Supplementary Information

Tweezers-like magnetic tip control of the local spin state in FeOEP/Pb(111) adsorption system: A preliminary exploration based on first-principles calculation

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S1. Structural deformation caused by magnetic tip and non-magnetic tip

Hubbard-like+U correction is applied to improve the prediction for band energies. U_{eff} is determined by reducing the delocalization error of DFT using the formula $U_{\text{eff}} = E_{\text{gap}}^{\text{int}} - E_{\text{gap}}^{\text{der}}$.[1] $U_{\text{eff}} \approx 2$ eV is adopted for calculating the junction geometries, electronic structures and magnetic anisotropy (MA). The same value of U_{eff} is adopted in Pb-tip controlled FeOEP/substrate system.[1]
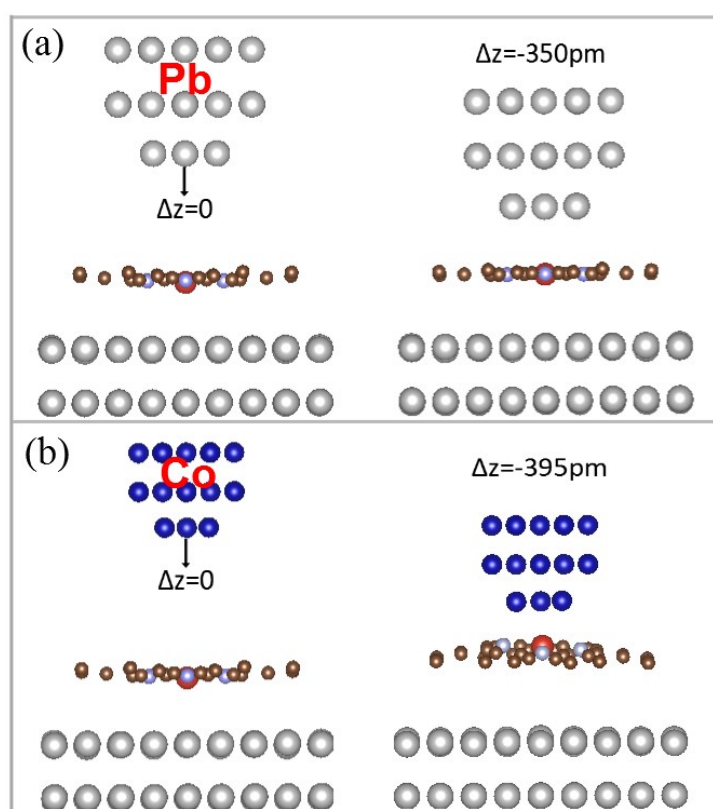

Fig. S1. Structure deformation induced by (a) Pb tip and (b) Co tip.

Fig. S1 shows the geometric deformation of FeOEP molecule induced by non-magnetic Pb-tip and magnetic Co-tip. At tip displacement of $\Delta z = 0$, for both magnetic tip and non-magnetic tip control systems, the Fe atom is attracted downwards by the substrate and forms a local depression in the middle of the molecule. The Fe

atom locates in an axial distorted square-planar ligand field. When approaching the tip to the molecule, tip potential exerts a strong attractive force to pull the molecule away from the substrate. For the nonmagnetic tip, the non-uniform deformation in different parts of the molecule shows a tendency to initialize the molecular plane. At $\Delta z = -350$ pm, Fe atom returns to the square-planar ligand field, but fails to pass through the porphyrin plane, see Fig. S1(a). Then the molecule moves with the tip towards the substrate. The maximum value of the attractive force exerted by the magnetic tip is estimated to be approximately ten times greater than that exerted by a non-magnetic tip. In the manipulation process of magnetic tip, the central part of the molecule is suddenly grabbed by the tweezers-like tip at $\Delta z = -395$ pm. Then Fe atom passes through the framework plane, and forms a local bulge in the molecular plane, as shown in Fig. S1(b).

S2. Projected density of states of the Fe $3d$ orbital

Fig. S2(a) shows the spin-resolved projected density of states (PDOS) of Fe $3d$-orbitals at $\Delta z = 0$. The black dotted line represents the Fermi level. The PDOS of orbital-d_{xz} and orbital-d_{yz} are mostly overlap with each other. The corresponding spin-resolved energy level is diagrammed in Fig. S2(b). To determine the local spin state on the Fe center, the electron occupation number on each $3d$ orbital is extracted from the PDOS and listed in Table S1. It is confirmed that among the five $3d$ orbitals, orbital-d_{xy} and orbital-d_{z^2} are fully-occupied, the unpaired spins reside on the two d_π orbitals. Orbital-$d_{x^2-y^2}$ is acknowledged as an empty orbital above the Fermi level, and the small fractional occupation on it has but negligible contribution to the magnetic moment of the junction.
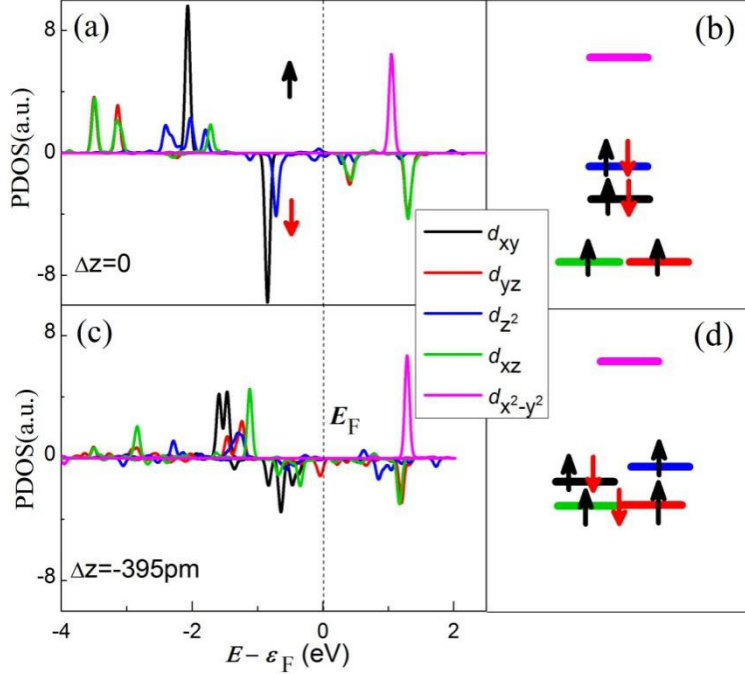

Fig. S2. The spin-resolved PDOS of Fe $3d$-orbitals at (a) $\Delta z = 0$ and (c) $\Delta z = -395$ pm. The corresponding spin-resolved energy level is diagrammed in (b) and (d), respectively.

Approaching the tip towards the molecule about 395 pm, we can see a remarkable change of PDOS shown in Fig. S2(c) and a rearrangement of d-orbitals shown in Fig. S2(d). Due to the strong hybridization with the magnetic tip, the PDOS shifts towards the Fermi level, localizes in the energy range of -2eV $\sim$ $+2$eV. The PDOS of orbital-d_{z^2} is distributed over a relatively broad energy range. In the meanwhile, the rearrangement of the energy level in the contact regime induces the fractional occupation on d_π and d_{z^2} orbitals. Hence, as the tip-sample distance decreases, the enhanced coupling between the molecule and the magnetic tip definitely changes the electronic structure of Fe $3d$ orbitals, particularly the orbitals polarized along the z axis.

Table S1. The electron occupation of each $3d$ orbital of the Fe atom at different tip displacement. For each orbital, $n_{\mathrm{occ}} = n_\uparrow + n_\downarrow$ and $S_z = 1/2(n_\uparrow - n_\downarrow)$ are also evaluated.

			$\Delta z = 0$			
	d_{xy}	d_{yz}	d_{z^2}	d_{xz}	$d_{x^2-y^2}$	tot
$n_\uparrow$	0.93	0.93	0.90	0.93	0.41	4.10
$n_\downarrow$	0.92	0.06	0.70	0.06	0.30	2.04
n_{occ}	1.85	0.99	1.60	0.99	0.71	6.14
S_z	0.005	0.44	0.1	0.44	0.05	1.03
			$\Delta z = -395\text{pm}$			
	d_{xy}	d_{yz}	d_{z^2}	d_{xz}	$d_{x^2-y^2}$	tot
$n_\uparrow$	0.92	0.92	0.84	0.90	0.36	3.94
$n_\downarrow$	0.90	0.37	0.36	0.49	0.28	2.40
n_{occ}	1.82	1.29	1.20	1.39	0.64	6.34
S_z	0.01	0.28	0.24	0.21	0.04	0.77

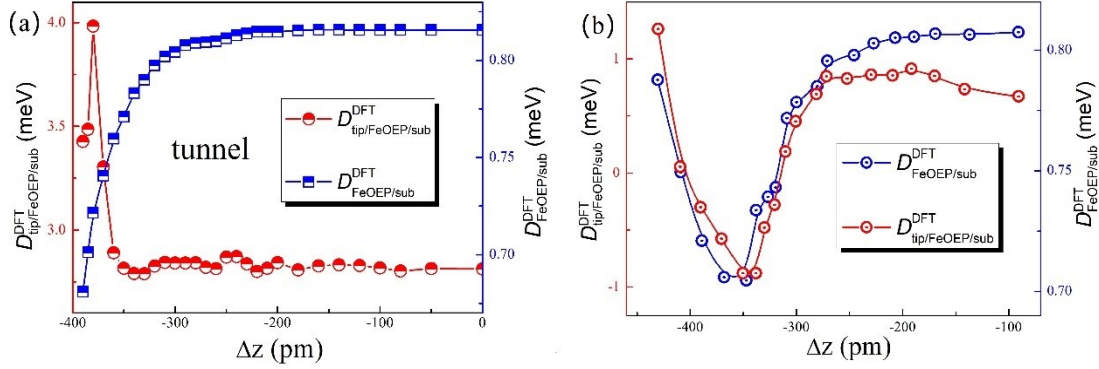## S3. Influence of magnetic tip on the calculated magnetic anisotropy.

Fig. S3. The DFT calculated magnetic anisotropy under the control of (a) magnetic Co tip and (b) non-magnetic Pb tip.

The DFT calculated MA is obtained by rotating the spin quantization axis along different directions and comparing the energy difference. In the control process of non-magnetic Pb tip, the MA $D^{\text{DFT}}_{\text{FeOEP/Pb(111)}}$ is calculated after eliminating the tip. The evolution of $D^{\text{DFT}}_{\text{FeOEP/Pb(111)}}$ is found to be consistent with the trend of $D^{\text{DFT}}_{\text{tip/FeOEP/Pb(111)}}$ for the system with the Pb-tip, as shown in Fig. S3(b). For the control process of magnetic Co-tip, the intrinsic magnetic moment of the 16-atoms tip is about $32\mu_B$. The calculated MA of FeOEP molecule is mixed with the intrinsic MA of the magnetic tip. When the tip is cut off, the evolution of $D^{\text{DFT}}_{\text{FeOEP/Pb(111)}}$ is roughly opposite to the total $D^{\text{DFT}}_{\text{tip/FeOEP/Pb(111)}}$, see Fig. S3(a). The coordination field around Fe atom returns to a planar structure at $\Delta z = -395$ pm. Therefore, the value of D should decline to a minimum value. In order to prevent the MA of magnetic tip from interfering with the calculation results, the tip is taken off when calculating the energy difference. The influence of the surrounding environment is assessed by comparing the MA of the FeOEP/sub system to that of an isolated FeOEP molecule, with the formula:

$$D_{\text{env}}^{\text{DFT}} = D_{\text{tip/FeOEP/sub}}^{\text{DFT}} - D_{\text{FeOEP}}^{\text{DFT}} - D_{\text{tip}}^{\text{DFT}}$$

$$\approx D_{\text{FeOEP/sub}}^{\text{DFT}} - D_{\text{FeOEP}}^{\text{DFT}} \qquad (1)$$

S4. Quantification of spin-polarized coupling strength.

The coupling of the impurity orbital to the environment (tip or substrate) is given by the so-called hybridization function $\Gamma_{i\alpha\sigma}(\omega)$, which can be obtained from the local Kohn-Sham Green Function. [2, 3]

$$G_i^0(\omega) = \sum_{\kappa} \frac{\langle\phi_i|\psi_\kappa\rangle\langle\psi_\kappa|\phi_i\rangle}{\omega - \epsilon_\kappa + i\delta} \tag{2}$$

Where ϕ_i is the local impurity orbital, ϵ_κ is the orbital level of the Bloch state ψ_κ. The reciprocal of the imaginary part of $G_i^0(\omega)$ is: $\Gamma_i(\omega) = IM[G_i^0(\omega)]^{-1}$, which describes the single-particle broadening of individual impurity orbital when it coupled to the conduction electrons.
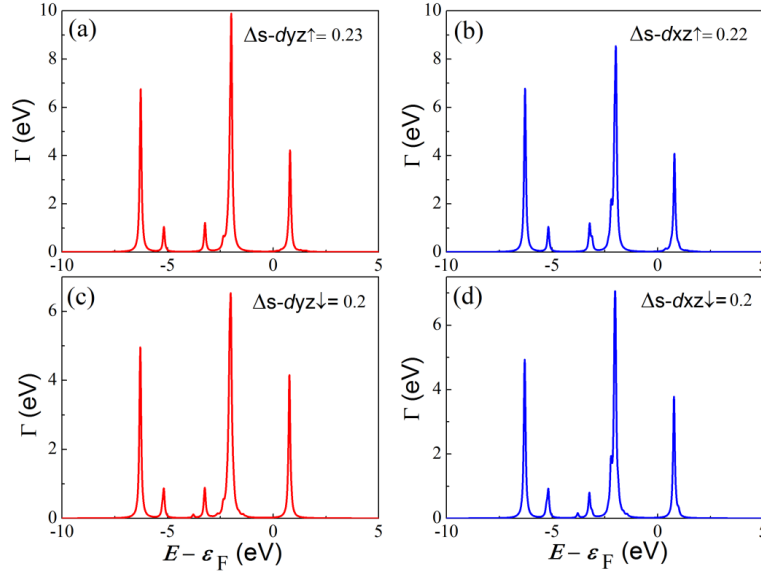

Fig. S4. The DFT calculated $\Gamma_{i\alpha\sigma}(\omega)$ function of molecule/substrate system at $\Delta z = -390$ pm.

The total coupling strength of the v-th spin-unpaired d orbital and the environment can be estimated from the average height of $\Gamma_i(\omega)$ function from the band edge to the Fermi level. By removing the tip or the substrate from the composite junction, while
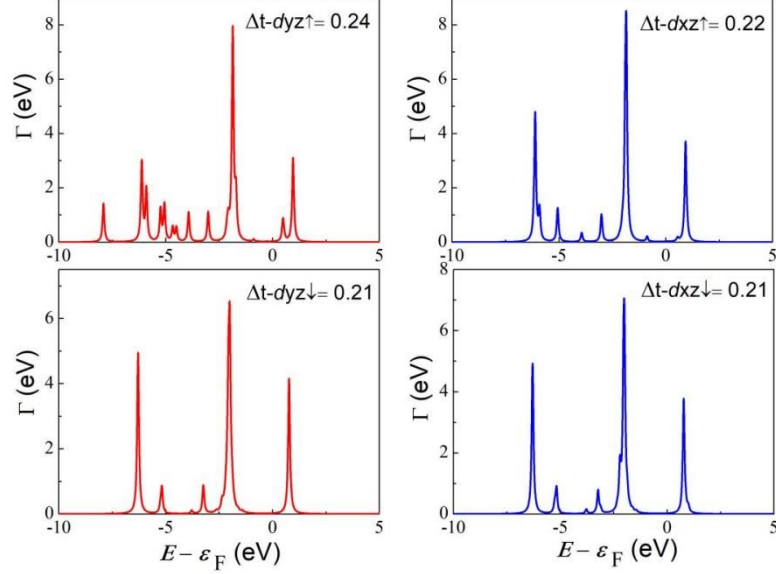

Fig. S5. The DFT calculated $\Gamma_{i\alpha\sigma}(\omega)$ function of tip/molecule system at $\Delta z = -390$ pm.

fixing the coordinates of the remaining atoms, the coupling strength $\Delta_{i\alpha\sigma}$ can be evaluated based on the calculated $\Gamma_{i\alpha\sigma}(\omega)$.

At $\Delta z = -390$ pm, the system is still in tunneling state. The tip-molecule distance is greatly shortened, and the interaction between the environmental electron and the impurity is significantly enhanced. We cut away the tip and calculate the $\Gamma_{i\alpha\sigma}(\omega)$ (in units of eV): $\Delta_{s1\uparrow} = 0.23$, $\Delta_{s1\downarrow} = 0.20$, $\Delta_{s2\uparrow} = 0.22$ and $\Delta_{s2\downarrow} = 0.20$, as shown in Fig. S4. Then, we remove the substrate and evaluate the tip-impurity coupling strength (in units of eV): $\Delta_{t1\uparrow} = 0.24$, $\Delta_{t1\downarrow} = 0.21$, $\Delta_{t2\uparrow} = 0.22$ and $\Delta_{t2\downarrow} = 0.21$, as shown in Fig. S5. Here, orbitals 1 and 2 represent the Fe d_{yz} and d_{xz} orbitals, respectively.
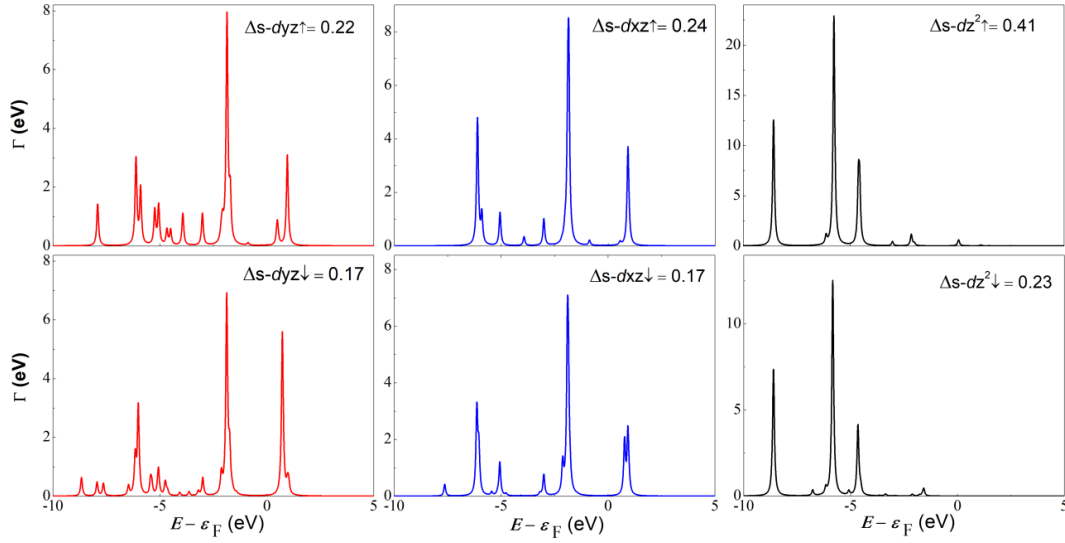
Fig. S6. The DFT calculated $\Gamma_{i\alpha\sigma}(\omega)$ function of molecule/substrate system at $\Delta z = -395$ pm.

Approaching the tip towards the molecule about 395 pm, the system transfers from tunneling state to contact state. The d_{xz} and d_{yz} orbitals together possess one spin-unpaired electron, and they thus can be combined and treated as a singly-occupied orbital in the Anderson impurity model. Here, orbital-2 represents the d_{z^2} orbital, while orbital-1 stands for a combination of d_{xz} and d_{yz} orbitals. From Fig. S6 we have the coupling of impurity and substrate (in units of eV): $\Delta_{s1\uparrow} = 0.23$, $\Delta_{s1\downarrow} = 0.17$, $\Delta_{s2\uparrow} = 0.41$ and $\Delta_{s2\downarrow} = 0.23$. We remove the substrate and evaluate the tip-impurity coupling strength (in units of eV): $\Delta_{t1\uparrow} = 0.29$, $\Delta_{t1\downarrow} = 0.25$, $\Delta_{t2\uparrow} = 0.49$ and $\Delta_{t2\downarrow} = 0.34$, as shown in Fig. S7.
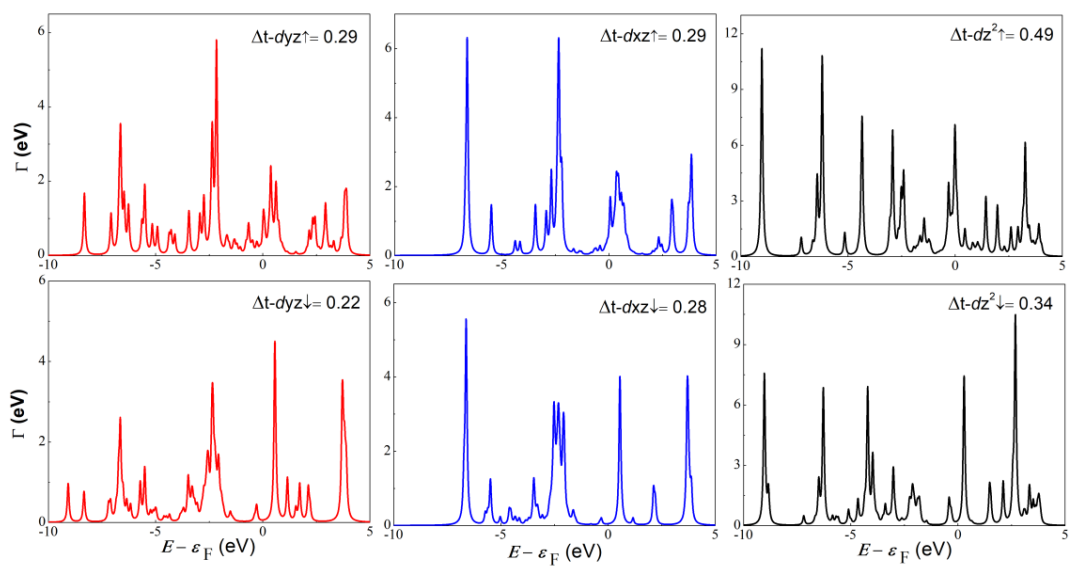
Fig. S7. The DFT calculated $\Gamma_{i\alpha\sigma}(\omega)$ function of tip/molecule system at $\Delta z = -395$ pm.

S5. Ferromagnetic interaction between the tip and the molecule

In this work, we have calculated the energy difference $\Delta E = E_{AFM} - E_{FM}$ of the composite system when the magnetic tip and molecule are in the ferromagnetic (FM) and antiferromagnetic (AFM) states; see Fig. S8. It is found that ΔE is positive and increases gradually as the tip gets closer to the molecule ($\Delta z < -200\,$pm), implying that the interaction between the magnetic tip and molecule is ferromagnetic and gradually enhances. The geometric deformation, charge transfer, the evolution of magnetic anisotropy and dI/dV spectrum discussed in the manuscript are all in the range of $\Delta z < -200$pm. Noted that in the range of $-200 < \Delta z < 0\,$pm, the tip is far from the molecule, so the spin polarization of the tip has little effect on the molecule and ΔE shows a negative but negligible value.
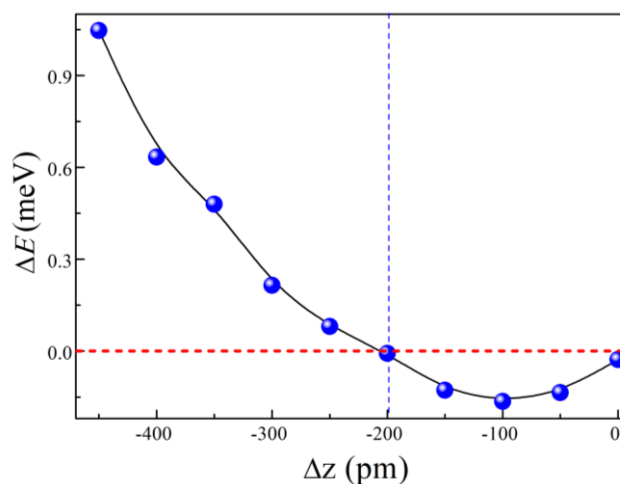

Fig. S8. The DFT calculated energy difference $\Delta E = E_{AFM}\text{-}E_{FM}$

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