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Abstract

Electron spin resonance (ESR) spectroscopy is a crucial tool in investigations of the chemical structure of materials, and of the electronic structure of materials associated with unpaired spins, through spin-labelling. ESR spectra measured in molecular systems, however, are established on large ensembles of spins and usually require complicated structural analysis. Recently, the combination of scanning tunneling microscopy (STM) with ESR has proven to be a powerful tool to image and coherently control individual atomic spins on surfaces. Here, we extend this technique single coordination complexes — iron phthalocyanines (FePc) — and investigate the magnetic interactions between their molecular spin with either another molecular spin (in FePc–FePc dimers) or an atomic spin (in FePc–Ti pairs). We show that the molecular spin density of

FePc is both localized at the central Fe atom and also distributed to the outer ligands, yielding a strongly molecular, geometry-dependent exchange coupling.

Main text

Introduction

Chemical engineering and fabrication of single molecular spins is of vital importance in molecule-based quantum devices.[1] To detect and control single molecular spins, there have been various approaches such as optical detection of diluted molecular spins[2-4], magnetic resonance force microscopy[5], nitrogen-vacancy magnetometry[6], and break junction-based molecular devices[7-9]. Nevertheless, these systems typically require embedding the molecule in a solid-state host and lack the flexibility to locate and access individual spins, or harness intra- and inter-molecular spin-spin interactions.

Conventional electron spin resonance (ESR) studies on chemical ensembles[10,11] are a very useful tool to elucidate the chemical structures at the molecular level, but they rely on the order of $\sim 10^{10}$ spins and often require complementary analysis techniques or theoretical calculations. Recent development of scanning tunneling microscopy (STM) combined with ESR have provided the advantage to investigate single molecular spins with atomic resolution. ESR-STM introduces a radio frequency (rf) electric field at the tunneling junction which can coherently drive individual atomic spins on surfaces[12-14]. The change in spin state is read out by a spin-polarized tip through tunneling magnetoresistance. This combined ESR-STM approach enables precise atom manipulation and imaging in sub-nanometer scale with sub-microelectronvolt (~10 MHz) energy resolution. Previous ESR-STM studies have focused on the spins of single transition metal adatoms[12,14-16] rather than those of single molecules, besides early attempts on the organic

molecule – α,γ-bisdiphenylene β-phenylallyl (BDPA) at room temperature and in ambient condition[17]. Coordination compounds in particular often have non-trivial spin distribution owing to the ligands[18], giving the unique opportunity to tune the spin distribution on the ligands for engineering spin-spin interaction with atomic resolution.

Metal phthalocyanines with various substitutional central metal atoms have been extensively employed as model systems in many-body quantum physics[18,19] and spin-dependent transport[20]. Here, we explore a system of spin-1/2 iron phthalocyanine (FePc) molecules, iron (Fe) atoms and titanium (Ti) atoms adsorbed on a bilayer magnesium oxide (MgO), itself grown atop a Ag(100) surface. We have performed ESR on individual FePc molecules and characterized the effects of ligand orientations on spin-spin interactions in FePc-FePc dimers and FePc-Ti pairs. This enables us to visualize the electronic configuration of molecular orbitals and characterize the role of the molecular ligands using nearby atoms as sensors, measuring magnetic dipolar and exchange coupling between the molecular spin and ESR-active species (FePc and Ti). DFT calculations, in good agreement with the experimental results, suggest that the spin density of the compound mainly located on the Fe centere spreads to the outer molecular ligands. These findings highlight the role of non-localized spins in the transfer of magnetic interactions, which can be crucial for fabricating molecular devices[21].

Results and discussion

Single-molecule ESR. Individual FePc molecules, Fe atoms, and Ti atoms were deposited in a step-wise manner onto a bilayer (2-ML) MgO surface on Ag(100) substrate and all measurements were performed at a temperature of 2 K in a commercial STM with vector magnetic fields. The molecules and atoms are well isolated from each other at a low coverage and can be distinguished

readily by their topographical appearance, as shown in Fig. 1a. Individual FePc molecules appear as a cross-like shape and lattice analysis indicates that the central Fe atom of FePc of the molecule sits atop an oxygen atom of MgO. The molecular axes are rotated by approximately 27° with respect to the underlying oxygen rows (inset of Fig. 1a). The Ti atoms in our experiment are mainly found on oxygen-oxygen bridge sites (marked as Ti_B) and appear taller than the Fe atoms atop the oxygen-site[22,23].

Previous studies have reported that FePc possesses a spin $S = 1$ in bulk and on several surfaces[24,25]. Surprisingly, our differential conductance (dI/dV) spectra measured on well-isolated FePc molecules on a MgO surface show a clear conductance maximum, reminiscent of the Kondo effect at zero bias when no magnetic field is applied, suggesting the FePc spin being $S = 1/2$ (Supplementary Fig. 1). This agrees with our DFT calculations, suggesting that an electron is transferred from the Ag substrate to the adsorbed FePc and the molecular spin becomes $S = 1/2$. The spin density of a negatively charged FePc (referred as $[FePc]^{1-}$ in the following) is plotted in Fig. 1b, indicating that the spin distributes mainly on the central Fe atom and partially extends along the ligands[19]. Further analysis of the frontier orbital indicates that it consists of about 71% dz^2 and 29% contributions from the ligands and other orbitals (Supplementary Information Section 8, 10, and 11).

We performed ESR on individual $[FePc]^{1-}$ molecules using rf frequency sweeps[12,14] at a fixed external magnetic field (Fig. 1c). The external magnetic field sets the Zeeman splitting of the $[FePc]^{1-}$ spin and the two Zeeman states of $[FePc]^{1-}$ spin (labeled as $|0\rangle$ and $|1\rangle$, inset of Fig. 1c) can be coherently driven when the frequency of the applied oscillating electric field V_{rf} matches the Larmor frequency, which is known as the angular frequency of the spin processing around the

external magnetic field axis. The spin Hamiltonian of a single $[FePc]^{1-}$ spin system can be written as:

$$H_0 = 2\mu_{\mathrm{FePc}}\boldsymbol{B}\cdot\boldsymbol{S}, \qquad (1)$$

where μ_{FePc} is the magnetic moment of FePc. $\boldsymbol{S}$ is the spin operator and the total magnetic field $\boldsymbol{B}$ which sets the Zeeman splitting is a sum of external magnetic field ($\boldsymbol{B}_{\mathrm{ex}}$) and tip field ($\boldsymbol{B}_{\mathrm{tip}}$): $\boldsymbol{B} = \boldsymbol{B}_{\mathrm{ex}} + \boldsymbol{B}_{\mathrm{tip}}$. When we apply an external magnetic field along the out-of-plane (z) direction, we simplify the external magnetic field and tip field as B_{z} and B_{tip}. The resonance frequency f_0 corresponding to the transition between $|0\rangle$ and $|1\rangle$ states is determined by

$$hf_0 = 2\mu_{\mathrm{FePc}}(B_{\mathrm{z}} + B_{\mathrm{tip}}). \qquad (2)$$

The continuous-wave ESR signal can be detected when the ESR driving Rabi time is comparable to a geometric mean of spin relaxation (T_1) and spin coherence time (T_2)[26] (see also Supplementary Section 15). Here, Rabi time describes the half-cycle time needed by a two-level quantum system to perform a cyclic behavior between the two quantum levels and is determined by $T_{Rabi} = \frac{1}{\Omega} \propto \frac{1}{V_{\mathrm{rf}}\langle 1|S_x|0\rangle}$, where Ω is the Rabi rate. While the time scale of T_1 and T_2 are given by a system, an optimal selection of the frequency range and V_{rf}, in principle, can allow the measurement of ESR signal on other spin systems. Therefore, the ESR-STM method can be applied to other atomic and molecular systems as long as the above condition ($T_{Rabi} \sim T_1, T_2$) is satisfied. Here, we note that the ESR peak intensity and linewidth are associated with the spin relaxation time (T_1), spin coherence time (T_2) and driving Rabi rate ($\Omega \propto V_{\mathrm{rf}}$). The low bound of T_2 can be extracted by measuring the ESR peak intensity and the linewidth as a function of V_{rf}[14], which is approximately 10 ns in our case (see Supplementary Section 15).

As shown in Fig. 1c and d, f_0 of a single FePc molecule shifts linearly to lower frequencies as the set tunneling current (I_{set}) increases at fixed DC bias (V) and B_z, indicating that the tip field (B_{tip}) is proportional to I_{set}[27,28] and opposite to the external magnetic field direction. This holds for all the tips used throughout this paper. In Fig. 1d, the vertical intercept, which is determined by extrapolating the curve of f_0 vs I_{set} to zero B_{tip} (I_{set}), corresponds to the Zeeman splitting in the absence of a tip magnetic field. We can thus extract the magnetic moment of an individual $[\mathrm{FePc}]^{1-}$ molecule (μ_{FePc}), 1.058±0.003 μ_{B}, free from the influence of any tip field. For a given tip at each set tunneling current, B_{tip} can be calculated precisely by using $B_{\mathrm{z}} - \frac{hf_0}{2\mu_{\mathrm{FePc}}}$ where the fitted μ_{FePc} is used, as shown by the double x-axes of Fig. 1d. We also found that the magnetic moment extracted from varied external fields at a fixed tip field gives consistent $[\mathrm{FePc}]^{1-}$ magnetic moment of approximately 1 μ_{B} and obtained an averaged μ_{FePc} of 1.028±0.023 μ_{B} by measuring 14 individual $[\mathrm{FePc}]^{1-}$ molecules (Supplementary Fig. 3). Moreover, we noted that μ_{FePc} differed by approximately 5% in two different directions of magnetic field (i.e. B_{x} and B_{z}, Supplementary Fig. 2) and a similar anisotropy in magnetic moment has been found in other systems, e.g. bulk cobalt phthalocyanine (CoPc)[29] and $[\mathrm{FePc}]^{1-}$ crystals[30] verified by standard ESR measurements. This anisotropy results from the spin-orbit coupling that mixes the quenched ($L = 0$) ground state with excited states of larger orbital moment. The comparison with those bulk measurements also shows that the averaged value of the g-factor for single $[\mathrm{FePc}]^{1-}$ molecule adsorbed on MgO/Ag is smaller and closer to that of a free electron. We note that the difference of g-factor between our work on individual $[\mathrm{FePc}]^{1-}$ molecule and bulk $[\mathrm{FePc}]^{1-}$ studies may be explained by different local environment (ligand field) and Kondo screening[31,32]. A detailed discussion is provided in Supplementary Section 12. Our results indicate that the magnetic moment of $[\mathrm{FePc}]^{1-}$ on MgO is

weakly anisotropic having spin-1/2 and the tip field can be utilized as a local magnetic field addressing an individual spin.

Magnetic interaction between molecules. To investigate the spin-spin interaction of the $[FePc]^{1-}$ molecular system, we performed ESR measurements on naturally formed $[FePc]^{1-}$-$[FePc]^{1-}$ dimers (one such dimer is outlined in white in Fig. 1a). We define the configuration of a dimer as (m, n) by labeling the separation between the two Fe centers in the dimer in increments of the oxygen lattice along $[01\bar{1}]$ and $[011]$, respectively. We found two dominant configurations, (3, 4) and (0, 5), which have the identical distance of 1.45 nm (given the MgO lattice constant: 0.29 nm) between the centers of the two molecules. The occurrence of each configuration is approximately 38% and 53%, respectively (see all Supplementary Fig. 5). When measuring on one of the $[FePc]^{1-}$ molecules in either dimer (3, 4) or (0, 5), we observed multiple ESR peaks as shown in Fig. 2a(ii) and b(ii). For each dimer, the splitting between two adjacent ESR peaks appears to be independent of the tip field, implying the splitting is purely associated with the intermolecular coupling while the intensity of each peak evolves differently as the tip field varies (Fig. 2a(iii) and b(iii)). Moreover, the ESR splitting on the (3, 4) and (0, 5) dimers is different although the center-center distance is the same in both configurations, which we will discuss later.

The two magnetically coupled $[FePc]^{1-}$ molecules can be demonstrated by a two-spin system interacting with exchange and dipolar coupling[33,34]. The corresponding Hamiltonian model is thoroughly discussed in Methods section. The presence of exchange and dipolar coupling terms (denoted as parameters J and D, respectively) in the two-spin model makes the quantum eigenstates deviate from the four pure Zeeman product states $|00\rangle$, $|01\rangle$, $|10\rangle$ and $|11\rangle$, giving rise to singlet-triplet states. While $|00\rangle$ and $|11\rangle$ remain as the eigenstates of H_{12}, the other two eigenstates become superpositions of the two Zeeman states $|01\rangle$ and $|10\rangle$ as defined below:

$$|-\rangle = -\frac{\alpha}{\sqrt{\alpha^2+1}}|01\rangle + \frac{1}{\sqrt{\alpha^2+1}}|10\rangle,$$

$$|+\rangle = \frac{1}{\sqrt{\alpha^2+1}}|01\rangle + \frac{\alpha}{\sqrt{\alpha^2+1}}|10\rangle$$

where α indicates the relative weight of $|01\rangle$, $|10\rangle$ component in the $|-\rangle$ and $|+\rangle$ states[22,33] and equals to $\frac{\delta+\sqrt{\varepsilon^2+\delta^2}}{\varepsilon}$, in which $\delta = 2(\mu_1-\mu_2)B_{\text{ex}} + 2\mu_1 B_{\text{tip}}$ and $\varepsilon = J - \frac{D}{2}(1-3\cos^2\theta)$. μ_1 and μ_2 represent the magnetic moment of the $[\text{FePc}]^{1-}$ molecule under the tip and the one apart from the tip, respectively. B_{ex} and B_{tip} are external magnetic field and tip field. θ is the angle between $\hat{\boldsymbol{r}}$ and $[\text{FePc}]^{1-}$ spin orientation. Figure 2g depicts a schematic diagram of eigenenergies for the given eigenstates $|00\rangle$, $|-\rangle$, $|+\rangle$ and $|11\rangle$ (denoted as E_{00}, E_-, E_+ and E_{11}) as a function of B_{ex} and B_{tip}. The four possible transitions between these states account for the ESR peaks shown in Fig. 2a(iii) and b(iii), labeled as $f_1 = \frac{E_- - E_{00}}{h}$, $f_2 = \frac{E_{11}-E_+}{h}$, $f_3 = \frac{E_+ - E_{00}}{h}$, and $f_4 = \frac{E_{11}-E_-}{h}$, respectively. Fitted ESR transitions based on this singlet-triplet model (dotted white curves in Fig. 2a(iii), b(iii)) show excellent agreement with the experimental data (Supplementary Information Section 5).

From the expression of α with δ, we note that the tip field can tune the relative weight of $|01\rangle$ and $|10\rangle$ in the $|-\rangle$ and $|+\rangle$ states at given B_{ex}, leading to different dominant ESR transitions at different tip fields (bold arrows in Fig. 2c at weak and strong tip fields). This accounts for the changes in the relative peak intensities of four ESR transitions. In particular, when B_{tip} is adjusted to achieve $\delta = 0$ (occurring at the avoided level crossing indicated by the dashed square in Fig. 2c) and $\alpha = 1$, meaning B_{tip} compensates the difference of Zeeman energy of two $[\text{FePc}]^{1-}$ spins (originated from the unequal magnetic moments), $|10\rangle$ and $|01\rangle$ are equally weighted in $|-\rangle$ and

$|+\rangle$, f_1 and f_4 have the same intensity and f_2, f_3 merge to one peak (when $D \ll J$ and thus negligible), as indicated by the white arrows in Fig. 2a(iii) and b(iii).

Using the above Hamiltonian model, we found that the ESR splitting Δf ($\Delta f = f_2 - f_1 = f_4 - f_3$) corresponds to the total coupling energy of the two-spin system,

$$\Delta f = J + D(1 - 3\cos^2\theta). \qquad (4)$$

Here, Δf depends on the angle between the external field and the sample plane due to an anisotropic dipolar distribution. We recorded Δf measured on a (3, 4) dimer with rotating external fields in order to differentiate the magnetic dipole interaction from the exchange interaction, as shown in Fig. 2d. By fitting to equation (4), we extracted J and D as 133±4 MHz and 16±3 MHz, respectively, which strongly suggests that the exchange coupling is the dominant interaction in the molecular spin pairs. The positive sign of J indicates that the coupling is antiferromagnetic (AFM). Moreover, we note that the measured dipolar coupling energy here is consistent with that expected from two ideal atomic spins having 1 μ_B with same center-center distance[22,33,34]. Based on this, we can extract the exchange coupling energy (J) of $[FePc]^{1-}$ dimers by subtracting the dipolar coupling energy (D) of an atomic dimer with same center-center distance from the measured ESR splitting (Δf).

Previous ESR-STM studies on spin-spin interaction for atomic spins have shown that the exchange coupling is determined exclusively by the interatomic distance, implying that the atomic spin can be treated as a point magnet[22,33,34]. However, we found that the exchange coupling energy of (3, 4) and (0, 5) molecular dimer are different despite having the same center-center distance. By measuring the ESR splitting (Δf) of approximately 20 dimers with B_z field only, we obtained a mean $\overline{\Delta f}$ of 134±19 MHz for the (3, 4) dimer while 64±7 MHz for the (0, 5) dimer (Supplementary Fig. 5). As mentioned above, the corresponding exchange coupling energy (J)

extracted from $\Delta\overline{f}$ is 117±19 MHz and 47±7 MHz, respectively, by subtracting a dipole contribution of 17 MHz (calculated with two atomic spins having 1 μ_B for each). The non-negligible spin density on the outer ligands of the molecule may produce such a difference by generating additional coupling path for the intermolecular magnetic interaction. This implies that the distance between nearby ligands plays a crucial role in determining the magnetic coupling energy of molecular spin systems.

DFT model. We performed DFT calculations to evaluate the influence of the ligand-ligand distance on the exchange coupling energy of $[FePc]^{1-}$ dimers. For both (3, 4) and (5, 0) dimers, the optimized adsorption configuration on a MgO surface was achieved when the two Fe centers are atop oxygen sites and the molecular lobes align along the (2, 1) lattice direction, in good agreement with our STM topographic images displayed in Fig. 2(a,i) and 2(b.i) . In subsequent calculations, we fixed one molecule in its optimized configuration (lower one in Fig. 3a) while rotating the other molecule (upper one in Fig. 3a) around its Fe center by an angle of ϕ with respect to the (2, 1) lattice direction. The center-center distance remains unchanged during such a rotation while the minimal ligand-ligand distance d_{min} (defined as the nearest distance between two hydrogen atoms in the benzene rings as shown in Fig. 3c) changes accordingly. The variation in d_{min} when ϕ changes in (3, 4) and (5, 0) configuration is exhibited in the inset of Fig. 3b. We note a small difference in the d_{min} of (3, 4) and (5, 0) dimers when they are in optimized configurations (*i.e.* $\phi = 0°$). We then calculated the energy difference between ferromagnetic (E_{FM}) and antiferromagnetic coupling (E_{AFM}), the value of which equals to $\frac{1}{2}J$ for a two spin-1/2 system[35], as a function of d_{min} (Fig. 3b). The calculated $|E_{\mathrm{FM}} - E_{\mathrm{AFM}}|$ obeys an exponential decay ($\propto \exp(-d_{\mathrm{min}}/d)$) as d_{min} increases, which can be attributed to an exchange interaction through the

molecular ligands. We extract a characteristic decay length of d = 0.0345 nm, which is similar to the length scale of exchange coupling in other molecular system[36]. In our calculations, we note that the exchange coupling energy only differs slightly with and without MgO substrate, implying the negligible role of the substrate in the intermolecular interaction. Notably, the exchange interaction between two molecular spins is mediated through the fully occupied orbitals of ligand, suggesting a superexchange mechanism (see Supplementary Section 14 for a detailed discussion). The calculated J decreases as d_{min} gets larger in optimized (3, 4), (0, 5) and (2, 5) dimer configurations, consistent with the trend observed in our experiments (Fig. 3d). Besides, we found a few dimers whose ligand-ligand distance (Supplementary Fig. 7) deviated significantly from the optimized dimer configurations. The exchange coupling energy was significantly larger at equal center-center distance but shorter ligand-ligand distances. This result indicates that the molecular spin-spin coupling can be engineered via tuning inter-ligand symmetry.

Sensing molecular spin distribution. To sense the spin distribution on the molecular ligands in greater detail, we substituted a spin-1/2 Ti_B atom for a FePc molecule and measured the exchange coupling energy in $[FePc]^{1-}$-Ti_B pairs. While $[FePc]^{1-}$ dimers prefer to arrange only in a few configurations as mentioned above, the relative spatial position of a Ti_B atom with respect to a $[FePc]^{1-}$ molecule can be controlled with atomic precision using atom manipulation. Here, the Ti_B atom is considered as a point magnet based on previous studies[33,34] and our DFT calculations (Supplementary Fig. 10). We applied only B_z field for measuring $[FePc]^{1-}$-Ti_B pairs in order to be able to ignore the angular dependence of the dipolar interaction. The measured exchange coupling energy is thus merely its component along the out-of-plane direction, simplified as J. Figure 4a, c and e show three $[FePc]^{1-}$-Ti_B pairs with the Ti_B atom sitting on different lattice sites: (2.5, 3), (2.5,

3) and (3.5, 1) with similar center-center (Fe-Ti_B) distances: 1.13 nm, 1.13 nm, and 1.06 nm. However, the relative angle between the connection of Fe-Ti_B and the molecular axes varies from 13.2° to 42.5°, corresponding to different Ti_B-ligand distances. As the angle becomes larger, i.e. the Ti_B is further away from the closest $[FePc]^{1-}$ ligand, we observed a drastic decrease in J by measuring ESR on $[FePc]^{1-}$, as exhibited in Fig. 4b, d and f. Referring to the $[FePc]^{1-}$-$[FePc]^{1-}$ dimer case, the J values shown here is the result after subtracting the dipolar coupling contribution (D) from the ESR splitting (Δf). The strong dependence on the relative Ti_B-ligand configuration of the exchange coupling energy indicates that the molecular ligands can influence the magnetic interaction significantly, which agrees with our measurements on $[FePc]^{1-}$-$[FePc]^{1-}$ dimers.

To map the molecular geometry-dependent spin distribution of the $[FePc]^{1-}$ molecules, we measured J of a total of 14 $[FePc]^{1-}$-Ti_B pairs and observed a drastic decay of J as both Fe-Ti_B distance (r) and ligand-Ti_B distance (l) increases (Supplementary Fig. 8). Figure 5 (lower panel) displays the spatial map of J measured in different $[FePc]^{1-}$-Ti_B pairs. Considering the D_{4h} symmetry of the $[FePc]^{1-}$ molecule with respect to the MgO lattice, we duplicated the J of each pair to those equivalent adsorption sites. To emphasize the spin distribution on both Fe center and outer ligands, we utilized a heuristic model that simplified the entire spin distribution as two spin centers sitting at the central Fe atom and the nearest ligand, respectively. In this model, the J of a $[FePc]^{1-}$-Ti_B pair with the Ti_B sitting at (r, l) with respect to the molecule can be described by a sum of two exponential functions, $J(r,l) = J_0(c_1 \cdot e^{-r/\lambda} + c_2 \cdot e^{-l/\lambda})$. Here, J_0 is the exchange coupling energy constant, which is assumed the same for Fe-Ti_B interaction and ligand-Ti_B interaction. c_1 and c_2 are fitting pre-factors. λ is the characteristic decay length toward the molecular center (Fe) and the ligand center, respectively. By choosing different lattice sites along the (2, 1) direction for determining l in the fitting, we note that c_1 and c_2 are optimized when the

reference spot on the ligand is set at (1.42, 0.71), giving a ratio of $\frac{c_2}{c_1}$ = 0.03 which is consistent with the <30% contribution of the spin density from the ligands (<7% for each ligand). The characteristic decay length is fitted as λ = 0.0506 nm (see Supplementary Information Section 7 for more details). This allows us to approximate the spatial distribution of the exchange interaction with a molecule when the Ti_B spin is positioned at different sites, as shown in the upper panel of Fig. 5. We found good agreement between this simple model and the experimental data by comparing the simulated contour lines with those measured data points, revealing the molecular geometry-dependence of exchange interaction with a molecular spin. These results highlight that the ligands play a crucial role in molecular spin-spin interactions.

In conclusion, we have demonstrated single-molecule ESR by driving the spin of an individual $[FePc]^{1-}$ molecule on a surface. ESR-STM measurements on molecular dimers and molecule-metal atom pairs enable us to investigate the crucial role of the molecular ligands on the exchange coupling between molecules. The spin-spin interaction energy that we measured is only in hundreds of MHz range (~100 neV) and the measurement on spin coherence time allows the molecular spin to be one of potential candidates for molecular quantum control experiments. Most importantly, we found that the magnetic exchange interaction with a molecule shows strong dependence on molecular geometry, emphasizing the important role of ligands for the transfer of spin-polarization in molecular systems. Our work extends ESR-STM from single atoms to a much larger class of matter – magnetic molecules. This allows synthetic chemistry to design the spin properties through engineering the ligand field and symmetry. In addition, one can utilize ESR-active atoms or molecules to detect the spin distribution of other general molecular systems via dipolar and exchange interaction. Our work suggests molecules as a potential platform to investigate magnetic interactions with non-localized spins, which has brought intensive interest in

the field of coordination networks and is essential for developing molecule-based spintronic and quantum information devices[37].

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Author Contributions Statement

T.C. and X.Z. designed the project. X.Z., Y.W., T.B. and P.W. performed the experiments. C.W. carried out DFT calculations. H.A. contributed to Hamiltonian model simulations. X.Z. and T.C. wrote the manuscript with help of all authors. T.C. and A.J.H. advised the project process. This work is corresponded to A.J.H (heinrich.andreas@qns.science) or T.C. (choi.taeyoung@qns.science).

Competing Interests Statement

The authors declare no competing interests.

Figure Legends/Captions

Fig. 1 | $[FePc]^{1-}$ molecules adsorbed on MgO/Ag(100) and ESR measurements with varied tip fields. a, STM images of $[FePc]^{1-}$ molecules (light grey cross), Fe (smaller white dot), and Ti_B (bigger white dot) atoms adsorbed on MgO surface (dark grey background). A naturally formed $[FePc]^{1-}$-$[FePc]^{1-}$ dimer is circled in white. Inset: Magnified view of $[FePc]^{1-}$ molecules, Fe and Ti_B atoms. The blue grids in the inset indicate oxygen sites of the underlying MgO surface throughout this paper. Black arrows describe the molecular axes pointing to the benzene rings and showing an azimuthal angle of 26.6° with respect to the oxygen rows. Scanning conditions:

V = 200 mV, I_{set} = 12 pA for bigger image and I_{set} = 10 pA for inset. **b,** Isosurface representation (in red) of the frontier orbital (isovalue: 10^{-5}) corresponding to the molecular frontier orbital (a_{1g} in the inset). Inset: electron occupancy and *d*-orbital components (%) of the molecular frontier orbitals. $d_\pi = 0.5(d_{zx} + d_{zy})$. Notably, the a_{1u} orbital has no contribution from *d* component. **c,** ESR spectra of an individual $[FePc]^{1-}$ molecule measured at different tunneling currents. ESR conditions: V = 100 mV, V_{rf} = 10 mV. Each spectrum is shifted vertically from one another by 0.75 pA for clarity. Colored lines are Lorentzian fits of raw ESR spectra (black dots). Inset: Schematic representation of ~~switching~~ controlling the electron spin resonance in a two-level system with an rf electric field. **d,** Linear fit (red line) of resonance frequencies obtained from (**c**) as a function of B_{tip} (I_{set}), showing the possibility of tuning local field by the tip. Notably, the error bars are smaller than the size of the data dots, thus not distinguishable. The errors shown in (**d**) originate from the 95% confidence intervals of the non-linear fits. The source data can be found through the link indicated by Data and Code Availability. ~~[Please provide source data for this panel]; [Please add error bars]~~.

Fig. 2 | Spin coupling in $[FePc]^{1-}$-$[FePc]^{1-}$ dimers. a, b, Dimers in configuration (3,4) (a) and (0,5) (b). **(i)** STM images showing that the (3, 4) and (0, 5) dimers have the same center-center distance (dashed lines). Scanning conditions: V = 180 mV, I_{set} = 20 pA. **(ii)** Representative ESR spectra of the upper $[FePc]^{1-}$ measured at yellow dots in (**a,i**) and (**b,i**), respectively. **(iii)** ESR spectra plotted in color scale measured at different B_{tip} (I_{set}), showing clearly the difference in the coupling energy (i.e. Δf) of (3, 4) and (0, 5) dimers. Blue arrows indicate each ESR spectrum presented in (**ii**). The dotted white curves represent fitted ESR transitions. **c,** Energy level diagram of a two-spin system considering exchange (J) and dipolar (D) interaction in the presence of B_{ex} and B_{tip}. **d**, Measured (blue dots) and fitted (red curve) ESR splitting Δf of a (3, 4) dimer while rotating the external field by θ with respect to the sample plane. The errors and error bars in (**iii**) and (**d**) denote the 95% confidence intervals of the non-linear fits. The total external field $|B_{tot}|$ was kept at 550 mT during the field rotation. All ESR spectra were taken with the same tip and V = 100 mV. (**a**) and (**b**) were obtained with an out-of-plane field

of B_z = 550 mT. V_{rf} was set as 50 mV for (**a,ii**), (**a.iii**), (**d**) and 40 mV for (**b,ii**), (**b,iii**). ESR spectra of the lower $[FePc]^{1-}$ in each dimer are provided in Supplementary Fig. 4.

Fig. 3 | DFT calculations of exchange coupling in $[FePc]^{1-}$-$[FePc]^{1-}$ dimer atop MgO only. a, Computational model of a $[FePc]^{1-}$-$[FePc]^{1-}$ dimer. Fe-Fe distance is set according to experimental Fe coordinates. One molecule is fixed while the other one is rotated around the Fe center by ϕ. The minimum distance between two close-by ligands is denoted as d_{min} and amplified in (**c**). **b,** Calculated energy difference between FM and AFM coupling as a function of d_{min} for (3, 4) (orange dots) and (0, 5) (blue dots) showing good linearity, indicating a dominant exchange coupling mechanism. Solid lines are fits based on $|E_{\mathrm{FM}} - E_{\mathrm{AFM}}| \propto \exp(-d_{\mathrm{min}}/d)$. Inset: d_{min}as a function of ϕ. The d_{min} of optimized (3, 4) and (0, 5) configurations and corresponding $|E_{\mathrm{FM}} - E_{\mathrm{AFM}}|$ are highlighted by dashed lines. **d,** Comparison of calculated (dots) and experimental (triangles) J for three different dimer configurations ((3,4), orange; (0,5), blue; (2,5), green), showing very similar trend of J vs d_{min}. The experimental data shown here is only the exchange coupling energy after subtracting the dipolar coupling energy (17 MHz for the (3, 4), (0, 5) configurations and 14 MHz for the (2, 5) configuration) from the mean ESR splitting $\Delta\overline{f}$. Error bars represent the standard deviation of all measured coupling energies on each dimer configuration with respect to the mean value (see also Supplementary Fig. 5)~~[Please add a description of the statistical treatment]~~. ESR spectra of (2, 5) dimer are provided in Supplementary Fig. 4.

Fig. 4 | Exchange coupling of $[FePc]^{1-}$-Ti_B pairs with different Ti_B-ligand distance. a, $[FePc]^{1-}$-Ti_B pair with a (2.5, 3) configuration. **b,** A second pair in a (2.5, 3) configuration. **c,** A pair in (3.5, 1) configuration. The three pairs have similar Fe-Ti_B distances but different angles between molecular axes and the connection of Fe-Ti_B. (**i**) STM images of three pairs ~~[Please add the colour code]~~. Scanning conditions: (a) V = 200 mV, I_{set} = 6 pA; (b) V = 200 mV, I_{set} = 10 pA; (c) V = 150 mV, I_{set} = 20 pA. (**ii**) Respective ESR

spectra measured on $[FePc]^{1-}$ (yellow spots in (**i**)) as a function of tip field by varying setpoint of the tunneling current. The exchange coupling energy J of each $[FePc]^{1-}$-Ti_B pair is labeled on the upper right corner, obtained by subtracting the dipolar coupling contribution (36 MHz for (2.5, 3) pair and 44 MHz for (3.5, 1) pair) from the measured ESR splitting. The significant change in J when Ti_B is positioned at different sites with respect to the molecular ligands implies a molecular geometry-depended exchange interaction. The errors were obtained from the 95% confidence intervals of the non-linear fits. The external magnetic field was along out-of-plane direction for all $[FePc]^{1-}$-Ti_B measurements in our work. ESR conditions: V = 100 mV for all three pairs and (**a,ii**) V_{rf} = 30 mV, B_z = 650 mT, (**b,ii**) V_{rf} = 10 mV, B_z = 600 mT, (**c,ii**) V_{rf} = 30 mV, B_z = 570 mT.

Fig. 5 | Molecular geometry-dependent exchange coupling in $[FePc]^{1-}$-Ti_B pairs. Lower panel: measured J of different $[FePc]^{1-}$-Ti_B pairs expressed by colored dots and labelled at corresponding Ti_B adsorption sites with respect to the central $[FePc]^{1-}$ model. In total, 14 pairs were measured and the data points corresponding to the measured J have been equivalently duplicated by a rotation and reflection process according to the molecular symmetry axes (dashed lines). The grey grids represent the oxygen lattice. J is the exchange coupling energy after subtracting the dipole contribution from the total ESR splitting. The contour lines are projected from the simulated spatial exchange coupling energy map choosing those J values obtained from the experiment. Upper panel: simulated spatial exchange coupling energy map by using a sum of two exponential terms representing r-dependence and l-dependence, respectively. The simulated results are in good agreement with the experimental data, unveiling the geometry-dependence of the exchange coupling with a molecule. The frequency range used in the simulation is set as 3,000 MHz (upper limit) and 5 MHz (lower limit).

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Methods

STM-ESR setup. ESR measurements were performed in a commercial low-temperature STM (Unisoku, USM1300). A radio frequency (rf) microwave which was generated by a signal generator (Keysight, E8257D) was added to a DC voltage (V) using a bias tee at the tip side. With this set-up, an oscillating electric field V_{rf} was applied at the tunneling junction. The magnetic tip was prepared by transferring 3~5 Fe atoms from MgO surface to the tip apex and allowed a readout of the spin state by the spin-polarized tunneling current. During an ESR frequency sweep, the rf voltage and DC bias were applied continuously but the rf voltage was modulated at 95 Hz. The modulated tunneling current was then recorded by lock-in technique. All voltages in this paper are referred to the sample.

Sample preparation. In our work, all the materials used for sample preparation were commercially purchased. Single crystalline Ag(100) was purchased from MaTek. FePc was purchased from Sigma-Aldrich with a purity of 90%. Highly-pure Fe and Ti rods (99.95%) were purchased from Goodfellow. Mg in dendritic pieces was purchased from Sigma-Aldrich with a purity of 99.998%. The O_2 (99.995%) used here was supplied by a local vendor. The Ag(100) substrate was pretreated by alternative Ar^+ sputtering and annealing cycles. During MgO growth,

Ag(100) was kept at 400°C and magnesium was evaporated onto clean Ag surface in an O_2 atmosphere of 1.1×10^{-6} torr. FePc was first deposited onto the MgO surface while the sample was kept at room temperature. The sample was then transferred to the cryostat for cooling down. Fe and Ti atoms were deposited subsequently onto the cold sample at 25-40 K. After the dosage of molecules and metal atoms, the sample was transferred to ~2 K environment for ESR measurements. The thickness of the MgO filmwas determined by performing point-contact measurements on individual Fe atoms[38] and varied from 2 to 4 monolayers (2-ML to 4–ML) in our case. Our experiments were all performed on 2 ML MgO. Also, we note that the MgO patches were found to be surrounded with large irregular Ag terraces. Detailed discussion on the sample morphology is provided in Supplementary Section 9.

All the STM images displayed in this work were processed by WSxM[39] in "Bone" color mode. A low-order Gaussian filtering function was applied to the images for better visual effect without hindering the authenticity. The original STM files and unprocessed images can be found in Ref. 40. All the ESR spectra plotted in color scale were dealt with "Copper" color mode.

Titanium atom manipulation. After titanium deposition, naturally formed $[FePc]^{1-}$-Ti_B pairs were abundant. In addition, we were able to position Ti_B atom using atom manipulation and construct $[FePc]^{1-}$-Ti_B pairs with various configurations. When the tunneling conductance was set as $V \approx 350$ mV, $I \approx 2.2$ nA, the Ti_B atom under the tip could follow the tip movement and be positioned at desired sites. In contrast, controllable manipulation of $[FePc]^{1-}$ molecule rarely occurs under our manipulation parameters.

Hamiltonian model of the two-molecule system. In order to understand the ESR spectra quantitatively, we used a Hamiltonian model of the two-spin system including exchange and dipolar coupling[33,34] between two FePc molecules:

$$H_{12} = 2\mu_1(\boldsymbol{B}_{\text{ex}} + \boldsymbol{B}_{\text{tip}}) \cdot \boldsymbol{S}_1 + 2\mu_2 \boldsymbol{B}_{\text{ex}} \cdot \boldsymbol{S}_2 + J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + D[\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 - \mathbf{3}(\boldsymbol{S}_1 \cdot \hat{\boldsymbol{r}})(\boldsymbol{S}_2 \cdot \hat{\boldsymbol{r}})]. \quad (3)$$

Here, the subscripts 1, 2 represent the two $[FePc]^{1-}$ spins in a dimer. The one under the tip is denoted as 1 whose Zeeman energy is set by both external magnetic field (B_{ex}) and tip field (B_{tip}). $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ are spin operators of the two molecular spins. The μ_1 and μ_2 are the magnetic moment of each $[FePc]^{1-}$. The first two terms describe the Zeeman energy of a dimer system. Both $[FePc]^{1-}$ spins align with the external magnetic field direction since both molecules are spin-1/2. The third and last term represent intermolecular exchange and dipolar coupling with the energy constant J and D, respectively. $\hat{\boldsymbol{r}}$ is the unit distance vector connecting the centers of two FePc spins. D is given by $\frac{\mu_0 \mu_1 \mu_2}{\pi r^3}$, where μ_0 is the vacuum permeability.

DFT calculations. All density functional theory (DFT) calculations were performed using Quantum Espresso (version 6.5) which implements DFT using plane waves and pseudopotentials[41,42]. Pseudopotentials were chosen based on the SSSP library and the basis set was expanded using a kinetic cutoff of 40 Rydberg[43]. All pseudopotentials use the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) and we treated van der Waals interaction using Grimme's D3[44,45]. For single FePc, the calculation model includes 4 ML of silver capped by 2 ML of MgO exposing the (100) surface. In z-direction, the cell is padded with 1.2 nm of vacuum. For FePc-FePc dimer, the cell was laterally expanded to accommodate both molecules and make sure that the separation of dimers and their periodic image is at least 5 times larger than the inter-dimer distance. The exchange coupling energy was calculated using the broken-symmetry approach introduced by Noodleman[35]. This approach maps the Kohn-Sham energies of the high-spin ($m_s = 1$) and the broken symmetry ($m_s = 0$) state to the diagonal elements of the Heisenberg Hamiltonian. More computational details can be found in Supplementary Information. The

computational models are provided as Additional Supplementary Files and also available in Ref. 40.

Data and Code Availability

All data that support the findings of this study are available in this manuscript and its Supplementary Information, or from the corresponding authors on reasonable request. The source data, code and DFT models supporting all figures displayed in main article and supplementary information[40] are also publicly available through the link https://doi.org/10.6084/m9.figshare.16574534.v1 that directs to Figshare.

References for Methods

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