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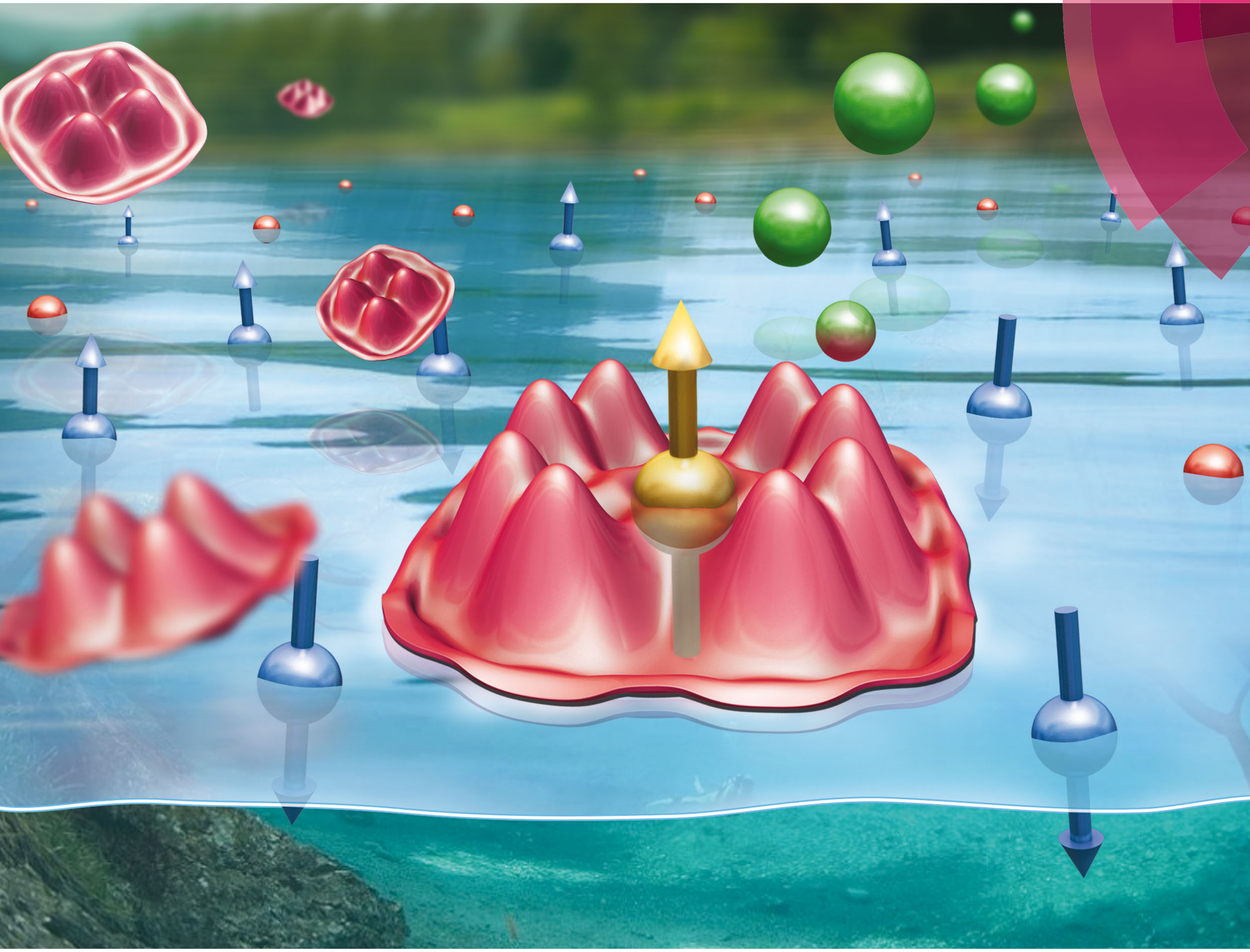

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# Vacuum synthesis of magnetic aluminum phthalocyanine on Au(111)†

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**Air-unstable magnetic aluminum phthalocyanine (AlPc) molecules are prepared by an on-surface metalation reaction of phthalocyanine with aluminum (Al) atoms on Au(111) in ultrahigh vacuum. Experiments and density functional theory calculations show that an unpaired spin is located on the conjugated isoindole lobes of the molecule rather than at the Al position.**

Magnetic molecules have attracted considerable attention due to their fascinating properties and potential applications in molecular spintronics.[1] Scanning tunneling microscopy (STM)[2–4] is a powerful tool to study the magnetic properties of single molecules by spectroscopy of Kondo resonance, inelastic spin transitions, and spin polarized tunneling.[5–14] In this context, small paramagnetic molecules (NO and $O_2$),[15,16] neutral organic radicals,[17,18] charged organic molecules,[19,20] and organometallic complexes[21–24] have been intensely investigated.

Metal phthalocyanine molecules are particularly versatile as the central nitrogen atoms of their macrocycles can coordinatively bond magnetic ions with various spins (*e.g.*, MPc with M = Mn,[25,26] Fe,[27] Co,[28] and Cu[29]). For these molecules, metal ions are stable in the +2 oxidation state and they could be synthesized in solution. When reactive metals tend to stabilize in other oxidation states such as K (+1), Al (+3), Tb (+3), and Ti (+4), simple MPc molecules are unstable in air because the Pc ring prefers to form a −2 state. Molecules can be stabilized by axial bonding of the metal ion to another atom (*e.g.*, ClAlPc) or another Pc ring (*e.g.*, $TbPc_2$), which changes the molecular properties. For example, $TbPc_2$ shows single molecule magnet behavior.[30] It is interesting and important to synthesize these pristine reactive MPc molecules, like AlPc, and study their particular properties. The newly developed vacuum synthesis method provides this possibility.[31–38]

Here, we present tunneling microscopy and spectroscopy data from magnetic AlPc (Fig. 1b) which was prepared in ultrahigh vacuum using on-surface metalation from $H_2Pc$ (Fig. 1a). It turns out that AlPc remains paramagnetic on Au(111) with its spin density distributed over the isoindole lobes. Axial bonding of Cl to the Al center suppresses this spin.

Fig. 1c shows an STM image of the Au(111) surface with its typical $(\sqrt{3} \times 22)$ reconstruction. After depositing a small amount of Al atoms on Au(111), the regular herringbone structure is highly distorted (Fig. 1d), possibly due to Al intermixing.[39]

$H_2Pc$ molecules deposited on pristine Au(111) at low coverages (Fig. 1e) remain isolated from each other. $H_2Pc$ adsorbs on the surface with the molecular conjugate plane parallel to Au(111), to maximize the interaction between π states and surface electrons.[40,41] Four bright protrusions in the STM image correspond to molecular isoindol groups, which is similar to other phthalocyanines on metal surfaces.[36,41] The molecules are stable enough to enable imaging at low temperature (4.3 K).

Upon depositing $H_2Pc$ molecules and Al atoms on the substrate sequentially, some of the phthalocyanine molecules are altered. The top-left molecule in Fig. 1f displays the characteristic structure of $H_2Pc$ with four featureless lobes. Its STM image and d$I$/d$V$ spectrum match the data from $H_2Pc$ deposited alone.[42] The isoindol groups of the bottom-right molecule, however, exhibit interesting substructures (see the ESI†). This suggests that a different type of phthalocyanine molecule formed. Previously, metalation of free-base porphyrins with Co, Ni, Cu, Zn, Ce and phthalocyanines with Fe, Cu atoms to form MTPP[31–33,37,38] and MPc[34,35,43] molecules was reported.

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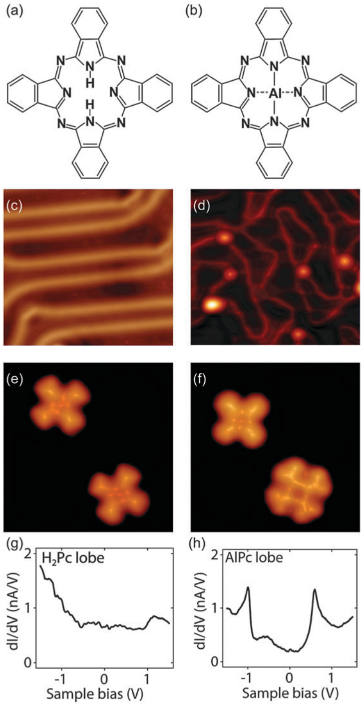

Fig. 1 Schematic molecular structures of (a) $H_2Pc$ and (b) AlPc. (c–f) display constant-current topographs in a pseudo three dimensional mode. (c) Pristine $\sqrt{3} \times 22$-reconstructed Au(111) surface (+1.0 V, 40 pA, (21 nm)$^2$). (d) After deposition of small amounts of Al, the reconstruction is disturbed and Al clusters are observed at kinks of the dislocation lines (−1.0 V, 14 pA, (15 nm)$^2$). (e) Two $H_2Pc$ molecules (−1.0 V, 20 pA, (5.2 nm)$^2$). (f) Two molecules after co-deposition of $H_2Pc$ and Al (−50 mV, 20 pA, (5.3 nm)$^2$). The top-left and bottom-right molecules are $H_2Pc$ and AlPc, respectively. The lobes of AlPc appear split, different from those of $H_2Pc$. (g and h) d$I$/d$V$ spectra recorded above the lobes of $H_2Pc$ and AlPc. Parameters before opening feedback: −1.5 V, 100 pA.

It therefore appears likely that the newly formed molecule is AlPc. Experimental XPS data also indicate the metalation of $H_2Pc$ with Al on Au(111) (ESI†). The reaction is selective insofar as Al reacts only with the nitrogens in the center causing dissociation of the N–H bonds, whereas the C–H, C–C and C–N bonds are not affected. Experimental and theoretical evidence for this interpretation is presented next.

Consistent with a previous observation,[42] the differential conductance (d$I$/d$V$) spectrum taken at a lobe of $H_2Pc$ (Fig. 1g) is rather featureless in the voltage range from −1.5 to 1.5 V. A broadened peak centered at 1.2 V is attributed to the lowest unoccupied molecular orbital (LUMO) based on the results of other phthalocyanine molecules.[44,45] By contrast, the spectrum of the supposed AlPc molecule (Fig. 1h) exhibits pronounced peaks. The peaks centered around −0.6 and 0.6 V are attributed to a singly occupied molecular orbital (SOMO) and a singly unoccupied molecular orbital (SUMO), respectively. The Coulomb repulsion separating these states is ≈1.2 eV, similar to values from other macrocycles with conjugated π-orbitals.[46]

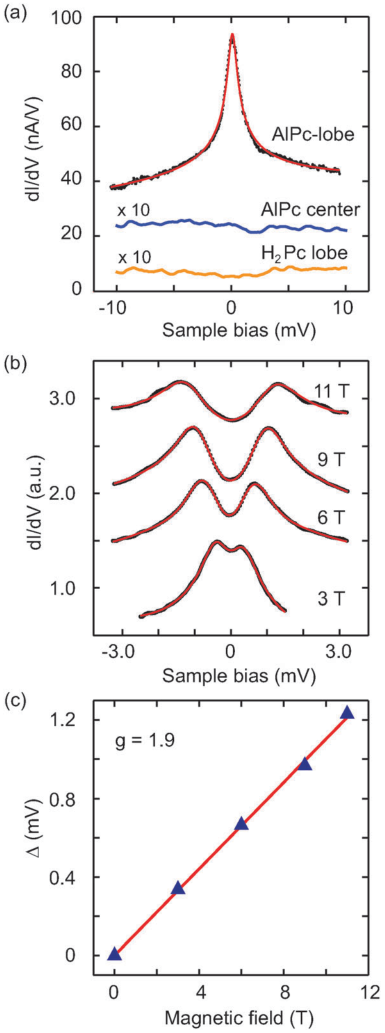

Fig. 2 Differential conductance spectra (d$I$/d$V$) of AlPc and $H_2Pc$ on Au(111). (a) Spectra taken with the tip placed above a lobe of AlPc (black dots), the Al center of AlPc (blue, shifted 10 nA $V^{-1}$ according to the black one), and a lobe of $H_2Pc$ (yellow, shifted 20 nA $V^{-1}$ according to the black one) at a temperature $T$ = 0.5 K. The spectra are vertically shifted for clarity. Fits with Frota (red curve) lineshape reproduce the data well. Feedback was opened at 30 mV and 1 nA. (b) Variation of spectra of an AlPc lobe with the magnetic field along the surface normal ($T$ = 0.5 K, feedback opened at 10 mV and 1 nA). An increasing splitting of the Kondo resonance peak is observed. (c) Zeeman energy *vs.* field strength. Points were extracted from the spectra in (b). A linear fit, constrained to zero splitting at $B$ = 0 yields a Landé $g$ = 1.9.

A more detailed spectrum around zero bias (Fig. 2a) recorded from the lobes of AlPc reveals a strong resonance in the differential conductance. No indication of this resonance is discernible at the center of the molecule or on the lobes of $H_2Pc$. We attribute this peak to a Kondo resonance,[5,6,12,14,17,19] which results from the screening of a localized spin by a delocalized electron gas. Indeed, the AlPc molecule has one unpaired electron (see calculated results below). The moderate strong molecule–surface interaction does not quench the molecular spin state and also leads to the detectable Kondo resonance. The spectrum may be modeled using a Frota function (Fig. 2a): $D(\varepsilon) \propto \mathrm{Im}\left(\frac{1}{i}\sqrt{\frac{i\Gamma_\mathrm{F}}{\varepsilon + i\Gamma_\mathrm{F}}}\right)$.[25,47] From the fit we obtain a half width at half maximum $\Gamma \approx 1.2$ meV corresponding to a Kondo temperature $T_\mathrm{K} = \Gamma/k_\mathrm{B} \approx 14$ K.

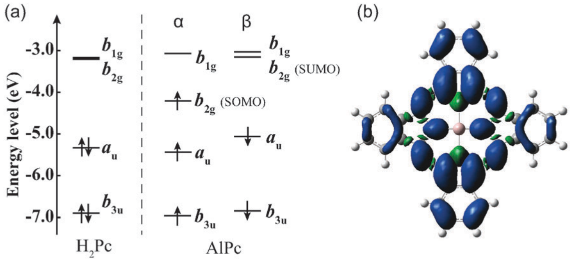

Fig. 3 Results of calculations for the isolated $H_2Pc$ and AlPc molecules at the UB3LYP/6-311+G(d,p) level. (a) Energy diagram of frontier molecular orbitals. (b) Spin density of AlPc. Blue and green indicate spin up and down.

To exclude alternative interpretations of the resonance its dependance on a magnetic field along the surface normal was investigated. Fig. 2b shows the spectra from AlPc lobes which are recorded at various field strengths. We find a splitting of the Kondo peak. To quantify this effect, we determined the peak splitting by fitting the data using Frota functions (Fig. 2c).[48] As expected, a linear increase of the splitting with the magnetic field strength is found with a Landé *g*-factor of ≈1.9.

The geometric and electronic structures of an isolated $H_2Pc$ and AlPc molecule were calculated by employing density functional theory (DFT) at the unrestricted B3LYP/6-311+G(d,p) level using the Gaussian09 code. The energy diagram of the calculated frontier molecular orbitals is shown in Fig. 3a. The HOMO of $H_2Pc$ is doubly occupied which explains the absence of Kondo resonance in the experiments. The optimized AlPc molecule is planar with $D_{2h}$ symmetry, but the difference between the two types of Al–N bond lengths (1.927 Å and 1.918 Å) is very small. The ground state of AlPc is a doublet where the SOMO and SUMO are both in a π* state with $b_{2g}$ symmetry and their energy difference is ≈1.1 eV. All molecular orbitals at energies below the SOMO are doubly occupied, implying that the spin density of the molecule (Fig. 3b) is mainly located on the lobes of the Pc ring. This is consistent with the experimental observation.

The DFT calculations in ref. 49 show that all molecular orbitals become doubly occupied when a Cl atom axially binds to Al in chlorinated AlPc (ClAlPc). This implies that Kondo resonance should not occur for ClAlPc. To test this expectation, ClAlPc was deposited on Au(111). In STM topographs (Fig. 4a) the molecule appears similar to tin phthalocyanine, and shows two distinct images.[41] The one with a protrusion corresponds to the configuration with the central Cl atom pointing upward (Cl-up).[49–51] The other one with a depression corresponds to the opposite case, with Cl pointing downward (Cl-down). The high resolution d*I*/d*V* spectra show no signature of a Kondo resonance thus confirming the scenario outlined above.

In summary, AlPc, which is unstable under ambient conditions, was prepared in ultrahigh vacuum by co-depositing $H_2Pc$ and Al atoms on Au(111). Scanning tunneling spectroscopy revealed a Kondo effect at the conjugated isoindole lobes. DFT calculations of the isolated molecule also showed that the spin of the molecule is distributed over these lobes. In contrast, most other reported free Pc or porphyrin derivatives show magnetic properties at metal sites of molecules. These results demonstrate the success of the vacuum synthesis of an air-unstable magnetic molecule.

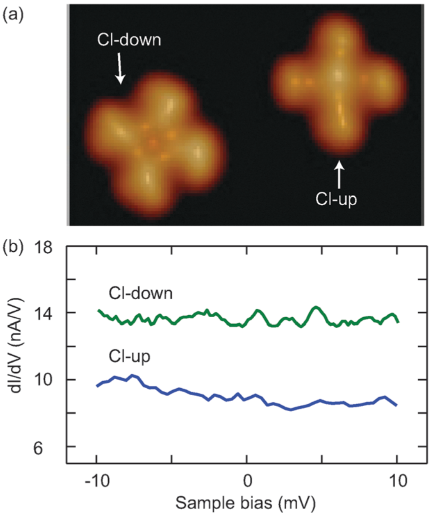

Fig. 4 (a) STM topograph of ClAlPc (100 mV, 100 pA, 5.0 nm × 3.2 nm). (b) d*I*/d*V* spectra of a lobe of ClAlPc. Blue: Cl-up (set point: 50 mV, 300 pA), green: Cl-down (set point: 50 mV, 1 nA). The Cl-down data have been offset for clarity.

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