Electronic Supplementary Information for "Persistent superconductivity in atomic layer-magnetic molecule van der Waals heterostructures: a comparative study"

Takashi Uchihashi[1*], Shunsuke Yoshizawa[2], Emi Minamitani[3], Satoshi Watanabe[3],
Yasumasa Takagi[4], Toshihiko Yokoyama[4],

[1] International Centre for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan
[2] Surface Characterization Group, Research Center for Advanced Measurement and Characterization, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan
[3] Department of Materials Engineering, the University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[4] Institute for Molecular Science, Myoudaiji Campus, 38 Nishigo-Naka, Myodaiji, Okazaki, Aichi 444-8585, Japan

*email: UCHIHASHI.Takashi@nims.go.jp

XAS/XMCD measurements on the FePc/Si(111)-($\sqrt{7}\times\sqrt{3}$)-In heterostructure

Note: In this section, θ represents the incident angle of X-ray beam, not the coverage as used in the main text of the paper.

XAS at N *K*-edge

Figure S1(A) shows the N *K*-edge XAS spectra obtained for a FePc monolayer on the ($\sqrt{7}\times\sqrt{3}$)-In surface with $\theta = 0°$ and $\theta = 55°$. They exhibit eight peaks similar to those reported for vanadium phthalocyanine[1]. The four peaks on the low- and high-energy sides are attributed to transitions from N 1*s* to π^* and σ^* molecular orbitals, respectively, both of which have *p* orbital characters [2,3]. At $\theta = 0°$ the peaks of π^* orbitals are negligibly small, while those of σ^* orbitals are enhanced. This means that the FePc molecules were adsorbed in the in-plane geometry, because a dipolar transition from 1*s* to p_z-like π^* orbitals is suppressed due to the selection rule when the X-ray beam is in the normal direction (see Fig. S1(B)). As shown in Figs. S1(C) and S1(D), the intensity of each peak is approximately proportional to the molecular coverage.

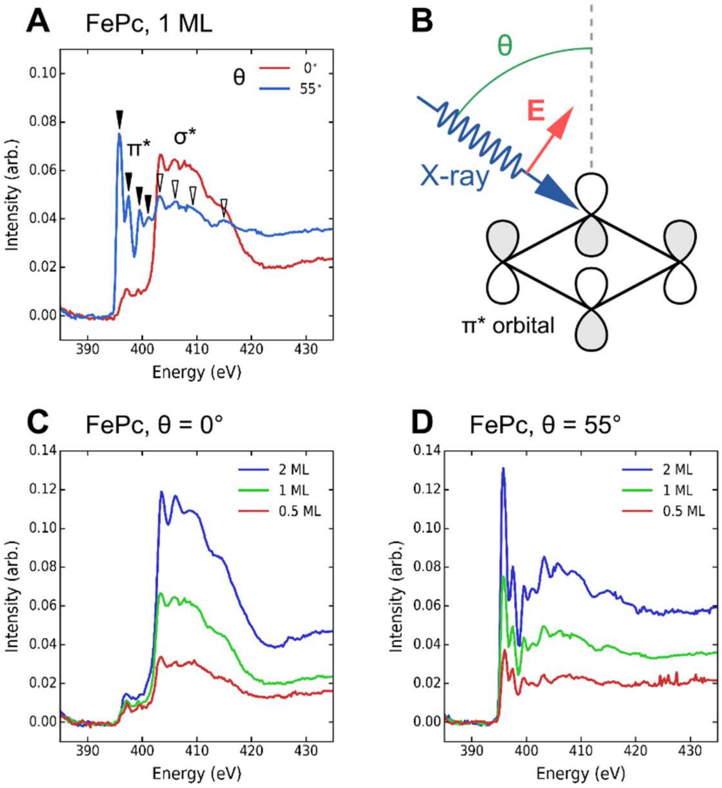

Figure S1 (A) N *K*-edge XAS spectra of FePc monolayers on the ($\sqrt{7}\times\sqrt{3}$)-In surface obtained with $\theta = 0°$ (red) and $\theta = 55°$ (blue). Filled (open) triangles indicate the positions of peaks corresponding to excitations from N 1*s* to π^* (σ^*) molecular orbitals. (B) Schematic illustration for the configuration of the XAS/XMCD measurement of FePc molecules. (C,D) N *K*-edge XAS spectra of FePc at $\theta = 0°$ (C) and $\theta = 55°$ (D) measured at different coverages.

Details of the sum rule analysis

The effective spin magnetic moment $\langle m_S^{\text{eff}}(\theta)\rangle$ is obtained from the XAS data by using the sum rule [4],

$$\langle m_S^{\text{eff}}(\theta)\rangle = -n_h \frac{9p(\theta) - 6q(\theta)}{r(\theta)} \mu_B, \tag{7}$$

where n_h is the number of holes in the d orbitals (assumed to be 4 for FePc) and μ_B is the Bohr magneton. The three functions $p(\theta)$, $q(\theta)$, and $r(\theta)$ are given by

$$p(\theta) = \int_{L3} [I^+(E,\theta) - I^-(E,\theta)]dE, \tag{8}$$

$$q(\theta) = \int_{L3,2} [I^+(E,\theta) - I^-(E,\theta)]dE, \tag{9}$$

$$r(\theta) = \int_{L3,2} [I^+(E,\theta) + I^-(E,\theta) + I^0(E,\theta)]dE\,. \tag{10}$$

Here, $I^+(E,\theta)$ and $I^-(E,\theta)$ are the XAS intensities measured with the photon helicity parallel and antiparallel to the applied magnetic field, respectively. $I^0(E,\theta)$ corresponds to the XAS intensity measured with a linear photon polarization parallel to the magnetization, which is approximated as described later. Note that $r(\theta)$ is an isotropic term and thus is independent of θ in principle.

The quantity $\langle m_S^{\text{eff}}(\theta)\rangle$ is composed of two terms:

$$\langle m_S^{\text{eff}}(\theta)\rangle = 2\langle S\rangle + 7\langle T(\theta)\rangle, \tag{11}$$

where $\langle S\rangle$ is the isotropic spin component and $\langle T(\theta)\rangle$ is the intra-atomic dipolar moment. The latter reflects the anisotropic distribution of spins within an atom and, in a system with a symmetry higher than D_{2h}, cancels out at the 'magic angle' of $\theta = 54.7°$[5]. This cancellation of the $\langle T(\theta)\rangle$ term at the magic angle has been demonstrated previously for FePc thin films on noble metals[6,7]. For the discussions on the spin magnetic moments in the main text, we used $\theta = 55°$ to minimise the contribution from the $\langle T(\theta)\rangle$ term.

The $r(\theta)$ term was evaluated for FePc as follows. Since the angular dependence of $I^+(E,\theta) + I^-(E,\theta)$ is small for FePc, I^0 can be approximated by $I^0 = (I^+ + I^-)/2$. Then, $r(\theta)$ is given by

$$r(\theta) = \frac{3}{2}\int_{L3,2} [I^+(E,\theta) + I^-(E,\theta)]dE. \tag{13}$$

Figure S2(A) shows the XAS spectrum of a FePc monolayer. An atomic background was simulated by integrating two Voigt functions placed at the $L_{3,2}$ peaks and was subtracted from the XAS spectrum before applying the sum-rule. The result of XAS integration is also plotted by the red curve in Figs. S2(A) where the small circles indicate the upper bound of the $r(\theta)$ integration range. Figure S2(B) shows the XMCD spectrum, $I^+(E,55°) - I^-(E,55°)$, and its integral evaluated for FePc. The integration ranges for $p(\theta)$ and $q(\theta)$ are indicated by the small squares and triangles, respectively.

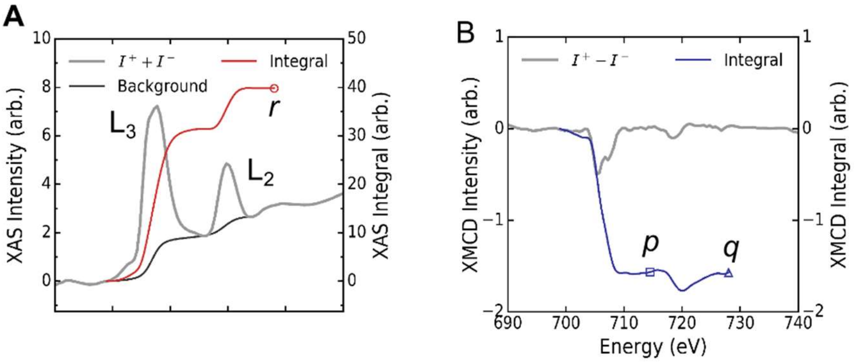

Figure S2 (A) XAS spectrum ($I^+ + I^-$) of FePc at $\theta = 55°$ (gray curves). The atomic backgrounds are plotted in thin black curves. The integrals of XAS spectra are plotted in red and the points defining the $r(\theta)$ integration is marked by circles. (B) XMCD spectra ($I^+ - I^-$) of FePc. The points defining the integrations for $p(\theta)$ and $q(\theta)$ are marked by squares and triangles, respectively.

References

1 Eguchi, K., Nakagawa, T., Takagi, Y. & Yokoyama, T. Direct Synthesis of Vanadium Phthalocyanine and Its Electronic and Magnetic States in Monolayers and Multilayers on Ag(111). *J. Phys. Chem. C* **119**, 9805-9815 (2015).

2 Koch, E. E., Jugnet, Y. & Himpsel, F. J. High-resolution soft x-ray excitation spectra of 3d-metal phthalocyanines. *Chem. Phys. Lett.* **116**, 7-11 (1985).

3 Rocco, M. L. M., Frank, K. H., Yannoulis, P. & Koch, E. E. Unoccupied electronic structure of phthalocyanine films. *The Journal of Chemical Physics* **93**, 6859-6864 (1990).

4 Carra, P., Thole, B. T., Altarelli, M. & Wang, X. X-ray circular dichroism and local magnetic fields. *Phys. Rev. Lett.* **70**, 694-697 (1993).

5 Stöhr, J. & König, H. Determination of Spin- and Orbital-Moment Anisotropies in Transition Metals by Angle-Dependent X-Ray Magnetic Circular Dichroism. *Phys. Rev. Lett.* **75**, 3748-3751 (1995).

6 Bartolomé, J. *et al.* Highly unquenched orbital moment in textured Fe-phthalocyanine thin films. *Phys. Rev. B* **81**, 195405 (2010).

7 Stepanow, S. *et al.* Giant spin and orbital moment anisotropies of a Cu-phthalocyanine monolayer. *Phys. Rev. B* **82**, 014405 (2010).