Vacuum Synthesis of Magnetic Aluminum Phthalocyanine on Au(111)

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1 Experimental details

Measurements were performed with an ultrahigh vacuum scanning tunneling microscope (UNISOKU USM-1300-^{3}He), at temperatures of 4.3 K and 0.5 K with a base pressure of 10^{-9} Pa, and magnetic fields up to 11 T. Au(111) surfaces were prepared by cycles of Argon ion sputtering and annealing. Metal free phthalocyanine (H_2Pc) molecules and Al atoms were thermally sublimated from two Knudsen cells, while ClAlPc were deposited using a Ta boat. The substrate was kept at room temperature during growth.

2 STM images and Kondo spectra of four other AlPc molecules

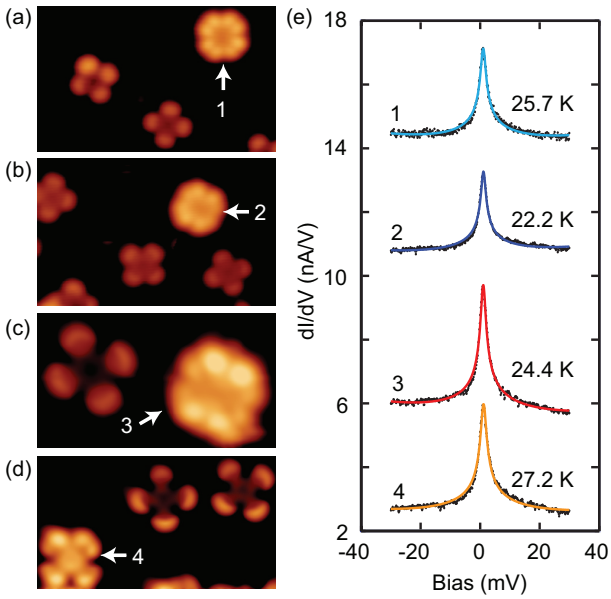

Fig. S1 (a-d) STM images recorded after co-deposition of H_2Pc and Al on Au(111). The AlPc molecules are marked by white arrows. Their lobes exhibit substructures. (e) DI/dV spectra of the marked AlPc molecules. Their Kondo temperature were obtained by fitting with Frota function and marked on the right of the spectra. Spectra 1-3 are shifted vertically. The spectra broadening induced by temperature is ignored during the fitting process. That is why the fitted Kondo temperatures here at 4.0 K are higher than that measured at 0.4 K. Image parameters are: (a) 9.6 nm × 5.8 nm, -1 V, 19 pA; (b) 9.8 nm × 6.1 nm, -1 V, 20 pA; (c) 5.2 nm × 2.9 nm, -0.06 V, 19 pA; (d) 7.2 nm × 4.0 nm, -0.1 V, 20 pA.

3 The details of Spectra fitting

Frota function was used for modeling the Kondo spectra of AlPc. A parabolic function was added as background.

$$F(\varepsilon) \propto \mathrm{Im}[\frac{1}{i}\sqrt{\frac{i\Gamma_F}{i\Gamma_F+\varepsilon}}] \tag{1}$$

Its half width half maximum is $\Gamma = 2.542\Gamma_F$. As for the spectra taken under magnetic field in Figure 2b, two Frota functions shifted by Zeeman energy Δ and a pair of step functions Z were applied. Its total fit function is

$$D(\varepsilon) = a[cF(\varepsilon+\Delta)+F(\varepsilon-\Delta)]+b[Z(\Delta+\varepsilon)+Z(\Delta-\varepsilon)] \tag{2}$$

, where $Z(\Delta\pm\varepsilon) = \frac{exp(\frac{\Delta\pm\varepsilon}{k_BT})(\frac{\Delta\pm\varepsilon}{k_BT}-1)}{(exp(\frac{\Delta\pm\varepsilon}{k_BT})-1)^2}$, and a, b, c are fitting parameters.

4 XPS experimental results

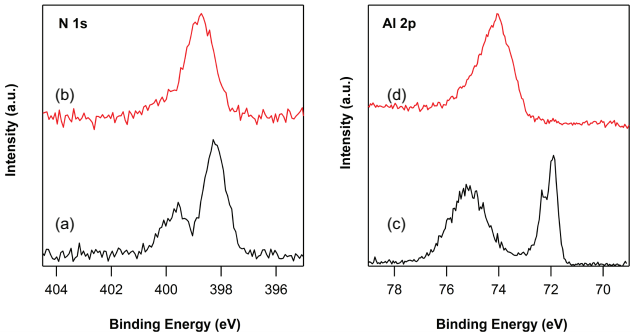

Fig. S2 N 1s and Al 2p X-ray photoelectron spectra of the metalation of a H_2Pc monolayer on Au(111) with Al at room temperature. (a) N 1s spectrum ($h\nu$ = 650 eV) of the H_2Pc monolayer (prepared by multilayer desorption) before metalation. The two components are assigned to aminic nitrogen -NH-(399.6 eV) and iminic nitrogen -N= (398.2 eV). (b) N 1s spectrum ($h\nu$ = 650 eV) of the H_2Pc monolayer after metalation with Al at room temperature. The single peak at 398.7 eV is attributed to -N-Al-. (c) Reference Al 2p spectrum of an Al foil with a surface oxide layer, showing the peaks of Al(0) at 72.0 eV and of Al(III) at 75.3 eV ($h\nu$ = 2500 eV). (d) Al 2p spectrum after deposition of Al onto the H_2Pc monolayer on Au(111) ($h\nu$ = 200 eV).

5 Manganese phthalocyanine and copper phthalocyanine on Ag(001)

A Ag(001) surface was cleaned by repeated cycles of Ar^+ sputtering and annealing. Manganese phthalocyanine (MnPc) and copper phthalocyanine (CuPc) were sublimated from standard Knudsen cells and deposited onto the Ag(001) surface kept at room temperature. These molecules can conveniently be discriminated by the different appearances of their central ions. As shown in Figure S3, MnPc exhibits a protrusion while CuPc shows a depression at the molecular center.[1] The lobes of CuPc molecules display substructures similar to that of AlPc. Interestingly a Kondo resonance is also observed for these lobes as the result of charge transfer from the substrate into the molecular π orbitals.[2] In contrast, the isoindol groups of MnPc appear featureless and no Kondo resonance is discernible. It seems that the substructures of lobes in STM image are due to the unpaired electron.

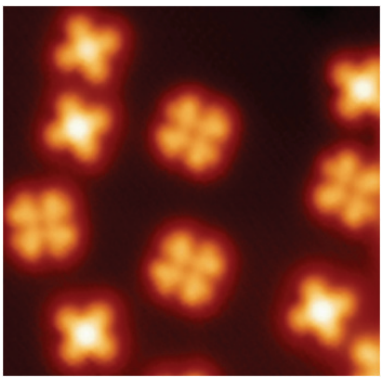

Fig. S3 Constant-current STM image of MnPc and CuPc on Ag(001) (−50 mV, 20 pA, 8 × 8 nm^2).

6 DFT calculation of an isolated AlPc molecule

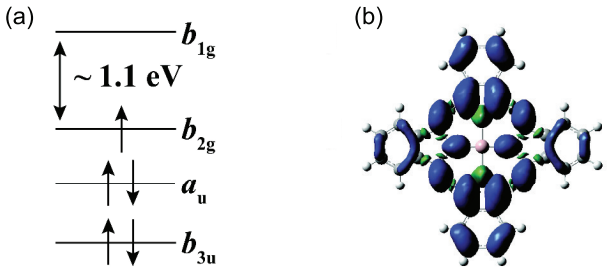

Fig. S4 Results of calculation for an isolated AlPc molecule at the UB3LYP/6-311+G(d,p) level. (a) Energy diagram of frontier molecular orbitals, the same data as Fig. 3a but redrawn to stress the single occupation of the b_{2g} orbital. (b) Spin density of AlPc. Blue and green indicate spin up and down.

References

1 J. Kügel, M. Karolak, J. Senkpiel, P.-J. Hsu, G. Sangiovanni and M. Bode, *Nano Letters*, 2014, **14**, 3895.
2 A. Mugarza, C. Krull, R. Robles, S. Stepanow, G. Ceballos and P. Gambardella, *Nat. Commun.*, 2011, **2**, 490.