On-surface synthesis of bis(benzenehexol)lanthanide sandwiches: chemical, electronic, and magnetic properties.

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Lanthanide-based organo-metallic and metal-organic nanoarchitectures are interesting low dimensional materials for a variety of applications such as nanomagnetism, information storage and quantum computing. From a magnetic point of view, the high spin-orbit coupling and the strong localization of 4f orbitals make lanthanides promising candidates for single molecular magnets.

In particular, a double-decker coordination is one possible strategy to induce a high anisotropic energy barrier between lanthanide spin states, magnetic remanence and long relaxation times due to their specific crystal field environment [1].

Here, we introduce a protocol to grow, from a bottom-up approach and in a step-wise manner, lanthanide-based double-deckers herein called bis(benzenehexol)lanthanides. The complexes consist on lanthanide atoms (either Dy or Er) sandwiched by two benzene-1,2,3,4,5,6-hexaol (BHO) molecules.

The bottom-up growth, tracked by means of Scanning Tunneling Microscopy, was performed on Au(111) single crystal by a consecutive sublimation of BHO species and lanthanide metal atoms. By DFT calculations, together with STS fingerprint of lanthanides, we were able to corroborate the formation of the complexes, and by XPS we could check the chemical status of the organic linker in this manner.

Magnetic properties were studied with XAS, XLD and XMCD measurements (Figure 1) by means of synchrotron radiation. We demonstrated the in-plane character of the magnetic anisotropy in the oblate Dy-BHO, and the more isotropic character in the prolate Er-BHO. We also reveal the +3 oxidation state of both lanthanide atoms. Our study paves avenues for the synthesis of novel organo-metallic complexes based on lanthanides, while revealing surface science insights about the decisive role of organo-metallic coordination in the magnetic properties.

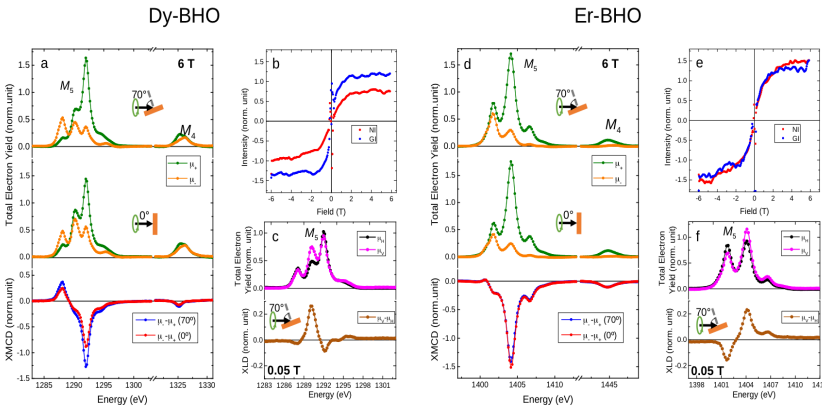

Fig. 1. a)-d) XAS and XMCD of Dy- and Er- BHO metallocenes; b)-e) Magnetic intensity versus external magnetic field in Dy-HBO and Er-BHO; c)-f) XLD for Dy- BHO and Er- BHO.

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