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Assembly and Manipulation of Rotatable Cerium Porphyrinato Sandwich Complexes on a Surface**

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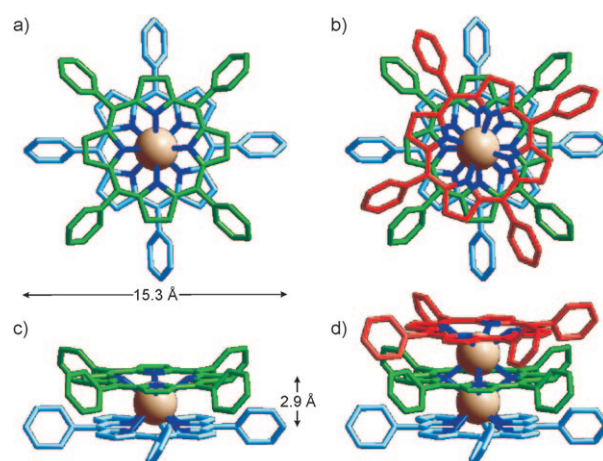
The comprehensive characterization and engineering of molecular nanostructures on surfaces is of great current interest, both from a scientific and technological point of view.[1] In particular, the significant potential of surface-confined supramolecular coordination chemistry has been recognized,[2] and

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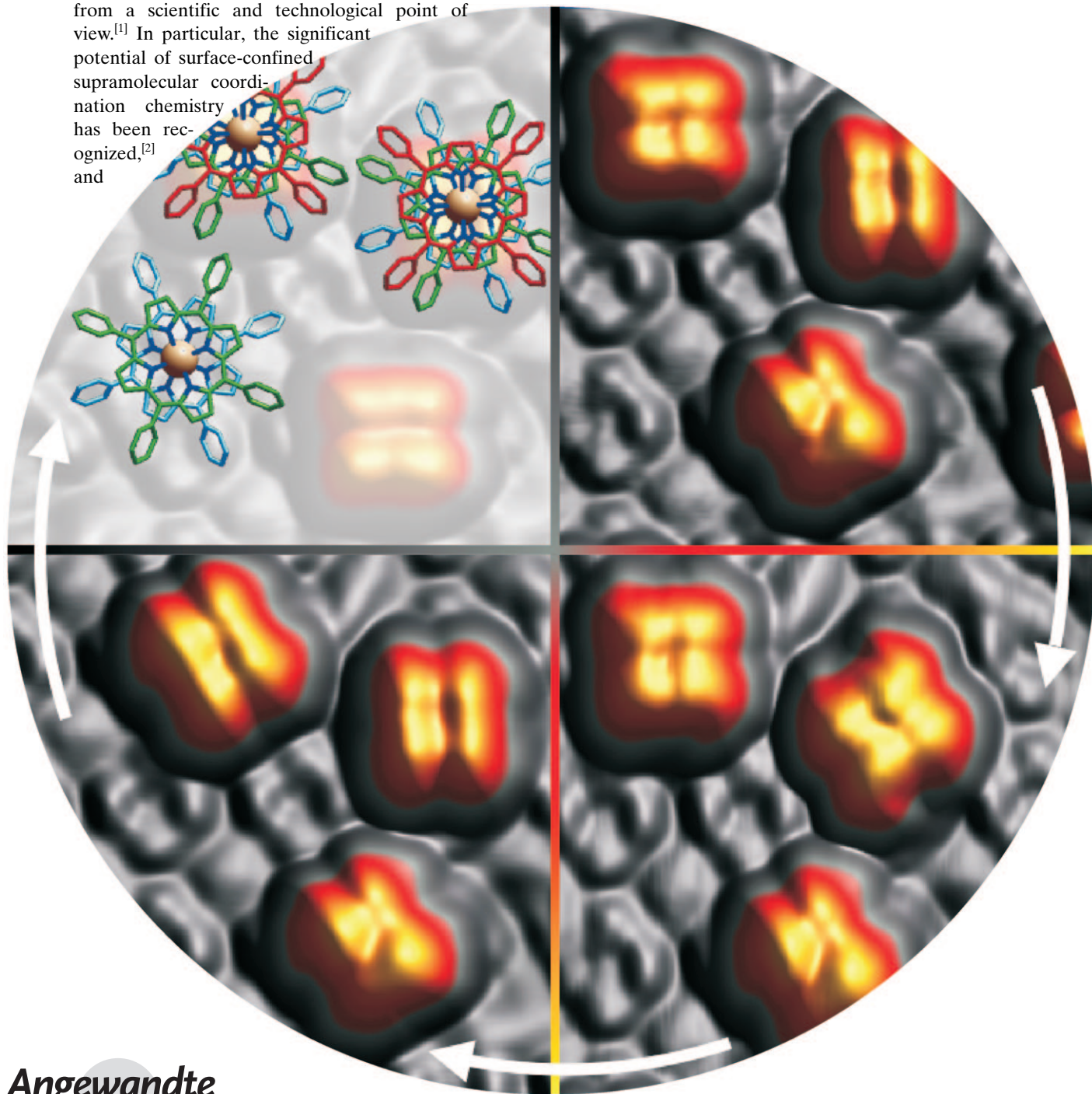
relies on metal-directed assembly protocols with suitable linkers and metal atoms that are combined on well-defined interfaces. Regarding their intriguing variety of functional properties,[3] which are exploited in both biological and artificial systems, porphyrin molecules are ideally suited as building blocks for these surface-anchored nanostructures. Tetrapyrrole-derived related sandwich compounds that comprise rare-earth metal centers are particularly interesting. Such complexes can play an important role as single-molecule magnets,[4] field-effect transistors,[5] artificial receptors for metal ions and functional units that express positive allosterism based on the rotation between the porphyrin planes,[6] and molecular multibit information storage, as a result of their rich redox properties.[7] Among the series of rare-earth double-decker complexes, those with cerium centers are especially versatile because they can exist in both +III or +IV oxidation states.[8]

Regarding future applications, molecular rotors have a special appeal and are considered as crucial elements for next-generation synthetic machines.[9] Promising candidates for surface-confined azimuthal molecular rotors[10] are double and triple-decker complexes with rare-earth ions that connect the adjacent phthalocyanine or porphyrin macrocycles (or a combination of both). These sandwich structures provide rotational degrees of freedom, where the top molecular plane (rotor) is able to rotate with respect to the bottom one (stator) that is anchored on the surface.[11, 12] These large double- and triple-decker molecules are generally susceptible to thermal decomposition and often unsuitable for high-temperature vapor deposition, indeed, only a few examples are reported.[13, 14] Alternatively, observations are possible at solid/liquid interfaces in an insulating organic solvent[12, 15] or under electrochemical control in an electrolyte solution.[16]

Herein we report a novel route for the synthesis of bis(porphyrinato)cerium double-decker complexes (Ce-(TPP)$_2$, TPP = tetraphenylporphyrin; Figure 1 a,c) directly on a Ag(111) surface under ultra-high-vacuum conditions by exposing a porphyrin precursor layer to an atomic beam of Ce followed by a temperature-programmed reaction and desorption of surplus material. In addition, the formation of tris(porphyrinato) Ce triple-decker complexes (Ce$_2$(TPP)$_3$,

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Figure 1. Models of cerium double- and triple-decker porphyrinato complexes. a,c) Top and perspective view of Ce(TPP)$_2$; b,d) top and perspective view of Ce$_2$(TPP)$_3$. Different colors are used to indicate the relative orientation of the porphyrin layers on Ag(111). Hydrogen atoms are omitted for clarity.

Figure 1 b,d) is strongly suggested. The nature of the formed double- and triple-decker compounds was studied by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), including a comparison with Ce(TPP)$_2$ layers generated by molecular beam epitaxy. Moreover, we address the motion of double- and triple-decker moieties in specific environments: the upper porphyrin of each molecular species can be rotated by STM manipulation, provided that spatial constraints do not interfere. These results pave the way for functional materials that rely on rare-earth double- and triple-decker systems at surfaces.

The in situ metalation of 2H-TPP monolayers by transition metals was recently reported,[17] as well as the interaction of Ce with mixed porphyrin arrays.[18] We now introduce a different procedure in which a precursor multilayer of 2H-TPP is deposited on the Ag(111) surface maintained at 330 K, and subsequently exposed to an atomic beam of Ce. As a second step, the sample is annealed at 500 K. By using this protocol (procedure 1) we aimed to synthesize sandwich complexes in situ by the reaction of Ce with 2H-TPP macrocycles. The thermal treatment is sufficient to overcome any formation activation barrier and simultaneously guarantees a complete desorption of the unreacted 2H-TPP multilayer.[19]

Figure 2a shows an STM image after the application of this procedure using a low Ce dose (0.05 ML). A compact island with an apparent height that clearly exceeds the surrounding first-layer 2H-TPP molecules is observed. In addition, individual bright molecules are embedded in the 2H-TPP layer. Compared to the apparent height of 2.7 Å of 2H-TPP on Ag(111) (at V_b = 2.4 V; see Figure 2b), both these individual bright molecules and the islands exhibit an identical apparent height of 6 Å relative to the Ag(111) surface and thus represent second-layer species that will be associated with Ce(TPP)$_2$, as discussed below. Moreover, the compact second-layer islands host an additional molecular species, which appears as single protrusion on the island.
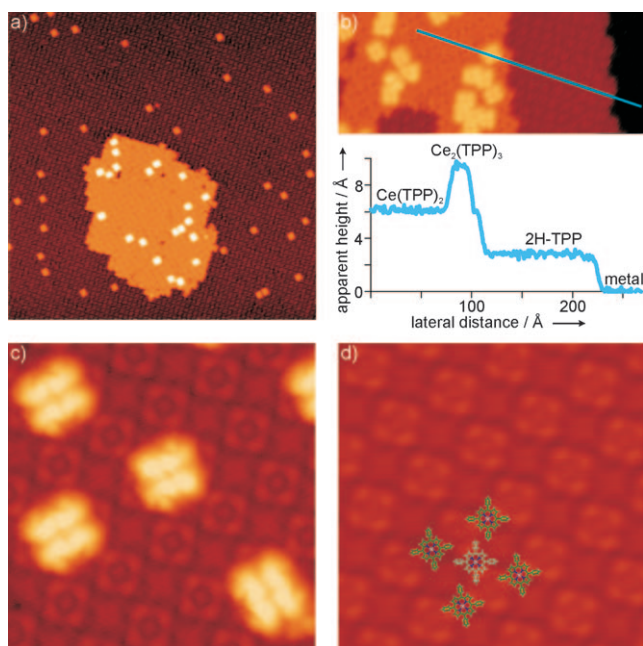
Figure 2. STM images of the self-assembly of double-decker cerium porphyrinato complexes on Ag(111). a–c) Islands of double-decker complexes grown by procedure 1 (see text), with some embedded triple-decker complexes. These double-decker islands coexist in-phase with 2H-TPP domains. Ce dosage was 0.05 ML in (a and c) and 0.2 ML in (b). A profile of apparent height in (b) shows the formation of molecular species of three different apparent heights. d) Double-decker domain on Ag(111), obtained by procedure 2 by depositing 0.2 ML of $Ce(TPP)_2$ on Ag(111). The double-decker assembly obtained with both procedures is identical. A molecular model of the unit cell is shown with the orientation of the upper porphyrin in light or dark green, respectively. Image size: a) 443×443 Å^2; b) 321×127 Å^2; c,d) 96×96 Å^2. Scanning conditions: a) $I_t = 0.2$ nA, $V_b = 2$ V; b) $I_t = 0.2$ nA, $V_b = 2.4$ V; c) $I_t = 0.1$ A, $V_b = 1.4$ V; d) $I_t = 0.2$ nA, $V_b = 1.4$ V. V_b refers to the bias voltage applied to the sample.

Based on their apparent height of about 9.4 Å, we assign these species to third-layer molecules that correspond to the formation of $Ce_2(TPP)_3$. This interpretation is in agreement with the comparison between the apparent heights of closely related bis- and tris(phthalocyaninato) lanthanoid systems on different surfaces.[14,20]

In order to clarify the nature of these second- and third-layer molecules, systematic control experiments were performed: 1) after annealing a multilayer of 2H-TPP, following procedure 1, but without Ce dosage, no second- or third-layer molecules are observed on top of the highly regular 2H-TPP monolayer on Ag(111). 2) Application of procedure 1 with an increased Ce dosage results in more extended second-layer islands and also a higher density of incorporated third-layer molecules (Figure S1), which suggest that second- and third-layer molecules require the presence of Ce. 3) 2H-TPP molecules deposited either on one monolayer of 2H-TPP on Ag(111) or on second-layer islands exhibit both a different adsorption site and a reduced bonding strength as compared to the second- and third-layer molecules obtained by procedure 1. 4) Finally, the direct sublimation of $Ce(TPP)_2$[21,22] complexes on Ag(111) and subsequent annealing to 500 K

(see the Supporting Information), designated procedure 2, results in the formation of islands with identical topographic STM appearance (compare Figure 2c and d) and electronic structure (Figure S3) as those obtained by procedure 1. Importantly, even third-layer molecules are observed by applying procedure 1. Altogether these control experiments prove the synthesis of $Ce(TPP)_2$ double-decker complexes on Ag(111) by procedure 1 and strongly indicate that the observed third-layer molecules correspond to $Ce_2(TPP)_3$ triple-decker complexes.

Focusing on the double-decker species, intramolecular resolution allows us to image the molecular centers for both the individual and the densely packed double-decker complexes together with the lattice of the surrounding 2H-TPP monolayer (see Figure 3a). At a bias voltage $V_b = 0.3$ V, double-decker complexes show a twofold symmetry with two bright central protrusions and four peripheral lobes that are attributed to the meso-phenyl rings. Both the individual and the densely packed double-decker complexes are placed on positions in registry with the 2H-TPP lattice (Figure 3b). This
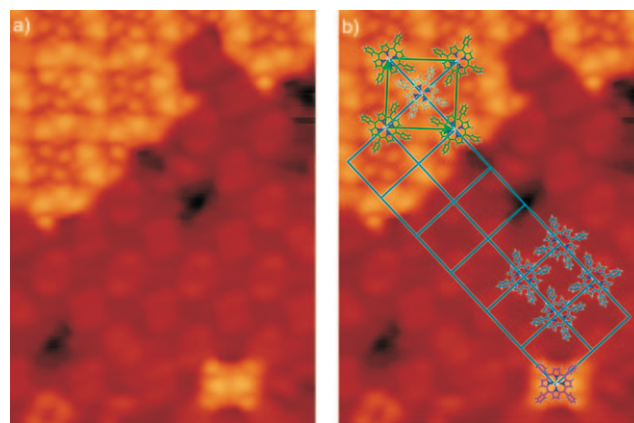
Figure 3. a) STM image of the boundary between a $Ce(TPP)_2$ and a 2H-TPP domain on Ag(111). b) Model of the registry between the lattices of double-decker complexes (green line) and adjacent 2H-TPP species (blue line). Different colors are used to outlined the orientation of the upper porphyrin in each complex: 2H-TPP is shown in blue, isolated $Ce(TPP)_2$ units in violet, and the two $Ce(TPP)_2$ units that make up the double-decker network are shown in light and dark green, respectively. Image size: 82×111 Å^2. Scanning conditions: $I_t = 0.4$ nA, $V_b = 0.3$ V.

result implies that the bottom porphyrins of the double-decker complexes exhibit a packing similar to the 2H-TPPs. In addition, the upper porphyrins are rotated about the azimuthal axis to yield densely packed $Ce(TPP)_2$ islands. While a precise determination of the double-decker conformation is elusive to STM measurements, we can rationalize the relative orientations of the $Ce(TPP)_2$ upper porphyrin versus the first layer of 2H-TPP and accordingly the bottom porphyrin: the upper porphyrin is rotated by $(15 \pm 5)°$ in the individual double-decker complex, and by $(-45 \pm 5)°$ or $(+45 \pm 5)°$ in the islands. Following this analysis, we identify the double-decker lattice based on a square unit cell with a $Ce(TPP)_2$ unit in every corner (dark-green molecules in Figure 3b) and a

central Ce(TPP)$_2$ unit where the top part is rotated by 90° (light-green molecule in Figure 3 b). The nearest-neighbor distance amounts to (13.9 ± 0.5) Å, which is in full agreement with the first layer of 2H-TPP.

In addition to Ce(TPP)$_2$ double-decker complexes, our synthesis results in third-layer molecular protrusions associated with Ce$_2$(TPP)$_3$ complexes, which, to the best of our knowledge, could not be realized to date. Figure 2 c, Figure 4 d,f, and Figure S2 show high-resolution STM images of triple-decker complexes embedded in a double-decker island. At $V_b = 1.4$ V, these complexes present a twofold symmetry, with four bright lobes separated by an equatorial dark depression, and each lobe ending in a hooklike shape. We observe two azimuthal orientations of the upper porphyrin in Ce$_2$(TPP)$_3$, each related by a 90° rotation. In addition, the STM images show that each triple-decker complex is placed exactly in registry with the surrounding double-decker molecular island. The orientation of the triple-decker complex depends on its position in the double-decker lattice: Since there are two inequivalent orientations for a double-decker complex, there are also two orientations for the triple-decker species. Assuming that the bottom and central

porphyrins of the Ce$_2$(TPP)$_3$ complex present the same orientation than the surrounding Ce(TPP)$_2$ species, the upper porphyrin of the triple-decker complex exhibits a rotation of $(-20 \pm 5)°$ with respect to the central porphyrin. Regarding these angles in both molecular species, the range of rotation of the upper porphyrin is in agreement with reported results for similar systems in crystalline form.[23]

Next we address the rotatibility of the upper porphyrin in both the double- and triple-decker species. Figure 4 a–c provides a direct proof for azimuthal rotation of a double-decker complex embedded in a 2H-TPP island induced by a lateral manipulation procedure using the STM tip (see the Supporting Information). Starting from an initial equilibrium configuration, the orientation of the upper porphyrin, as indicated by two bright protusions (see red circles in figure 4 a,b) can be rotated $(20 \pm 5)°$ counterclockwise and then be moved reversibly back (clockwise). Remarkably, such rotations were performed repeatedly without any lateral displacement or desorption of the top porphyrin, thus reflecting the cohesion of the Ce(TPP)$_2$ complex where the upper porphyrin revolves about the Ce center. As for any azimuthal molecular rotor, the interaction of the rotor (upper porphyrin) with its surroundings can block the rotation. In this sense, manipulation procedures on the Ce(TPP)$_2$ in the compact islands were not successful, because the intermolecular steric constraints between the closely arranged meso-substituents of the upper porphyrins prevent any individual rotation.

Similar to the rotation in the double-decker complex, it is also possible to induce rotations of isolated Ce$_2$(TPP)$_3$ species embedded in an island of double-decker complexes, however, a different manipulation procedure must be applied (see the Supporting Information). Single upper porphyrin units of Ce$_2$(TPP)$_3$ complexes are rotated $(57 \pm 5)°$ to a new orientation, and then in subsequent manipulations they are rotated back to their initial orientation. The exact conformation of the central porphyrin of the triple-decker complex during the manipulation procedure cannot be determined by STM, though it is highly likely that any rotation of this porphyrin is blocked by intermolecular interactions with the surrounding double-decker complexes. Figure 4 d–g exemplifies one such rotation step (a complete series of reversible rotations is presented in Figure S4). Hundreds of these rotation steps could be performed without destruction of the compound. Nevertheless, a desorption or lateral displacement of the upper porphyrin is possible, which is in agreement with a recent report.[24]

It is important to note that the manipulation procedures were performed at 6 K, where thermal motions are frozen. It is plausible to assume that the demonstrated rotational rearrangements occur spontaneously at elevated temperatures, where the rotation barrier given by intramolecular interactions can be overcome. In particular, with the induced rotation of the upper porphyrin of the Ce$_2$(TPP)$_3$ complex, the phenyl groups of the top and central ligands are presumably crossed during motion under cryogenic conditions (Figure 4 e–g), thus suggesting that the steric hindrance between phenyl groups may be easily overcome at higher temperatures. Accordingly, the realized surface-anchored
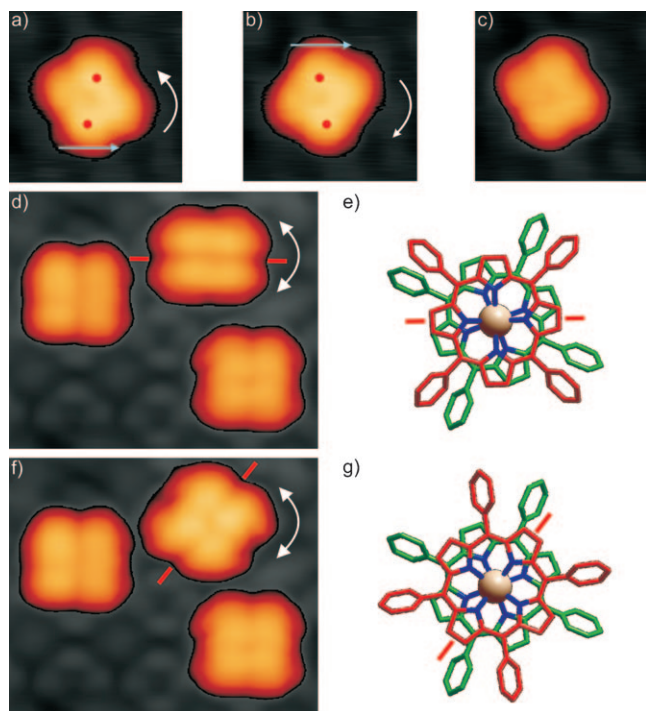
Figure 4. Molecular rotation of the upper porphyrin of Ce(TPP)$_2$ and Ce$_2$(TPP)$_3$ species on Ag(111). a–c) By lateral manipulation (path of the tip from left to right drawn by a blue line) the upper porphyrin of a CeTPP$_2$ complex embedded in a 2H-TPP island is rotated 20° counterclockwise from (a) to (b) and clockwise from (b) to (c). The red circles depict the two brighter lobes of the double-decker complexes, defining an orientation for rotation. d–g) The upper porphyrin of a Ce$_2$(TPP)$_3$ species embedded in a Ce(TPP)$_2$ island is rotated 57° from position 1 (d,e) to position 2 (f,g) by scanning at $V_b = 0.3$ V, with a tunneling current of 0.1 nA. For clarity, in the top-view model, only the top (red) and medium (green) porphyrins of the Ce$_2$(TPP)$_3$ complex are displayed. Image sizes: a–c) 40×40 Å^2; d,f) 71×59 Å^2. Scanning conditions: a–d) $I_t = 0.1$ nA, $V_b = 1.4$ V.

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double- and triple-decker species are potential thermal rotors. The incorporation of the lanthanide center introduces the versatility of rare-earth coordination chemistry and offers an alternative to "pinwheel" systems based on zinc tetra(3,5-di-*tert*-butylphenyl)porphyrins.[25] Therefore, this study highlights the promise of surface coordination architectures regarding design and control of rotamers.[26]

In conclusion, we have reported a new synthesis protocol for the fabrication of homoleptic cerium bisporphyrinato (Ce(TPP)$_2$) directly on a smooth Ag(111) substrate under ultra-high-vacuum conditions, and provide evidence for the formation of a cerium trisporphyrinato (Ce$_2$(TPP)$_3$) species. Rotational motions of the upper porphyrin of these double- and triple-decker sandwich complexes were demonstrated by STM manipulation with exquisite control. It is suggested that the described approach can be extended to synthesize and anchor other homoleptic or heteroleptic multidecker complexes based on different porphyrins and phthalocyanines, or other suitable compounds, as bottom and top layers. The employed tetrapyrrole species can be designed according to specific requirements, thus providing novel avenues in situations where organic synthesis or thermal sublimation of entire species fail. These results thus pave the way for the design of novel functional molecular architectures incorporating adaptive and rotatable sandwich compounds and furthermore extend supramolecular assemblies at surfaces to the third dimension.

Experimental Section

All STM experiments were performed in a custom-designed ultra-high-vacuum (UHV) system that provides a base pressure below 1×10^{-10} mbar.[27] The monocrystalline Ag(111) substrate was cleaned by repeated Ar$^+$ sputtering cycles at an energy of 800 eV, followed by annealing at 730 K for 10 min. Procedure 1 for the growth of Ce(TPP)$_2$ and Ce$_2$(TPP)$_3$ on Ag(111) is based on three steps: 1) A multilayer coverage of 2H-TPP was deposited by organic molecular beam epitaxy from a thoroughly degassed quartz crucible held at 600 K; 2) Ce atoms were evaporated from a homemade water-cooled cell by resistively heating a W filament enclosing a Ce ball of high purity (99.9999%, MaTecK GmbH, 52428 Juelich, Germany); 3) the sample was annealed at 500 K for 10 min. In procedure 2, Ce(TPP)$_2$[22] was dosed on Ag(111) by organic molecular beam epitaxy from a thoroughly degassed quartz crucible held at 700 K. In both experiments, during deposition, the Ag(111) surface was kept at 330 K. For the control experiment, 2H-TPP was deposited on top of 1 ML of 2H-TPP with the sample held at 173 K. During the growth experiments the pressure remained less than 5×10^{-10} mbar. Regarding coverage, 1 ML is defined as one surface fully covered by 2H-TPP species. Accordingly, 1 ML of Ce is defined as one Ce atom attached to each 2H-TPP molecule. All data were acquired by employing a low-temperature CreaTec-STM[28] with the sample held at 6 K using electrochemically etched W tips.

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