How Contacting Electrodes Affect Single π-Conjugated Molecular Electronic States: Local Density of States of Phthalocyanine Nanomolecules on MgO(001), Cu(111), Ag(001), Fe(001), and Mn(001)

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Single molecules have attracted much interest as new materials for future spin electronic devices; however, many open questions still remain. One of them is how the electronic local density of states (LDOS) of single molecules is affected when they are in contact with electrodes. We show a systematic study of the LDOS of π-conjugated phthalocyanine (H_2Pc) nanomolecules adsorbed on various electrodes, namely, (1) MgO(001) thin films grown on Ag(001), (2) noble metals of Cu(111) and Ag(001), and (3) 3d magnetic metals of Fe(001) and Mn(001), adupting scanning tunneling spectroscopy techniques with an ultrahigh-vacuum scanning tunneling microscopy setup at room temperature. Since MgO thin films cut the electronic coupling from the substrate Ag(001), we could observe H_2Pc molecular states at -1.5 and $+1.0$ eV. H_2Pc molecules on the noble metal substrates form a pattern with a square unit cell of about 1.5×1.5 nm^2 and have similar LDOS peaks near the Fermi energy. Strong hybridizations between the substrate 3d spin-polarized states and the molecular π orbitals produce new molecular states of H_2Pc molecules adsorbed on Fe(001) and Mn(001) near the energy positions of the Fe(001) minority spin state and the Mn(001) majority spin state, respectively.
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1. Introduction

The realization of a sustainable society is nowadays one of the most important issues in saving our environment. Since a huge increase in the human population in the next decades is predicted, a reduction in energy consumption is required. Energy consumption in small electronic devices will play a major role. The minimization of electronic devices is expected to be a trump. This is the reason why nanoscience and nanotechnology have been markedly advanced over the last decades. Single molecular electronics and spintronics are considered to be new breakthroughs in the development of future nanodevices with low energy consumption, low cost, and high performance.[1–9]

However, many open questions still remain in realizing single molecular electronic devices. One of them is how the electronic local density of states (LDOS) of single molecules is affected when the molecules are brought into contact with substrate electrodes. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of molecules in the gas phase are frequently calculated by molecular orbital simulations. Previously, the electronic states of molecules adsorbed on metallic electrodes were assumed to be the same as those of molecules in the gas phase. This assumption is acceptable for thick bulk-like molecular films. Surface and interface effects have been considered to be minor problems.

However, for future nanoelectronic devices, surface and interface effects determine the electronic properties. Studies of single molecules and molecular monolayer films have been carried out using noble metal substrates.[3,5–11] Quantum spin states of single molecular magnets have been widely studied.[3,4,6–9] Electronic couplings from the noble metal substrates have been considered not to affect strongly the quantum spin states of the molecules. However, we have recently found that properties of Fe-based spin-crossover molecules are affected by the electronic coupling from a Cu(001) substrate.[5] We succeeded in detecting molecular low-spin and high-spin states of the spin-crossover mole-cules by inserting a CuN layer between the substrate and the molecules to cut the coupling from the substrate, which means that even with noble metal electrodes, electronic or spin states of single molecules can be modified. Such a decoupling layer is required to observe intrinsic molecular orbitals. MgO (2–3 ML) and NaCl (2 ML) thin films have also been used as decoupling layers.[12–14]

On the other hand, strong electronic couplings between substrates and molecules can also be useful for new molecular spintronics. Strong hybridizations between 3d spin-polarized LDOS and molecular π-orbitals result in a magnetoresistance effect through a single molecule,[1,2] i.e., spin current through single molecules can be controlled by switching the magnetization directions of magnetic electrodes.

In this work, we report a systematic study of the LDOS of low-dimensional π-conjugated phthalocyanine (H_2Pc) molecules on various substrates by scanning tunneling spectroscopy techniques with an ultrahigh-vacuum scanning tunneling microscopy (STM) setup at room temperature. MgO(001) ultrathin films, noble metal Cu(111) and Ag(001) surfaces, and 3d magnetic metal Fe(001) and Mn(001) surfaces were used as substrate electrodes.

2. Experimental Procedure

STM and spectroscopy (STS) experiments were performed at 300 K in ultrahigh-vacuum (UHV; base pressure $<8 \times 10^{-9}$ Pa). STS measurements were performed by opening the feedback loop of the tunneling current, i.e., fixing the tip–sample separation (z). The tunneling current was measured at each pixel by varying the sample voltage within ±1.5 V. $I(V)$ curves averaging more than 1000 single $I(V)$ curves were used in this study. Differential conductivity (dI/dV) curves were obtained by numerical differentiation of the $I(V)$ curves. Although a lock-in amplifier was used to obtain the dI/dV signals indicated in our previous papers,[1] here we do not use a lock-in amplifier so that we can distinguish between real and pseudogaps around the Fermi energy. A dI/dV curve normalized by its fitted

tunneling probability function (T) corresponds to the sample LDOS.[15–18]

Nonmagnetic tungsten (W) tips were electrochemically etched from W wires ($\phi = 0.3$ mm, purity 99.9%) in air using KOH aq., while the etching process was monitored by optical microscopy. Subsequently, the tip was rinsed with hot water, then transferred into the load lock chamber of our STM setup. The apex of the W tip was sputtered with Ne$^+$ in UHV and annealed at temperatures of up to 2000 K to obtain a clean apex. Fcc-Cu(111) and fcc-Ag(001) single crystals (purity 99.999%) were used as conductive noble metal substrates. A clean and atomically flat surface was obtained after several sputtering and annealing cycles in UHV. A MgO(001) ultrathin film was grown on Ag(001). Mg was deposited on Ag(001) at 500 K at an oxygen (purity 99.995%) pressure of 1×10^{-4} Pa. A clean and atomically flat bcc-Fe(001) surface was obtained on Fe-whisker single crystals by Ar$^+$ sputtering and annealing cycles up to 870 K. Mn(001) ultrathin films were grown on an Fe(001)-whisker single crystal substrate at 370 K.

H$_2$Pc molecules were used as a representative of π-conjugated molecules. Commercial H$_2$Pc powder (Alfa Aesar, purity 95%) was purified by sublimation at 653 K and recrystallization at 473 K at a pressure of 1×10^{-3} Pa (yield 30%). Nuclear magnetic resonance (NMR) and infrared spectra confirmed the absence of impurities after the purification. The clean H$_2$Pc powder was placed in a crucible that was set in a molecule chamber and heated to 550 K. The H$_2$Pc powder was deposited on single crystal surfaces at 300 K by opening the shutter valve between the preparation and molecule chambers. The deposition rate was 0.03 ML/min.

3. Results and Discussion

Firstly, we investigated the LDOS of π-conjugated H$_2$Pc molecules adsorbed on MgO(001) ultrathin islands with a thickness of 2 ML grown on atomically flat Ag(001) terraces. (MgO in bulk is known to be insulator.) The MgO thin film was used to suppress electronic coupling between Ag(001) and the molecules. Using such decoupling layers, we observed true electronic structures of H$_2$Pc molecules.

Figure 1(a) shows an STM topographic image of MgO islands on the Ag(001) substrate. A dI/dV map obtained at $+2$ V in the same area as Fig. 1(a) shows a strong black-white contrast [see Fig. 1(b)]. Dark areas correspond to MgO islands, which clearly indicate that the LDOS of MgO islands is much lower than that of Ag(001). Figure 1(c) shows a dI/dV curve obtained on MgO islands. dI/dV values at around the Fermi energy are approximately 0 nA/V, which indicates a very low LDOS. dI/dV increases exponentially below -2 eV and above $+1.5$ eV. This experimental result is comparable to the dI/dV spectrum obtained in Ref. 14. Schintke et al. reported that MgO (1–10 ML) thin films have an unoccupied state at around $+2.5$ eV, an occupied state at around -4.0 eV, and a gap width of about 6.2 eV.[14] (The gap width of bulk MgO is 7.8 eV.) Thin films have smaller gaps. The theoretically calculated LDOS of MgO (2–3 ML) thin films is very low near the Fermi energy, but it starts to increase at around $+1.5$ and -1.5 eV, i.e., the calculation showed a gap width of about 3 eV.[14] The calculated LDOS nicely fits our experimentally obtained
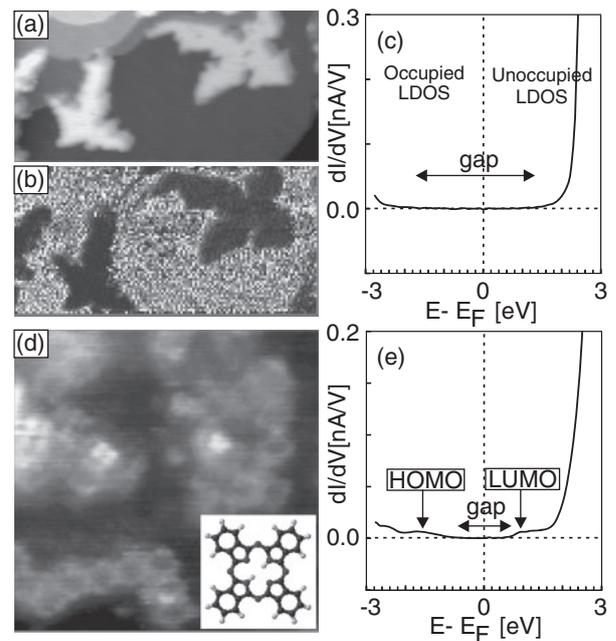

Fig. 1. (a–c) Obtained on the surfaces of MgO(001) bilayer islands grown on Ag(001). (a) STM topographic image (55×28 nm^2, $V_s = +2.8$ V, $I = 50$ pA). (b) dI/dV map at $+2.0$ V. MgO islands appear dark. (c) dI/dV curve obtained on MgO islands at $V_s = +2.8$ V and $I = 500$ pA. (d) and (e) Obtained on the surfaces of 1 ML H$_2$Pc molecules on MgO(001) bilayer islands. (d) STM topographic image (15×15 nm^2, $V_s = +2.8$ V, $I = 50$ pA). The inset image is a model of a H$_2$Pc single molecule. (e) dI/dV curve obtained on 1 ML H$_2$Pc on MgO islands at $V_s = +2.8$ V and $I = 200$ pA.

dI/dV curve in Fig. 1(c). To obtain spectroscopy curves with a better signal-to-noise ratio, we used low-noise current amplifiers and cables with low capacitance (about 50 pF/m), which reduced the total current noise of our homemade STM setup down to about 200 fA. The current noise amplitude in dI/dV was below 0.001 nA/V.[18] Although, in Fig. 1(c), dI/dV values at around the Fermi energy are very low, we can detect the tunneling electrons from the substrate Ag(001), i.e., when we set the sample bias voltage, for example at $+1$ V, we can observe the Ag(001) surface through the MgO thin film while paying attention to avoid crashing the tip into the MgO thin film. (We needed to set the current at 1–5 pA.) Therefore, the dI/dV conductance in Fig. 1(c) near the Fermi energy is not zero, but the LDOS between -2 and $+1.5$ eV is very low [gap in Fig. 1(c)] since the LDOS near the Fermi energy of Ag(001) decays rapidly into the MgO film. The 2 ML MgO film likely cuts the electronic coupling from Ag(001). If we observe new LDOS peaks within the gap when we deposit H$_2$Pc molecules on the MgO thin films, these new peaks can be identified as molecular HOMO and LUMO states.

We deposited 1 ML H$_2$Pc molecules on MgO islands. An observed STM image is shown in Fig. 1(d), in which single H$_2$Pc molecules connect with each other and form molecular chains. dI/dV curves were measured on the molecules. Within the MgO gap, we found two peaks. H$_2$Pc molecules have a LUMO peak at $+1.0$ eV and a HOMO peak at -1.5 eV, as shown in Fig. 1(e). Furthermore, since dI/dV values between -0.8 and $+0.6$ eV are very low (close to 0 nA/V), we consider that the molecules on the MgO films

have a gap width of about 1.4 eV, i.e., the molecules on the MgO films can have semiconductor-like properties.

Secondly, we deposited H_2Pc molecules on noble metal substrates of fcc-Ag(001) and fcc-Cu(111). Electronic coupling from the noble metals to the molecules will affect molecular electronic states.

Figure 2(a) shows an STM topographic image obtained on a clean and atomically flat Cu(111). Atomic terraces larger than 20 nm are observed. Figure 2(b) shows an experimentally obtained dI/dV curve on a clean terrace. A surface state peak is observed at around -200 meV [marked by an arrow in Fig. 2(b)]. This peak is known to be an sp surface state and electrons on Cu(111) show free-electron-like behavior.[19,20] Unlike the MgO(001) surface, Cu(111) surface has a higher LDOS near the Fermi energy.

H_2Pc molecules were deposited on this Cu(111) surface at room temperature. Single molecules diffused on the Cu(111) surface and formed two-dimensional islands or films, which indicates that the coupling between Cu(111) and the molecules is not strong. Figure 2(c) shows a molecular pattern obtained on the terrace. Single dots correspond to single molecules. The molecules have a unit cell size of about 1.5×1.5 nm^2, which is very similar to the pattern observed on FePc films (1 ML) on Cu(111).[11] Similar patterns were even observed on CuPc films on Au(111).[10] These suggest that phthalocyanine molecules adsorbed on a sixfold-symmetry fcc(111) noble metal substrate form an ordered pattern with a square unit cell. The fact that the molecular patterns are independent of the noble metal substrate also indicates a weak coupling between the molecules and the noble metals.

Tunneling spectroscopy measurements were performed on this surface. Figure 2(d) shows the obtained LDOS of the molecular film. New peaks were found near the Fermi energy at -300, $+300$, and $+600$ meV. In the case of decoupling, MgO layers cut the electronic coupling from the substrate, and HOMO and LUMO are separated by about 2.5 eV; however, owing to the coupling, HOMO and LUMO peaks appear near the Fermi energy, which increases the LDOS at the Fermi energy, and H_2Pc molecules on Cu(111) have metal-like properties.[3]

Figures 2(e)–2(h) show STM/STS results obtained on Ag(001) substrates. Figure 2(e) shows an STM topographic image obtained on a clean and atomically flat Ag(001) surface. Atomic terraces are observed.

Figure 2(f) shows a dI/dV curve obtained on Ag(001). In contrast to the case of Cu(111), there is no clear LDOS peak since Ag(001) does not have a surface state near the $\bar{\Gamma}$ point and bulk bands are dominant near the Fermi energy.[21,22] [Outermost electron shells of Ag(001) are 4d and 5s electron orbitals.]

We deposited H_2Pc molecules on the Ag(001) surface at room temperature. Similarly to the case of the Cu(111) surface, H_2Pc molecules diffused on the Ag(001) surface and formed a two-dimensional film. Figure 2(g) shows an STM topographic image obtained on the 1 ML H_2Pc film grown on Ag(001). A molecular pattern with a square unit cell with dimensions of about 1.5×1.5 nm^2 can be observed in the enlarged image in Fig. 2(g); the dimensions are the same as those of the 1 ML H_2Pc molecules on Cu(111). This result is surprising. Since fcc(001) has a different symmetry from
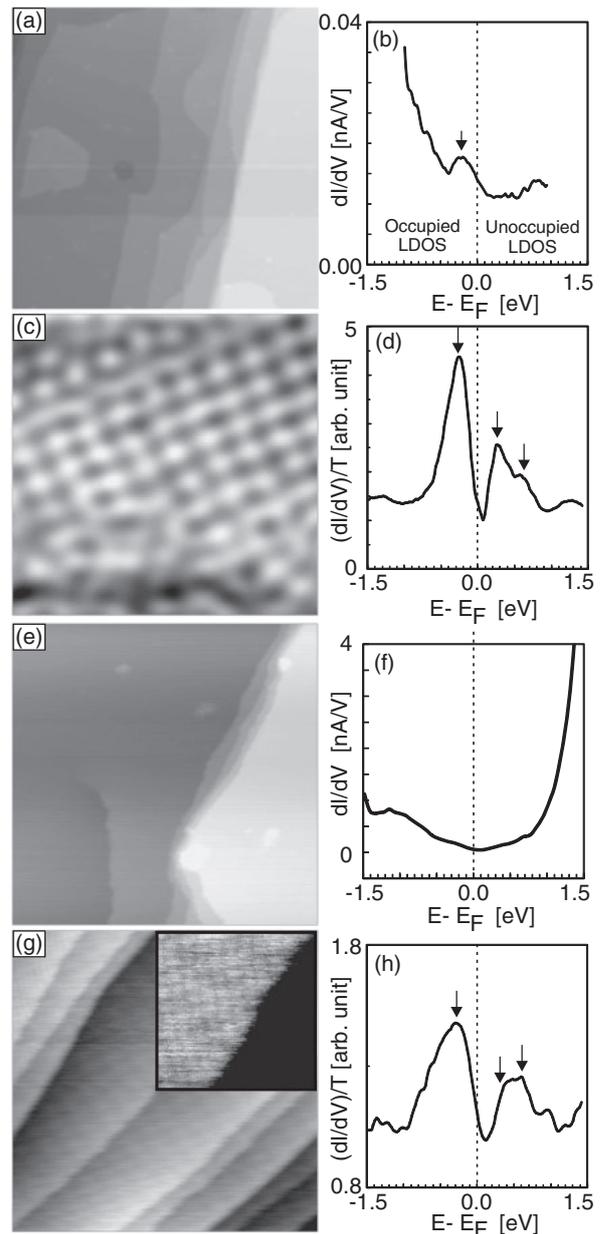

Fig. 2. STM topographic images (a, c, e, g) and spectroscopy curves (b, d, f, h) corresponding to LDOS values obtained on (a, b) Cu(111), (c, d) 1 ML H_2Pc on Cu(111), (e, f) Ag(001), and (g, h) 1 ML H_2Pc on Ag(001). (a) 125×125 nm^2, $V_s = -2.0$ V, and $I = 300$ pA. (c) 12×12 nm^2, $V_s = +870$ meV, and $I = 1.1$ nA. (e) 51×51 nm^2, $V_s = -2.0$ V and $I = 50$ pA. (g) 70×70 nm^2, $V_s = -900$ mV, and $I = 500$ pA. The inset (14×14 nm^2) is an enlarged image showing a 2D molecular array with a periodicity of about 1.5 nm.

fcc(111), we expected different molecular patterns. These results indicate weak coupling between Ag(001) and H_2Pc, and it seems that Pc molecules physisorb on noble metal surfaces.

The LDOS obtained on the 1 ML H_2Pc on Ag(001) is shown in Fig. 2(h). H_2Pc molecules have peaks at -300, $+300$, and $+600$ meV. These peak positions are almost the same as the LDOS peak positions obtained on $H_2Pc/$ Cu(111). This proves that H_2Pc molecules do not chemisorb on Cu(111) and Ag(001). Since HOMO and LUMO peaks appear near the Fermi energy, 1 ML H_2Pc molecules on Ag(001) could have metal-like properties.

Finally, we performed STM/STS measurements on single H_2Pc molecules adsorbed on 3d magnetic metal substrates. Here, we used bcc-Fe(001) and bct-Mn(001) substrates, which are well-known model systems for ferromagnetic and layerwise antiferromagnetic order substrates for STM studies.[17,23]

Figure 3(a) shows an STM topographic image obtained on an Fe(001)-whisker single crystal substrate. Atomic terraces larger than 100 nm are observed. The LDOS obtained by tunneling spectroscopy is shown in Fig. 3(b). A peak is observed at +300 meV above the Fermi energy, which is known to be a highly spin-polarized 3d minority spin state.[24]

Single H_2Pc molecules were deposited on this Fe(001) surface at room temperature. Figure 3(c) shows an STM topographic image obtained on the surfaces of H_2Pc single molecules on Fe(001). In contrast to the noble metal surfaces, single molecules adsorbed on Fe(001) do not diffuse even at room temperature, which indicates a relatively strong coupling between the Fe(001) substrate and the molecules. If the H_2Pc molecules chemisorb on Fe(001), molecular electronic structures are expected to change markedly. The LDOS of H_2Pc/Fe(001) is shown in Fig. 3(d). Only one clear peak can be observed at +300 meV; this energy position is the same as that of the spin-polarized 3d surface state of the Fe(001) substrate, i.e., the new molecular state appears near the 3d surface state. A similar phenomenon can be observed in the case of CoPc molecules on Co(111), where Co(111) has a 3d spin-polarized surface state peak at −300 meV and the adsorbed CoPc has a spin-polarized surface state peak at −150 meV; this energy position is close to that of the Co(111) surface state. This is considered to be due to the strong hybridization between the 3d state and the π orbitals.[20] If a similar hybridization occurs in the case of Fe(001) and H_2Pc, the +300 meV peak of H_2Pc/Fe(001) is likely spin-polarized. Since the new peak appears near the Fermi energy, H_2Pc/Fe(001) could have metal-like properties.

If the molecular π orbitals tend to hybridize strongly with the 3d states, we will find a new molecular state near the energy position of the 3d state when we use different magnetic substrates. Here, we used Mn(001) thin films. One unique reason for using this Mn(001) thin film is that Mn(001) has majority and minority spin states below and above the Fermi energy, respectively. In the case of Fe(001), molecular π orbitals likely couple with the minority spin state at +300 meV. In the case of Mn(001), it is unclear which spin state (minority or majority) is more favorable to couple with H_2Pc molecular orbitals. Figures 3(e)–3(h) show STM/STS results obtained on the Mn(001) substrate. The Mn(001) film with a thickness of about 5 ML was grown on the Fe(001)-whisker single crystal. An STM topographic image shows several atomic terraces on the surface due to a layer-plus-island growth mode [Fig. 3(e)].[16,17] LDOS obtained on Mn(001) shows two peaks at −150 and +500 meV, which are attributed to spin-polarized $3d_{z^2}$-like majority LDOS and minority LDOS, respectively [see Fig. 3(f)].[17]

H_2Pc molecules were deposited on the Mn(001) film at room temperature. Similarly to the case of H_2Pc on Fe(001), single molecules adsorbed on Mn(001) do not diffuse even at
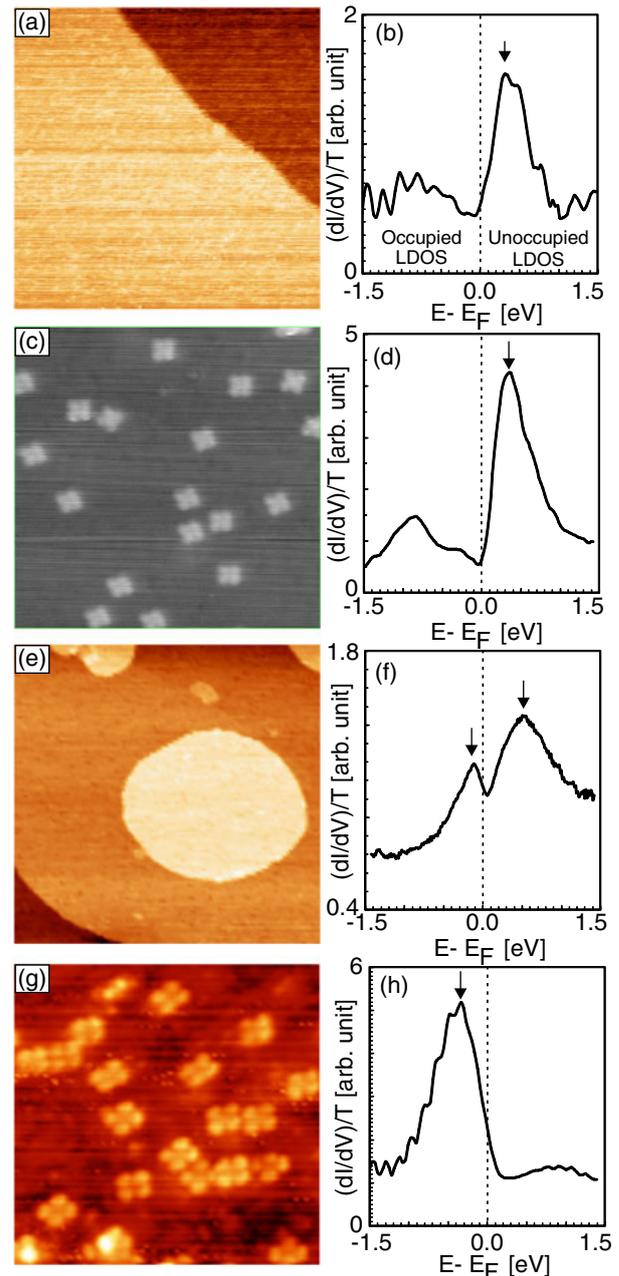

Fig. 3. (Color online) STM topographic images (a, c, e, g) and $(dI/dV)/T$ curves (b, d, f, h) corresponding to LDOS values obtained on (a, b) Fe(001), (c, d) single H_2Pc molecules on Fe(001), (e, f) Mn(001), and (g, h) single H_2Pc molecules on Mn(001). (a) 100×100 nm^2, $V_s = -1500$ mV, and $I = 500$ pA. (c) 20×20 nm^2, $V_s = -1000$ mV, and $I = 200$ pA. (e) 100×100 nm^2, $V_s = -1500$ mV, and $I = 80$ pA. (g) 16×16 nm^2, $V_s = -1500$ mV, and $I = 200$ pA.

room temperature [see Fig. 3(g)]. As we expected, 3d metals seem to couple strongly with the molecules. The obtained LDOS on H_2Pc/Mn(001) is shown in Fig. 3(h), in which a new peak is observed at −300 meV close to the majority peak position of the Mn(001) substrate. The calculated spin-resolved LDOS of H_2Pc/Mn(001) was reported (supplementary information in Ref. 2). The peak at −300 meV corresponds to the peak energy position of the molecular spin-polarized LUMO state, which is attributable to the strong hybridization between the Mn(001) majority state and the molecular LUMO state.[2] These experimental and
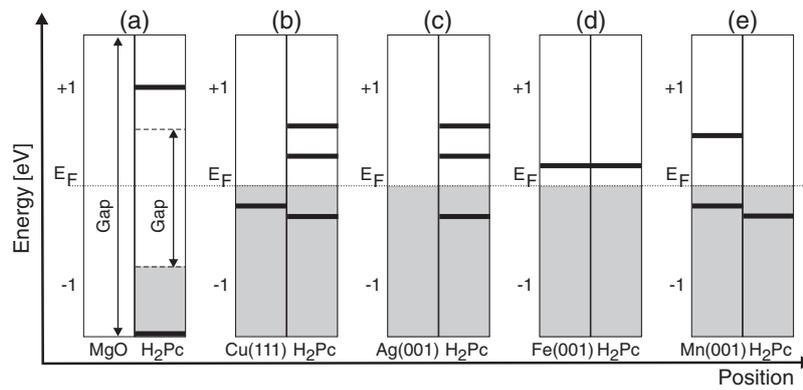
Fig. 4. LDOS peak positions of H$_2$Pc molecules adsorbed on (a) MgO(001) thin film (2 ML), (b) Cu(111), (c) Ag(001), (d) Fe(001)-whisker single crystal, and (e) Mn(001) thin-film (about 5 ML) substrates. Solid lines denote surface state peak positions. Shaded areas denote the occupied density of state. Dotted lines denote onsets of increasing LDOS.

theoretical results prove that 3d spin-polarized surface states couple strongly with the molecular π orbitals and that new molecular spin states near the energy positions of the 3d states are formed. In contrast to H$_2$Pc on noble metals, H$_2$Pc on 3d magnetic metals have molecular states at different energy positions: $+300$ meV for H$_2$Pc/Fe(001), -300 meV for H$_2$Pc/Mn(001), and -150 meV for H$_2$Pc/Co(111).[20] We could control the energy position of the H$_2$Pc molecular state by choosing different magnetic electrodes. Also, the presence of the spin-polarized molecular state on H$_2$Pc/3d metals means that nonmagnetic H$_2$Pc molecules exhibit magnetic properties upon contact with 3d magnetic metals. Since the new peak appears near the Fermi energy, the molecules adsorbed on Mn(001) could have metal-like properties.

Figure 4 shows a summary of energy positions of the surface state peaks obtained on the H$_2$Pc molecules adsorbed on various electrodes. The MgO(001) thin film grown on Ag(001) has a very low LDOS ($=$ gap) near the Fermi energy. The electronic coupling from Ag(001) is decoupled by the 2 ML MgO thin film. The dI/dV curve in Fig. 1(c) and the calculated LDOS in Ref. 14 showed that the 2 ML MgO thin film has a gap between -2 and $+1.5$ eV. The H$_2$Pc molecules adsorbed on the MgO thin film have LDOS peaks at -1.5 and $+1.0$ eV, and the LDOS near the Fermi energy is very low [Fig. 4(a)]. Since this electronic structure is similar to the calculated electronic states of H$_2$Pc molecules in the gas phase,[25] we believe that the MgO thin film cuts the electronic coupling from the Ag substrate.

H$_2$Pc single molecules adsorbed on the noble metal substrates diffused and formed two-dimensional islands or films. In spite of the fact that different types of noble metal substrates were used, namely Ag(001), Cu(111), and Au(111),[10,11] Pc molecules always formed a similar pattern with a square unit cell with dimensions of about 1.5×1.5 nm^2, indicating that Pc molecules do not couple strongly with noble metal substrates. Pc molecules likely physisorb on noble metal surfaces. The LDOS values of H$_2$Pc adsorbed on Ag(001) and Cu(111) show peaks at similar energy positions of -300, $+300$, and $+600$ meV [see Figs. 4(b) and 4(c)]. Since the molecular electronic states are not changed by the different noble metal substrates, we could conclude

that the H$_2$Pc molecules physically adsorb on the noble metal surfaces.

Figures 4(d) and 4(e) show the LDOS values of H$_2$Pc on Fe(001) and Mn(001). H$_2$Pc molecules have new peaks near the energy positions of the substrate 3d states. In contrast to Figs. 4(b) and 4(c), the energy positions of molecular states in Figs. 4(d) and 4(e) are changed by the different 3d substrates. Another interesting point observed on the 3d metal substrates is that, even at room temperature, H$_2$Pc molecules do not diffuse on the substrate surface, which was not observed on the noble metal and MgO film surfaces. The origin of these unique properties is considered to be the stronger coupling between the molecular π orbitals and the 3d magnetic metal substrates. Calculations also suggest the strong hybridizations between the 3d states and the molecular π orbitals.[2] H$_2$Pc molecules adsorbed on Fe(001) show an LDOS peak at the same energy position as the 3d minority spin state of the Fe(001) substrate, i.e., minority spins can pass through the molecules. H$_2$Pc molecules adsorbed on Mn(001) show a LUMO peak at an energy position near the Mn(001) 3d majority spin state, i.e., majority spins can pass through the molecules. These suggest that π-conjugated molecules adsorbed on magnetic metals with 3d spin-polarized states likely have a spin-polarized molecular state at an energy position near the substrate 3d state. Such new properties of π-conjugated single molecules could be useful for near-future single molecular spintronics.

4. Conclusions

We showed a systematic study on how the LDOS of low-dimensional π-conjugated H$_2$Pc molecules is affected by different substrate electrodes. LDOS values were measured by using STM/STS techniques in UHV at room temperature. The decoupling of a 2 ML MgO(001) thin film from a Ag(001) substrate and its effects were examined. H$_2$Pc molecules adsorbed on the MgO thin film show H$_2$Pc molecular states at -1.5 and $+1.0$ eV. H$_2$Pc molecules adsorbed on Cu(111) and Ag(001) have similar patterns with a square unit cell (about 1.5×1.5 nm^2) and similar LDOS peaks near the Fermi energy. These results indicate a weak coupling between the noble metal substrates and the H$_2$Pc molecules. The molecules likely physisorbed on the noble metals.

H$_2$Pc molecules was found to couple strongly with the 3d magnetic metal substrates. H$_2$Pc molecules likely chemisorbed on Fe(001) and Mn(001). H$_2$Pc molecules on Fe(001) and Mn(001) could have new spin-polarized molecular states near the energy positions of the Fe(001) minority spin state and the Mn(001) majority spin state, respectively.

Acknowledgments

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