and (b) side views of the structure of FeTBrPP. The highlighted areas denote the pyrroles pointing upwards. (c - j) STM topographs of FeTBrPP at different sample voltages. Image size (1.8 nm)². Tunneling current *I* = 30 pA.

Figure S1 shows top and side views of the molecular structure and STM topographs of a FeTBrPP molecule at different sample voltages. The pyrroles pointing upward exhibit bright lobes at small positive sample voltage *V*. The lobes turn into crescents when *V* is increased to approximately 1.2 V. Further increase to +2.5 V leads to a pattern of four lobes, similar to those previously observed from TPP molecules.¹ The contrast at the position of the Fe ion is inverted from a depression to a protrusion when the voltage polarity is changed from positive to negative.

2. Adsorption of FeTBrPP on Au(111)



Figure S2. (a) Atomic resolution topograph of the substrate with a depression serving as a landmark. Topographic maxima are marked by black dots and the center of the depression is indicated by a white dot. (b) and (c) show the adsorption positions of molecules H and L in the same region as (a). The molecules were moved from a neighboring island to the imaged area via tip manipulation using V = 5 mV and I = 8 nA. (d) Topograph of a different area with atomic resolution. (e) Image of a different H molecule. White circles in (d) and (e) depict the same hollow position and the black dots mark the surface lattice in an fcc region. The area exhibiting atomic resolution in (d) is denoted by a dashed rectangle in (e). (f – h) Series of STM images recorded after manipulation steps of the bottom molecule. The molecular center is indicated by black circles in (b), (c), and (e – h). (i) Model proposed for the molecular arrangement. Imaging parameters: (a) 5 mV, 6 nA; (b, c) 5 mV, 10 pA; (d) –10 mV, 6 nA; (e) – 300 mV, 100 pA; (f – h) –30 mV, 70 pA.

To determine the adsorption site of the molecule, we used the following approach. First, we searched a surface area that included a defect that would serve as a landmark and acquired an atomically resolved image. Second, we marked the topographic maxima, which

presumably correspond to atomic positions, as well as the landmark (Figure S2 a). Third, we moved the molecule into the imaged area. Fourth, the lattice obtained in step 2 was transferred (Figure S2 b and c). Figures S2 b and c suggest that the metal center of the H (L) molecule is located at a bridge (top) site of the substrate. We moved the molecule to approximately 50 positions inside the area *via* tip manipulation and identified the type of the molecule (H or L) and the position of its center after each manipulation. We always found the H and L states at bridge and top sites, respectively, consistent with the observations in Figures S2 b and c. The same approach was also used in a different region (Figures S2 d and e) with the same result.

Uncertainties of the method result from the determination of the location of the surface atom and landmarks, thermal drift, creep of the piezoelectric scanner, and possible tip changes. To minimize errors arising from the tip state we made sure that multiple scans with stable tips gave identical results, independent of the scanning speeds and directions used. All sources add up to an estimated uncertainty below 80 pm, largely due to the determination of the center position in the images. This uncertainty is small enough to not interfere with the conclusions drawn.

Figures S2 f – h show two molecules in the same scanning frame recorded after manipulation steps of the lower molecule. The center of the molecule in the H (L) state is still located at a bridge (top) site when the two molecules touched each other, indicating that this interaction between the molecules does not drastically affect their adsorption structure. Finally, the adsorption model of the self-assembly is proposed (Figure S2 i).



3. dI/dV Spectra Along the Pyrrole[up]-Fe-Pyrrole[up] Axis

Figure S3. Series of differential conductance spectra recorded along the line pyrrole[up]–Fe–pyrrole[up] (dashed line in the inset) on (a) H and (b) L molecules. The measurements were performed at constant tip height after disabling current feedback at V = -50 mV and I = 100 pA. Voltage modulation: $V_{\rm rms} = 500$ μ V. Image size: (1.8 nm)²; imaging parameters: V = -100 mV, I = 50 pA.

Figure S3 demonstrates that the shape of dI/dV spectra turns from asymmetric to symmetric when the tip is moved away from the Fe ion to the upward pyrrole, for both H and L molecules. The same evolution was observed on FeTPP on Au(111) and attributed to a change of the ratio of potential and exchange scattering amplitudes.²

4. Magnetic Anisotropy Energies of FeTBrPP on Different Regions of the Au(111) Reconstruction



Figure S4. MAEs of H (red triangles) and L (blue triangles) molecules adsorbed on fcc (left), soliton wall (middle) and hcp (right) regions of the surface. The red (blue) dashed lines stand for the average values of MAEs of the H (L) molecules in each region. The underlying measurements were performed at constant tip height after disabling current feedback at V = -30 mV and I = 100 pA.

Slight variations of the magnetic anisotropy of the molecules were observed. Figure S4 shows the magnetic anisotropy energies of 32 molecules in the same molecular island. In the same region of the Au(111) reconstruction (fcc, hcp or soliton wall), the variation of the magnetic anisotropy energies remain below 0.8 meV. Interestingly, the average MAE of the molecules adsorbed on the soliton wall is smaller than those on fcc and hcp regions. We assume that the different regions slightly change the occupation of the Fe 3d-orbitals, leading to the small MAE differences between molecules in different regions.

5. dI/dV Spectra of FeTBrPP-Cl



Figure S5. (a) Constant-current STM image of two FeTBrPP-Cl molecules. Set point: V = -1 V, I = 100 pA. (b) Spin excitation spectra recorded at fixed tip height at the tip positions depicted by red and blue dots, which correspond to the Cl ions. Spectroscopy was performed at constant tip height after disabling current feedback at V = -30 mV and I = 100 pA and using a sinusoidal modulation of the sample voltage $V_{rms} = 500 \mu$ V.

d*I*/d*V* spectra obtained on Cl ligands show significantly lower excitation energies, 2.6 (blue) and 2.5 meV (red). The variation of the excitation energy of FeTBrPP-Cl molecules observed in our experiments is tiny, indicating that the influence of surface on the magnetic anisotropy of FeTBrPP-Cl is negligible. The magnetic anisotropy energies here are rather close to that of FeTPP-Cl molecules on Au(111), which is 1.7 meV.²

6. Spectra of the LUMO

When the tip moved from the upward pyrrole to the center Fe ion, the conductance of the LUMO is gradually suppressed for both H and L molecules. This change explains that the center of the FeTBrPP appears as a depression in STM images recorded at low positive voltages (Figure S1).



Figure S6. dI/dV spectra of the LUMO as function of tip positions on L (up) and H (down) molecules. Spectroscopy was performed at constant tip height after disabling current feedback at V = -300 mV and I = 60 pA and using a sinusoidal modulation of the sample voltage $V_{\rm rms} = 7$ mV. For clarity, the spectra from H have been multiplied by 2. The dashed line in the inset shows the tip trace from the upward pyrrole to the Fe ion. The STM images were recorded at -300 mV and 100 pA.





Figure S7: Projected density of states on d-orbitals of Fe and and p-orbitals of Br atoms for H molecules (top panels) and L molecules (bottom panels).

Figure S7 shows the density of states projected on the Fe d-orbitals, including the contributions from d_{xy} and $d_{x^2-y^2}$, as well as on Br atoms. Note that a wider energy range than in Figure 3 is used here. The results for both molecular configurations, H and L, are presented. It is clearly observed that Br atoms have a negligible contribution around the Fermi level.

8. Fe d-orbital Occupation of a Four FeTBrPP Cell



Figure S8: (Left) The unit cell used, represented by black dashed lines, consists of two FeTBrPP molecules placed in H and two in L configurations on Au(111). (Right) Simplified scheme showing the occupation of Fe *d*-orbitals for each of the four molecules.

We also carried DFT simulations using the unit cell shown in the left panel of Figure S8. This unit cell contains four FeTBrPP molecules (two each in H and L configurations). As shown in the right panel of Figure S8, the occupation of the d-orbitals for both configurations is the same as for the isolated molecules on Au (see Figure 3 in main text). Therefore, our DFT results further confirm that the magnetization of the molecules is not modified by the interaction with the neighboring molecules.

9. H and L Conformations of FeTBrPP on Au(111)



Figure S9: Upper panels: Top view of H and L molecules on Au(111), including the labels for the N atoms. The dashed red boxes indicate the orientation of the up pyrroles. Bottom panels: Vertical displacement of all atoms with respect to the Fe atom ($\Delta z = 0$) in H (left) and L (right) molecules, as relaxed on Au(111).

Distance (in pm)	Fe-N ₁	Fe-N ₂	Fe-N ₃	Fe-N ₄
H molecule	198.0	197.3	199.8	199.6
L molecule	198.3	198.1	198.4	199.7

Table S1: Distances between the central Fe atom and the surrounding N atoms for H and L molecules as relaxed on Au(111). N_1 and N_2 are from the up pyrroles. N_3 and N_4 are from down pyrroles.



10. Changing the magnetic anisotropy of molecules

Figure S10. Tuning the magnetic anisotropy by modifying the position of the molecules. (a - i), STM topographs recorded after each manipulation of the molecule marked by the white dashed circle. The type of the molecule and its MAE is shown nearby. The close-packed directions of the surface are shown by the white arrows in (a). Imaging parameters V = -30 mV, I = 70 pA.

The molecule type can be switched freely between L and H via manipulating its adsorption site/orientation. When the orientation of the molecule is parallel (perpendicular) to the close-packed direction of the surface, the molecule type is L (H) and a low (high) MAE is obtained.

References

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