

In-situ growth of gadolinium phthalocyaninato sandwich complexes on the Ag(111) surface

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We report a low-temperature scanning tunneling microscopy investigation of the in-situ growth of gadolinium phthalocyaninato complexes by co-depositing free-base phthalocyanines and gadolinium atoms on a smooth Ag(111) substrate. A careful control of the stoichiometry allows the expression of a reticular supramolecular architecture composed of irregularly distributed $Gd_{x-1}(Pc)_x$ complexes, $x=2-5$, thus paving new avenues for surface-confined columnar growth.

1. Introduction

Porphyrinoid compounds such as porphyrins and phthalocyanines are functional pigments that have attracted much interest in the last decades due to their importance in biology and technology.^[1] Specifically, phthalocyanines (Pcs) are attractive synthetic molecules for nanotechnology^[2-5] presenting an appealing variety of functional properties in pigments, organic solar cells and optoelectronics.^[6] In the last decade, scanning tunneling microscopy (STM) as well as scanning tunneling spectroscopy (STS) techniques have facilitated the study and characterization with atomic-scale precision of the surface assembly and electronic properties of such compounds.^[7-15]

Contemporarily, the successful synthesis of phthalocyanine sandwich-type double and triple-decker lanthanide complexes reveals distinctive features that cannot be achieved for their non-sandwich analogues, *i.e.*, single-molecule magnetism and axial molecular rotation. On one hand, rare-earth metal atoms promote octa-coordinated sandwich-type complexes^[16-21] that have been recently under the spotlight due to the large magnetic moment and anisotropy^[22,23] of the lanthanide elements, which results in the expression of single molecular magnetism,^[24-29] thus with great potential for organic field-effect transistors,^[30] molecular magnets,^[26] chemical sensors and liquid crystals,^[31] and single-molecule qu-bits. Steered by these functionalities, surface science studies have addressed the sublimation, self-assembly, electronic and magnetic properties of such compounds when deposited on surfaces.^[17,22,23,32-39] On the

other hand, surface-confined multi-decker species have revealed their capability to be used as axial molecular rotors,^[40–43] while simultaneously introducing columnar growth on surfaces, though limited to triple-deckers.^[18]

In this work, we demonstrate the formation of homoleptic gadolinium phthalocyaninato complexes, up to stacked penta(phthalocyaninato) species, on a smooth Ag(111) substrate under ultra-high-vacuum (UHV) conditions.

2. Results and Discussion

Figure 1a shows a large-scale high-resolution STM image after deposition of 0.02 ML of Gd atoms onto a precursor multilayer of phthalocyanine species and subsequent annealing treatment to 550 K on the Ag(111) substrate. Herein, three molecular layers of different apparent heights are recognized. A detailed analysis of the first-layer reveals four-lobed species attributed to 2H-Pc molecular entities with a two-fold symmetry, D_1 axis deviating by 3° and from the dense-packed crystallographic directions of the Ag(111) substrate (Figure 1b and atomistic model in Figure 1d). Figure 1c shows the coexistence of 2H-Pc species with individual eight-fold molecular species or small patches thereof, with apparent heights of ~ 2.02 Å relative to the neighboring 2H-Pc first-layer (cf. Figure S11). Since these higher species could not be removed by voltage pulses or tip-assisted lateral manipulation procedures, they are assigned to $Gd(Pc)_2$ complexes as depicted in the atomistic model of Figure 1e. Furthermore, additional third-layer molecular species with an apparent height of ~ 4.8 Å respect to adjacent 2H-Pc first-layer and contained within packed $Gd(Pc)_2$ islands are occasionally observed (cf. Figure S11). Based on their apparent height and their robustness to STM manipulation, we attribute these third-layer structures to $Gd_2(Pc)_3$ complexes. Importantly, we performed control experiments by depositing on pristine Ag(111) a multilayer of Pc species followed by annealing at 550 K, which afforded the formation of a monolayer of Pc, without the presence of any other species, thus reinforcing our argumentation. Furthermore, our investigations are in agreement with complementary lanthanide-based porphyrinoid double- and triple-decker complexes on different substrates as YPC_2 on Au(111),^[19] $TbPc_2$ on Cu(111)^[22] or $Ce(TPP)_2$ / $Ce_2(TPP)_3$ on Ag(111)^[18] where closely related apparent heights for such systems are presented. Importantly, a related protocol employing 2H-TPP and Ce resulted in the formation of $Ce(TPP)_2$ and $Ce_2(TPP)_3$ species.

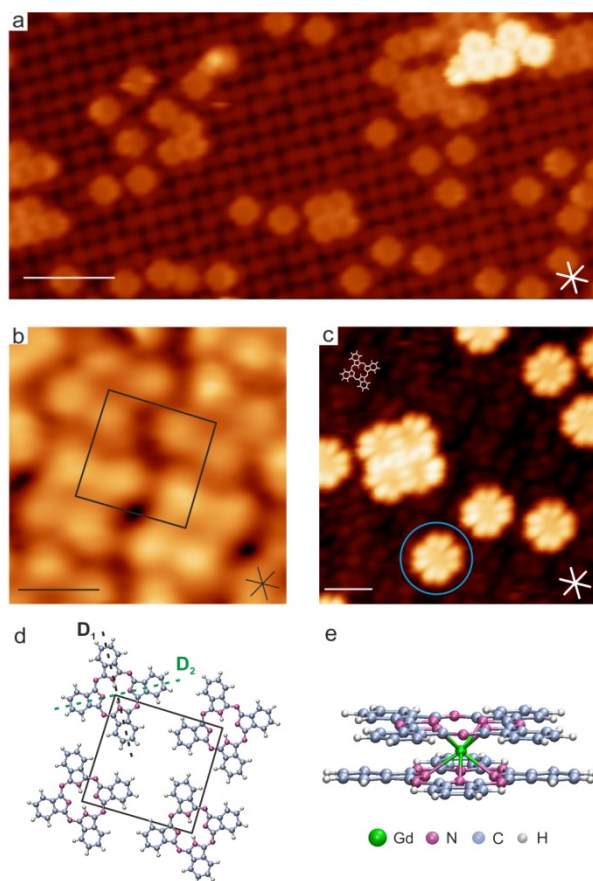


Figure 1. 2H-Pc layer and gadolinium phthalocyaninato sandwich complexes on the Ag(111) surface. (a) Large-scale high-resolution STM image of the first-, second- and third-layer species observed on the Ag(111) substrate. ($V_b = 2$ V, $I = 50$ pA and scale bar: 6 nm). (b) High-resolution STM image that shows the two-fold symmetric 2H-Pc species. ($V_b = -0.8$ V, $I = 80$ pA). (c) Zoom-in high-resolution STM image of (a) highlighting the eight-lobed second-layer structures ($\text{Gd}(\text{Pc})_2$). Atomistic model in white represents a 2H-Pc molecule and its orientation respect to the Ag(111) surface. Blue circle highlights an individual $\text{Gd}(\text{Pc})_2$ species. ($V_b = -1$ V, $I = 100$ pA and scale bar: 2 nm). (d) Atomistic model of (b) that shows the molecular orientation of the 2H-Pc species on the silver substrate. The dashed lines represent the D_1 and D_2 molecular symmetry axes, with D_1 deviating 3° with respect to the close-packed directions of the substrate (indicated by stars in (a-c)). (e) Atomistic model of a $\text{Gd}(\text{Pc})_2$ species. Gd, N, C and H atoms are shown in green, fuchsia, purple and white respectively.

Figure 2a shows high-resolution data with recognition of intramolecular features of $\text{Gd}(\text{Pc})_2$ and $\text{Gd}_2(\text{Pc})_3$ species, where the molecular orbitals of the topmost Pc ligands are observed. Herein, a weak interaction of the upper Pc and the Ag(111) substrate is expected due to the presence of the Gd atom and the lower Pc species. Figures 2b-d present a detailed analysis of the $\text{Gd}_{x-1}(\text{Pc})_x$ ($x = 2,3$) complexes introduced in Figure 1. By assuming that all phthalocyanines in contact with the surface have the same orientation, the relative orientation of the distinct phthalocyanines in the multi-decker species can be estimated. Topmost Pc species in $\text{Gd}(\text{Pc})_2$ complexes present a molecular axis A_1 aligned with its isoindole groups along the four pairs of bright spots while the axis of lower Pc moieties (A_2) is rotated by $40^\circ \pm 5^\circ$ with respect to the topmost Pc species. Remarkably, the rotation of the upper Pc with respect to the lower one is only $3^\circ \pm 9^\circ$ for $\text{Gd}_2(\text{Pc})_3$ complexes. We tentatively attribute these molecular rotations to the reduction of the molecular steric hindrance between Pc species coordinated via

Gd atoms. Importantly, rotation of the upper Pc with respect to the bottom ones could not be induced by lateral manipulation procedures.

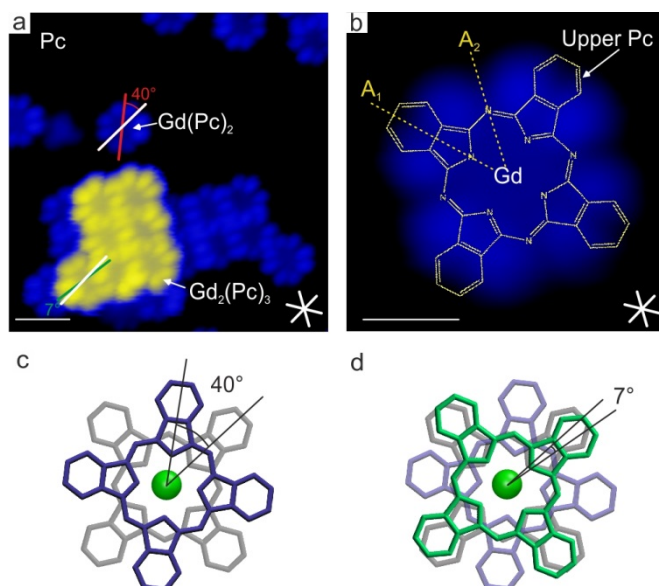


Figure 2. Molecular orientation of gadolinium phthalocyaninato sandwich complexes on the Ag(111) surface. (a) High-resolution STM image of $\text{Gd}(\text{Pc})_2$ and $\text{Gd}_2(\text{Pc})_3$ species and their molecular orientation with respect to the lower Pcs species. ($V_b = -0.8$ V, $I = 100$ pA and scale bar: 2nm). (b) Zoom-in high-resolution STM image of (a). ($V_b = -1$ V, $I = 80$ pA and scale bar: 1nm). (c,d) Atomistic models of $\text{Gd}(\text{Pc})_2$ and $\text{Gd}_2(\text{Pc})_3$ complexes and their molecular orientations. Grey, blue and green colors indicate bottom, intermediate and top Pc layers respectively.

Next, we have increased the coverage of Gd atoms to 0.05 ML. In this context, five distinctive types of STM contrasted molecular islands or individual species with increasing apparent heights are distinguished (cf. Figures 3a,b). As a result, the lowest in height of these species is assigned to phthalocyanine, whereas the higher species are attributed to bis-, tris-, tetra and penta(phthalocyaninato)gadolinium complexes, namely $\text{Gd}(\text{Pc})_2$, $\text{Gd}_2(\text{Pc})_3$, $\text{Gd}_3(\text{Pc})_4$ and $\text{Gd}_4(\text{Pc})_5$, respectively (cf. Figure 3c for experimental height profile), with the second or higher layer Pc molecules being perpendicularly stacked in a perfectly centered fashion. Remarkably, lateral displacement or rotation of the different species could not be performed by tip-induced lateral manipulation (scanning parameters: $V_b = 0.3$ V, $I_t = 0.1$ nA). At this point, it is worthwhile to mention that the in-situ fabrication of multi-deckers with a height surpassing triple-deckers is unprecedented.^[18] DFT modelling reveals the structure and height of the different individual multi-deckers in gas phase (see Figure 3d), while remarkably illustrating that the terminal deckers for each species are the most corrugated, i.e., deviate most from planarity (cf. Figure SI2). Figure 3e shows the occurrence of each level of decker species (first, second, third, fourth and fifth decker's, respectively) which decreases significantly as more intricate complexes are formed, a result that is in agreement with the calculated formation energy of the multi-decker complexes (cf. Figure SI3). Additionally, Figure 3e presents a comparison of the experimental and DFT theoretical molecular orientation of the different topmost Pc ligands for every phthalocyaninato sandwich complex, highlighting an excellent match. The rotation of $\text{Gd}(\text{Pc})_2$ and $\text{Gd}_2(\text{Pc})_3$ complexes is described in Figure 2. Herein, one can observe how the upper Pc in $\text{Gd}_3(\text{Pc})_4$ and $\text{Gd}_4(\text{Pc})_5$ complexes are rotated by $50^\circ \pm 11^\circ$ and $1^\circ \pm 7^\circ$

with respect to the lowest Pc. Interestingly, $\text{Gd}(\text{Pc})_2$ and $\text{Gd}_3(\text{Pc})_4$ (even multi-deckers), and $\text{Gd}_2(\text{Pc})_3$ and $\text{Gd}_4(\text{Pc})_5$ (odd multi-deckers), respectively, exhibit almost the same orientation of the top decker.

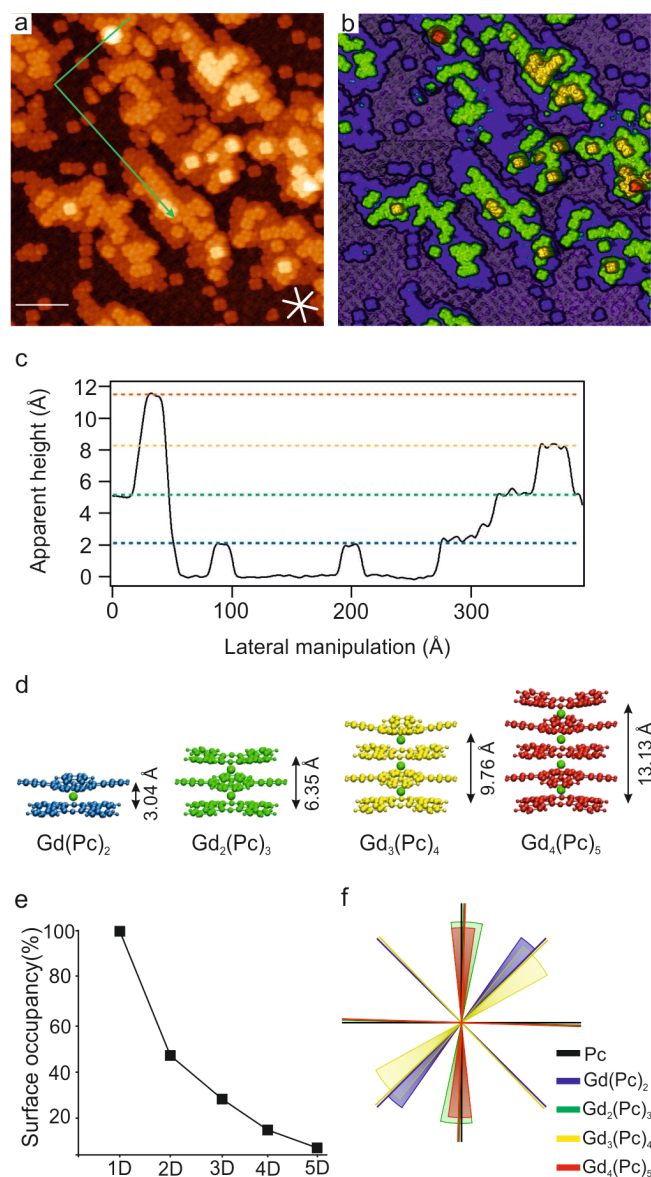


Figure 3. Three-dimensional growth of $\text{Gd}_{x-1}(\text{Pc})_x$ complexes on Ag(111). (a,b) Long-range STM images of the gadolinium phthalocyaninato sandwich complexes formed on the Ag(111) substrate. ($V_b = 2$ V, $I = 50$ pA and scale bar: 8 nm). The color code in (b) was introduced to highlight the distinct height levels and is applied in (c), (d) and (f). (c) Constant current height profile along the L-shaped green arrow in (a) revealing the distinct decker levels and the corresponding apparent heights at 2 V. (d) DFT atomistic models of the different species formed on the surface. The vertical arrow indicates the height of each species (measured between the N_4 mean planes). (e) Surface occupancy vs. different species formed on the substrate. 1D-5D labelled in x-axis indicates Pc to $\text{Gd}_4(\text{Pc})_5$ complexes. (f) Graph showing the molecular orientation of each $\text{Gd}_{x-1}(\text{Pc})_x$ complex with respect to the lower Pc species. Fixed lines correspond to the theoretical values, whereas dashed cones to the experimental ones.

3. Conclusions

In summary, we have reported an STM observation of the in-situ fabrication of homoleptic gadolinium multiple-decker complexes directly onto a smooth Ag(111) surface under ultra-high-vacuum conditions. The formation of a supramolecular reticular architecture was observed, in which each of the constituents was either a Pc or a multi-decker species. Thus, our results pave novel avenues for the engineering of columnar growth on surfaces. Furthermore, our results could be extended the design of innovative homoleptic and/or heteroleptic three-dimensional molecular nanoarchitectures incorporating flexible sandwich-type compounds and lanthanide elements with potential in single molecular magnetism, single-molecule qubits and molecular machinery.

Methods Section

The experiments were performed in a custom designed ultra-high vacuum system that hosts a low-temperature STM (www.lt-stm.com), where the base pressure was below 5×10^{-10} mbar. The Ag(111) substrate was prepared using standard cycles of Ar⁺ sputtering (800 eV) and subsequent annealing to 723 K for 10 minutes. All STM images were taken in constant-current mode with electrochemically etched tungsten tips, and applying a bias (V_b) to the sample at 4K. The procedure for the growth of Gd_{x-1}(Pc)_x complexes on the Ag(111) substrate is based in three steps: 1) A multilayer coverage of 2H-Pc was deposited by organic molecular beam epitaxy from a thoroughly degassed quartz crucible held at 600 K; 2) Subsequently, Gd atoms were evaporated by means of electron beam evaporation onto the sample held at ~300 K from an outgassed Gd rod; 3) the sample was annealed at 550 K for 10 min.

Non-spin polarized density functional calculations were performed using the projector-augmented plane wave method.^[44] A plane wave basis set with a maximum kinetic energy of 400 eV was used. For the Gd atoms, the f electrons have been included in the core and not treated explicitly. The multi-decker Gd complexes were relaxed until atomic forces were smaller than 0.05 eV per Å and energy differences were smaller than 1 μeV. The PBE exchange–correlation potential^[45] as implemented in VASP^[46-48] was employed. Long-range van der Waals interactions were taken into account by the DFT-D3 approach proposed by Grimme.^[49] All structures were optimized at the Γ point of the Brillouin zone of a cubic unit cell with a size of 25 Å³ in real space.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Lanthanides, sandwich complexes, supramolecular architectures, scanning probe microscopy

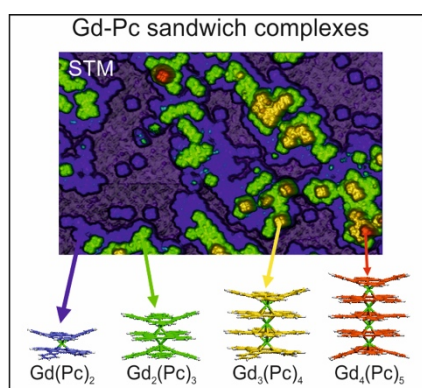
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The codeposition of free-base phthalocyanines and gadolinium atoms on a smooth Ag(111) substrate and subsequent annealing results in the expression of a reticular supramolecular architecture composed of irregularly distributed $Gd_{x-1}(Pc)_x$ complexes, $x=2-5$, thus paving new avenues for surface-confined columnar growth.