Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information
© Wiley-VCH 2011
69451 Weinheim, Germany

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

David Écija, Willi Auwärter,* Saranyan Vijayaraghavan, Knud Seufert, Felix Bischoff, Kentaro Tashiro, and Johannes V. Barth*

anie_201007370_sm_miscellaneous_information.pdf

Supporting Information.

List of contents.

Integrity of $Ce(TPP)_2$ species on Ag(111).

The direct sublimation of $Ce(TPP)_2$ by organic beam epitaxy at T = 700 K (deposition rate ~ 0.15 ML/h) on a clean Ag(111) surface held at 373 K, followed by annealing to 500 K, resulted in the formation of rectangular shaped islands of $Ce(TPP)_2$ complexes. Additionally, minority islands assembled from single-layer porphyrin species were observed (apparent height ~2.7 Å at V_b = 2.4 V). As extended degassing close to the sublimation temperature of $Ce(TPP)_2$ did not considerably reduce the number of these parasite species, we assume that they originate from a cracking of a small percentage of $Ce(TPP)_2$ molecules in the quartz crucible during deposition.

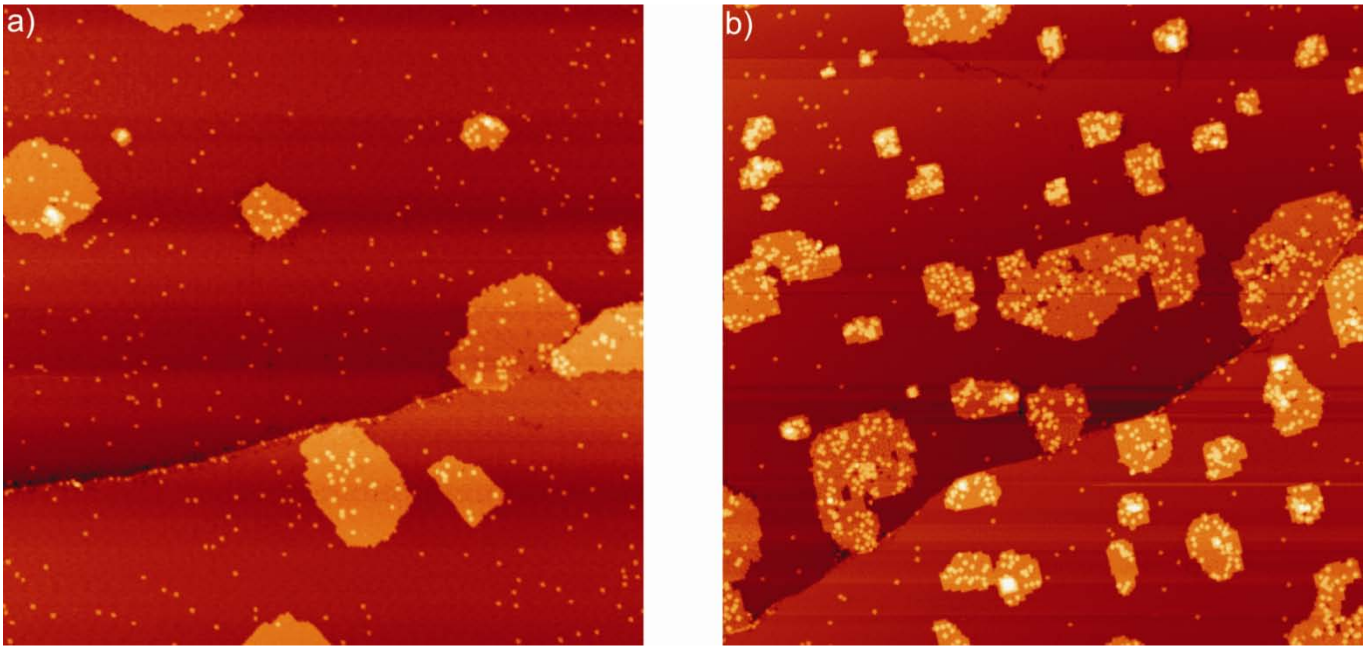

Figure S1. STM images of the growth of double-decker islands on Ag(111) following the new synthesis procedure described in the manuscript, by keeping fixed the deposition of H_2TPP (5 ML) and increasing the dose of Ce: a) 0.05 ML and b) 0.15 ML, respectively. The amount of $Ce_2(TPP)_3$ complexes found within the $Ce(TPP)_2$ islands also increases while rising the Ce dose. Images size: 2953 x 2953 $Å^2$. Scanning conditions: $I_t = 0.2$ nA, $V_b = 2$ V.

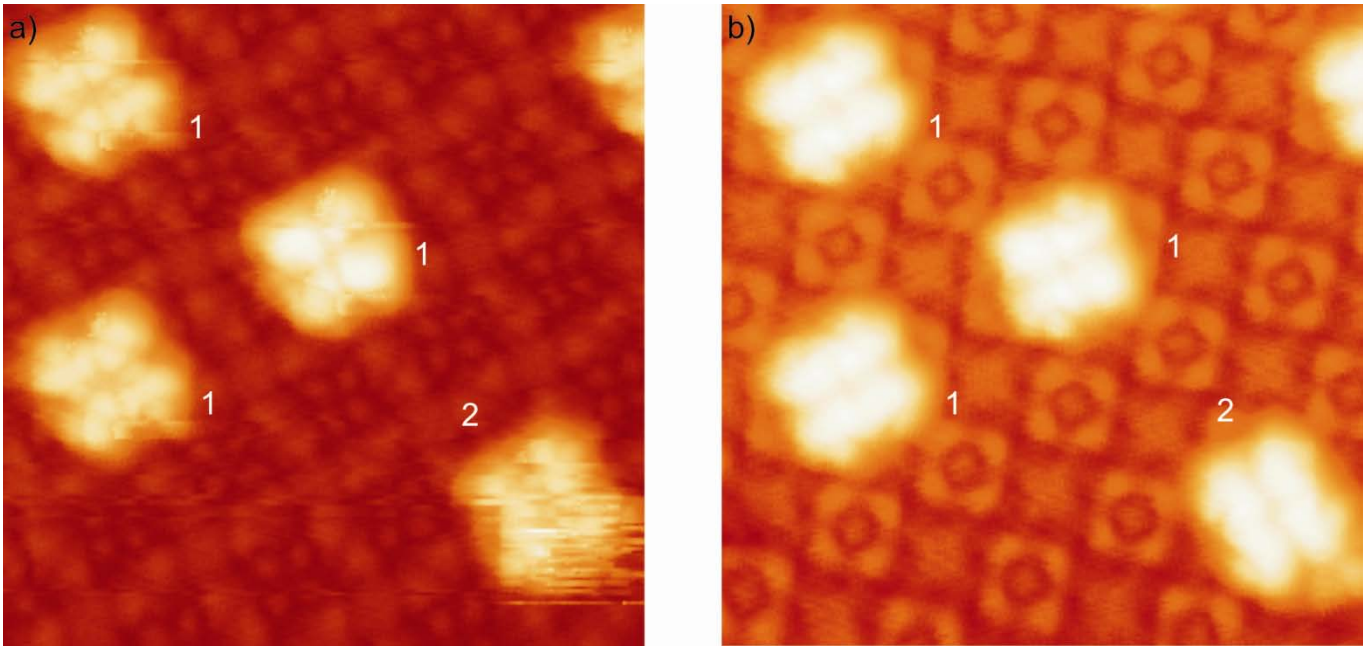

Figure S2. STM image of triple-deckers embedded in a double-decker island taken at different bias voltages. Each triple-decker is placed exactly in a vacancy of the double-decker molecular island, with two possible orientations of its top porphyrin (depicted by numbers 1 and 2, respectively). Since there are two different orientations of the double-deckers in the network, there can be two types of vacancies, regarding the supramolecular environment. Depending in which type of vacancy the triple-decker is placed, its bottom and medium porphyrin will interact with the surrounding environment of double-deckers, affecting the final orientation of the top molecule, resulting at the end in two different types of orientation, one per type of vacancy. Scanning conditions: a-b) I_t = 0.2 nA; a) V_b = 0.65 V, b) V_b = 1.4 V. Image size: 98 x 98 Å^2.

STS of double-deckers complexes.

To explore the electronic characteristics of the double-deckers complexes we employed scanning tunneling spectroscopy (STS). The peaks in the dI/dV spectra summarized in Figure S3 reflect major contributions to the tunneling current, mediated by molecular orbitals, whereby the negative (positive) bias regime represents the occupied (unoccupied) states. For the $Ce(TPP)_2$ species, the spectra are dominated by an intense, sharp peak around 1.9 V, while the lowest unoccupied electronic state is detected at 1.1 V. The following conclusion are supported by our spectroscopic data: i) The spectra of $Ce(TPP)_2$ obtained by *procedure 1* (red) or by direct sublimation (dark red) are essentially identical, confirming a successful synthesis of $Ce(TPP)_2$ by *procedure 1*. ii) In comparison to the reference spectrum of 2H-TPP (blue line) that presents a broad resonance at 800 mV, as previously reported,[1] the Ce compounds exhibit lower conductivity around the Fermi level and sharper resonances. This indicates a reduced electronic interaction with the metallic substrate, a prerequisite to preserve the intrinsic electronic and magnetic properties of rare-earth sandwich compounds anchored on surfaces.[2]

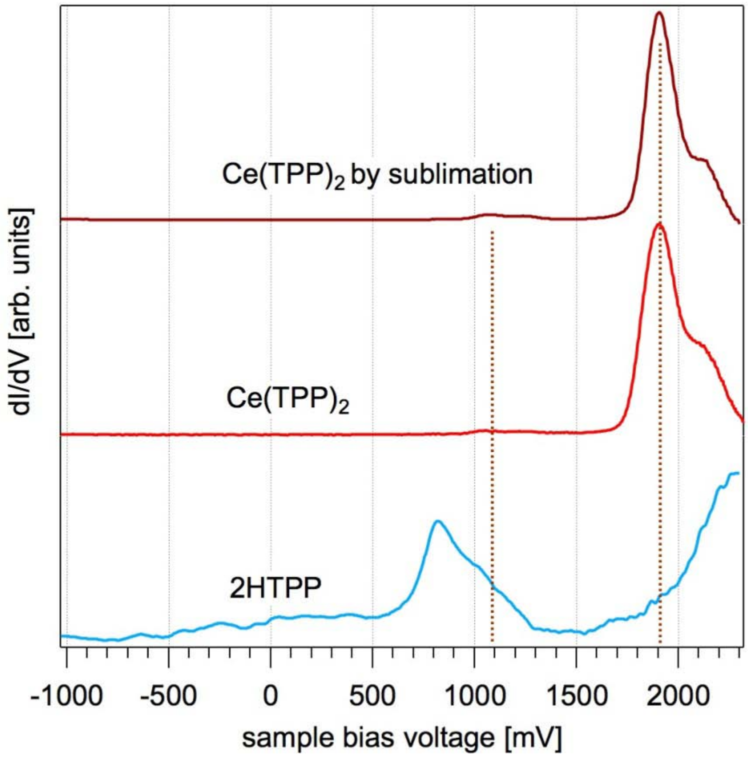

Figure S3. Scanning tunneling spectra representing porphyrin-based species on Ag(111): 2H-TPP (blue curve), $Ce(TPP)_2$ obtained by in-situ synthesis via procedure 1 (light red) and $Ce(TPP)_2$ deposited by sublimation (dark red). The spectra taken on the double-decker species show identical features (dotted lines) corroborating a successful in-situ synthesis of $Ce(TPP)_2$ directly on the Ag(111) surface. See text for further discussion.

Induced rotation in double and triple-decker complexes.

The rotation of the top porphyrin of Ce(TPP)$_2$ and Ce$_2$(TPP)$_3$ was induced by two different lateral STM manipulation procedures:

i) Ce(TPP)$_2$

Starting from regular imaging conditions (typical tunneling resistance R ~ 10 GΩ) in which the Ce(TPP)$_2$ and 2H-TPP species are unaffected by the STM tip, the tip is approached to the surface to increase the interaction with the adsorbates (R ~ 10 MΩ), and laterally translated across the top porphyrin of the Ce(TPP)$_2$ complex (the tip path is indicated by the blue arrows in Figures 4a and b of the manuscript). After this manipulation step, the surface is imaged again to detect the changes in the molecular orientation.

ii) Ce$_2$(TPP)$_3$

To induce rotations, the area of interest is scanned at a low bias voltage (typically V_b = 0.3 V) to increase the interaction of the tip and molecules (keeping a tunneling current of 0.1nA, used for normal scanning). Subsequently, the area is scanned again at regular imaging conditions to detect changes in the molecular orientation (cf. Figure S4).

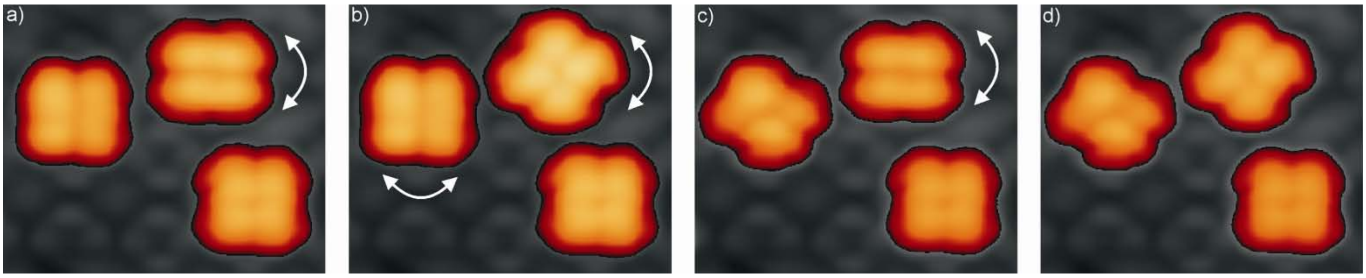

Figure S4. Molecular rotation of the top porphyrin of Ce$_2$(TPP)$_3$ complexes embedded in a Ce(TPP)$_2$ island on Ag(111). By a lateral manipulation procedure based on scanning at V_b = 0.3 V with a tunneling current of 0.1 nA, the top porphyrins of two Ce$_2$(TPP)$_3$ species presenting different initial orientations are rotated forward and backward between two positions. Images size: 71 x 59 Å^2. Scanning conditions: I_t = 0.1 nA, V_b = 1.4 V.

References

[1] A. Weber-Bargioni, J. Reichert, A. P. Seitsonen, W. Auwarter, A. Schiffrin, J. V. Barth, *J. Phys. Chem. C* **2008**, 112, 3453.
[2] L. Vitali, S. Fabris, A. M. Conte, S. Brink, M. Ruben, S. Baroni, K. Kern, *Nano Lett.* **2008**, 8, 3364.