Supporting Information

Spatially Resolving Electron Spin Resonance of π-Radical in Single-molecule Magnet

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S1. Details of the experimental setup

All experiments were performed in an ultrahigh-vacuum condition and at the sample temperature of 0.4 K achieved by the $^3$He cooling system (Unisoku USM1300). The cooling system was also equipped with a superconductor magnet (Cryogenic Ltd.) which was able to generate the out-of-plane magnetic field up to 11 T. We introduced the RF signal through the high-frequency cables connected to the tip bias line (Figure S1). The SMP-type feedthrough (Solid Sealing Technology, FA33179-1FF) create the connection between the ambient and the internal vacuum chamber (IVC), which had a lower insertion-loss performance than that of the standard SMA-type. We employed the semi-rigid cable of SC-219/50-SCN-CN (COAX Co., Ltd.) from this connector to the 1 K pot (orange line), and from the 1 K pot to the ultrahigh vacuum (UHV) feedthrough (green line), SC-119/50-SCN-CN (COAX CO., LTD). In the UHV chamber, the connection to the STM tip (blue line) was established by using the flexible coaxial cable (Cooner Wire, CW2040-3650F). For the line of the tunneling current, we used a SMA-type connector (COSMOTEC Co., C34SMR1) and flexible coaxial cable (same as that used for the RF line, as shown by the blue line in Figure S1). The continuous sinusoidal signal from the RF generator (Keysight, N5193A) was applied to the tunneling junction ($V_{RF}$) through the bias Tee (SigaTek, SB15D2) and combined with the DC bias voltage ($V_{DC}$). The cable shown with the yellow line in the figure is flexible coaxial cable (Mini-Circuits, TMP40-6FT-KMKM+).

For the lock-in detection, we modulated the amplitude of the RF signal (hence the RF bias voltage ($V_{RF}$)) in a chopping scheme at a frequency of $f_{mod} = 431$ Hz. The resulting $V_{RF}$-induced tunnel current was detected with a lock-in amplifier (NF, LI5650) after an amplification by using the current amplifier (Femto, DLPCA-200) with the bandwidth.
which covered the $f_{\text{mod}}$. The lock-in output ($V_{\text{lock-in}}$) corresponded to the root-mean-square value of the $V_{\text{RF}}$-induced tunnel current; it is defined as the $V_{\text{RF}}$-induced variation in the tunnel current ($\Delta I$). The ESR signal was acquired with a relatively weak feedback loop with the spin-polarized tip prepared by picking up a few Fe atoms from the Cu surface, while STM images were obtained at the constant-current mode.

**Figure S1.** Schematic of radiofrequency (RF) cabling in the cryostat and outside of the measurement setup area used for electron spin resonance measurements.
**S2. Spin-polarized tip with $dI/dV$ spectra**

Figure S2(a) shows the $dI/dV$ spectrum acquired with a nonmagnetic PtIr tip at the lobe position of the TbPc$_2$ molecule absorbed on the Cu(100) surface in the absence of the magnetic field. The sharp peak near the Fermi level corresponds to the Kondo peak. In the magnetic field ($B_{\text{ext}} = 500$ mT), as shown by the black curve in Figure S2(b), this peak splits into two peaks marked by arrows, thus resulting in the symmetric spectrum concerning the bias polarity. The obtained splitting was caused by spin excitation inelastic tunneling spectroscopy (IETS) owing to the transition between the Zeeman split state $m = \pm 1/2$ of the $\pi$-radical electron of $S = 1/2$. Conversely, the $dI/dV$ spectrum obtained with the spin-polarized tip, which was prepared by picking up a few Fe atoms from the Cu surface (red curve in Figure S2b), shows the asymmetric shape owing to the selection rule for spin excitation with tunneling electron$^{1,2}$. By using this method, we confirmed the tip polarization before we conducted the ESR measurements.

The prepared spin-polarized tip is used in the ESR-STM measurements to read-out the population difference of the up and down spins, where difference between the on- and off-resonance conditions is given by the tunneling magnetoresistance (TMR). The tip also contributes to the driving of surface spin resonance.

(1) Read out of spin resonance state
The change in the population of the Zeeman splitting states due to the ESR was read out as the change of tunneling current ($\Delta I$) compared to the background tunneling current during the off-resonance condition between the spin polarized tip and $\pi$-radical electron spin on the surface. The tunneling conductance was determined by the relative spin alignment of spin polarized tip and $\pi$-radical electron due to the TMR described as

$$G = G_j(1 + \alpha <S_{\text{tip}}> \cdot <S_{\pi}>),$$

where $\alpha$ is a constant proportional to the tip polarization, $G_j$ is the spin averaged junction conductance, and $<S_{\text{tip}}>$ and $<S_{\pi}>$ are the spin value for tip and $\pi$-radical electron, respectively. The read out of spin state in the ESR-STM measurement can be understood as a modification of $S_{\pi}$ at the on-resonance condition created by RF signal. To read out the changing spin state, the RF bias voltage ($V_{RF}$) is applied to the tunneling junction with usual DC bias voltage ($V_{DC}$) in STM. The total applied bias voltage is

$$V = V_{DC} + V_{RF}\cos(\omega t + \Phi),$$

where $\omega$ and $\Phi$ indicate the frequency and the phase of RF signal.

The tunneling current can be written as

$$I(t) = GV = G_j(1 + \alpha <S_{\text{tip}}> \cdot <S_{\pi}>)(V_{DC} + V_{RF}\cos(\omega t + \Phi)).$$

Finally, the read out of ESR signal is determined by the difference in $I(t)$ between on- and off-resonance conditions of the $\pi$-radical electron spin.
(2) Driving the ESR of a target spin

The $V_{RF}$ modulated the magnetic-field gradient generated by the spin-polarized tip. At the $V_{RF}$ frequency corresponding to the Zeeman energy lifted by the external magnetic field, the effective oscillating magnetic field imposed by $V_{RF}$ drives the ESR transition between the Zeeman split states. The ESR-STM driving mechanism using the spin-polarized tip is understood by considering the spin interactions between the tip and the surface spin$^4$. In ESR-STM measurement, the RF electric filed was applied from the spin-polarized tip to surface spin, whereas application of the oscillating magnetic field is generally required to drive the ESR. The mechanism of converting the RF electric field into the oscillating effective magnetic field is still under debate, and several experimental and theoretical investigations have been reported.
Figure S2. Preparation of spin-polarized scanning tunneling microscopy (STM) tip. (a) $dI/dV$ spectrum acquired at the lobe position of TbPc$_2$ molecule absorbed on the Cu(100) surface in the absence of a magnetic field. (b) $dI/dV$ spectra acquired with (red curve) and without (black curve) a magnetic tip in the presence of a magnetic field ($B_{\text{ext}} = 500$ mT). All $dI/dV$ spectra were acquired at the same conditions ($V_{\text{DC}} = 25$ mV, $I = 500$ pA, $V_{\text{mod}} = 1$ mV, $f_{\text{mod}} = 431$ Hz).
**S3. Acquisition and compensation of transmission**

The transmission of the entire RF signal line (Figure S1) has a specific frequency dependency owing to the characteristics of the RF components (such as cables, connectors, and feedthrough). As this frequency-dependent transmission makes the identification of the ESR peaks difficult, it is required to calibrate the transmission characteristics prior to ESR measurements. In frequency sweeping ESR-STM measurements with the constant RF source power ($P_{RF}$), frequency-dependent transmissions modify the amplitude of the RF voltage ($V_{RF}$) applied to the tunneling junction, and hence alter the ESR signal obtained as the tunnel current enhancement ($\Delta I$), thus leading to the artifact in the ESR spectrum. This artifact can be misinterpreted as an ESR signal, thus making it difficult to identify the actual ESR signal.

To compensate for the frequency-dependent influence of the transmission, we tuned $P_{RF}$ by the following procedure, as reported previously\(^5\). First, we quantified the $V_{RF}$ amplitude by rectifying the nonlinearity in the $I$–$V$ characteristic obtained from the Ag(111) surface state\(^6\). The Ag(111) surface was prepared with repeated Ar\(^+\) ion sputtering and annealing at 773 K. As shown in the STM images (Figure S3(a)), the prepared surface shows the monolayer steps with hexagonal atomic structures (inset), which constitute evidence that an atomically clean surface was prepared. The $dI/dV$
spectrum obtained on the Ag(111) surface (blue spectrum in Figure S3(b)) shows the step-like structure and indicates the onset of the surface state. The application of the continuous wave RF signal \((P_{RF} = -5 \text{ dBm}, f = 19 \text{ GHz})\) broadens the step structure (black spectrum in Figure S3(b)). We fitted both spectra with an arcsine function and determined the \(V_{RF}\) amplitude to be 25 mV at the specific RF condition. To evaluate the \(V_{RF}\) variation as a function of \(P_{RF}\), we first measured the \(\Delta I\) based on the \(V_{\text{lock-in}}\), as described in S1, while we swept \(P_{RF}\) at a constant RF frequency \((f = 19 \text{ GHz})\). The \(V_{\text{lock-in}}\) was then scaled to \(V_{RF}\) by using the relation between \(V_{RF}\) and \(V_{\text{lock-in}}\) obtained by the surface-state measurement described above. By using this method, we determined the \(P_{RF}\) which corresponded to any required \(V_{RF}\). 

Next, we acquired the RF transmission on the Ag(111) surface by sweeping the frequency in the range of 18–25 GHz at a constant power setting equal to \(P_{RF} = +5 \text{ dBm}\). The tunneling condition of \(V_{DC}\) was adjusted to the Ag(111) surface state onset of −70 mV (see Figure S3(b)) during the application of an RF signal for rectification of nonlinearity of the \(I-V\) curve. Herein, we set the tunneling current to 500 pA, which was higher than that used in our ESR measurement (10 pA). The higher tunneling current increased the \(V_{RF}\) and thus allowed us to obtain a more accurate relative intensity of the RF signal over the entire frequency range, especially in the frequency region in which
the signal was strongly attenuated within the RF line. The RF transmission can be determined by dividing $V_{\text{lock-in}}$ by the source power of $P_{\text{RF}}$. Figure S3(c) shows the RF transmission measured on an Ag(111) surface in the frequency range of 18–25 GHz at a constant $P_{\text{RF}} = +5$ dBm.

Finally, to compensate for the RF transmission, we tuned $P_{\text{RF}}$ (as plotted in Figure S3(d)) which was calculated from the obtained transmission function based on a method described previously. The result (Figure S3(e)) obtained on the NaCl/Cu(100) surface demonstrates that we can produce a constant $V_{\text{RF}} = 5$ mV over the frequency range of 18–25 GHz used in our ESR-STM measurements.
Figure S3. Compensation of RF transmission at the tunneling junction. (a) Typical large-scale STM image of Ag(111) surface (scanning condition: \( V_{\text{DC}} = 0.9 \) V and \( I = 18 \) pA). The inset shows an image at an atomic resolution (scanning condition: \( V_{\text{DC}} = 70 \) mV and \( I = 500 \) pA). (b) \( dI/dV \) spectra of step-like Ag(111) surface state with (black curve) and without (blue curve) RF signal (\( P_{\text{RF}} = -5 \) dBm, \( f = 19 \) GHz). The applied continuous RF signal broadened the step-like surface state of Ag(111) owing to the application of the \( V_{\text{RF}} \) at the tunnel junction; the \( V_{\text{RF}} \) amplitude was estimated to be 25 mV. (c) RF transmission of frequency range 18–25 GHz at a constant RF source power equal to \( P_{\text{RF}} = 5 \) dBm. (d) The RF source power used to compensate the frequency-dependent RF transmission and create constant \( V_{\text{RF}} \) at tunnel junction. (e) The constant \( V_{\text{RF}} \) amplitude of 5 mV was achieved by utilizing a compensated source power.
S4. Statistical analysis of the number of isolated TbPc2 molecules on the surface

As shown in Figure 1(b) in the main text, there are several isolated single TbPc2 molecules over the Cu(100) surface, while a few isolated single molecules exist on the NaCl surface where most molecules either aggregate at the edge of the NaCl island or make clusters. The same tendency was observed in other areas of the same sample as shown in Figure S4. We estimated the densities of the isolated molecule on the Cu and NaCl surfaces to be 17 molecules per 1618 nm$^2$ ~ $1.1 \times 10^{-3}$ nm$^{-2}$, and 2 molecules per 482 nm$^2$ ~ $4.1 \times 10^{-3}$ nm$^{-2}$, respectively. We performed the same analysis in ten different areas, including those shown in Figures 1b and S4. The averaged density ratio of the isolated molecules found on the Cu and NaCl surfaces was equal to 3:1.

**Figure S4.** STM image of TbPc2 molecules adsorbed on bare Cu(100) and 2 ML NaCl/Cu(100) surfaces. Scanning conditions: $V_{DC} = 1.4$ V and $I = 10$ pA.
REFERENCES

(1) Loth, S.; von Bergmann, K.; Ternes, M.; Otte, A. F.; Lutz, C. P.; Heinrich, A. J. Controlling the State of Quantum Spins with Electric Currents. Nat. Phys. 2010, 6 (5), 340–344.

(2) von Bergmann, K.; Ternes, M.; Loth, S.; Lutz, C. P.; Heinrich, A. J. Spin Polarization of the Split Kondo State. Phys. Rev. Lett. 2015, 114 (7), 076601.

(3) Wiesendanger, R. Spin Mapping at the Nanoscale and Atomic Scale. Rev. Mod. Phys. 2009, 81 (4), 1495–1550.

(4) Chen, Y.; Bae, Y.; Heinrich, A. J. Harnessing the Quantum Behavior of Spins on Surfaces. Adv. Mater. 2022, 2107534.

(5) Paul, W.; Baumann, S.; Lutz, C. P.; Heinrich, A. J. Generation of Constant-Amplitude Radio-Frequency Sweeps at a Tunnel Junction for Spin Resonance STM. Rev. Sci. Instrum. 2016, 87 (7), 074703.

(6) van Weerdenburg, W. M. J.; Steinbrecher, M.; van Mullekom, N. P. E.; Gerritsen, J. W.; von Allwörden, H.; Natterer, F. D.; Khajetoorians, A. A. A Scanning Tunneling Microscope Capable of Electron Spin Resonance and Pump–Probe Spectroscopy at MK Temperature and in Vector Magnetic Field. Rev. Sci. Instrum. 2021, 92 (3), 033906.