Supporting Information

Magnetic Interactions of Vanadyl Phthalocyanine with Ferromagnetic Iron, Cobalt, and Nickel Surfaces

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Contents

A. Details of sample preparation……...…….2

B. LEED images of VOPc on the ferromagnetic films……..……...….4

C. XAS/XMCD spectra of the Fe film before/after deposition of VOPc….....5

D. XAS/XMCD spectra of VOPc on Fe, Co, and Ni at remanence……...……6

E. References……...……...8

F. Supplementary References in Main Text….……...……...8

A. Details of sample preparation

All the sample preparation was conducted under ultrahigh vacuum conditions (P~4×10^{-8} Pa). A clean Cu(001) surface was prepared from a commercial Cu(001) single crystal by repeated cycles of Ar^+ sputtering (~2 μA, 1 kV) and annealing at 800 K. Low-energy electron diffraction (LEED) observation of the Cu substrate yielded a sharp (1×1) pattern (Figure S1a). The amount of carbon contamination was estimated to be less than 2% by using Auger electron spectroscopy (Figure S1b). A Fe film was prepared on Cu(001) by electron bombardment evaporation. During the evaporation, the substrate was kept at a temperature of ~110 K by using liquid nitrogen. Epitaxial growth of the Fe film was monitored by the reflection high-energy electron diffraction (RHEED) and the thickness was controlled by monitoring the RHEED oscillations (Figure S2a). Similarly, Co and Ni films were prepared using above-mentioned procedure, but the substrate temperature was maintained at room temperature (T~300 K) during the evaporation of Co or Ni. The thickness of the Co and Ni films was estimated to be 3 ML and 4 ML, respectively, from the RHEED oscillations (Figure S2b and c).

Commercial VOPc was purified by sublimation before mounting in a preparation chamber. The VOPc put in a homemade Knudsen cell evaporator was degassed at 450 K for 5 hours and deposited onto the ferromagnetic films at 530 K. During the deposition of VOPc, the pressure was not exceeded 4×10^{-8} Pa. The temperature was monitored by an alumel−chromel (K-type) thermocouple attached to the outside of the bottom of the cell. The molecular density of monolayer was defined as 0.5 molecules/nm^2 and was estimated from the LEED pattern of 1 ML VOPc on Ag(111) [1]. The amount of deposited VOPc was corresponding to 0.9 ML which was estimated using a quartz crystal oscillator and the deposition rate of VOPc was ~0.1 ML/min. The samples were transferred to a measurement chamber without dosing the air and cooled to 5 K without thermal treatment such as annealing.

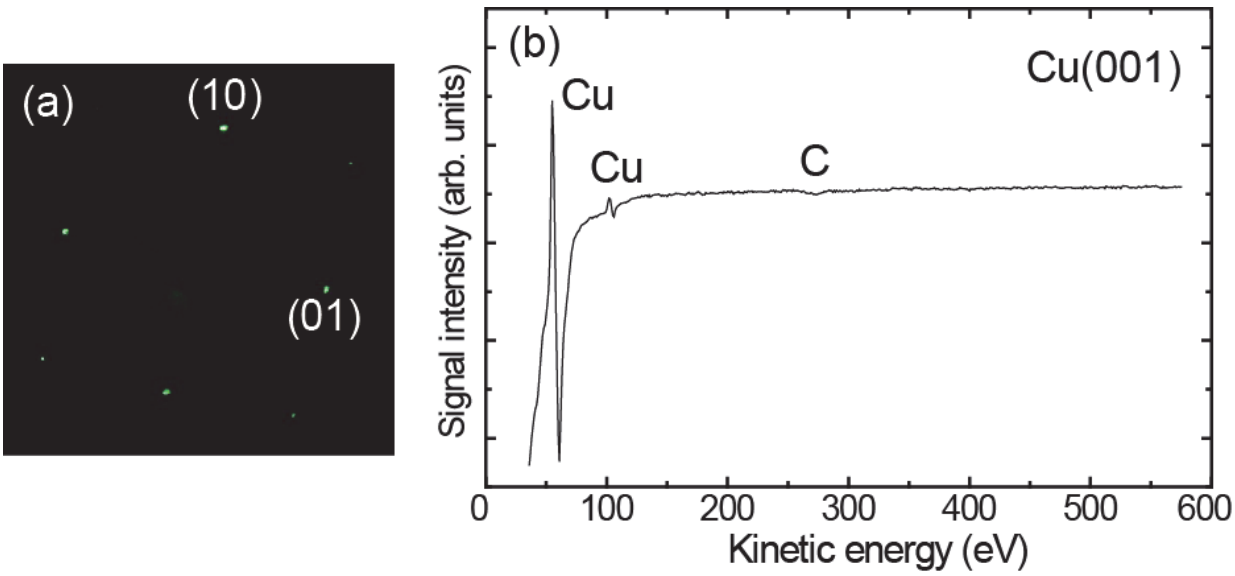

Figure S1. (a) A LEED image (E = 90 eV) and (b) Auger electron spectrum of Cu(001) after the cleaning procedure.

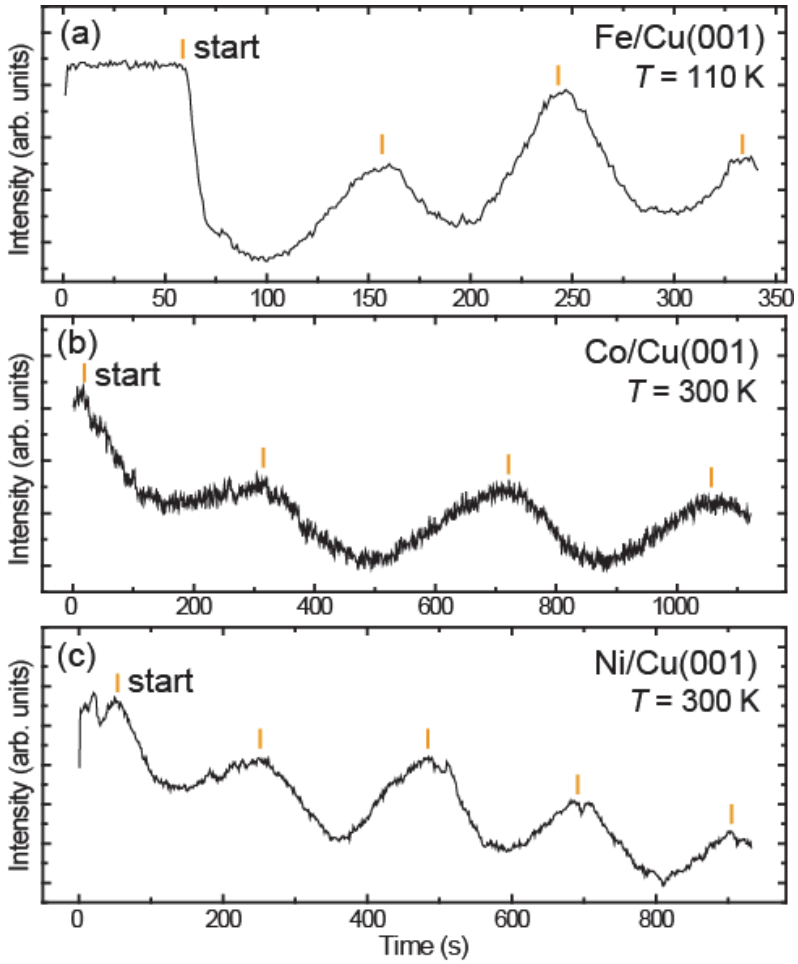

Figure S2. RHEED intensity oscillations on epitaxially grown ferromagnetic (a) Fe, (b) Co, and (c) Ni films.

B. LEED images of VOPc on the ferromagnetic films

LEED measurements were performed for the samples of VOPc deposited onto the ferromagnetic films and the images are shown in Figure S3. A LEED image originated from the Ni/Cu(001) substrate is given to show the [110] direction of the substrate. The LEED pattern of VOPc on the Fe film is not clear, indicating a disorder structure of VOPc. On the other hand, diffused LEED spots were observed in the samples of VOPc on Co and Ni films. This implies that the partially self-assembled structure was formed. The intensity of the diffraction is strong around the <110> directions. Most intense spots are located at both the side of the <110> axes and the angle between the axis and the spot is ~23° in the sample of VOPc on Ni. The circle patterns seen at the central part of LEED images are caused by the lack of long-range order of VOPc.

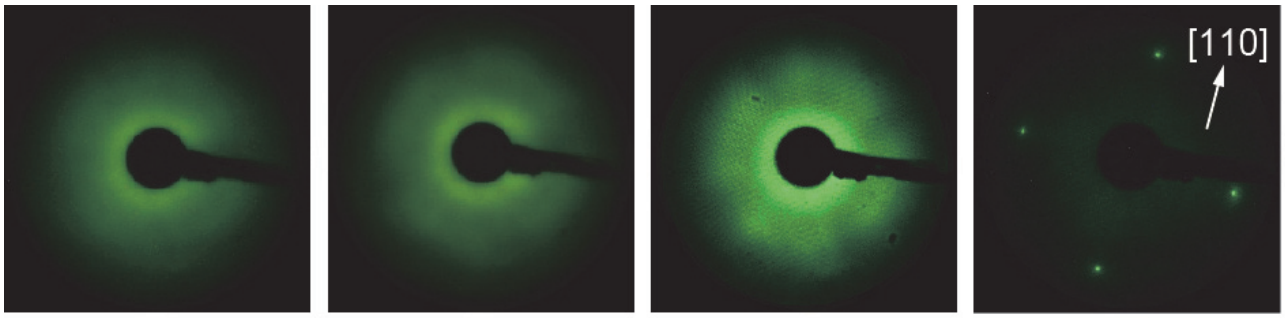

Figure S3. LEED images of 0.9 ML VOPc on (a) Fe, (b) Co, and (c) Ni films taken at the incident electron beam energy of 14 eV. (d) A LEED image of VOPc/Ni/Cu(001) taken at 80 eV. The [110] direction is shown in the image.

C. XAS/XMCD spectra of the Fe film before/after deposition of VOPc

We measured Fe L edge XAS and XMCD spectra of the Fe film before and after deposition of VOPc (Figure S4). There was no significant difference between them under the experimental condition.

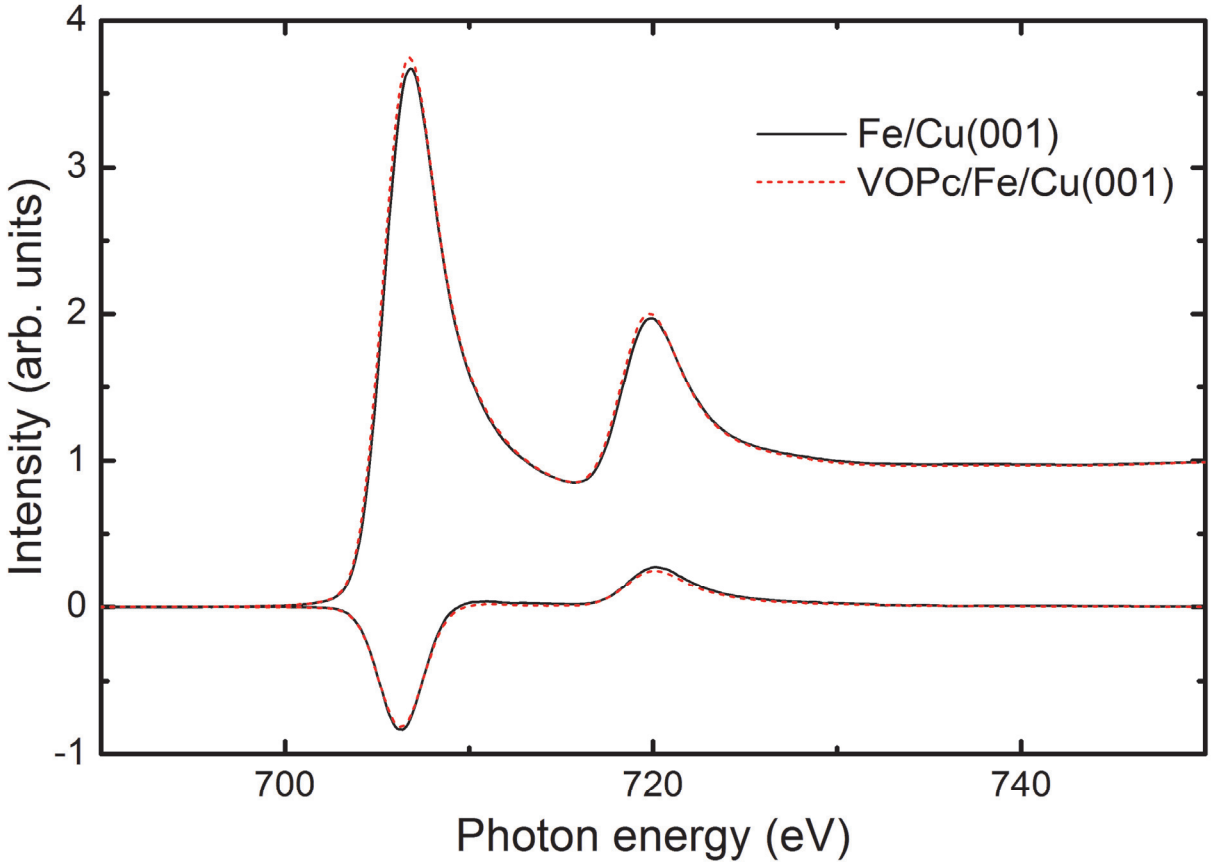

Figure S4. XAS ($\mu^+/2+\mu^-/2$) and XMCD ($\mu^+-\mu^-$) spectra of Fe before (black) and after (red) deposition of VOPc. These spectra were taken at θ = 55°, T = 5 K, and $\mu_0 H$ = 0 T. The energy resolution ($E/\Delta E$) was 1000.

D. XAS/XMCD spectra of VOPc on Fe, Co, and Ni at remanence

Magnetization curves of the ferromagnetic Fe, Co, and Ni films in the samples were shown in Figure S5a, S6a, and S7a, respectively. These magnetization curves were obtained by recording the electron yield with the photon energy fixed at Fe, Co, or Ni L_3 peak top. The data in the vicinity of $\mu_0 H$=0 are omitted due to strong suppression of the electron yield by the Lorentz force. From the differences of the magnetization curves between the normal (θ=0°) and grazing (θ=55°) configurations, it is found the magnetization of the ferromagnetic films are anisotropic and the easy magnetization direction of the Fe (Co, Ni) film is perpendicular (in-plane) to the surface. These magnetic anisotropies of ferromagnetic films are good agreement with those in previous reports [2,3].

XAS and XMCD spectra of VOPc on Fe taken at remanent magnetization are shown in Figure S5b and c. Although no magnetic field was applied to the sample, XMCD signals were obtained for not only the Fe film but also VOPc molecules. This indicates antiferromagnetic coupling of V with Fe. In the case of VOPc on Co, XMCD signals of Co and V were vanished at the 0° configuration while those at 55° configuration were weaken but observed (Figure S6b and c). So, VOPc was antiferromagnetically coupled with Co. In contrast to the cases of VOPc on Fe and Co, no clear XMCD signal at V L edge was observed in the sample of VOPc on Ni although XMCD signal of Ni at 55° was obtained. This means that the magnetic interaction of VOPc with Ni is not effective.

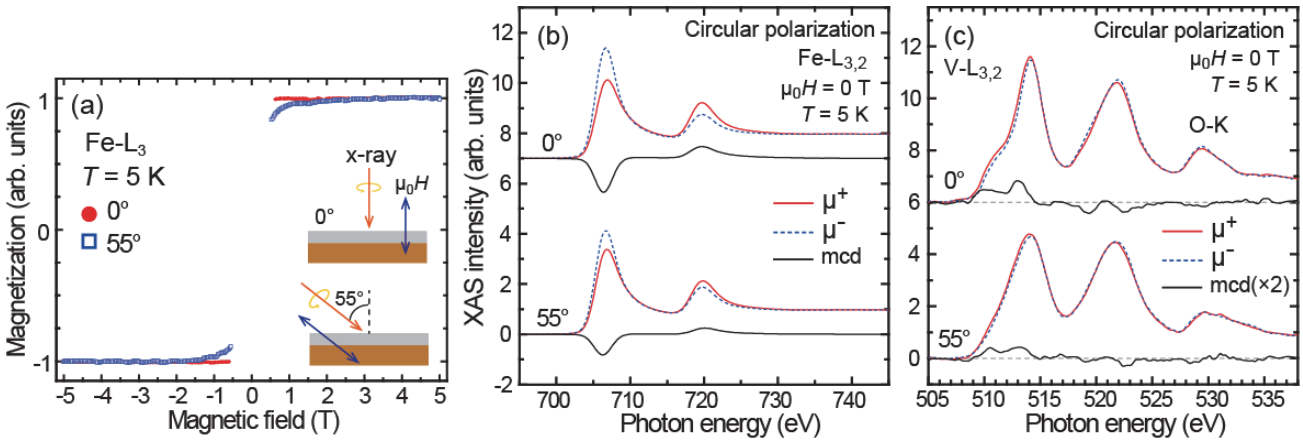

Figure S5. (a) Magnetization curves of the Fe film on Cu(001) taken at 0° (red) and 55° (blue). XAS and XMCD spectra at (b) Fe L edge and (c) V L edge taken at remanence.

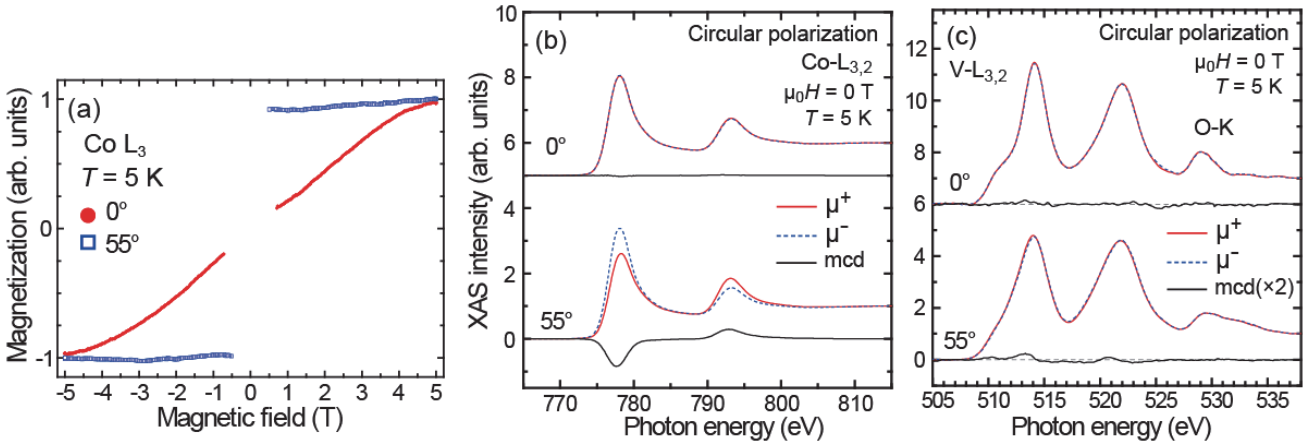

Figure S6. (a) Magnetization curves of the Co film on Cu(001) taken at 0° (red) and 55° (blue). XAS and XMCD spectra at (b) Fe L edge and (c) V L edge taken at remanence.

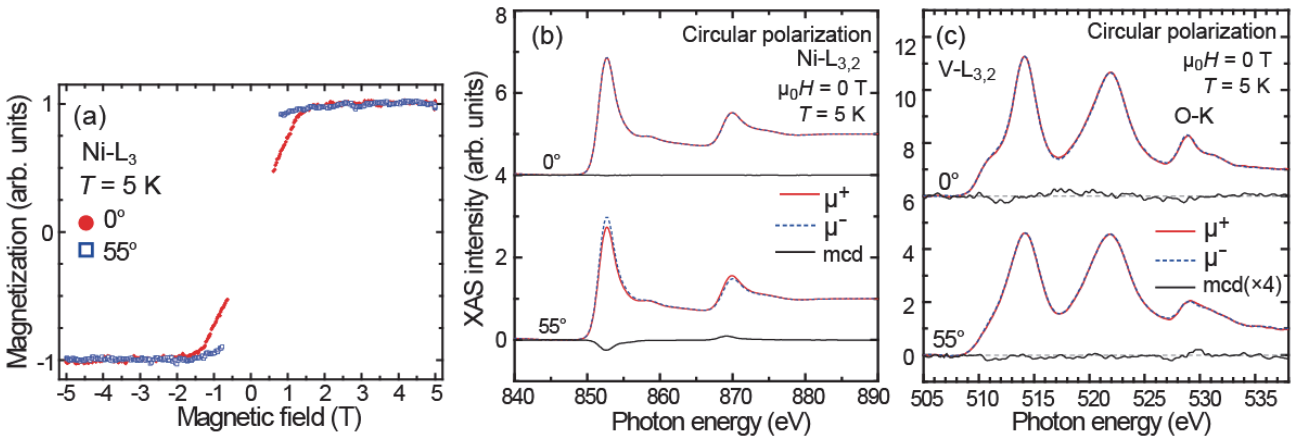

Figure S7. (a) Magnetization curves of the Ni film on Cu(001) taken at 0° (red) and 55° (blue). XAS and XMCD spectra at (b) Fe L edge and (c) V L edge taken at remanence.

E. References

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F. Supplementary References in Main Text

The complete author list for the references in the main text, where the number of authors are more than ten, are given below.

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