

SUPPLEMENTARY INFORMATION

Symmetry mediated tunable molecular magnetism on a 2D material

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Supplementary Note 1:

Symmetry of Cobalt phthalocyanine(CoPc) molecules on 2H-NbSe₂

The two adsorption geometries of the CoPc molecules on the 2H-NbSe₂ substrate can be well understood within point-group theory. Starting from the gas phase CoPc molecule which has D_{4h} symmetry, the symmetry reduces during adsorption due to the broken symmetry perpendicular to the surface to C_{4v} . Similarly, neglecting the charge density wave at low temperatures, the surface of 2H-NbSe₂ is reduced from the D_{3h} to the C_{3v} point group [1].

Combining these two highly symmetric entities reduces drastically possible symmetry operations. In particular, all non-trivial cyclic operations, i. e. rotations by $360^\circ/n$, are broken by the incommensurability between the allowed C_4 operations on the molecule and C_3 operations on the substrate. Additionally, the inversion symmetry operation is also broken, leaving mirror symmetries as the only residual ones in the system.

Here, the surface with C_{3v} point group symmetry contains three mirror planes (σ_v) (see Fig. S1a), while the CoPc molecule with C_{4v} symmetry has four mirror planes: two vertical σ_v and two dihedral, i.e. by 45° rotated, σ_d planes (see Fig. S1b). To minimize its energy the CoPc will prefer highly symmetrical adsorption sites. Therefore, we find the following two configuration sites in our experiment in which one of the substrate's σ_v planes is either aligned with one of the molecule's σ_v planes (Fig. S1c), or with one of the molecule's σ_d planes (Fig. S1d). The former symmetry describes the nonmagnetic CoPc_v, while the latter in which the molecule is 15° rotated describes the doubly degenerate $S = 1/2$ CoPc_d system.

Supplementary Note 2:

Simulating Yu-Shiba-Rusinov (YSR) states measured on CoPc_d with a superconducting tip

Both tip and sample are superconductors with a quasiparticle excitation spectrum described in the framework of the Bardeen-Cooper-Schrieffer (BCS)-theory of superconductivity as:

$$\rho_{\text{BCS}}(\varepsilon) = \rho_{\text{S}} \text{Im} \left(\frac{\varepsilon + i\Gamma}{\sqrt{\Delta^2 - (\varepsilon + i\Gamma)^2}} \right), \quad (\text{S1})$$

where Δ is the superconducting gap width of either sample or tip, and a small imaginary part $i\Gamma$ ($\Gamma \ll \Delta$) is added to the energy to account for finite lifetime effects of the quasiparticles at the gap edge [2]. The differential conductance (dI/dV) spectrum recorded between both superconductors is then given by:

$$\frac{dI}{dV}(V) \propto \frac{d}{dV} \int_{-\infty}^{+\infty} \rho_{\text{BCS}_\text{S}}(\varepsilon) \rho_{\text{BCS}_\text{T}}(\varepsilon - eV) [f(\varepsilon) - f(\varepsilon - eV)] d\varepsilon, \quad (\text{S2})$$

with $f(\varepsilon) = [1 + \exp(\varepsilon/k_{\text{B}}T)]^{-1}$ as the Fermi-Dirac distribution, k_{B} as the Boltzmann constant, and T as the effective temperature of our experiment.

The interaction between the superconducting Cooper pairs and the unscreened spin of the molecule lead in the dI/dV spectrum to a pair of YSR peaks symmetrically around the Fermi energy. By approximating the spin as a classical magnetic moment, the energy E_{YSR} and intensities $I_{\pm}$ of the peaks are given by the following equations derived by Šmakov and Salkola [3–5]:

$$E_{\text{YSR}} = \Delta_{\text{S}} \frac{1 - w^2 + u^2}{\sqrt{(1 - w^2 + u^2)^2 + 4w^2}}, \quad (\text{S3})$$

$$I_{\pm} = -\rho_{\text{S}} \frac{2w(1 + (w \mp u)^2)}{((1 - w^2 + u^2)^2 + 4w^2)^{3/2}}, \quad (\text{S4})$$

where Δ_S is the effective superconducting gap of the 2H-NbSe₂ substrate, S is the local impurity spin, J_S is the antiferromagnetic exchange coupling, U is the local Coulomb interaction, and w and u are their corresponding dimensionless parameters $w = \frac{1}{2}\pi\rho_S J_S S < 0$, and $u = \pi\rho_S U$. The quasiparticle excitation spectrum detected above the magnetic impurity is then calculated using Gor'kov-Nambu spinors:

$$\rho_{\text{YSR}}^{nn}(\varepsilon) = -\frac{1}{\pi}\text{Im}G^{R,nn}(\varepsilon), \quad (\text{S5})$$

Here $\rho_{\text{YSR}}^{nn}(\varepsilon)$ are the diagonal elements of the spectral function with $n = 1, 2$ describing electron ($n = 1$) and hole ($n = 2$) components of the YSR state.

The full retarded Green's function at finite temperature in the presence of a magnetic impurity $G^R(\varepsilon)$ is defined in the standard way in terms of the Dyson series as:

$$G^R(\varepsilon) = G_0^R(\varepsilon) + G_0^R(\varepsilon)V G^R(\varepsilon), \quad G^R(\varepsilon)^{-1} = G_0^R(\varepsilon)^{-1} - V,$$

with $G_0^R(\varepsilon)$ being the free finite temperature Green's function and V the impurity Hamiltonian for a homogeneous superconductor:

$$G_0^R(\varepsilon) = \frac{-\pi\rho_S}{\sqrt{\Delta_S^2 - (\varepsilon + i\Gamma)^2}} \begin{pmatrix} \varepsilon + i\Gamma & \Delta_S \\ \Delta_S & \varepsilon + i\Gamma \end{pmatrix}, \quad V = \frac{1}{\pi\rho_S} \begin{pmatrix} w + u & 0 \\ 0 & w - u \end{pmatrix}.$$

In the above equations, ρ_S is the density of states of the sample at Fermi energy in the normal conducting state.

Probing the YSR states with the superconducting tip lead to a spectrum which is a convolution of equation S1 and S5 which we additionally broaden by a Gaussian distribution function $g(\varepsilon) = \frac{1}{\sqrt{\pi}\gamma}e^{-(\frac{\varepsilon}{\gamma})^2}$ to account for an additional energy broadening of $\gamma \approx 0.2$ meV [6, 7].

$$\begin{aligned} \frac{dI}{dV}(V) \propto \frac{d}{dV} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} & [\rho_{\text{BCS}_T}(\varepsilon)\rho_{\text{YSR}}^{11}(\varepsilon' - eV)(f(\varepsilon) - f(\varepsilon' - eV)) \\ & + \rho_{\text{BCS}_T}(\varepsilon' - eV)\rho_{\text{YSR}}^{22}(\varepsilon)(f(\varepsilon' - eV) - f(\varepsilon))]g(\varepsilon - \varepsilon')d\varepsilon'd\varepsilon. \end{aligned} \quad (\text{S6})$$

Supplementary Note 3:

Kelvin probe force microscopy results and charge states of CoPc molecules

A significant difference between the energies of dips of the Kelvin probe force microscopy data on CoPc_d and CoPc_v demonstrates the different charge states [8] between CoPc_d and CoPc_v (see Fig. S3). The charge transfer between the

CoPc_v and the NbSe₂ is delocalized over the ligands, instead of the Co²⁺ ion, leading to a negligible shift of the local work function. Similar results are observed over the ligands. We further prove that the different spin states are due to the charge transfer by eliminating the influence of an additional hydrogen ligand on a molecule (see Fig. S5).

Supplementary Note 4:

Hamiltonian with an anisotropic Heisenberg exchange coupling

The Hamiltonian in Eq.(1) of the main paper is simplified from:

$$\hat{H}_{\text{dimer}} = \sum_{i=1,2} g_i \mu_B \hat{S}_z^i B_z + \hat{S}^1 T \hat{S}^2, \quad (\text{S7})$$

where $T = \begin{pmatrix} J_x & D_z & D_y \\ -D_z & J_y & -D_x \\ -D_y & D_x & J_z \end{pmatrix}$ is the coupling matrix that is linear with both spins and which includes anisotropic Heisenberg as well as Dzyaloshinskii-Moriya (DM) interactions. The general form of equation S7 allows us to discuss and exclude possible interaction schemes and their spectral evolution with the external magnetic field B_z .

First, we consider isotropic Heisenberg exchange coupling $J_x = J_y = J_z = J_{\text{ST}} = 21.6$ meV and $g_1 = g_2 = 2$, neglecting any DM interaction ($\mathbf{D}_{\text{ST}} = \vec{0}$). Fig. S6a shows the expected state energies versus B -field. At zero field only transitions at an energy of J_{ST} between the $(S, S_z) = \langle 0, 0 \rangle$ singlet and the three degenerated triplet states $(S, S_z) = \langle 1, 0 \rangle$ and $(S, S_z) = \langle 1, \pm 1 \rangle$ are possible, while at large enough B_z the triplet state splits in three independent states with equal excitation probabilities. The resulting dI^2/dV^2 spectra are shown in Fig. 3g of the main text and are incompatible with the experimental data.

Fig. S6b shows the evolution of the state energies using the same Heisenberg interaction term as in Fig. S6a, but with an additional DM term in-plane with the molecule ($D_x = 0.45 J_{\text{ST}}$, $D_y = D_z = 0$) and perpendicular to the applied B_z -field. Coloured dots correspond to the energies of the simulated d^2I/dV^2 peaks in Fig. 3d,f of the main text. These model fits our observed spectroscopic data well because the relative short lifetime of the excitations lead to a significant broadening so that at $B = 0$ all three excitations merge to only one detectable peak and at $B_z \geq 5$ T they merge into two peaks with $\approx 1 : 2$ intensity ratio.

Even though this model fits our experimental data well, it is not evident that it is the physically only possible solution. Therefore, we will discuss in the following other coupling schemes which, as we will see, do not lead to a description consistent with our observations. Note, due to the inherent symmetry of

the molecule we restrict our search to cases where the intramolecular in-plane coupling constants J_x and J_y are identical.

Therefore, we now want to assume pure Ising-like coupling, i. e. $J_x = J_y = 0$, $J_z = J_{\text{ST}}$. At zero field the eigenstates are doubly degenerated with $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ as the ground, and $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ as the excited states. While the ground state doublet is not influenced by the magnetic field as long as $g_1 = g_2$, the excited states split (Fig. S6c) leading to two excitations with equal intensity which does not correspond to the experimental observations (Fig. S6e).

Note, however, that an asymmetry in the gyromagnetic factors, i. e. $g_1 \neq g_2$ would lead to a lifting of the ground state degeneracy. Because this shifts the state occupancy by the thermal Boltzmann factor towards the state in with the spin with the larger g -factor is aligned with the B -field, an asymmetry in the intensity of the two excitation occurs. However, this spectroscopic features should be different on both spin centers contrary to our observation that on the central spin (Fig. 3 main text) as well as on the ligand spin (Fig. 2) the energetically lower transition has stronger weight.

Because the molecule is highly symmetric in its plane, we next check if an exclusively planar coupling of the form $J_x = J_y = J_{\text{ST}}$, $J_z = 0$ could be a reasonable description of the spin system. As Fig. S6d illustrates such a coupling lead to a $(S, S_z) = \langle 0, 0 \rangle$ ground state, two in zero field degenerated excited states $(S, S_z) = \langle 1, \pm 1 \rangle$ at an energy of $J_{\text{ST}}/2$, and an additional state $(S, S_z) = \langle 1, 0 \rangle$ at an energy of J_{ST} (Fig. S6d). At $B = 0$ this would result into two excitations from the ground state (Fig. S6f) contrary to our observation.

From the above two models it is apparent that any XXZ -model with arbitrarily values of $J_x = J_y$ and J_z can not describe our observations because such a model would interpolate between the two situations. This points to the model discussed in the main text with additional significant non-collinear DM interaction.

Supplementary Note 5:

Effective spin and transport model for the singlet-triplet transition in CoPc_v

To model the spin excitation spectrum and the observed singlet-triplet transition of the CoPc_v molecules, we describe the total tunneling current as:

$$I = I_{\text{el.}} + I_{\text{inel.}}, \quad (\text{S8})$$

with the elastic current as:

$$I_{\text{el.}} = \sigma_{\text{el.}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[\rho_{\text{BCS}_S}(\varepsilon' - eV) \rho_{\text{BCS}_T}(\varepsilon) f(\varepsilon' - eV) (1 - f(\varepsilon)) \right. \\ \left. + \rho_{\text{BCS}_S}(\varepsilon) \rho_{\text{BCS}_T}(\varepsilon' - eV) f(\varepsilon) (1 - f(\varepsilon' - eV)) \right] g(\varepsilon - \varepsilon') d\varepsilon d\varepsilon' \quad (\text{S9})$$

and the additional inelastic current as

$$I_{\text{inel.}} = \sum_{i=1}^3 \frac{1}{3} \sigma_{\text{inel.}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[\rho_{\text{BCS}_S}(\varepsilon'' - eV + V_{\text{ST}}^i) \rho_{\text{BCS}_T}(\varepsilon) f(\varepsilon'' - eV + V_{\text{ST}}^i) \right. \\ \times (1 - f(\varepsilon)) + \rho_{\text{BCS}_S}(\varepsilon) \rho_{\text{BCS}_T}(\varepsilon'' - eV - V_{\text{ST}}^i) f(\varepsilon) \\ \left. \times (1 - f(\varepsilon'' - eV - V_{\text{ST}}^i)) \right] g(\varepsilon - \varepsilon') h(\varepsilon' - \varepsilon'') d\varepsilon d\varepsilon' d\varepsilon'' \quad (\text{S10})$$

with V_{ST}^i as the threshold voltage of the spin excitation, $V_{\text{ST}}^1 = V_{\text{ST}}^2 < V_{\text{ST}}^3$ in zero magnetic field. An additional Cauchy-Lorentz distribution $h(\varepsilon) = (\pi\delta)^{-1} [1 + 2(\varepsilon/\delta)]^{-1}$ is added to account for a finite lifetime of the excited state [9]. We found $\delta = 0.30$ meV in Fig. 3a of the main text, corresponding to a lifetime $\tau = h/\delta \approx 14$ ps, where h is the Planck constant. The fitting in Fig. 3a of the main text results in the threshold voltage of spin excitation $V_{\text{ST}}^1 = V_{\text{ST}}^2 = 22.7$ meV and $V_{\text{ST}}^3 = 23.8$ meV which corresponds to an intramolecular Heisenberg term $J_{\text{ST}} = 21.7$ meV assuming $|\mathbf{D}_{\text{ST}}| = 0.45 \times J_{\text{ST}}$.

Supplementary References

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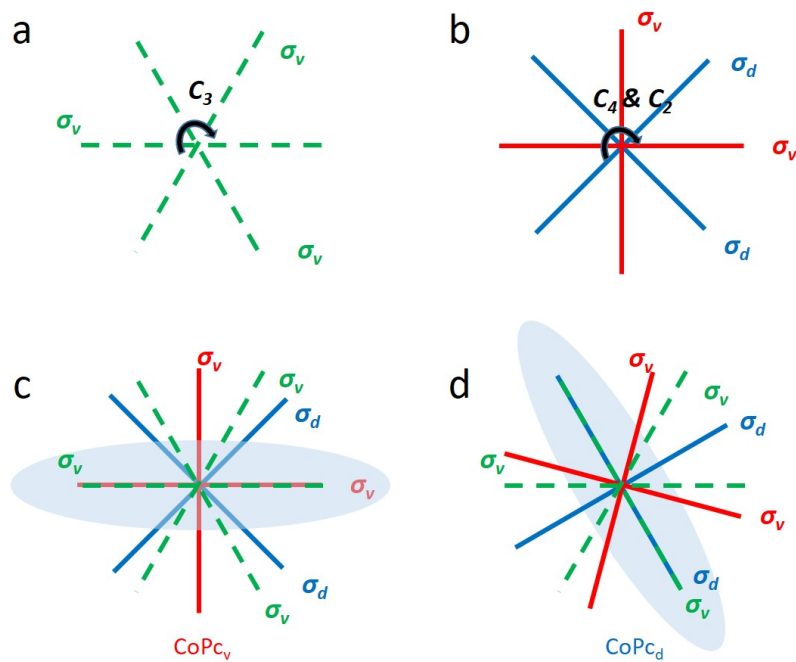


Figure S1: **Symmetry reduction by adsorption of CoPc on NbSe₂.** **a,b**, The symmetric elements of the C_{3v} and C_{4v} point group of the NbSe₂ surface and the adsorbed CoPc molecule, respectively. **c,d**, Sketch of the two highly symmetric alignments between the symmetry elements of the C_{3v} and C_{4v} point groups.

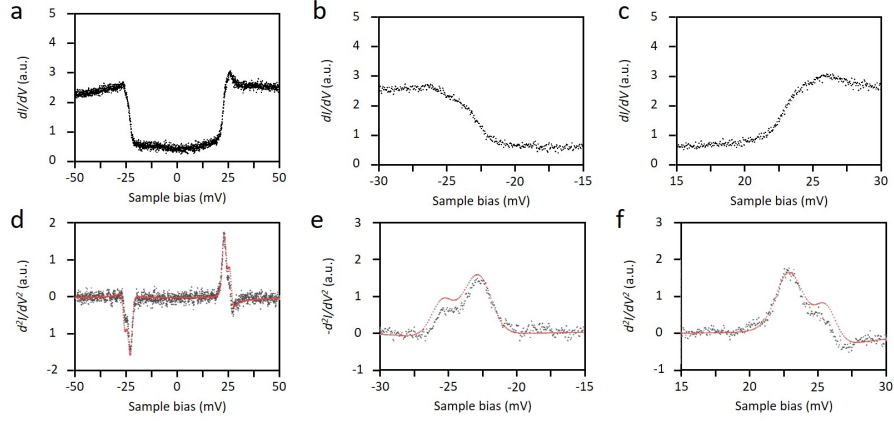


Figure S2: **Measured and modeled spin excitation spectra of CoPc_v at $B_z = 13$ T.** **a-c**, dI/dV measured at the ligands of a CoPc_v molecule. **d-f**, Numerically derived d^2I/dV^2 (black dots) and modeled d^2I/dV^2 (red dots). $J_{ST} = 22.4$ meV, $|\mathbf{D}_{ST}| = 0.45 \times J_{ST}$.

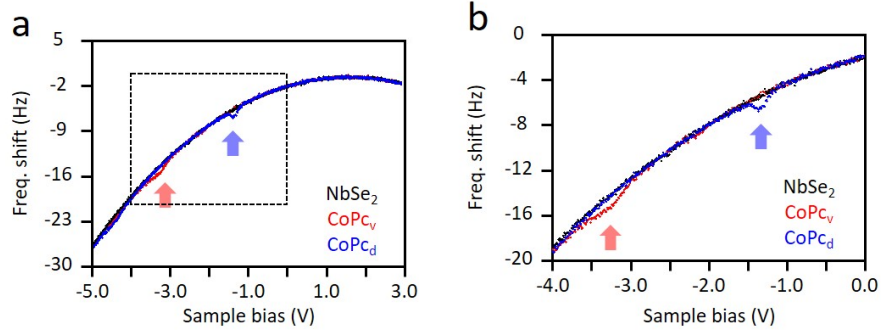


Figure S3: **Kelvin probe force microscopy on CoPc molecules.** **a**, Kelvin probe force microscopy data obtained on the NbSe₂ surface (black) and on the adsorbed CoPc molecules (red and blue), respectively. **b**, A zoom-in as marked in **a**. All spectra were measured with the same tip at the tip-sample distance. Dips on-top of the general parabolic spectra indicates the charging of CoPc_v (CoPc_v⁰ → CoPc_v⁺) and CoPc_d (CoPc_d⁰ → CoPc_d⁺), respectively.

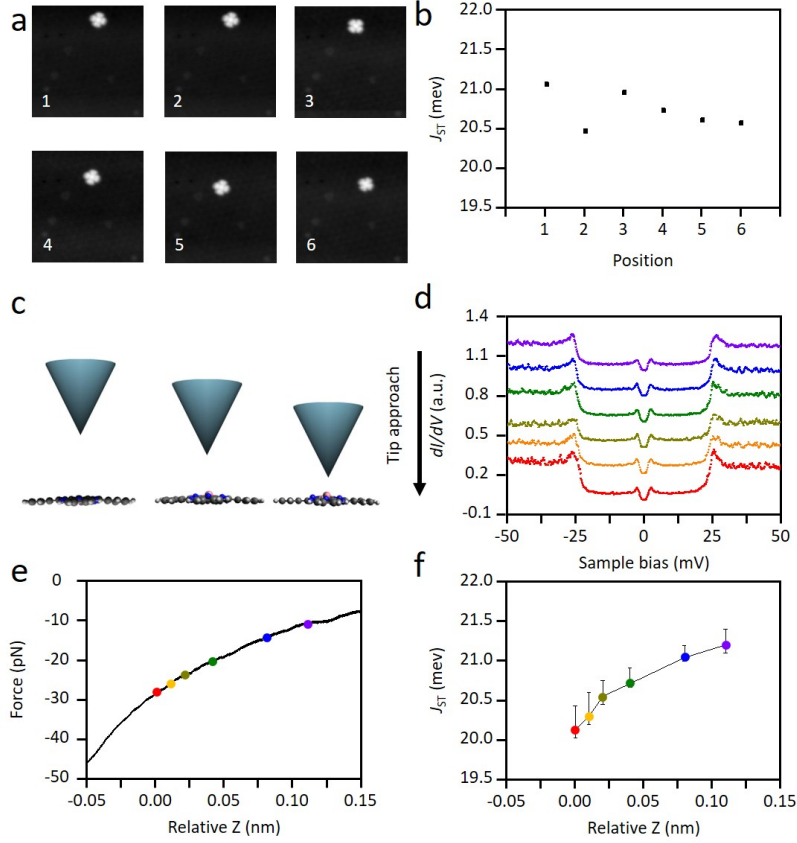


Figure S4: Surface and tip influences on the intra-molecular spin coupling. **a**, Successively measured constant-current scanning probe microscopy (SPM) images of one CoPc_v molecule during lateral manipulation by the tip. **b**, The magnetic exchange coupling strength J_{ST} extracted from dI/dV spectra measured at the central metal-ion at the corresponding positions in (a). J_{ST} varies between different adsorption sites by ± 0.5 meV. Note that the position of the molecule relative to the charge density wave of the surface has only marginal influence on J_{ST} . **c**, Sketch showing the influence of the approaching tip on the metal-organic complex. The attractive short-range force F pulls the central Co²⁺ ion towards the tip, which is equivalent to an increase of the center-ligand distance. **d**, dI/dV spectra obtained at different tip-sample distances z . **e**, Tip-molecule short-range force $F(z)$ calculated from frequency shift $df(z)$ data (not shown) of the tuning fork. Coloured circles mark the z distance at which the corresponding spectra in (d) are taken. **f**, Extracted intra-molecular Heisenberg interaction term $J_{ST}(z)$ from the spectra in (d). The height $z = 0$ correspond to $I = 0.5$ nA at $V = -50$ mV. The attractive force between the tip and the central Co-ion increases the center-ligands distance by changing the shape of the molecule, which leads to a weaker intra-molecular spin coupling.

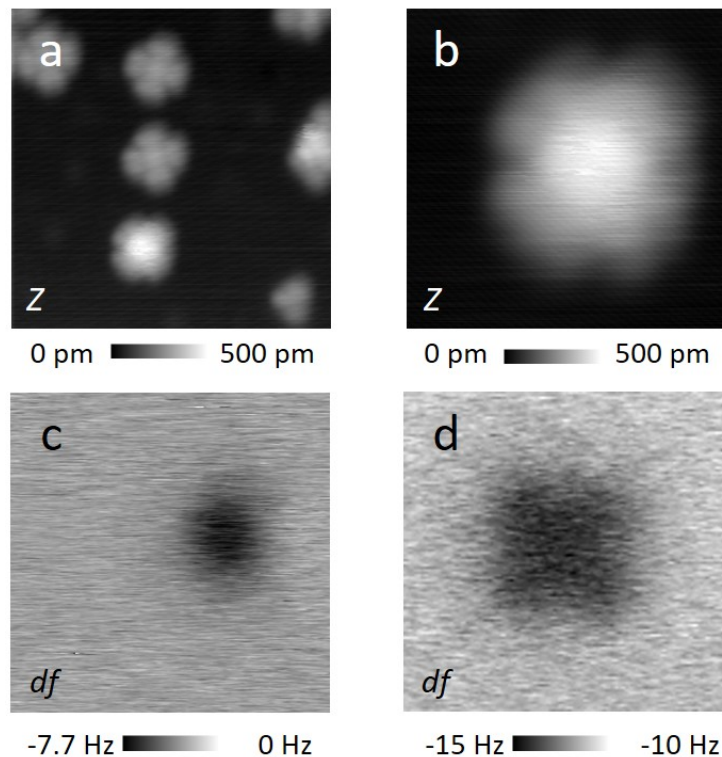


Figure S5: **Hydrogenated CoPc.** **a**, Constant current SPM image (size 10×10 nm²) of several CoPc molecules and one H-CoPc complex (lower left molecule). **b**, Zoom-in SPM image of the H-CoPc complex ($V = -500$ mV, $I = 10$ pA). **c,d**, Constant height df image of a H-CoPc (c) and a bare CoPc_v molecule (d). Both molecules have a $S = 0$ ground state but a significant difference in the topographical appearance. Set point parameters at molecular center of the H-CoPc complex: $V = -500$ mV $I = 10$ pA. Set point parameters at molecular center of the bare CoPc_v: $V = -20$ mV, $I = 20$ pA.

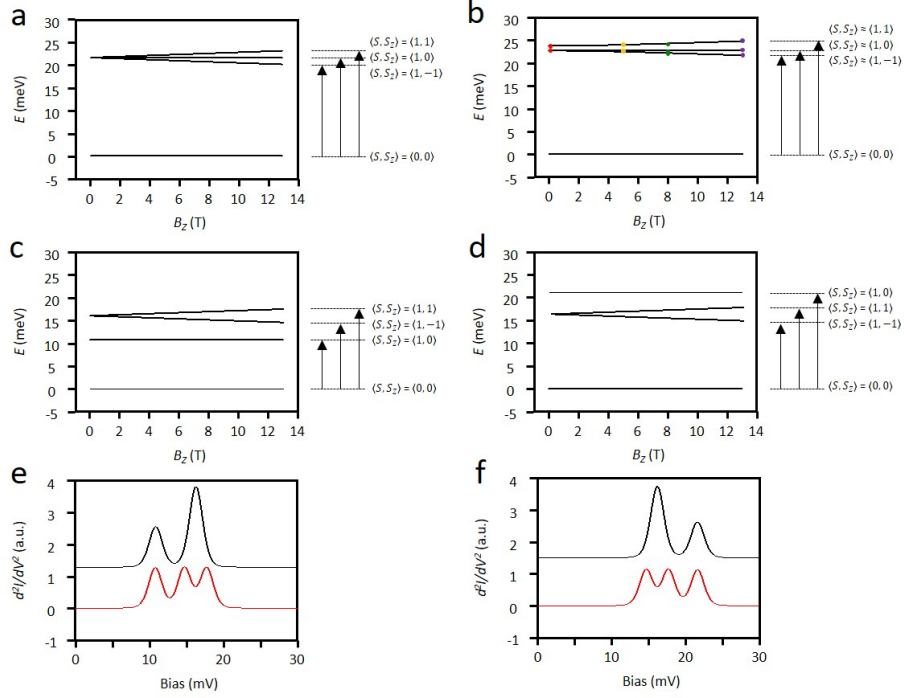


Figure S6: **Simulation of the spin excitations under magnetic fields and the corresponding d^2I/dV^2 spectra.** **a**, Energies of the eigenstates versus out-of-plane magnetic field strength using an isotropic Heisenberg interaction $J_x = J_y = J_z = J_{ST} = 21.6$ meV. **b**, Energies of the eigenstates versus out-of-plane magnetic field strength using the isotropic Heisenberg interaction as in (a) and an additional in-plane DM term with $|\mathbf{D}_{\parallel}| = 0.45 \times J_{ST}$. The coloured dots are the energies of the modeled d^2I/dV^2 in fig. 3 of the main text. **c**, **d**, Same as (a) for an anisotropic Heisenberg exchange coupling with $J_x = J_y = 0$ and $J_z = 21.6$ meV (c) and $J_x = J_y = 21.6$ meV and $J_z = 0$ (d), respectively. **e**, **f**, Modelled d^2I/dV^2 spectra for the simulations in (c) and (d), without magnetic field (black line) and with $B_z = 13$ T (red line), respectively. The arrows on the right-hand side of the panels (a-d) mark the possible transition between the energy levels labeled with the total spin (S) and its magnetic moment in z -direction (S_z).