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多層フタロシアニン錯体の分子形状操作とスピン制御

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Abstract: Molecular spintronics has attracted attentions, which combines molecular electronics with the spin degree of freedom in electron transport. Among various molecules as candidates of the molecular spintronics, single molecule magnet (SMM) is one of the most promising material. SMM molecules show a ferromagnetic behavior even as a single molecule and hold the spin information even after the magnetic field is turned off.

Here in this report, we show the spin behavior of SMM molecules adsorbed on the Au surface by combining the observation of Kondo peak in the STS and ESR-STM measurement. Kondo resonance state is formed near the Fermi level when degenerated spin state interacts with conduction electrons. ESR-STM detects the Larmor frequency of the spin in the presence of a magnet field. The sample include MPc_2 and M_2Pc_3 molecules (M = Tb^{3+}, Dy^{3+}, and Y^{3+}; Pc=phthalocyanine, Fig. 1) whose critical temperature as a ferromagnet reaches 40 K. A clear Kondo peak was observed which is originated from an unpaired π electron in the ligand of the molecule, which is the first demonstration of the Kondo peak originated from π electron observed in the STS measurement. We also observed corresponding peaks in ESR-STM spectra.

In addition we found that the Kondo peak intensity shows a clear variation with the conformational change of the molecule; namely the azimuthal rotational angle of the Pc planes. This indicates that the Kondo resonance is correlated with the molecule electronic state. We examined this phenomena by using STM manipulation technique, where pulse bias application can rotate the relative azimuthal angle of the Pc planes. The result indicates that an application of ~1V pulse to the bias voltage can rotate the Pc plane and the Kondo peaks shows a clear variation in intensity by the molecule's conformational change. (see Fig. 2)

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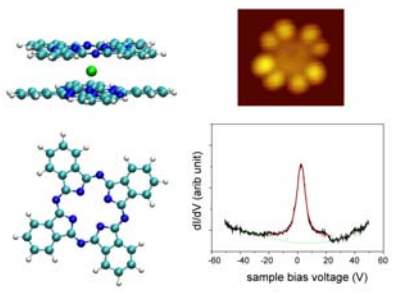

Fig. 1
Schematics of TbPc2 molecule and Pc plane, together with STM image and Kondo peak near Fermi level.

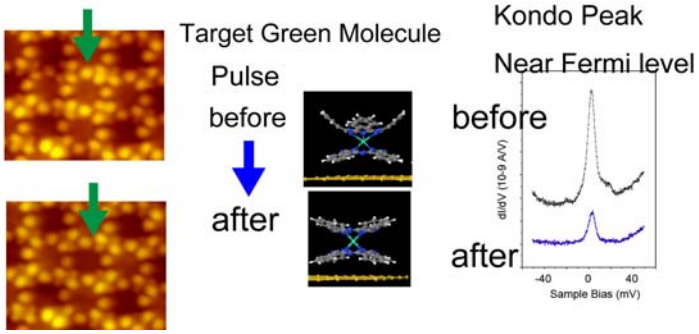

Fig. 2
STM manipulation for TbPc2 molecule in a monolayer film. By pulse application, Pc plane rotates and the relative azimuthal angle changes, which induces a clear change in Kondo peaks.

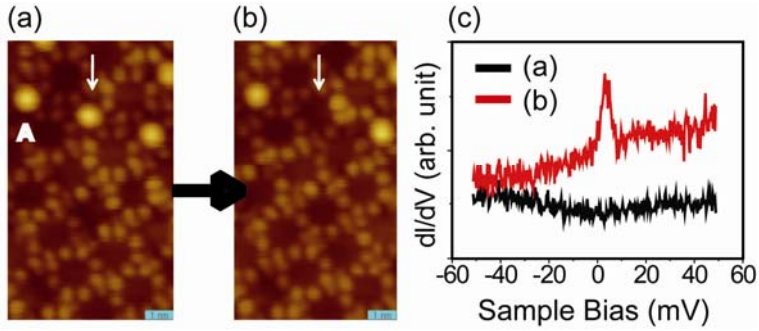

Fig. 3
STM manipulation for TbPc2 molecule in a monolayer film. By pulse application, Pc plane rotates and the relative azimuthal angle changes, which induces a clear change in Kondo peaks.

The presence of the spin in the Pc ligand can be explained by counting the valence electrons. While the molecule is neutral, the center Tb atom tends to be 3+ and the three electrons should be shared with the two Pc ligands. This makes one of the Pc ligands unpaired and the spin center. The presence of SOMO level by this scenario can survive on the metal surface in case the interaction between the molecule and the surface is weak. Actually for the $TbPc_2$ adsorbed on Cu(111) surface, which provides stronger bonding compared to the Au(111) surface, the Kondo peak was not observed. That is due to an electron transfer to from the substrate to the molecule which fills the SOMO level. Similar change can be seen in case the azimuthal rotational angle of the two Pc is rotated from the bulk value of 45o. Our DFT calculation indicated that the SOMO level moves closer to the Fermi level in case the rotation angle is reduced to 30^{o}, which makes the SOMO level filled with electron and diminishes the ligand-derived spin.

Another method of control of the molecule spins is to make a local doping of an electron donor or an acceptor near the spin. Since the SOMO level of the Pc ligand is responsible for the appearance of the spin, it should be possible to eliminate the spin by filling the SOMO. This was examined by depositing Cs atoms on the film of $TbPc_2$ film. Figure 3(a) shows three bright spots, indicated by 'A', that correspond to the deposited Cs atom. The adsorption of the Cs atom is apparently weak bonding on the TbPc2 film, and the Cs atom can be removed easily by applying a pulse of ~2.0 V from the STM tip. The removal of Cs atom by the pulse application is shown in Fig. 3(a) and (b); the Cs atom marked by the arrow in Fig. 3(a) was removed by the pulse in Fig. 3(b). The change of the spin structure is shown in Fig. 3(c); the apparent Kondo peak recovered after removing the Cs atom. This can be explained by the electron transfer from Cs to SOMO level and diminish the spin of the Pc ligand.

References

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