

Metallation by lanthanides of surface-confined multipyrroles

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Metallation of surface-confined porphyrinoid architectures have emerged as an important research topic due to its importance for biological phenomena and potential applications including optoelectronics, nanomagnetism, sensing and catalysis [1].

Hereby, the in-situ design of mutant porphyrinoids, either by selection of unconventional metal centers like lanthanides or by choosing expanded backbones, is attracting great attention.

In this talk we report our latest research regarding the metallation by dysprosium, an archetype lanthanide metal, of porphyrinoid species of distinct cavity size.

On one hand, the deposition of Dy on top a submonolayer of fluorinated 2HTPP species on Au(111) affords the expression of four different compounds, which are identified as physisorbed Dy-2H-TPP, Dy-1H-TPP, Dy-0H-TPP and 2HTPP species. Importantly, the Dy-2H-TPP complexes exhibit a zero bias resonance at Fermi level that is assigned to a molecular Kondo resonance and which can be switched off by voltage pulses transforming Dy-2H-TPP into Dy-1H-TPP species.

On the other hand, the self-assembly on Au(111) of an expanded aza-porphyrin, namely, an “expanded hemiporphyrazine”, through a unique growth mechanism gives rise to a long-range orientational self-assembly. Furthermore, a spatially controlled “writing” protocol on such self-assembled architecture is presented based on the STM tip-induced deprotonation of the inner protons of individual macrocycles. Finally, the capability of these surface-confined macrocycles to host lanthanide elements is assessed, introducing a novel off-centered coordination motif [2].

The presented findings represent a milestone in the fields of porphyrinoid chemistry and surface science, revealing a great potential for novel surface patterning, opening new avenues for molecular level information storage, and boosting the emerging field of surface-confined coordination chemistry involving f-block elements.

References:

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- [2] W. Auwärter, D. Écija, Nat. Chem. 7, 105 (2015).