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## Electron spin resonance of single iron phthalocyanine molecules and role of their non-localized spins in magnetic interactions

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1 **Electron spin resonance of single iron–phthalocyanine molecules and role of their**  
2 **non-localized spins in magnetic interaction**

3  
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14  
15 **Abstract**

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

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

3

#### 4 **Main text**

#### 5 **Introduction**

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

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

1 molecule –  $\alpha,\gamma$ -bisdiphenylene  $\beta$ -phenylallyl (BDPA) at room temperature and in ambient  
2 condition<sup>17</sup>. Coordination compounds in particular often have non-trivial spin distribution owing  
3 to the ligands<sup>18</sup>, giving the unique opportunity to tune the spin distribution on the ligands for  
4 engineering spin-spin interaction with atomic resolution.

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

18

## 19 **Results and discussion**

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

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

7 Previous studies have reported that FePc possesses a spin  $S = 1$  in bulk and on several  
8 surfaces<sup>24,25</sup>. Surprisingly, our differential conductance ( $dI/dV$ ) spectra measured on well-isolated  
9 FePc molecules on a MgO surface show a clear conductance maximum, reminiscent of the Kondo  
10 effect at zero bias when no magnetic field is applied, suggesting the FePc spin being  $S = 1/2$   
11 (Supplementary Fig. 1). This agrees with our DFT calculations, suggesting that an electron is  
12 transferred from the Ag substrate to the adsorbed FePc and the molecular spin becomes  $S = 1/2$ .  
13 The spin density of a negatively charged FePc (referred as  $[FePc]^{1-}$  in the following) is plotted in  
14 Fig. 1b, indicating that the spin distributes mainly on the central Fe atom and partially extends  
15 along the ligands<sup>19</sup>. Further analysis of the frontier orbital indicates that it consists of about 71%  
16  $dz^2$  and 29% contributions from the ligands and other orbitals (Supplementary Information Section  
17 8, 10, and 11).

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

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

$$3 \quad H_0 = 2\mu_{\text{FePc}}\mathbf{B} \cdot \mathbf{S}, \quad (1)$$

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

$$9 \quad hf_0 = 2\mu_{\text{FePc}}(B_z + B_{\text{tip}}). \quad (2)$$

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

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

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

3

4 **Magnetic interaction between molecules.** To investigate the spin-spin interaction of the  $[\text{FePc}]^{1-}$   
5 molecular system, we performed ESR measurements on naturally formed  $[\text{FePc}]^{1-}$ - $[\text{FePc}]^{1-}$  dimers  
6 (one such dimer is outlined in white in Fig. 1a). We define the configuration of a dimer as  $(m, n)$   
7 by labeling the separation between the two Fe centers in the dimer in increments of the oxygen  
8 lattice along  $[01\bar{1}]$  and  $[011]$ , respectively. We found two dominant configurations, (3, 4) and (0,  
9 5), which have the identical distance of 1.45 nm (given the MgO lattice constant: 0.29 nm) between  
10 the centers of the two molecules. The occurrence of each configuration is approximately 38% and  
11 53%, respectively (see all Supplementary Fig. 5). When measuring on one of the  $[\text{FePc}]^{1-}$   
12 molecules in either dimer (3, 4) or (0, 5), we observed multiple ESR peaks as shown in Fig. 2a(ii)  
13 and b(ii). For each dimer, the splitting between two adjacent ESR peaks appears to be independent  
14 of the tip field, implying the splitting is purely associated with the intermolecular coupling while  
15 the intensity of each peak evolves differently as the tip field varies (Fig. 2a(iii) and b(iii)).  
16 Moreover, the ESR splitting on the (3, 4) and (0, 5) dimers is different although the center-center  
17 distance is the same in both configurations, which we will discuss later.

18 The two magnetically coupled  $[\text{FePc}]^{1-}$  molecules can be demonstrated by a two-spin system  
19 interacting with exchange and dipolar coupling<sup>33,34</sup>. The corresponding Hamiltonian model is  
20 thoroughly discussed in Methods section. The presence of exchange and dipolar coupling terms  
21 (denoted as parameters  $J$  and  $D$ , respectively) in the two-spin model makes the quantum  
22 eigenstates deviate from the four pure Zeeman product states  $|00\rangle$ ,  $|01\rangle$ ,  $|10\rangle$  and  $|11\rangle$ , giving rise  
23 to singlet-triplet states. While  $|00\rangle$  and  $|11\rangle$  remain as the eigenstates of  $H_{12}$ , the other two  
24 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  $\alpha$  indicates the relative weight of  $|01\rangle$ ,  $|10\rangle$  component in the  $|-\rangle$  and  $|+\rangle$  states<sup>22,33</sup> 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  $\varepsilon = J - \frac{D}{2}(1 - 3\cos^2\theta)$ .  $\mu_1$  and

$\mu_2$  represent the magnetic moment of the  $[\text{FePc}]^{1-}$  molecule under the tip and the one apart from

the tip, respectively.  $B_{\text{ex}}$  and  $B_{\text{tip}}$  are external magnetic field and tip field.  $\theta$  is the angle between

$\hat{r}$  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  $B_{\text{ex}}$

and  $B_{\text{tip}}$ . 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  $\alpha$  with  $\delta$ , 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  $B_{\text{ex}}$ , 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  $B_{\text{tip}}$  is adjusted

to achieve  $\delta = 0$  (occurring at the avoided level crossing indicated by the dashed square in [Fig.](#)

[2c](#)) and  $\alpha = 1$ , meaning  $B_{\text{tip}}$  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

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

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

$$5 \quad \Delta f = J + D(1 - 3 \cos^2 \theta). \quad (4)$$

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

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

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

7

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

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

13  
14 **Sensing molecular spin distribution.** To sense the spin distribution on the molecular ligands in  
15 greater detail, we substituted a spin-1/2  $\text{Ti}_B$  atom for a FePc molecule and measured the exchange  
16 coupling energy in  $[\text{FePc}]^{1-}\text{-Ti}_B$  pairs. While  $[\text{FePc}]^{1-}$  dimers prefer to arrange only in a few  
17 configurations as mentioned above, the relative spatial position of a  $\text{Ti}_B$  atom with respect to a  
18  $[\text{FePc}]^{1-}$  molecule can be controlled with atomic precision using atom manipulation. Here, the  $\text{Ti}_B$   
19 atom is considered as a point magnet based on previous studies<sup>33,34</sup> and our DFT calculations  
20 ([Supplementary Fig. 10](#)). We applied only  $B_z$  field for measuring  $[\text{FePc}]^{1-}\text{-Ti}_B$  pairs in order to be  
21 able to ignore the angular dependence of the dipolar interaction. The measured exchange coupling  
22 energy is thus merely its component along the out-of-plane direction, simplified as  $J$ . [Figure 4a, c](#)  
23 and [e](#) show three  $[\text{FePc}]^{1-}\text{-Ti}_B$  pairs with the  $\text{Ti}_B$  atom sitting on different lattice sites: (2.5, 3), (2.5,

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

10 To map the molecular geometry-dependent spin distribution of the [FePc]<sup>1-</sup> molecules, we  
11 measured  $J$  of a total of 14 [FePc]<sup>1-</sup>-Ti<sub>B</sub> pairs and observed a drastic decay of  $J$  as both Fe-Ti<sub>B</sub>  
12 distance ( $r$ ) and ligand-Ti<sub>B</sub> distance ( $l$ ) increases (Supplementary Fig. 8). Figure 5 (lower panel)  
13 displays the spatial map of  $J$  measured in different [FePc]<sup>1-</sup>-Ti<sub>B</sub> pairs. Considering the  $D_{4h}$   
14 symmetry of the [FePc]<sup>1-</sup> molecule with respect to the MgO lattice, we duplicated the  $J$  of each  
15 pair to those equivalent adsorption sites. To emphasize the spin distribution on both Fe center and  
16 outer ligands, we utilized a heuristic model that simplified the entire spin distribution as two spin  
17 centers sitting at the central Fe atom and the nearest ligand, respectively. In this model, the  $J$  of a  
18 [FePc]<sup>1-</sup>-Ti<sub>B</sub> pair with the Ti<sub>B</sub> sitting at ( $r, l$ ) with respect to the molecule can be described by a  
19 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  
20 coupling energy constant, which is assumed the same for Fe-Ti<sub>B</sub> interaction and ligand-Ti<sub>B</sub>  
21 interaction.  $c_1$  and  $c_2$  are fitting pre-factors.  $\lambda$  is the characteristic decay length toward the  
22 molecular center (Fe) and the ligand center, respectively. By choosing different lattice sites along  
23 the (2, 1) direction for determining  $l$  in the fitting, we note that  $c_1$  and  $c_2$  are optimized when the

1 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  
2 with the <30% contribution of the spin density from the ligands (<7% for each ligand). The  
3 characteristic decay length is fitted as  $\lambda = 0.0506$  nm (see [Supplementary Information Section 7](#)  
4 for more details). This allows us to approximate the spatial distribution of the exchange interaction  
5 with a molecule when the  $T_{IB}$  spin is positioned at different sites, as shown in the upper panel of  
6 [Fig. 5](#). We found good agreement between this simple model and the experimental data by  
7 comparing the simulated contour lines with those measured data points, revealing the molecular  
8 geometry-dependence of exchange interaction with a molecular spin. These results highlight that  
9 the ligands play a crucial role in molecular spin-spin interactions.

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

1 the field of coordination networks and is essential for developing molecule-based spintronic and  
2 quantum information devices<sup>37</sup>.

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6 We thank N. Lorente for fruitful discussions.

#### 8 **Author Contributions Statement**

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

#### 15 **Competing Interests Statement**

16 The authors declare no competing interests.

#### 18 **Figure Legends/Captions**

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

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

13

14

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



1 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  
2  $[\text{FePc}]^{1-}$  in each dimer are provided in Supplementary Fig. 4.

3  
4

5 **Fig. 3 | DFT calculations of exchange coupling in  $[\text{FePc}]^{1-}$ - $[\text{FePc}]^{1-}$  dimer atop MgO only. a,**

6 Computational model of a  $[\text{FePc}]^{1-}$ - $[\text{FePc}]^{1-}$  dimer. Fe-Fe distance is set according to experimental Fe  
7 coordinates. One molecule is fixed while the other one is rotated around the Fe center by  $\phi$ . The minimum  
8 distance between two close-by ligands is denoted as  $d_{\text{min}}$  and amplified in (c). b, Calculated energy

9 difference between FM and AFM coupling as a function of  $d_{\text{min}}$  for (3, 4) (orange dots) and (0, 5) (blue  
10 dots) showing good linearity, indicating a dominant exchange coupling mechanism. Solid lines are fits

11 based on  $|E_{\text{FM}} - E_{\text{AFM}}| \propto \exp(-d_{\text{min}}/d)$ . Inset:  $d_{\text{min}}$  as a function of  $\phi$ . The  $d_{\text{min}}$  of optimized (3, 4) and

12 (0, 5) configurations and corresponding  $|E_{\text{FM}} - E_{\text{AFM}}|$  are highlighted by dashed lines. d, Comparison of

13 calculated (dots) and experimental (triangles)  $J$  for three different dimer configurations ((3,4), orange; (0,5),  
14 blue; (2,5), green), showing very similar trend of  $J$  vs  $d_{\text{min}}$ . The experimental data shown here is only the

15 exchange coupling energy after subtracting the dipolar coupling energy (17 MHz for the (3, 4), (0, 5)

16 configurations and 14 MHz for the (2, 5) configuration) from the mean ESR splitting  $\Delta\bar{f}$ . Error bars

17 represent the standard deviation of all measured coupling energies on each dimer configuration with respect

18 to the mean value (see also Supplementary Fig. 5) [Please add a description of the statistical treatment]. ESR

19 spectra of (2, 5) dimer are provided in Supplementary Fig. 4.

20  
21

22 **Fig. 4 | Exchange coupling of  $[\text{FePc}]^{1-}$ - $\text{Ti}_B$  pairs with different  $\text{Ti}_B$ -ligand distance. a,**  $[\text{FePc}]^{1-}$ - $\text{Ti}_B$  pair

23 with a (2.5, 3) configuration. b, A second pair in a (2.5, 3) configuration. c, A pair in (3.5, 1) configuration.

24 The three pairs have similar Fe- $\text{Ti}_B$  distances but different angles between molecular axes and the

25 connection of Fe- $\text{Ti}_B$ . (i) STM images of three pairs [Please add the colour code]. Scanning conditions: (a)

26  $V = 200$  mV,  $I_{\text{set}} = 6$  pA; (b)  $V = 200$  mV,  $I_{\text{set}} = 10$  pA; (c)  $V = 150$  mV,  $I_{\text{set}} = 20$  pA. (ii) Respective ESR

1 spectra measured on  $[\text{FePc}]^{1-}$  (yellow spots in (i)) as a function of tip field by varying setpoint of the  
2 tunneling current. The exchange coupling energy  $J$  of each  $[\text{FePc}]^{1-}$ - $\text{Ti}_B$  pair is labeled on the upper right  
3 corner, obtained by subtracting the dipolar coupling contribution (36 MHz for (2.5, 3) pair and 44 MHz for  
4 (3.5, 1) pair) from the measured ESR splitting. The significant change in  $J$  when  $\text{Ti}_B$  is positioned at different  
5 sites with respect to the molecular ligands implies a molecular geometry-dependence of exchange interaction.  
6 The errors were obtained from the 95% confidence intervals of the non-linear fits. The external magnetic field  
7 was along out-of-plane direction for all  $[\text{FePc}]^{1-}$ - $\text{Ti}_B$  measurements in our work. ESR conditions:  $V = 100$   
8 mV for all three pairs and (a,ii)  $V_{\text{rf}} = 30$  mV,  $B_z = 650$  mT, (b,ii)  $V_{\text{rf}} = 10$  mV,  $B_z = 600$  mT, (c,ii)  $V_{\text{rf}} = 30$   
9 mV,  $B_z = 570$  mT.

10

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

23

24

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## 7 8 **Methods**

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

18 **Sample preparation.** In our work, all the materials used for sample preparation were  
19 commercially purchased. Single crystalline Ag(100) was purchased from MaTek. FePc was  
20 purchased from Sigma-Aldrich with a purity of 90%. Highly-pure Fe and Ti rods (99.95%) were  
21 purchased from Goodfellow. Mg in dendritic pieces was purchased from Sigma-Aldrich with a  
22 purity of 99.998%. The O<sub>2</sub> (99.995%) used here was supplied by a local vendor. The Ag(100)  
23 substrate was pretreated by alternative Ar<sup>+</sup> sputtering and annealing cycles. During MgO growth,

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

11 All the STM images displayed in this work were processed by WSxM<sup>39</sup> in “Bone” color mode.  
12 A low-order Gaussian filtering function was applied to the images for better visual effect without  
13 hindering the authenticity. [The original STM files and unprocessed images can be found in Ref.](#)  
14 [40](#). All the ESR spectra plotted in color scale were dealt with “Copper” color mode.

15 **Titanium atom manipulation.** After titanium deposition, naturally formed [FePc]<sup>1-</sup>-Ti<sub>B</sub> pairs  
16 were abundant. In addition, we were able to position Ti<sub>B</sub> atom using atom manipulation and  
17 construct [FePc]<sup>1-</sup>-Ti<sub>B</sub> pairs with various configurations. When the tunneling conductance was set  
18 as  $V \approx 350$  mV,  $I \approx 2.2$  nA, the Ti<sub>B</sub> atom under the tip could follow the tip movement and be  
19 positioned at desired sites. In contrast, controllable manipulation of [FePc]<sup>1-</sup> molecule rarely  
20 occurs under our manipulation parameters.

21 **Hamiltonian model of the two-molecule system.** In order to understand the ESR spectra  
22 quantitatively, we used a Hamiltonian model of the two-spin system including exchange and  
23 dipolar coupling<sup>33,34</sup> between two FePc molecules:

1 
$$H_{12} = 2\mu_1(\mathbf{B}_{\text{ex}} + \mathbf{B}_{\text{tip}}) \cdot \mathbf{S}_1 + 2\mu_2\mathbf{B}_{\text{ex}} \cdot \mathbf{S}_2 + J\mathbf{S}_1 \cdot \mathbf{S}_2 + D[\mathbf{S}_1 \cdot \mathbf{S}_2 - 3(\mathbf{S}_1 \cdot \hat{\mathbf{r}})(\mathbf{S}_2 \cdot \hat{\mathbf{r}})]. \quad (3)$$

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

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



1 computational models are provided as Additional Supplementary Files and also available in Ref.  
2 40.

### 7 **Data and Code Availability**

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

### 14 **References for Methods**

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