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Actinide Coordination Chemistry on Surfaces: Synthesis, Manipulation, and Properties of Thorium Bis(porphyrinato) Complexes

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Erik Rheinfrank, Mathias Pörtner, Maria del Carmen Nuñez Beyerle, Felix Haag, Peter S Deimel, et al.. Actinide Coordination Chemistry on Surfaces: Synthesis, Manipulation, and Properties of Thorium Bis(porphyrinato) Complexes. *Journal of the American Chemical Society*, 2021, 143 (36), pp.14581-14591. 10.1021/jacs.1c04982 . hal-03432277

HAL Id: hal-03432277

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Cite This: <https://doi.org/10.1021/jacs.1c04982>



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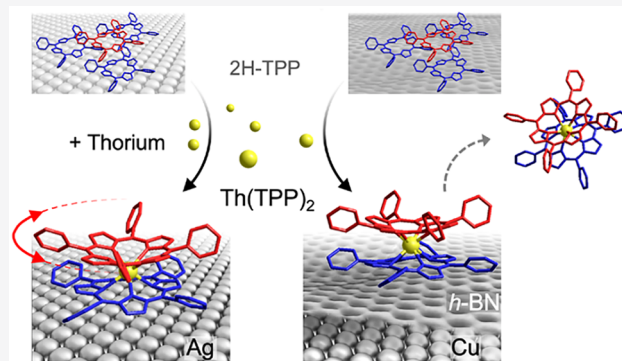


Article Recommendations



Supporting Information

7 **ABSTRACT:** Actinide-based metal–organic complexes and coordi-
8 nation architectures encompass intriguing properties and function-
9 alities but are still largely unexplored on surfaces. We introduce the
10 in situ synthesis of actinide tetrapyrrole complexes under ultrahigh-
11 vacuum conditions, on both a metallic support and a 2D material.
12 Specifically, exposure of a tetraphenylporphyrin (TPP) multilayer to
13 an elemental beam of thorium followed by a temperature-
14 programmed reaction and desorption of surplus molecules yields
15 bis(porphyrinato)thorium ($\text{Th}(\text{TPP})_2$) assemblies on Ag(111) and
16 hexagonal boron nitride/Cu(111). A multimethod characterization
17 including X-ray photoelectron spectroscopy, scanning tunneling
18 microscopy, temperature-programmed desorption, and complemen-
19 tary density functional theory modeling provides insights into
20 conformational and electronic properties. Supramolecular assemblies
21 of $\text{Th}(\text{TPP})_2$ as well as individual double-deckers are addressed with submolecular precision, e.g., demonstrating the reversible
22 rotation of the top porphyrin in $\text{Th}(\text{TPP})_2$ by molecular manipulation. Our findings thus demonstrate prospects for actinide-based
23 functional nanoarchitectures.



24 ■ INTRODUCTION

25 Understanding the organometallic and coordination chemistry
26 of actinide elements has drawn considerable interest in recent
27 years.^{1–8} High coordination numbers, a variety of available
28 oxidation states, and the presence of 5f orbitals allow actinides
29 to access reactivity modes and coordination environments that
30 differ from the characteristics of d-block elements and
31 lanthanides. As elemental metals, actinides are less homoge-
32 neous than their 4f counterparts. Their 5f electrons are
33 localized exclusively for the late members of the series from
34 Am through Lr. The early actinides through Pu show, in
35 contrast to all lanthanides, itinerant 5f electrons that take part
36 in bonding and screening, causing a parabolic dependence of
37 the Wigner–Seitz radii on the atomic numbers similar to d-
38 block elements, 5f density of states (DOS) directly at the
39 Fermi edge seen in ultraviolet photoelectron spectroscopy
40 (UPS), and well-screened inner-shell vacancies in X-ray
41 photoelectron spectroscopy (XPS) (see ref 9 and references
42 therein). These volatile 5f electrons enable oxidation states up
43 to +7 for Np.¹⁰ Comparing compounds with corresponding
44 lanthanide and actinide atoms, bonds with actinide partners are
45 generally considered to show increased covalent versus ionic

character, whereas for the early group members Ce and Th, 46
reversed results have been reported.^{11,12} These properties, and 47
the actinides' larger ionic radii that affect bond character and 48
geometry, open prospects for novel functional materials, 49
including single-molecule magnets^{13–15} and coordination 50
architectures, covering metal–organic coordination frame- 51
works.^{16–18} The latter structures are expected to play a 52
relevant role in nuclear waste management.¹⁹ Uranium- and 53
thorium-based complexes and molecular materials have 54
received the main attention, e.g., because of their interesting 55
catalytic chemistry^{20–24} and intriguing coordination structures 56
reported.^{6,17,18,25–32} Specifically, thorium tetrapyrrole com- 57
plexes (including porphyrins, phthalocyanines, and corroles) 58
were achieved,^{6,33–35} affording double-decker bis- 59
(porphyrinato)thorium complexes, where a single thorium 60

Received: May 13, 2021

61 center is sandwiched between two macrocyclic ligands.^{36–38} In
62 addition, the large half-lives of ²³²Th (1.4 × 10¹⁰ years) and
63 ²³⁸U (4.47 × 10⁹ years) minimize radiation hazards compared
64 to other, more short-lived actinides.

65 So far, most of this work on metal–organic actinide
66 complexes has been carried out in solution or solid state.
67 Single-molecule characterization, supramolecular assembly,
68 and chemistry directly on surfaces remain unexplored—in
69 stark contrast to the lanthanide counterparts (see below)—
70 mainly because of safety restrictions due to radiation. Metal
71 surfaces, however, provide excellent platforms to assemble and
72 synthesize metal–organic complexes and functional molecular
73 architectures and to control and monitor the structural,
74 electronic, and magnetic properties under ultrahigh-vacuum
75 (UHV) conditions.^{39–42} Moreover, two-dimensional materials
76 and ultrathin films can be used to reduce molecule–metal
77 interactions that can adversely affect or mask intrinsic
78 molecular properties, with a monolayer of insulating hexagonal
79 boron nitride (*h*-BN) being a prominent example of such a
80 decoupling layer.^{43,44} Indeed, surface science experiments and
81 complementary theoretical modeling have provided exciting
82 insights into lanthanide-based tetrapyrrole complexes and
83 coordination architectures on model surfaces,⁴⁵ with pioneer-
84 ing studies on double-decker and multidecker structures,^{46–52}
85 including TbPc₂ as an exemplary single-ion molecular
86 magnet.^{53–56} Thin decoupling layers were applied to improve
87 the stability of the magnetic properties^{51,55} or to manipulate
88 the charge state of lanthanide–tetrapyrrole double-deckers.⁵⁰
89 As a downside, the intact deposition of such complexes by
90 sublimation in a UHV environment poses severe challenges,
91 with thermally induced molecular fragmentation or modifica-
92 tions often interfering with clean, homogeneous adsorbate
93 structures,^{46,52,57} even though molecular functionalization can
94 favor successful deposition.⁴⁹ In situ synthesis of lanthanide
95 tetrapyrrole double-deckers and multideckers was resorted to
96 as a remedy and alternative, e.g., yielding Ce(TPP)₂,
97 Ce₂(TPP)₃,⁵⁸ Gd_{x-1}Pc_x (*x* = 1–5),⁵⁹ TbPc₂, and Tb(tbu-
98 Pc)₂⁶⁰ complexes directly on noble metal supports.

99 Here, we introduce the in situ synthesis of Th(TPP)₂ (see
100 Figure 1a–c) in a solvent-free UHV environment on two
101 distinctly different substrates, namely, Ag(111) and *h*-BN/
102 Cu(111). Our work thus expands on-surface metalation
103 protocols, which are well-established for 3d metals,^{61,62} alkali
104 metals,⁶³ nonmetals,^{64,65} and lanthanides,^{58–60,66} to the
105 actinide series. Along with extending tetrapyrrole surface
106 science,^{67,68} this study provides a rare example of a successful
107 reaction on *h*-BN.^{69–74}

108 The in situ synthesis process, inspired by the pioneering
109 studies on lanthanide metalation,^{45,58–60} is schematically
110 illustrated in Figure 1d and e. It encompasses three steps:
111 (1) growth of a precursor multilayer of 2H-TPP molecules on
112 the substrate of choice; (2) deposition of elemental Th at
113 room temperature (rt); and (3) thermal annealing at 500 K for
114 several minutes to desorb unreacted multilayer components.
115 The *h*-BN monolayer is prepared by chemical vapor deposition
116 prior to the deposition of the molecules.⁷⁵ As sketched in the
117 bottom panels of Figure 1d and e, the emerging surface
118 morphologies are different for the two supports (Ag(111),
119 Figure 1d; *h*-BN/Cu(111), Figure 1e). Furthermore, *h*-BN
120 enables desorption and detection of the reaction products. The
121 resulting Th(TPP)₂ sandwich complexes were investigated
122 using X-ray photoelectron spectroscopy (XPS), scanning
123 tunneling microscopy (STM), scanning tunneling spectroscop-

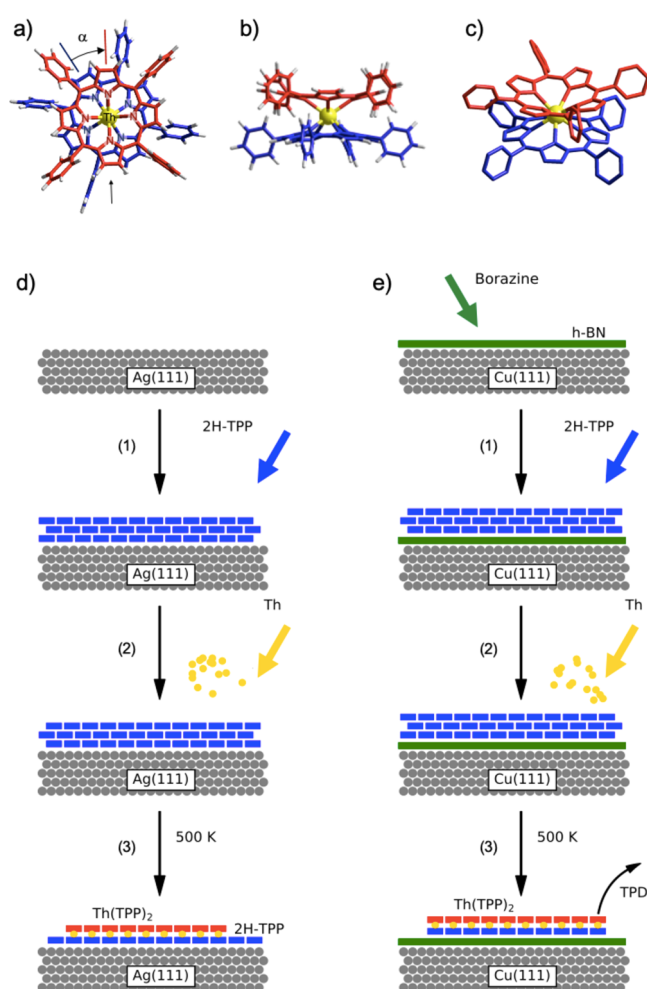


Figure 1. (a–c) DFT-optimized structure of a bis(porphyrinato)-thorium double-decker complex (Th(TPP)₂) in vacuum. The two TPP units connected via the Th center (yellow) are colored in red and blue, respectively. (a) Top view. α denotes the twist angle between the two macrocycles. (b) Side view (in the direction of the arrow in panel a). (c) 3D view (hydrogens omitted for clarity). (d, e) Schematic of the three-step synthesis route (1–3) for the formation of Th(TPP)₂ on Ag(111) (d) and *h*-BN/Cu(111) (e). See text for details.

py (STS), and temperature-programmed desorption (TPD).
124 On both supports, regular Th(TPP)₂ arrays are observed
125 without a discernible difference in packing and molecular
126 appearance. However, the electronic structure represented in
127 dI/dV spectra reveals distinct differences, e.g., featuring a larger
128 apparent electronic gap on *h*-BN/Cu(111). The twist angles
129 between the two macrocyclic ligands were determined for
130 Th(TPP)₂/Ag(111) and hint to a deviation from a perfect
131 square antiprismatic coordination of the Th center. Comple-
132 mentary density functional theory (DFT) modeling reveals
133 details of the molecular conformation, e.g., demonstrating an
134 inverted dome shape of the upper TPP. Molecular
135 manipulation applied to individual Th(TPP)₂ units anchored
136 in a 2H-TPP layer induced the reversible rotation of the top
137 porphyrin, thus demonstrating basic properties of a molecular
138 rotational switch.⁷⁶ To this end, the large size of the Th center
139 (ionic radius exceeding, e.g., the one of Tb)⁷⁷ might be
140 instrumental in providing well-distanced macrocycles. 141

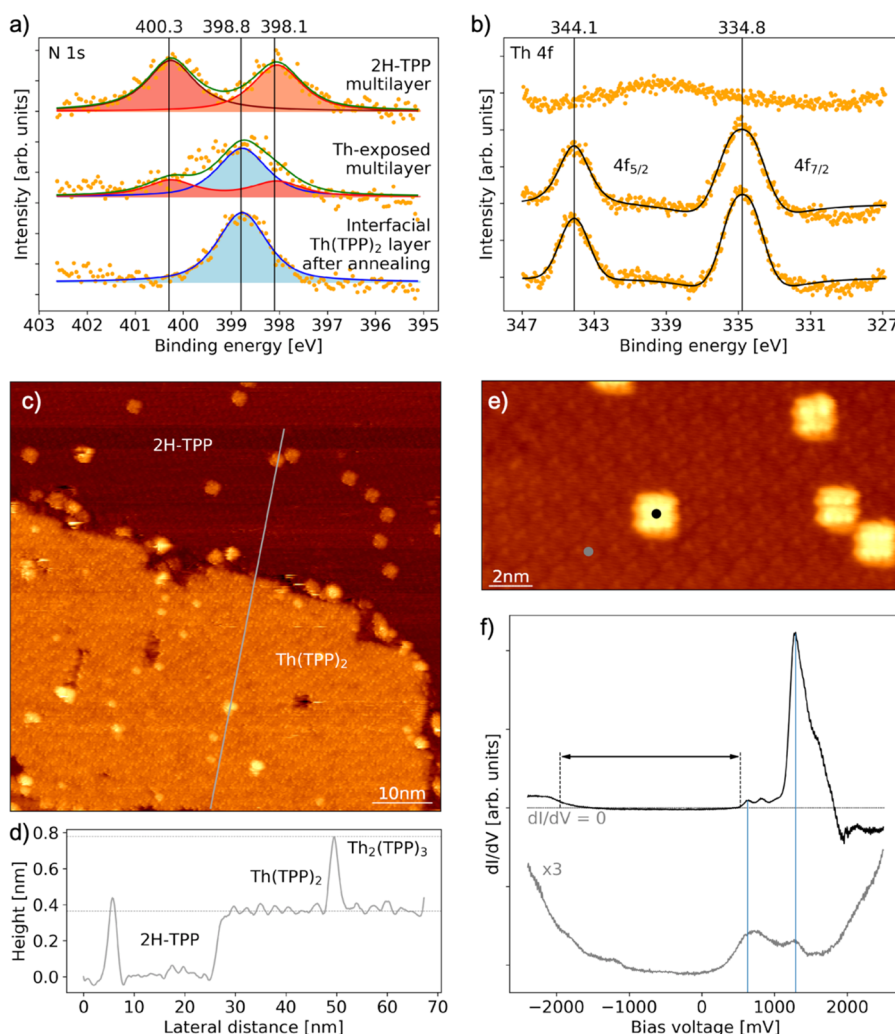


Figure 2. (a) Series of N 1s XP spectra representing a 2H-TPP multilayer on Ag(111) (top panel), the multilayer exposed to Th at rt (middle panel), and the resulting interfacial layer after thermal desorption of unreacted multilayer species (bottom panel). For each spectrum, fits are included for the individual components (see text for discussion). The respective binding energies are marked by the vertical lines with the values specified in eV. The maximum intensities of the spectra are normalized for better comparability. (b) Series of spin–orbit split Th 4f spectra representing the three synthesis steps described in panel a. (c) STM image of a $\text{Th}(\text{TPP})_2$ island in a 2H-TPP array embedding individual $\text{Th}(\text{TPP})_2$ units. (d) Apparent height profile along the path marked by the gray line in panel c. (e) Close-up STM image of individual $\text{Th}(\text{TPP})_2$ in the 2H-TPP layer. The colored dots represent positions where dI/dV spectra were recorded (see panel f). (f) (Top panel) Characteristic dI/dV spectrum of $\text{Th}(\text{TPP})_2$ revealing a large gap (marked by the arrow) and pronounced spectral features (see text for discussion). (Bottom panel) dI/dV reference spectrum of 2H-TPP. Tip stabilized at $I_t = 60$ pA and $V_b = 2.5$ V. Scanning conditions: (c) $I_t = 0.7$ nA, $V_b = 1.7$ V; (d) $I_t = 0.7$ nA, $V_b = 1.7$ V.

142 ■ RESULTS AND DISCUSSION

143 Thorium Bis(porphyrinato) Complexes on Ag(111).

144 The formation of $\text{Th}(\text{TPP})_2$ complexes on Ag(111) was
 145 monitored by XPS, following each step of the synthesis
 146 process. The corresponding N 1s and Th 4f signatures
 147 including fits are shown in parts a and b of Figure 2,
 148 respectively. The evolution of the N 1s core-level spectrum
 149 clearly reflected the metalation of the TPP. Before the
 150 deposition of Th (Figure 2a, top panel), two separate peaks
 151 arose from the two inequivalent nitrogen atoms in 2H-TPP,
 152 i.e., the pyrrolic ($-\text{NH}-$) and iminic ($-\text{C}=\text{N}-$) species.⁷⁸
 153 The binding energies ($E_b = 400.3$ and 398.1 eV) matched the
 154 reported values for 2H-TPP multilayers on Ag(111) (400.2
 155 and 398.1 eV).⁷⁹ After dosing Th, the N 1s signature changed
 156 considerably (Figure 2a, middle panel), reflecting a super-
 157 position of signals from unreacted 2H-TPP and a new species
 158 tentatively assigned to Th-metalated TPP. Following annealing

to 500 K, the width of the spectral feature was clearly reduced,
 159 and the signal could be described by a main peak at $E_b = 398.8$
 160 eV (Figure 2a, bottom panel). This indicates the desorption of
 161 unreacted TPP multilayer components and a dominating
 162 contribution of metalated TPP, where all four nitrogen atoms
 163 in the macrocycle are chemically equivalent. Such behavior is
 164 well-known from the in situ metalation of tetrapyrroles^{61,62,78}
 165 and consistent with the formation of $\text{Th}(\text{TPP})_2$ complexes.
 166 The resulting N 1s binding energy compares well with values
 167 reported for Fe-TPP (398.7 eV⁷⁹ and 398.4 eV⁸⁰), Ti-TPP
 168 (398.6 eV⁸¹), Ru-TPP (398.6 eV⁸²), and Co-TPP (398.8
 169 eV⁷⁸) on Ag(111). However, it is considerably larger than the
 170 N 1s binding energy (398.1 eV) attributed to the N–Tb
 171 component in TbPc_2 double-deckers on Ag(111).⁶⁰ Figure 2b
 172 depicts the Th 4f_{7/2} and 4f_{5/2} core levels that exhibit strong
 173 spin–orbit splitting. The binding energies (see Figure 2b)
 174 match the ones reported for oxidized Th (ThO_2 , $E_b = 344.2$
 175

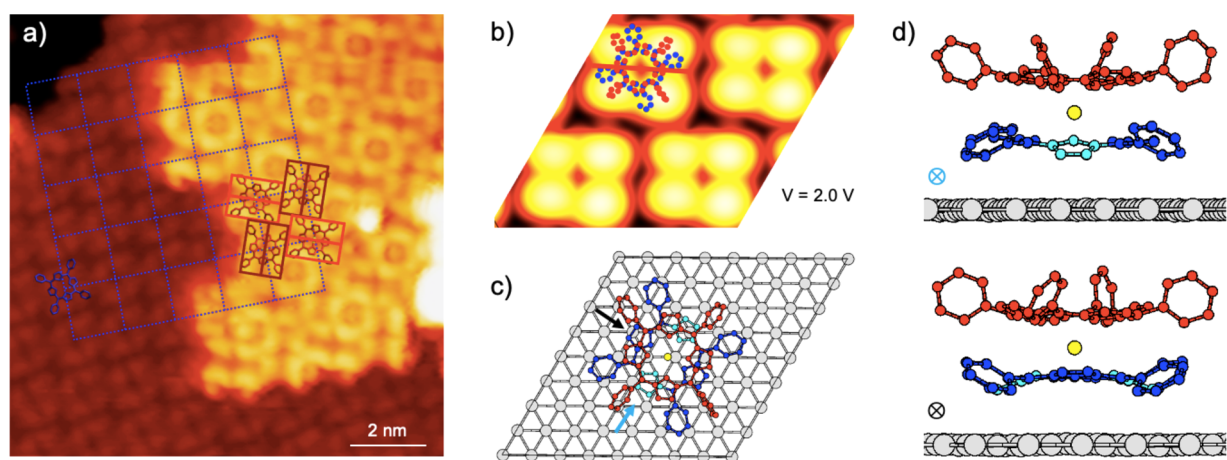


Figure 3. (a) STM image of a Th(TPP)₂ island embedded in a 2H-TPP array revealing submolecular contrast. The Th(TPP)₂ centers are in registry with the surrounding dense-packed 2H-TPP lattice (blue grid). The orientations of the upper porphyrin in adjacent Th(TPP)₂ units differ by $\sim 90^\circ$, as indicated by the molecular models framed in two shades of red. The main axis of the top ligand is marked by a line. A comparison to 2H-TPP (blue model) reveals a rotation of the upper porphyrin in Th(TPP)₂ by $(33 \pm 6)^\circ$ or $(-56 \pm 6)^\circ$ with respect to the bottom one. Scanning conditions: $I_t = 0.1$ nA, $V_b = 2.0$ V. (b) STM image simulation based on the DFT-optimized structure of Th(TPP)₂/Ag(111) (see panels c and d) computed at 2 V bias voltage. (c, d) Structural model with top ligand, bottom ligand, Th center, and Ag surface colored in red, blue, yellow, and light gray, respectively. (c) Top view. The κ -pyrroles are highlighted in turquoise. (d) Side views in the two directions indicated by the colored arrows in panel c. Hydrogens are omitted for clarity.

176 and 334.9 eV) rather than the ones of the pure metal species
177 ($E_b = 342.4$ and 333.1 eV).⁸³ This finding shows that the Th is
178 incorporated into the porphyrin's macrocycle and consistent
179 with a Th oxidation state +IV, as expected for Th(TPP)₂
180 complexes.³⁵

181 Because the XPS experiments point to a successful synthesis
182 of Th(TPP)₂, STM measurements were performed to get
183 insight into the surface morphology of the resulting system.
184 Figure 2c shows an STM image recorded after applying the
185 synthesis procedure described earlier using a low Th dose. The
186 silver surface was completely covered by well-ordered
187 molecular arrays. The top part was identified as a 2H-TPP
188 monolayer. The bottom part featured a compact island with an
189 apparent height exceeding the surrounding 2H-TPP film.
190 Because only a homogeneous monolayer and no second layer
191 species were observed after annealing the 2H-TPP multilayer
192 without the addition of Th,⁵⁸ this island was assigned to
193 Th(TPP)₂. Both the 2H-TPP layer and the Th(TPP)₂ array
194 hosted individual units of larger apparent height that were
195 scattered across the surface. The data showed no indication of
196 Th-modified single-decker species.⁶⁶ Taking a height profile
197 along the gray line revealed that the individual species
198 embedded in the 2H-TPP monolayer and the compact
199 Th(TPP)₂ island exhibited the same apparent height (see
200 Figure 2d). Accordingly, the former were assigned to
201 Th(TPP)₂ units. The coexistence of compact Th(TPP)₂ arrays
202 and individual Th(TPP)₂ units was reminiscent to the
203 situation of in situ synthesized Ce(TPP)₂⁵⁸ and Gd(Pc)₂⁵⁹
204 on Ag(111). Similar to other tetrapyrrole double-decker
205 complexes,^{52,59} the apparent height of Th(TPP)₂ was strongly
206 bias-dependent because it reflected the electronic structure of
207 the complex (see below). Accordingly, a meaningful
208 comparison of apparent heights of chemically different
209 M(TPP)₂ units was not straightforward. It is noted that the
210 apparent height of M(TPP)₂ increased with increasing positive
211 sample bias voltage until a height value was reached that stayed
212 roughly constant with further moderate increase of the bias.
213 When considering the apparent height at bias voltages where

214 this "plateau" was reached (1.9 V for Th(TPP)₂, 2.4 V for
215 Ce(TPP)₂), the values for Th(TPP)₂ (0.34 nm) and
216 Ce(TPP)₂ (0.33 nm)⁵⁸ measured relative to the surrounding
217 2H-TPP layer compared well. Given the similar covalent⁸⁴ and
218 ionic radii⁷⁷ of Th and Ce, this finding was not surprising.
219 Because of their apparent height of 0.78 nm (with regard to
220 2H-TPP), the additional bright species within the Th(TPP)₂
221 island were tentatively assigned to Th₂(TPP)₃ triple-decker
222 species.

223 The electronic properties of Th(TPP)₂/Ag(111) were
224 explored by STS. Figure 2f represents a typical dI/dV spectrum
225 taken above the center of an individual Th(TPP)₂ double-
226 decker (see black marker in Figure 2e), showing well-defined
227 features. The unoccupied spectral region ($V_b > 0$ V) was
228 dominated by a distinct peak at 1290 mV trailed by a shoulder
229 and a negative differential resistance (NDR) region. At ~ 670
230 mV a faint double protrusion was observed. Because its lower-
231 energy peak (onset at ~ 540 mV) was the first unoccupied
232 feature detected, it was associated with the lowest unoccupied
233 molecular orbital (LUMO). The occupied spectral region (V_b
234 < 0 V) revealed an onset at approximately -1950 mV, which
235 was tentatively assigned to the highest occupied molecular
236 orbital (HOMO). Consequently, the apparent HOMO-
237 LUMO gap amounted to ~ 2490 mV. Within an experimental
238 accuracy of ± 30 mV (i.e., given by the lateral and vertical
239 positions of the tip), the spectra recorded on several Th(TPP)₂
240 units provided consistent values for the characteristic spectral
241 features. While their assignment to distinct molecular orbitals
242 was not straightforward, some conclusions could be drawn
243 from the spectra. The low conductivity around the Fermi level
244 (E_F , $V_b = 0$ V) and the corresponding emergence of an
245 electronic gap, as well as the NDR signature, indicated a weak
246 interaction of the probed molecular states with the metallic
247 support. Reference spectra recorded on 2H-TPP (gray marker
248 in Figure 2e) did not show a gap but rather broad resonances.
249 Interestingly, the onset of the prominent feature in the
250 unoccupied range that was previously assigned to the LUMO

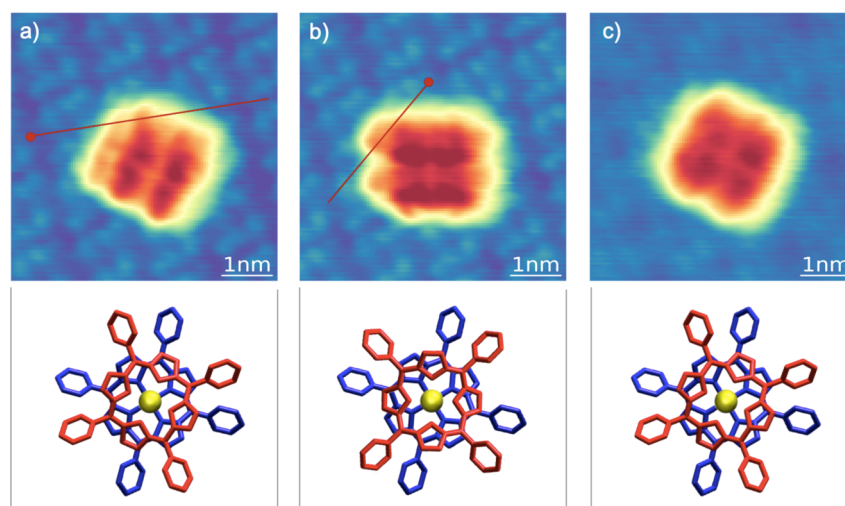


Figure 4. Reversible tip-induced mechanical rotation of the top porphyrin in individual $\text{Th}(\text{TPP})_2$ units. (Top row) STM images of a double-decker embedded in a 2H-TPP array. (Bottom row) Corresponding structural models (top view). (a) Initial configuration. By laterally moving the tip from the position marked by the red dot along the red line, a rotation of the top porphyrin is induced. (b) $\text{Th}(\text{TPP})_2$ after this first manipulation step. The red line marks the subsequently applied manipulation path. (c) In this second manipulation step, the $\text{Th}(\text{TPP})_2$ returned to its initial configuration. The apparent change in resolution is related to a minor modification of the STM tip apex. Lateral manipulation parameters: $I_t = 3.5$ nA, $V_b = 0.05$ V. Scanning parameters: $I_t = 0.11$ nA, $V_b = 1.7$ V.

251 of 2H-TPP^{66,85} coincided with the onset of the LUMO of
252 $\text{Th}(\text{TPP})_2$.

253 On a more general note, the overall spectral shape including
254 the features described earlier for $\text{Th}(\text{TPP})_2$ was reflected in
255 several different bis(tetrapyrrole)lanthanoid systems on
256 $\text{Ag}(111)$ and $\text{Cu}(111)$,^{47,57} even if the energies of the features
257 depended on the specific center atom, the tetrapyrroles, and
258 the substrate involved. Nonetheless, as far as we know, a
259 conclusive interpretation of these features is lacking in the
260 literature to date. The apparent HOMO–LUMO gap of
261 $\text{Th}(\text{TPP})_2/\text{Ag}(111)$ exceeded the ones of $\text{Ce}(\text{TPP})_2/\text{Ag}(111)$
262 (~ 2160 mV)⁴⁷ and $\text{CePcTPP}/\text{Ag}(111)$ (~ 1550 mV).⁵⁷
263 Whereas the latter case highlighted the influence of the Pc
264 ligand in the heteroleptic complex, the two homoleptic TPP
265 systems revealed the influence of the central atom.

266 In a next step, we aimed for a detailed insight into the self-
267 assembled $\text{Th}(\text{TPP})_2$ arrays and shed some light on the
268 conformation of the double-deckers. Figure 3 a shows an STM
269 image of a $\text{Th}(\text{TPP})_2$ island embedded in a 2H-TPP array
270 featuring intramolecular resolution. At a bias voltage of $V_b =$
271 2.0 V, the 2H-TPPs showed a square-like shape with four
272 protrusions and a central depression, as previously reported.⁸⁶
273 The $\text{Th}(\text{TPP})_2$, on the other hand, featured a more rectangular
274 shape with four extended protrusions, peripheral lobes, and a
275 central depression. Because of the apparent 2-fold symmetry of
276 the double-decker at this specific bias voltage, we defined a
277 main symmetry axis along the dark central line crossing the
278 $\text{Th}(\text{TPP})_2$ (see Figure 3a). A model overlay of the top
279 porphyrin showed that this main axis represented the N–Th–
280 N directions and indicated that the phenyl ring orientations as
281 well as a nonplanar macrocycle distortion contributed to the 2-
282 fold appearance. Importantly, two distinct orientations of the
283 porphyrin top ligand of $\text{Th}(\text{TPP})_2$ were observed, differing by
284 $\sim 90^\circ$ (see dark and light-red rectangular outlines in Figure 3a).
285 In the molecular array, the orientation alternated from
286 molecule to molecule. The centers of $\text{Th}(\text{TPP})_2$ were placed
287 on positions in the registry with the surrounding 2H-TPP
288 lattice with a nearest-neighbor distance of 1.39 nm (see blue

grid in Figure 3a), implying that the $\text{Th}(\text{TPP})_2$'s bottom 289
ligands followed the packing of the 2H-TPPs. On the basis of 290
this assumption, one could determine the twist angle α 291
between the bottom and top macrocycles of $\text{Th}(\text{TPP})_2$, which 292
amounted to $(33 \pm 6)^\circ$ for the dark-red species. This value 293
matched the twist angle of $\sim 30^\circ$ reported for crystalline 294
 $\text{Th}(\text{TPP})_2$ and indicated deviations from a square, anti- 295
prismatic coordination geometry.³⁷ For the bright-red species, 296
 $\alpha = (-56 \pm 6)^\circ$ (with “–” signaling counterclockwise 297
rotation), reflecting the same macrocycle registry if a 4-fold 298
symmetry of the macrocycle was assumed. Additionally, 299
 $\text{Th}(\text{TPP})_2$ featuring the opposite chirality, i.e., twist angles of 300
 $(-33 \pm 6)^\circ$ or $(56 \pm 6)^\circ$, occurred in islands with identical 301
packing. The same twist angles were found for individual 302
double-deckers embedded in 2H-TPP, which signaled that 303
packing effects did not play a dominant role. The conformation 304
of $\text{Th}(\text{TPP})_2$ thus differed from that of $\text{Ce}(\text{TPP})_2$, where twist 305
angles of $(15 \pm 5)^\circ$ and $(45 \pm 5)^\circ$ were reported for individual 306
and dense-packed double-deckers, respectively.⁵⁸ Nonetheless, 307
the packing scheme featuring alternating orientations of top 308
ligands differing by 90° was reminiscent of self-assembled 309
 $\text{Ce}(\text{TPP})_2$ islands on $\text{Ag}(111)$.⁵⁸ 310

A more detailed insight into the structure of $\text{Th}(\text{TPP})_2$ 311
adsorbed on $\text{Ag}(111)$ was provided by DFT (Figure 3b–d and 312
Figure S1 in the Supporting Information). The calculations 313
revealed that the top and bottom ligands displayed different 314
geometries. The bottom porphyrin, coupled to the metallic 315
substrate, exhibited a saddle conformation and a moderate tilt 316
of the peripheral phenyl groups (dihedral angles $\sim 40^\circ$). The 317
top ligand adopted an inverted dome shape and a larger tilt of 318
the phenyl rings (dihedral angles from 64° to 86° , average = 319
 74°). From the superposition of the STM image simulation 320
and the double-decker structure (see Figure 3b), one could see 321
that the STM contrast was entirely governed by the four 322
phenyl rings of the top ligand. The quantitative agreement 323
between STM simulations and experiments indeed allowed 324
one to assign the dark central line (characteristic of the 325
 $\text{Th}(\text{TPP})_2$ appearance at 2 V) to a N–Th–N axis, with the 2- 326

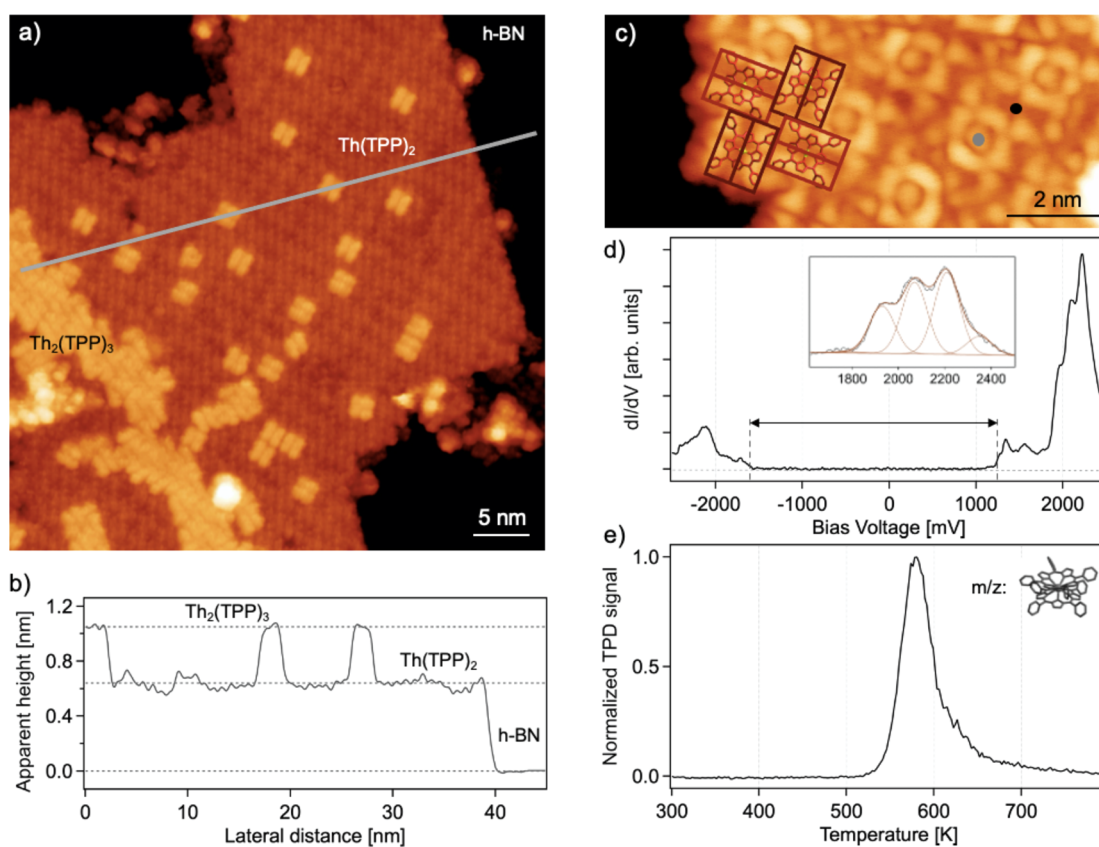


Figure 5. (a) STM image of a self-assembled $\text{Th}(\text{TPP})_2$ island on $h\text{-BN}/\text{Cu}(111)$. Third-layer species within the island are tentatively attributed to $\text{Th}_2(\text{TPP})_3$. (b) Height profile along the line highlighted in panel a. (c) STM image of a $\text{Th}(\text{TPP})_2$ island revealing the same packing as on $\text{Ag}(111)$. Two orientations of top porphyrins rotated by $\sim 90^\circ$ with respect to each other are observed, as highlighted by the superimposed rectangles and models (compare to Figure 3a). (d) dI/dV spectrum of $\text{Th}(\text{TPP})_2$ (averaged from three individual spectra) recorded above the center of the molecule (see black marker in panel c). The arrow marks the apparent gap. The inset shows a magnification of the substructure of the main peak (recorded above the position represented by the gray marker in panel c) after subtracting a polynomial background. The signal is fitted by four Gaussians with fixed separation and fixed width. Tip stabilized at $I_t = 100$ pA, $V_b = 2.0$ V, $z\text{-approach} = 0.5$ Å. (e) TPD spectrum of the relevant mass-to-charge ratio m/z , showing the desorption of $\text{Th}(\text{TPP})_2$ around 580 K. Scanning parameters: (a) $I_t = 0.8$ nA, $V_b = 1.725$ V; (c) $I_t = 0.5$ nA, $V_b = 2.0$ V.

327 fold symmetry induced by the phenyl groups tilted in opposite
 328 directions (see Figure 3b–d). Interestingly, DFT yielded a
 329 higher stability (by 60 meV) for a $\text{Th}(\text{TPP})_2$ configuration
 330 with a twist angle $\alpha = 30^\circ$ than for the one with $\alpha = 45^\circ$, thus
 331 confirming the experimental observation (which seems
 332 counterintuitive when only considering steric repulsion).
 333 Additional structural information (such as Th–N bond lengths
 334 and $\text{Th}(\text{TPP})_2$ adsorption heights) extracted from the DFT
 335 optimization is provided in Figure S1, including a comparison
 336 of $\text{Th}(\text{TPP})_2$ on $\text{Ag}(111)$, $\text{Cu}(111)$, and $h\text{-BN}$. It is noted that
 337 the inverted dome shape observed for the top decker might
 338 promote distinct interactions with nonplanar guest species,
 339 such as fullerenes.⁴⁷

340 Next, we experimentally addressed the structural stability of
 341 $\text{Th}(\text{TPP})_2$ and demonstrated the rotatability of the upper
 342 porphyrin by applying an STM-based molecular manipulation
 343 procedure. First, an STM image with scanning parameters not
 344 affecting the $\text{Th}(\text{TPP})_2$ was taken. Then, the STM tip
 345 approached the surface and laterally moved across the
 346 periphery of the upper porphyrin of the double-decker to
 347 exert a torque, keeping the current constant. Subsequently, the
 348 tip was retracted, and another STM image with the original
 349 parameters was taken to check whether the manipulation was
 350 successful. Figure 4 shows the reversible azimuthal rotation of

the top ligand of a $\text{Th}(\text{TPP})_2$ anchored in the 2H-TPP 351
 network by applying said procedure. Starting from the position 352
 marked by a red dot, the STM tip was moved along the red 353
 path, rotating the upper TPP out of its equilibrium orientation. 354
 From the initial configuration in Figure 4a, an apparent 355
 clockwise rotation of $\sim 70^\circ$ led to the configuration in Figure 356
 4b. Using the same manipulation procedure but a different tip 357
 path, the process could be reversed, as shown by the apparent 358
 counterclockwise rotation from panel b to panel c of Figure 4, 359
 after which the molecule was again in its initial state. During 360
 the whole procedure, the top porphyrin remained in registry 361
 with the unaffected 2H-TPP network. The two distinct 362
 configurations (Figure 4a and b) reflected the twist angles as 363
 discussed earlier. These lateral manipulation experiments were 364
 performed successfully on several molecules. In some cases, the 365
 removal of the complete $\text{Th}(\text{TPP})_2$ occurred, exposing a bare 366
 $\text{Ag}(111)$ patch.⁵² Apparently, the interaction between the Th 367
 center and the upper porphyrin macrocycle was sufficiently 368
 strong to prevent decomposition of $\text{Th}(\text{TPP})_2$ upon 369
 interaction with the STM tip under the applied manipulation 370
 parameters. This experiment also showed that the vertical 371
 separation of the two TPP units by the Th center was large 372
 enough to allow reversible rotational switching of the upper 373
 porphyrin, even though details of the process (such as the 374

sense of rotation) remained elusive to the STM methodology. Nonetheless, STM measurements of this system carried out at room temperature showed a rectangular outline of the individual molecules as in the low-temperature imaging (not shown), indicating that the rotation barrier was high enough to inhibit thermally induced rotation on the time scale of the STM imaging, even at room temperature. Indeed, a DFT-calculated energy profile between two configurations revealed a considerable energy barrier with a transition state featuring aligned phenyl moieties of upper and lower porphyrin ligands (see Figure S2). In summary, we concluded that surface-anchored Th(TPP)₂ represented a molecular rotor switchable by an external stimulus, in agreement with findings for surface-confined lanthanide tetrapyrrole sandwich compounds.^{58,87,88}

Thorium Bis(porphyrinato) Complexes on *h*-BN/Cu(111). After demonstrating the successful assembly of Th(TPP)₂ double-decker complexes on the Ag(111) surface, we now discuss the results of applying the same synthesis protocol to the *h*-BN/Cu(111) support (see Figure 1e), again yielding the targeted Th(TPP)₂ complexes. The *h*-BN spacer layer was introduced to access intrinsic molecular properties, reducing potentially detrimental effects on electronic and magnetic characteristics caused by interaction with a metallic support.^{50,51,55} Figure 5a shows an STM image of the resulting surface structure. Dense-packed islands of Th(TPP)₂ embedding individual, as well as aggregated, third-layer molecules were observed. However, no surrounding 2H-TPP layer remained on the surface. This allowed for determination of the apparent height of the complexes relative to the bare *h*-BN support. The line profile in Figure 5b reveals an apparent height of 0.64 nm (at $V_b = 1.725$ V) for the island assigned to Th(TPP)₂ and of 1.05 nm for the third-layer species.

Submolecularly resolved STM images exhibited the same order of the Th(TPP)₂ islands as on Ag(111) (Figure 5c). Specifically, a 2-fold appearance of Th(TPP)₂ was observed at $V_b = 2$ V, and every second upper TPP ligand was rotated by $\sim 90^\circ$ with respect to its neighbors, as reflected by the framed dark- and light-red models superimposed on the STM image in Figure 5c. Because no 2H-TPP was left as a “marker” for the orientation of the bottom TPP, the twist angle of Th(TPP)₂/*h*-BN/Cu(111) remained elusive in our experiment. DFT modeling (Figure S1) revealed a similar conformation for Th(TPP)₂ on Ag(111) and *h*-BN, with a larger adsorption height on the latter support.

The absence of 2H-TPP after annealing the Th-exposed 2H-TPP multilayer at 500 K showed that unreacted 2H-TPP readily desorbed from *h*-BN/Cu(111) at this temperature, whereas Th(TPP)₂ only efficiently desorbed at higher temperature (see below). Indeed, the desorption of a somewhat smaller tetrapyrrole (2H-porphine) from *h*-BN/Cu(111) occurred at 470 K.⁸⁹

A characteristic STS signature of a Th(TPP)₂ complex on *h*-BN/Cu(111) is shown in Figure 5d. Even though the key features already discussed for the dI/dV spectrum of Th(TPP)₂/Ag(111) remained clearly discernible, the spectrum on Th(TPP)₂/*h*-BN showed distinct modifications. The dominant resonance in the unoccupied spectral region appeared at ~ 2000 mV and showed a pronounced substructure with a series of peaks separated by an average spacing of (142 ± 5) mV (see inset in Figure 5d). A faint feature with an onset at ~ 1240 mV was assigned to the LUMO, following the notation introduced earlier for Th(TPP)₂/Ag(111). The occupied spectral feature comprised a subtle increase in

conductivity at approximately -1650 mV, the HOMO, which followed by a peak at -2130 mV. Accordingly, the apparent HOMO–LUMO gap (2890 mV) of Th(TPP)₂/*h*-BN/Cu(111) was noticeably increased by ~ 400 mV compared to Th(TPP)₂ adsorbed on Ag(111), pointing to an efficient electronic decoupling of Th(TPP)₂ from the Cu(111) by the *h*-BN spacer. Indeed, the substructure of the main resonance was reminiscent of vibronic excitations, as reported for phthalocyanines on *h*-BN/Ir(111) and *h*-BN/Rh(111).^{90,91} However, both the intensity sequence and the peak separation were distinct. The measured energy spacing (142 mV, 1145 cm^{-1}) and the rescaled energy spacing, considering the voltage drop across the *h*-BN layer⁹¹ (118 mV, 952 cm^{-1}), fell in a range of different vibrational modes reported for Th(TPP)₂.³⁸ It should be noted that the energy of Th(TPP)₂'s spectral features could vary with lateral position due to the corrugated electronic landscape provided by the *h*-BN/Cu(111) support.⁹²

To corroborate the in situ formation of Th(TPP)₂ complexes and to study the corresponding desorption characteristics, a qualitative TPD characterization was carried out. A Th(TPP)₂/*h*-BN/Cu(111) sample was prepared by the procedure described earlier and subsequently annealed with a linear heating rate (1 K/s), recording the signal that corresponded to the mass-to-charge ratio of the thorium porphyrinato double-decker (1456 amu). Specifically, due to the limited resolution at such a high mass, we integrated over a small mass range (1456 ± 10 amu). A typical desorption spectrum is depicted in Figure 5e, revealing a maximum at a temperature of ~ 580 K. The TPD experiment thus provided two important messages. (1) The detection of the Th(TPP)₂ proved the successful in situ synthesis of bis(porphyrinato) thorium on *h*-BN/Cu(111), complementing the STM data. (2) The *h*-BN support afforded the thermal desorption of intact, interfacial tetrapyrrole adsorbates and reaction products that could subsequently be characterized, e.g., by mass spectrometry, complementing TPD results on porphyrin multilayers and films.^{63,64}

CONCLUSIONS

We introduced actinides for interfacial coordination chemistry. Specifically, we reported the fabrication of homoleptic thorium bis(porphyrinato) complexes, namely, Th(TPP)₂, on well-defined model surfaces under UHV conditions. The N 1s and Th 4f XPS data revealed the bonding of the Th center to the TPP macrocycles. Submolecular resolution in STM imaging combined with complementary DFT modeling gave insight into the conformation of Th(TPP)₂, characterized by distinct twist angles between bottom and top porphyrin ligands (33° and 56°), an inverted dome shape of the latter, and tilted terminal phenyl moieties. The twist angles deviated from the ones reported for its lanthanide counterpart, Ce(TPP)₂ on Ag(111), reflecting the character of the actinide center. The self-assembled Th(TPP)₂ arrays on Ag(111) and *h*-BN/Cu(111) showed the same packing, with alternating orientations of the top ligands differing by 90° , consistent with reports on the Ce(TPP)₂ islands. The reversible rotation of the top porphyrin by tip manipulation demonstrated the potential of actinide-based tetrapyrrole double-deckers for molecular switching and machinery, with the large size of the Th ion facilitating rotational dynamics by separation of the two macrocycles. From a different perspective, this study showed for the first time the formation of a supramolecular double-

500 decker complex on a two-dimensional material, namely,
501 monolayer *h*-BN, and demonstrated the benefits of such a
502 decoupling layer. Specifically, the *h*-BN support permitted the
503 thermal desorption of intact double-decker units, corroborat-
504 ing the successful in situ Th(TPP)₂ synthesis, and allowed one
505 to observe details of the double-deckers' electronic structure
506 including vibronic signatures by STS. Thus, no metal surface
507 was needed as a catalyst for this multistep synthesis of actinide-
508 based metal–organic complexes.

509 We anticipate that the reported synthesis protocol is
510 generally applicable to diverse tetrapyrrole derivatives, addi-
511 tional actinide elements, and other supports (including two-
512 dimensional materials), thus opening pathways to actinide
513 complexes and nanostructures with tailored properties and
514 functionalities. Accordingly, surface-confined actinide-based
515 metal–organic complexes and supramolecular architectures
516 might perfectly complement lanthanide-based systems for
517 potential application in molecular magnetism, quantum
518 technologies, sensing, and heterogeneous catalysis.

519 ■ EXPERIMENTAL SECTION

520 **Experimental Setup and Data Processing.** XPS measurements
521 were conducted in a custom-built UHV chamber incorporating a XPS
522 system with a lab-based X-ray source and a hemispherical electron
523 analyzer from SPECS (Phoibos 100). All data were acquired using a
524 Mg anode (1253.6 eV) with a pass energy of 10 eV in normal
525 emission. During the acquisition of the XP spectra, the base pressure
526 was $<1 \times 10^{-9}$ mbar and the sample was kept at rt. The spectra were
527 calibrated against the binding energy of the Ag 3d_{5/2} core level.
528 Pseudo-Voigt functions were used to fit the spectra. The background
529 in the Th 4f spectra was corrected by subtracting a Shirley
530 background following the method of Herrera-Gomez et al.⁹³ For
531 the N 1s spectra, the background subtraction was performed by fitting
532 the clean Ag(111) signal with a polynomial function and subtracting
533 this adjusted curve from the data.

534 STM measurements were carried out in a separate custom-built
535 UHV system housing a commercial low-temperature CreaTec STM
536 operating at 7 K with a base pressure of $<3 \times 10^{-10}$ mbar. All images
537 were recorded in constant-current mode using a chemically etched W
538 tip.

539 The TPD experiments were performed in a custom-designed UHV
540 chamber with a base pressure of low 10^{-10} mbar, which could be
541 lowered to 6×10^{-11} mbar during the TPD acquisition by employing
542 liquid nitrogen cooled traps. A K-type junction, which was in direct
543 contact with the Cu(111) crystal, was used to measure the
544 temperature of the sample. The quadrupole mass spectrometer
545 (QMS) used in the TPD experiments was a Balzers QMA 160 rod
546 system enclosed within a copper cap,⁹⁴ in front of which the Cu(111)
547 crystal was positioned as close as 1 mm. A mass range up to 3000 amu
548 was covered with 400 kHz Extrel electronics. The temperature was
549 varied linearly, exploiting radiative heating from a glowing W filament
550 placed behind the sample and using a purpose-built PID controller
551 (Schlichting Physikalische Instrumente HS 130). The experimental
552 chamber also contained XPS equipment (a dual-anode X-ray source
553 and a SPECS Phoibos 100 hemispherical electron analyzer with 2D-
554 CCD detector) for optimization of the preparation procedures and
555 consistency checks. STM data were processed using Gwyddion,⁹⁵
556 python3, and the WSxM software (www.wsxm.es). A Gaussian filter
557 was applied to Figure 3a.

558 **Sample Preparation.** The Ag(111) and Cu(111) single crystals
559 were cleaned by repeated cycles of Ar⁺ or Ne⁺ sputtering at an energy
560 of 800–1000 eV and annealing to ~ 730 K (silver) and ~ 830 K
561 (copper) for several minutes. The 2H-TPP molecules (Sigma-Aldrich,
562 $\geq 99\%$ purity) were evaporated via organic molecular beam epitaxy
563 (OMBE) from a quartz crucible that was resistively heated to $T_{\text{evap}} \approx$
564 260 °C, while the sample was kept at rt. Th atoms were deposited
565 from a home-built water-cooled evaporator with integrated temper-

ature-stabilized quartz microbalance. Our source was a 0.2 mm Th 566
wire (Goodfellow, 99.5% purity) wrapped by multiple windings (0.5 567
mm pitch) of a 0.1 mm W wire onto a 0.3 mm W support wire. The 568
whole assembly was resistively heated, and the evaporation rate was 569
measured with the microbalance; see ref 96 for details. The *h*-BN 570
monolayer was grown by chemical vapor deposition of borazine 571
(B₃N₃H₆, Katchem, Czech Republic), following a published recipe.⁷⁵ 572

Theoretical Methodology. DFT calculations were carried out 573
using the Vienna Ab Initio Simulation Package (VASP)⁹⁷ with the 574
Perdew–Burke–Ernzerhof (PBE) exchange correlation.⁹⁸ The 575
projector-augmented wave potential with a cutoff energy of 400 eV 576
was used to describe the electron–ion interaction.⁹⁹ We considered 577
the metallic lattice parameter $a_{\text{Ag}} = 4.07$ Å (corresponding to a Ag– 578
Ag distance of 2.878 Å). Hence, we used the GGA PBE-D3 579
method¹⁰⁰ to achieve structural and electronic convergence of the 580
large supercells at Gamma point. The simulated STM images were 581
carried out by applying the Tersoff and Hamann theory in a plane- 582
wave basis set as implemented in the STMpw code.¹⁰¹ To visualize 583
the simulations, we used Crystal Maker 10 software ([www. 584](http://www.crystallmaker.com)
[crystallmaker.com](http://www.crystallmaker.com)).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at 588
<https://pubs.acs.org/doi/10.1021/jacs.1c04982>. 589

Additional structural information from DFT calcula- 590
tions, including coordinates of Th(TPP)₂ (PDF) 591

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<https://pubs.acs.org/doi/10.1021/jacs.1c04982> 625

626 **Notes**

627 The authors declare no competing financial interest.

628 ■ **ACKNOWLEDGMENTS**

629 We thank Nicolas Lorente for fruitful discussions. This work
630 was supported by the European Research Council Consol-
631 idator Grant NanoSurfs (no. 615233), the ANR-DFG project
632 RidePorph, and the Deutsche Forschungsgemeinschaft (DFG)
633 via the Cluster of Excellence e-conversion. M.-L.B. acknowl-
634 edges granted access to the French HPC resources of TGCC
635 and CINES under Grant A7-A0070807364 by GENCI. F.H.,
636 F.A., and J.V.B. are grateful for funding from the TUM
637 International Graduate School of Science and Engineering
638 (IGSSE) via the DFG, GSC 81. W.A. acknowledges funding by
639 the DFG via a Heisenberg professorship.

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