Engineering of organolanthanide sandwich complexes by on-surface synthesis

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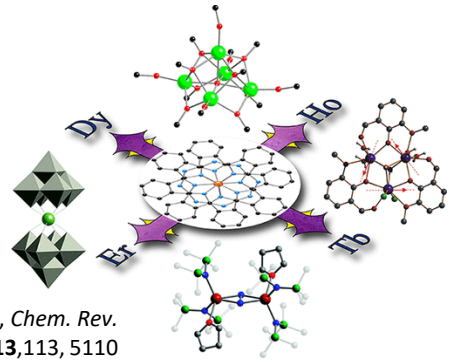
Single Molecule Magnets (SMMs)

- "Finite molecular unit capable of displaying slow relaxation of magnetization without the need for long range ordering"

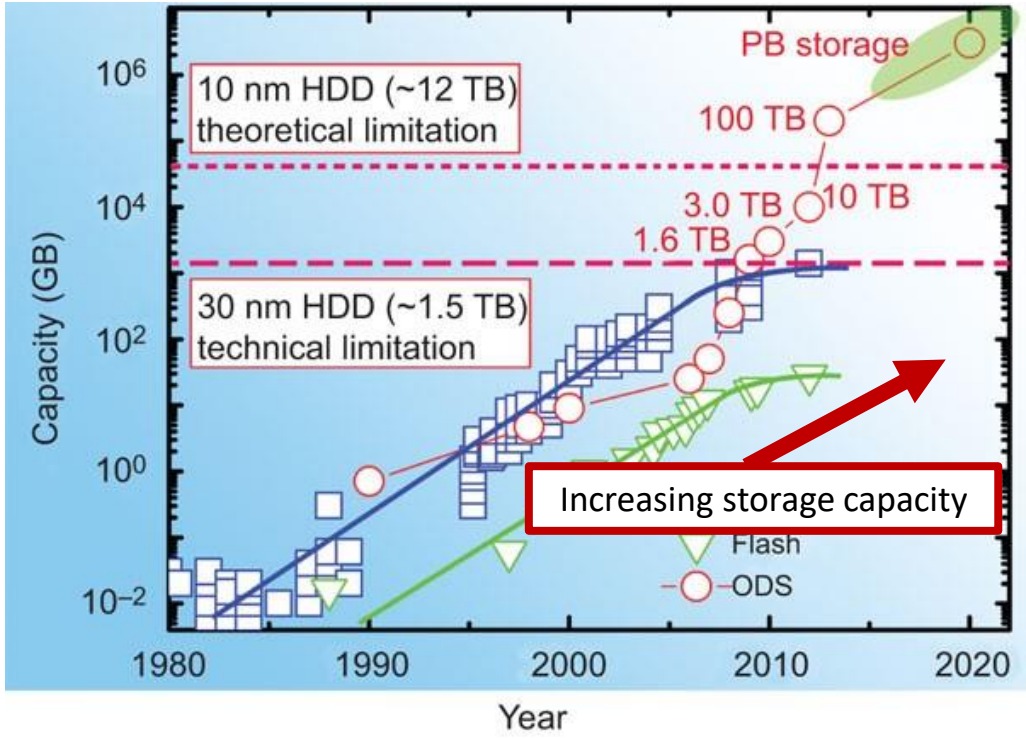
- High potential for technological applications
  - High density information storage
  - Molecular spin qubits
  - Spintronics devices

- Lanthanide-based SMMs
  - High magnetic moments
  - High magnetic anisotropy
  - Large spin lifetimes



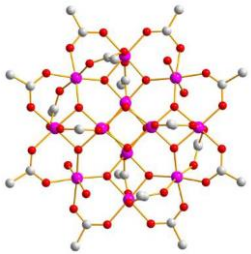
D. N. Woodruff et al., *Chem. Rev.* **2013**,113, 5110

Data storage limit



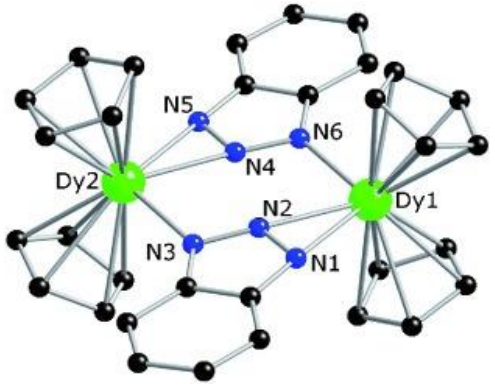
Decreasing bit size

SMM

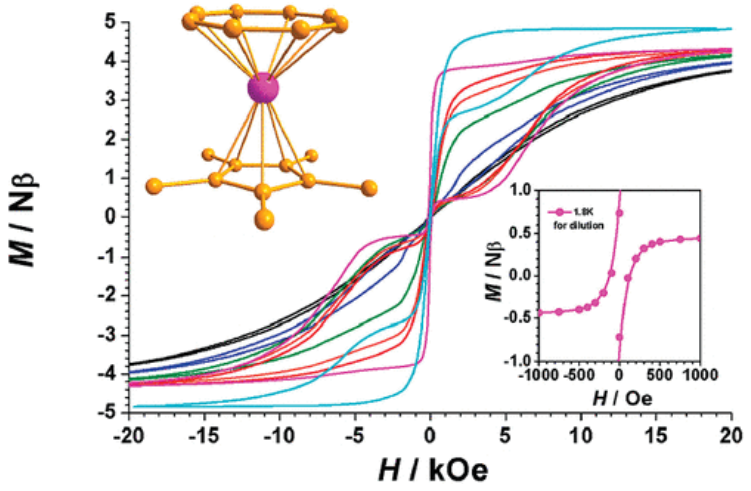


Organolanthanide SMMs

- Molecular complexes that present least one chemical bond between a carbon and metal atom
- Ligands synthesized up to now have been typically five (metallocenes) or eight member rings ($Ln[COT]_2$)
- Usually synthesized in solution



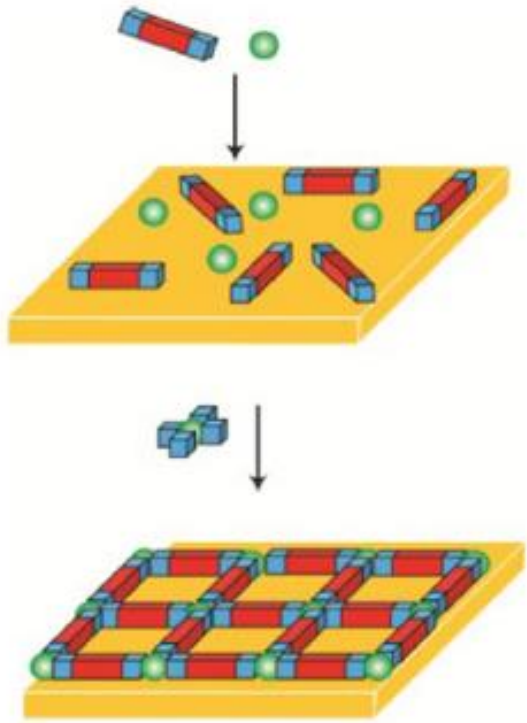
R. A. Layfield et al., *Chem. Eur. J.* **2010**, 16, 4442



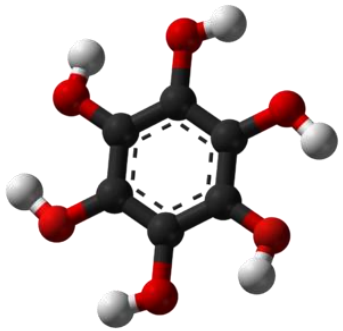
S. Jiang et al., *J. Am. Chem. Soc.* **2011**, 133, 4730

On-surface synthesis of organolanthanide complexes

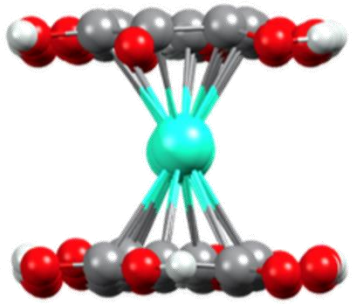
- On-surface synthesis:
  - Bottom-up approach to synthetize carbon-based materials with low dimensionality (0D, 1D and 2D)
  - Regular arrays with long range order
  - Flexibility and tunability to engineering tailorable functional nanomaterials



- Synthesis of organolanthanide sandwich complexes based on six-membered ring H_6HOB molecules and Dy/Er atoms on a Au(111) surface

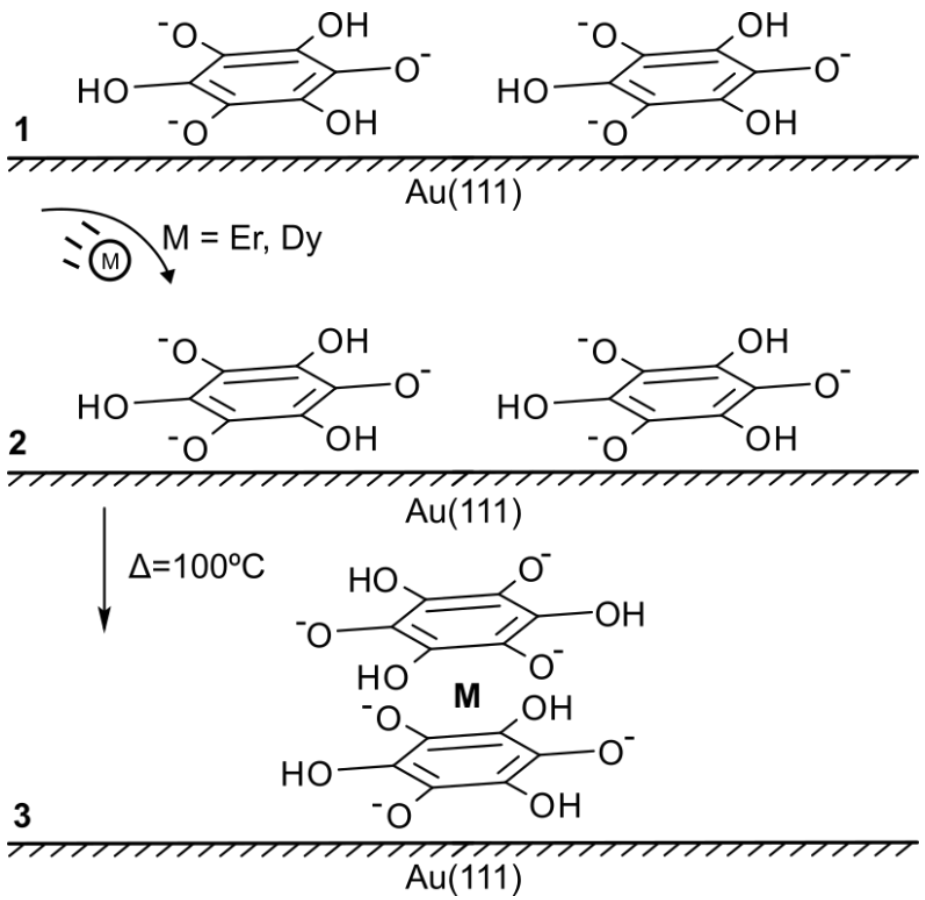


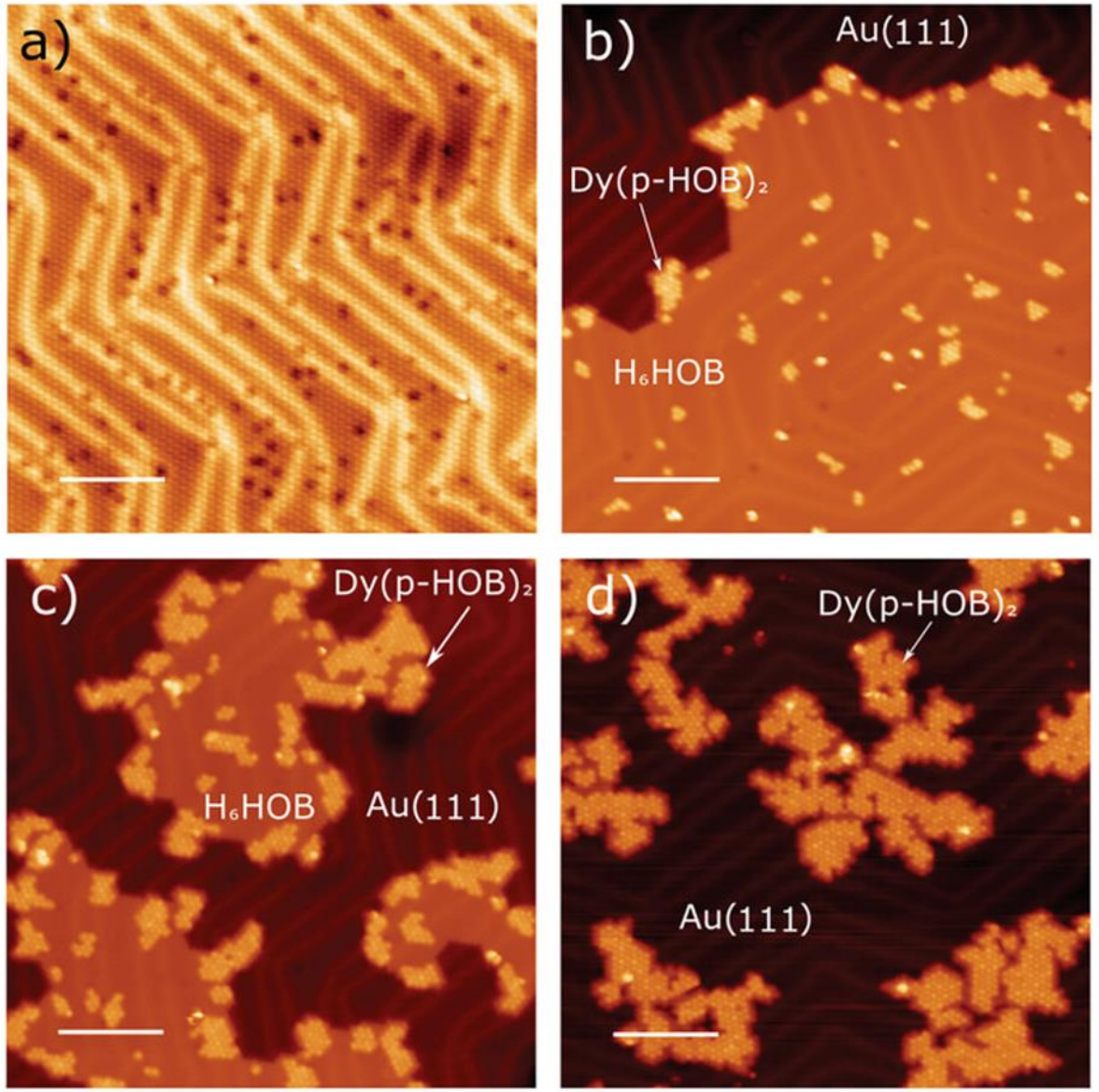
Hexahydroxybenzene: H_6HOB



Organolanthanide mononuclear sandwich: $Ln(p\text{-}HOB)_2$

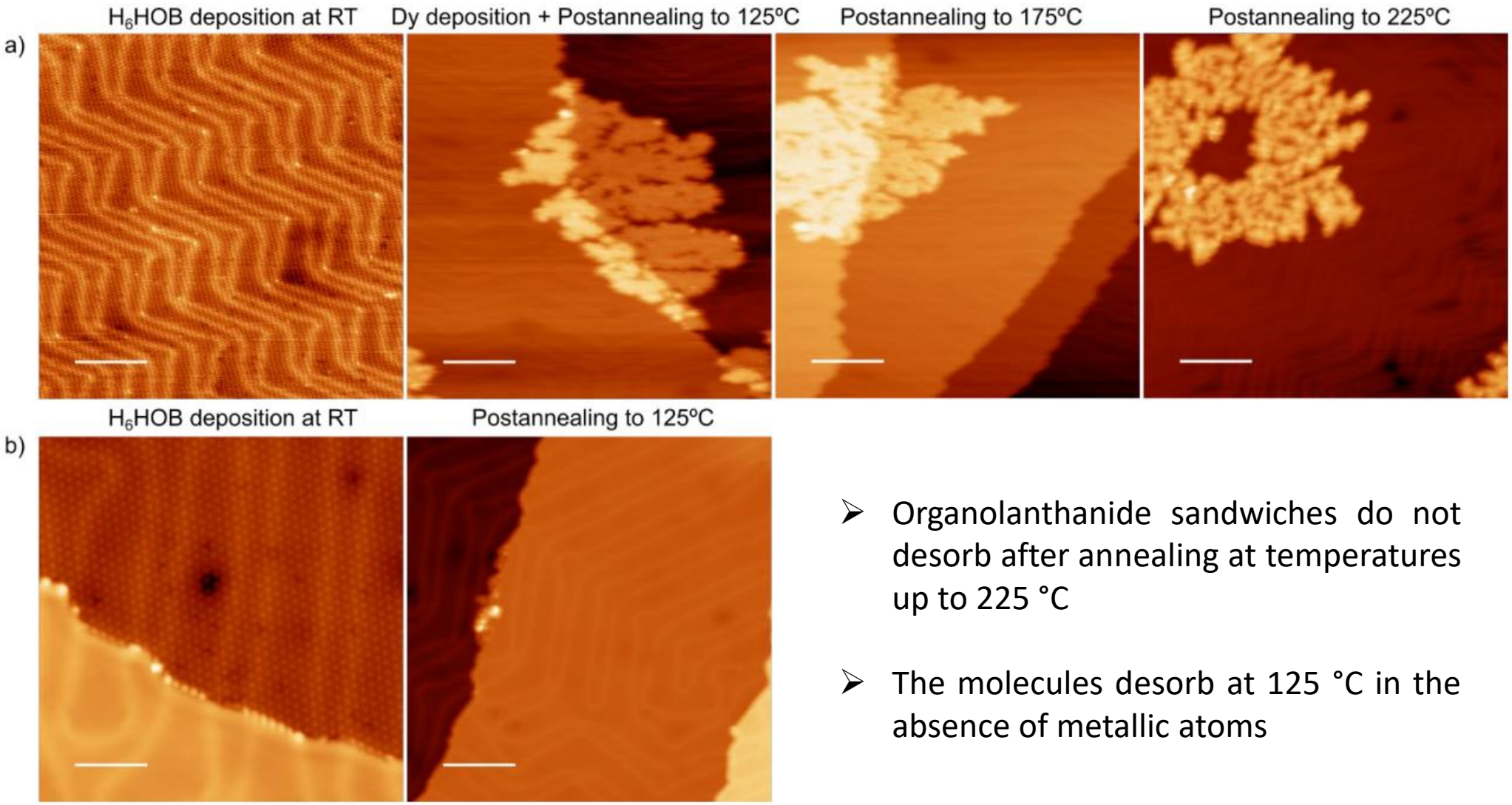
On-surface synthesis of organolanthanide sandwiches





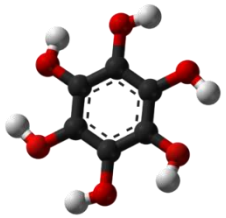
Unprecedent organometallic sandwich complexes

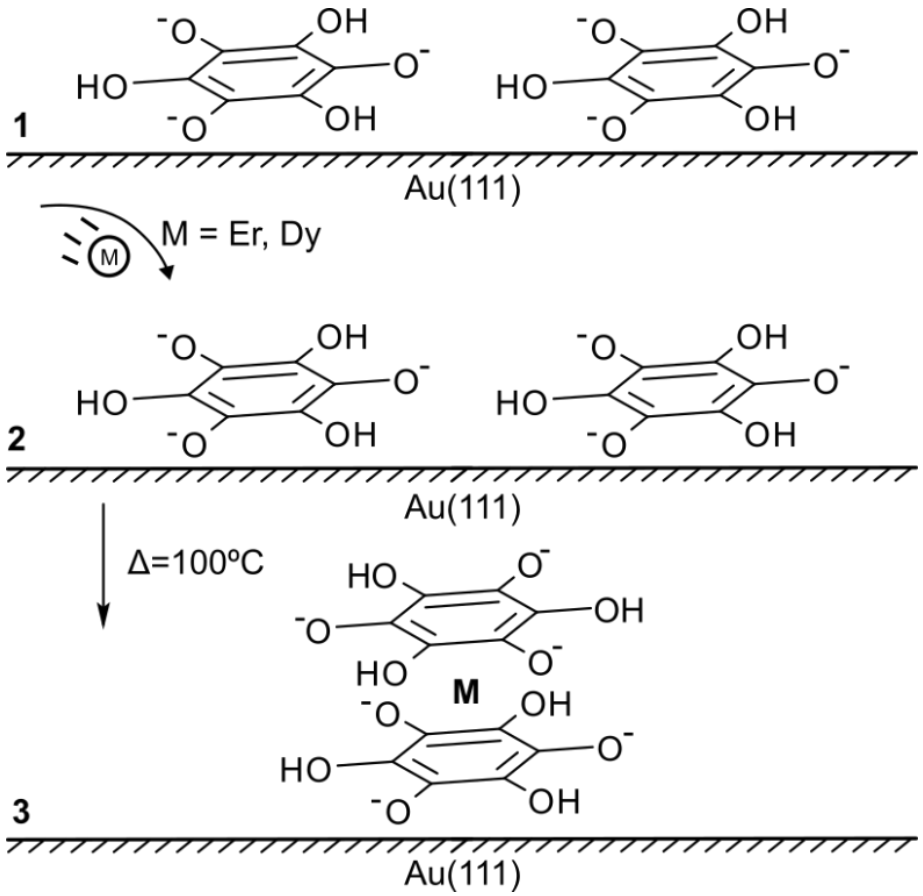
Temperature stability

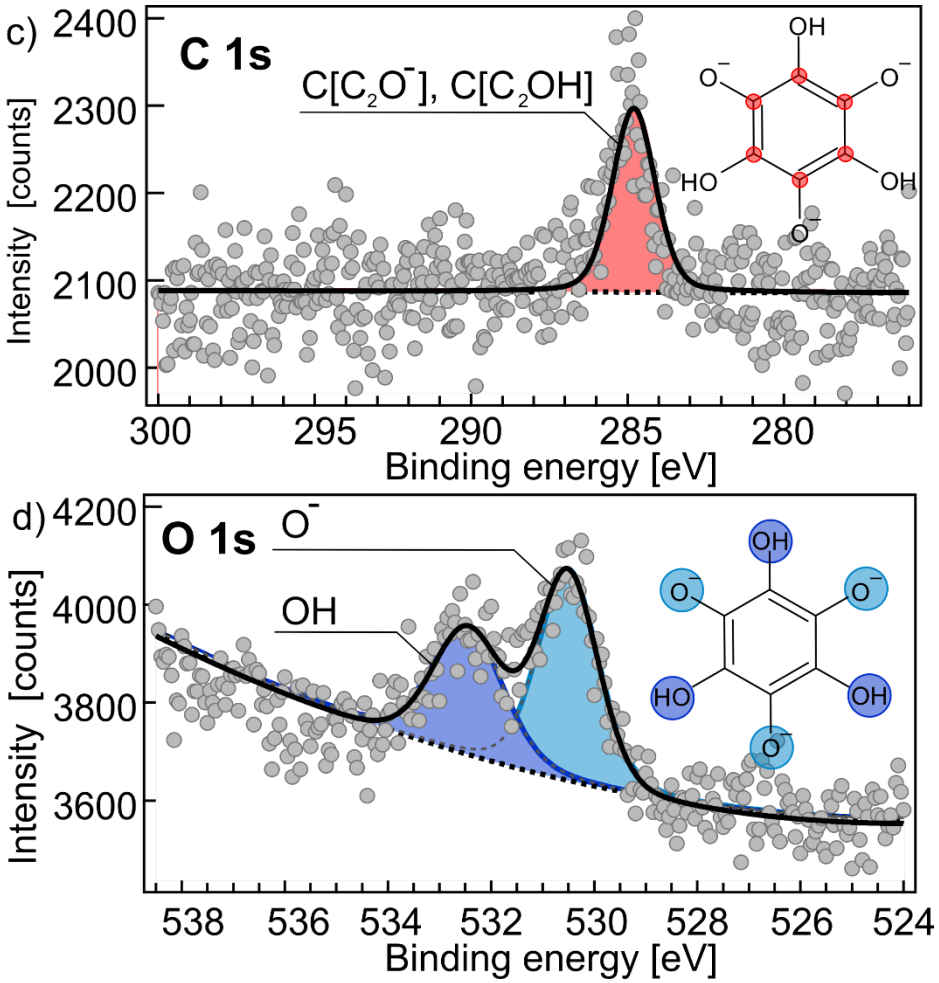


- Organolanthanide sandwiches do not desorb after annealing at temperatures up to 225 °C
- The molecules desorb at 125 °C in the absence of metallic atoms

Chemical analysis



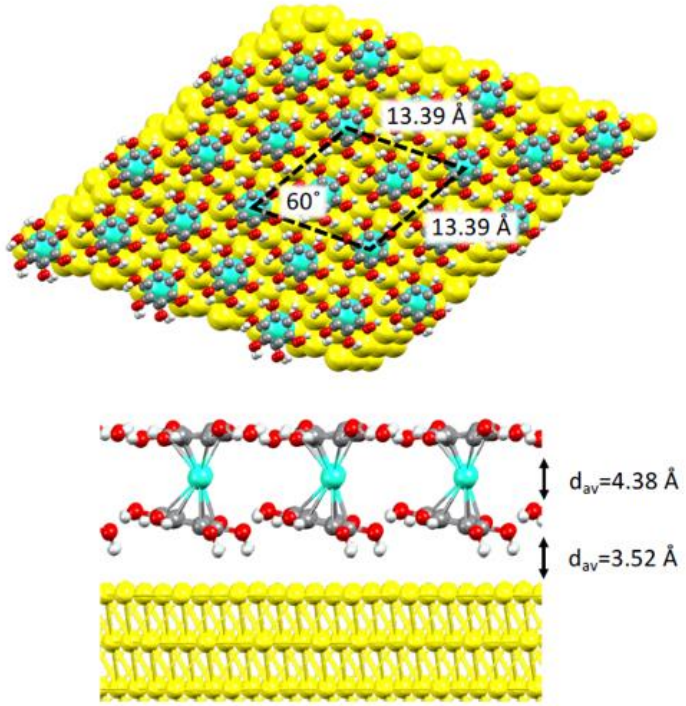




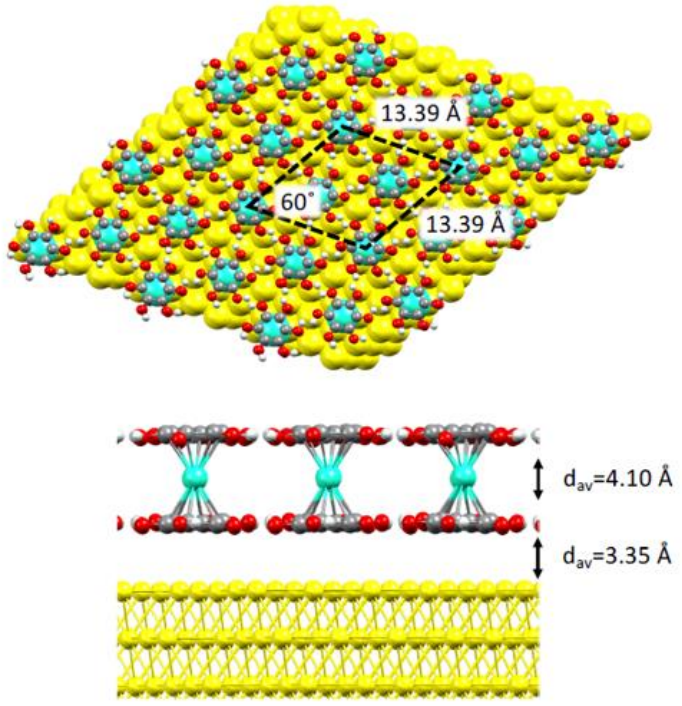
Partially deprotonated molecules

DFT calculations

Non-deprotonated molecules

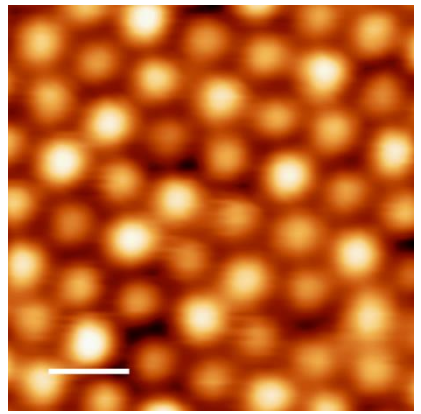


Partially deprotonated molecules

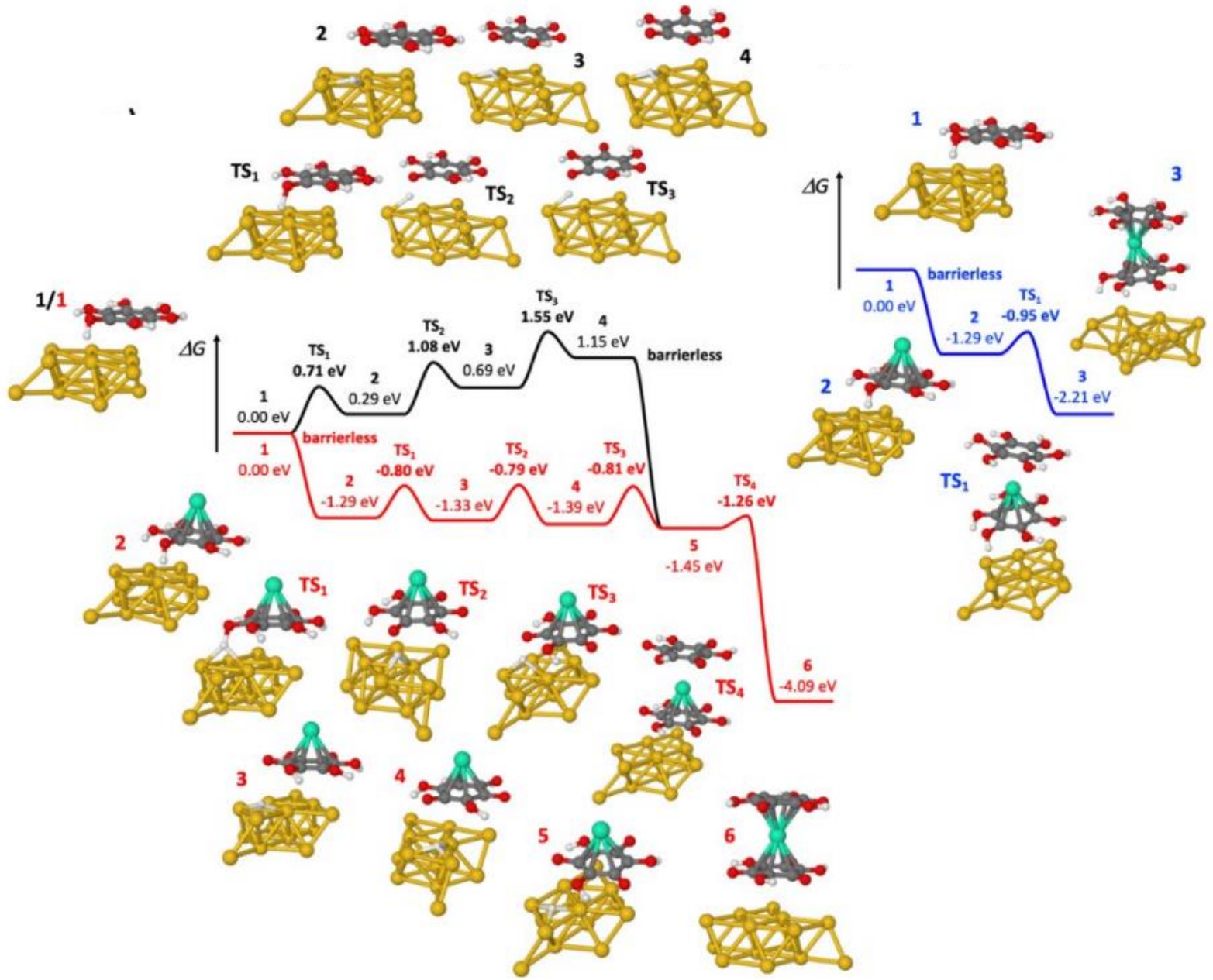


- Simulated STM images for partially deprotonated molecules shows perfectly round molecules in agreement with the experimental images

Experimental STM image



Atomistic reaction pathways



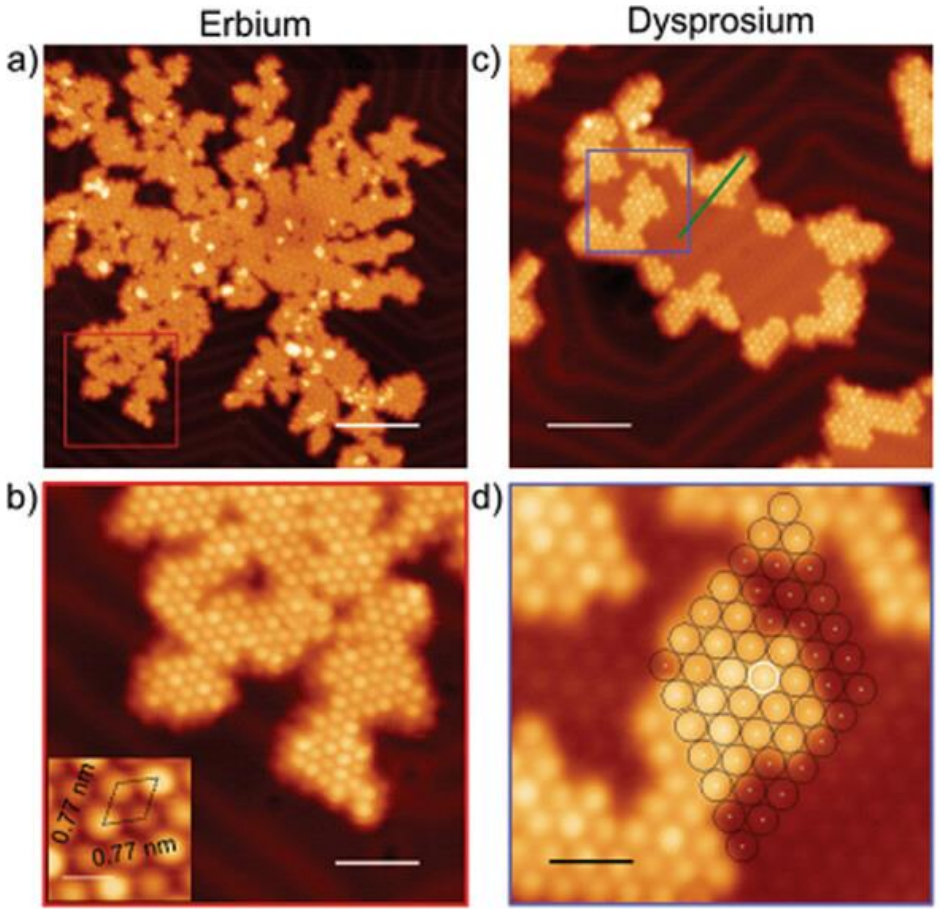
Energy barrier: 0.34 eV
Free-energy gain: -2.21 eV

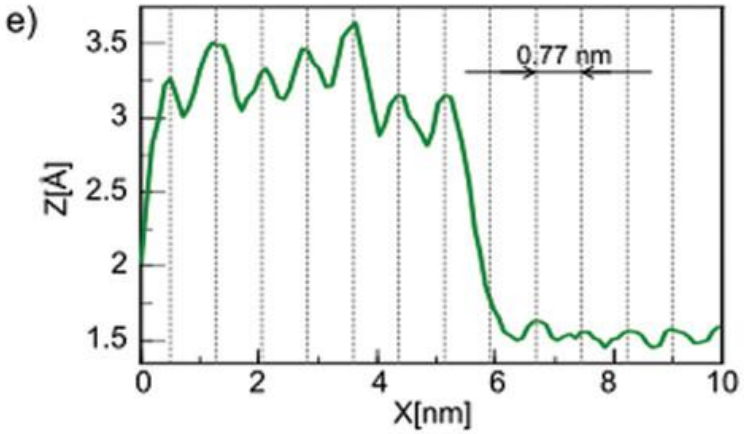
Energy barrier: 1.55 eV
Free-energy gain: -4.09 eV

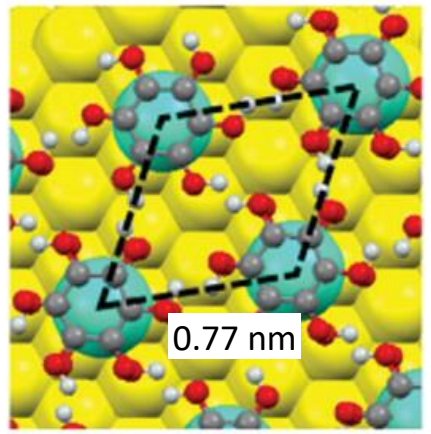
Energy barrier: 0.58 eV
Free-energy gain: -4.09 eV

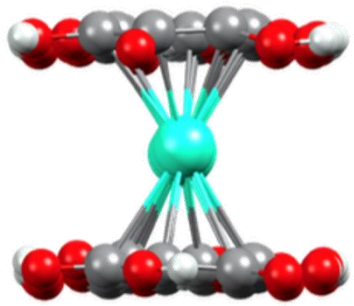
Most favorable process: formation of partially deprotonated species

Structural analysis



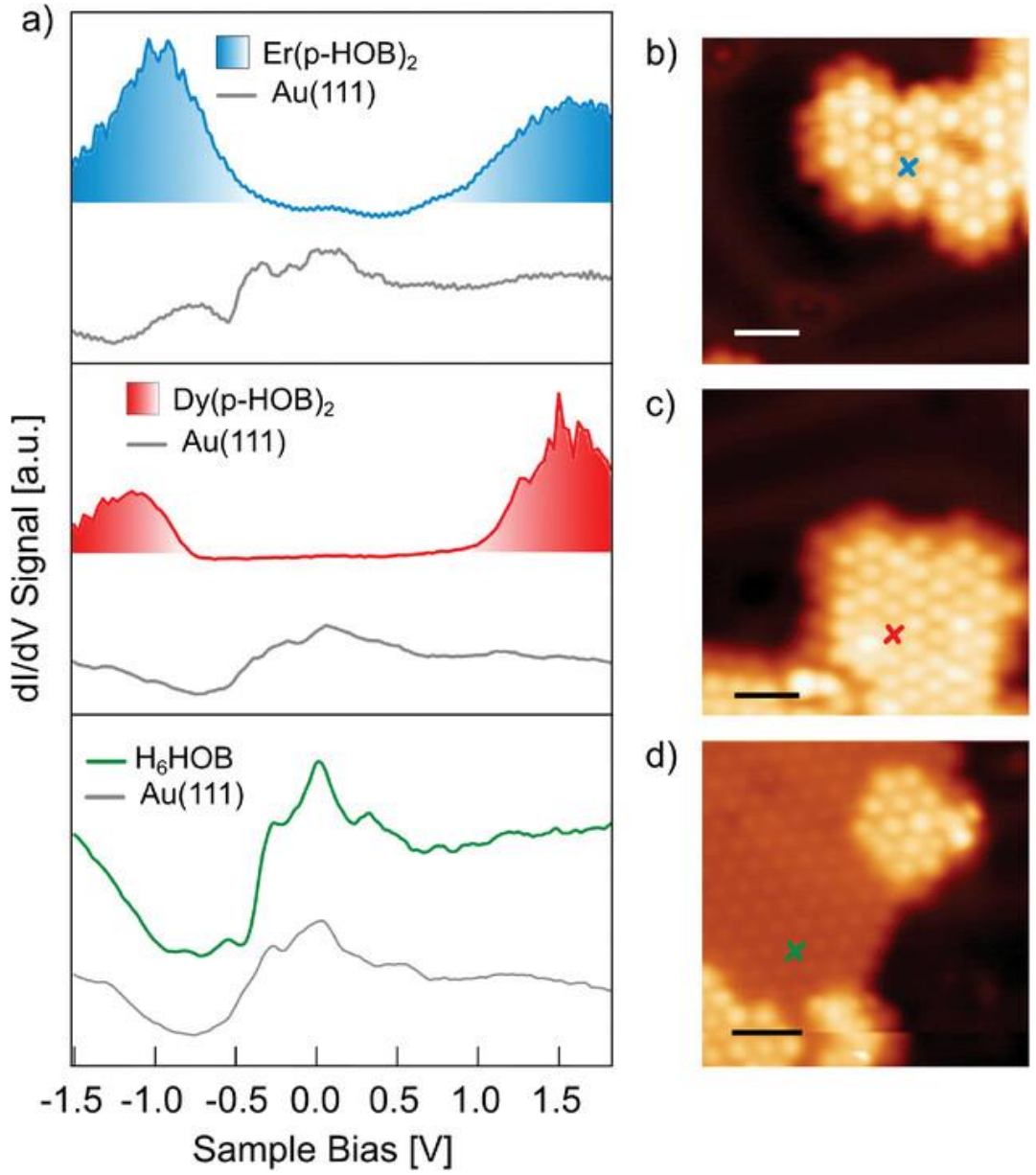






- Dysprosium and Erbium form the same sandwich structure
- In both cases the molecules of the second layer are perfectly aligned with the first layer

Electronic properties



- Both Dy and Er sandwich complexes present similar electronic structure
  - Two prominent peaks at negative (HOMO) and positive bias (LUMO)

- The monolayer of molecules doesn't present any significant feature

Magnetic properties

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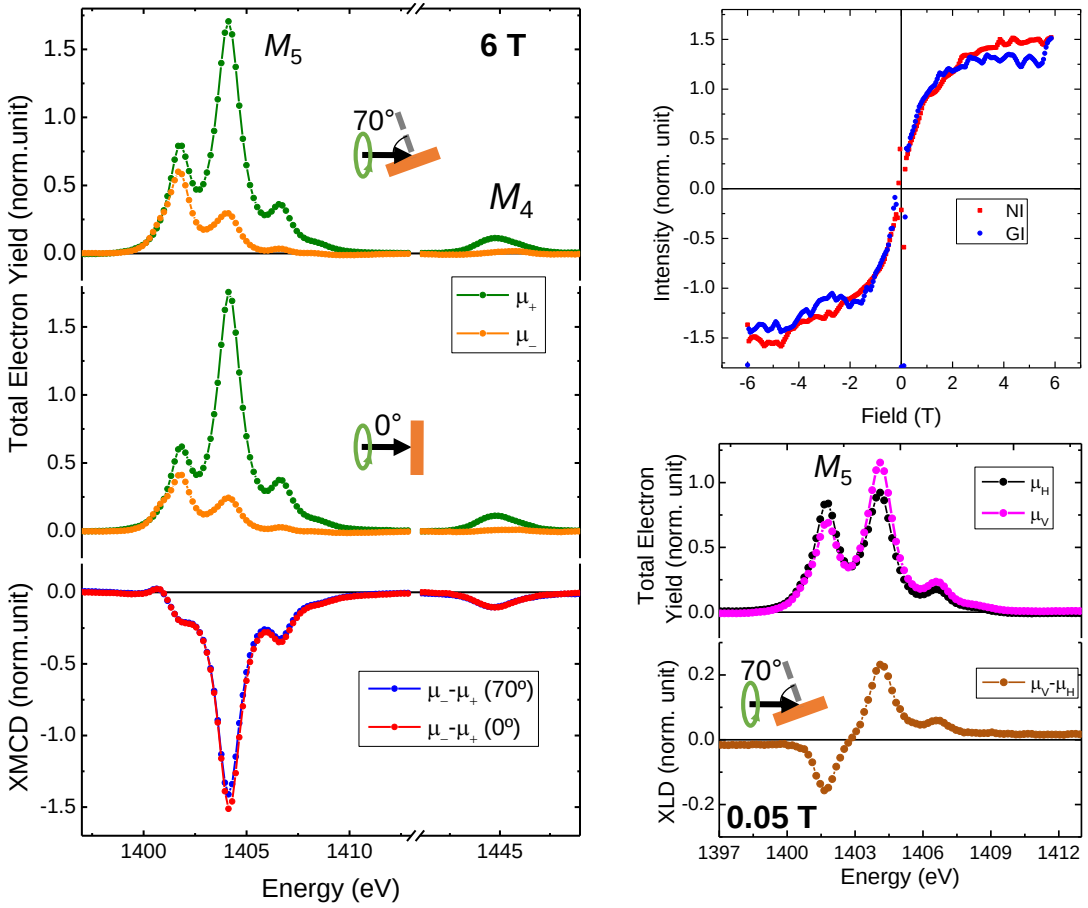
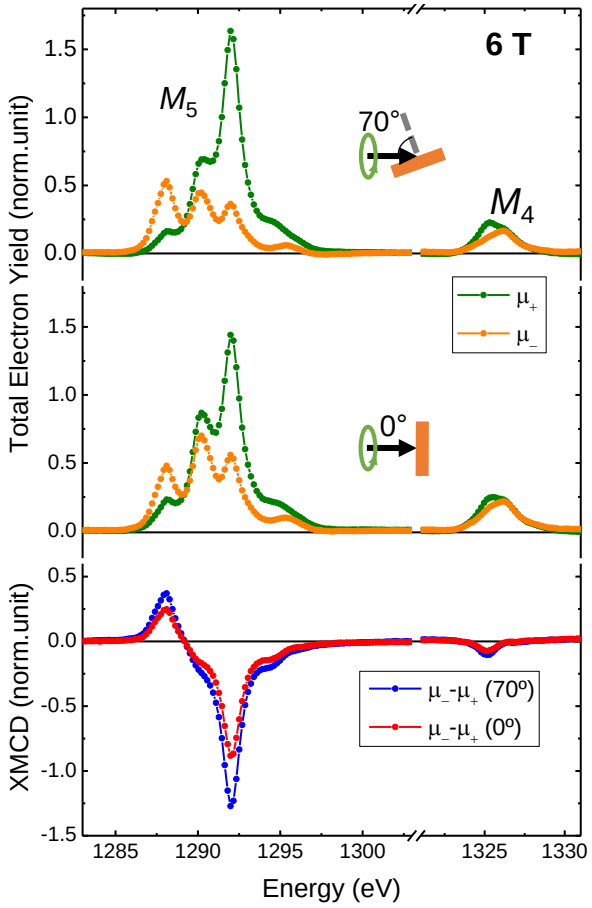
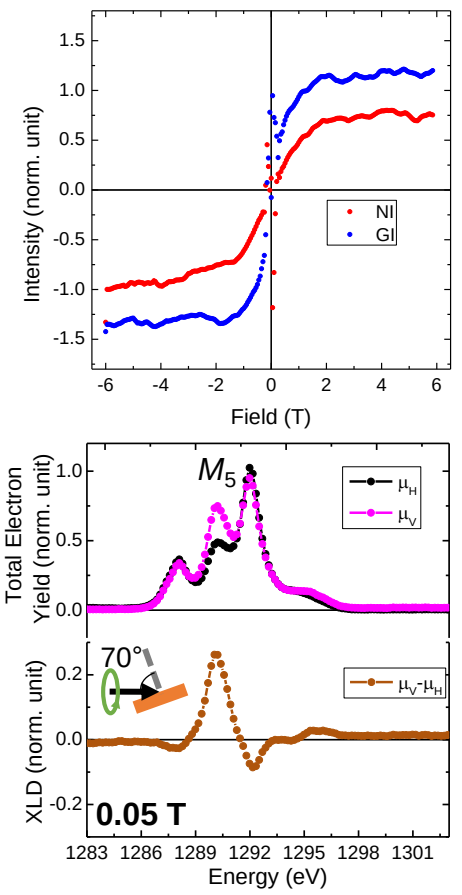
Erbium



Dysprosium





- Oxidation state: +3 for both Er and Dy
- Different magnetic properties: nearly isotropic for Er and in-plane anisotropy for Dy

Magnetic moments

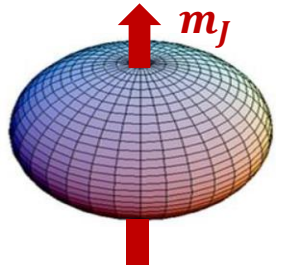
	$Dy(p\text{-}HOB)_2$		$Er(p\text{-}HOB)_2$	
Incidence angle (°)	70	0	70	0
$\langle S_z \rangle$	1.9(2)	1.1(1)	0.9(1)	1.0(1)
$\langle L_z \rangle$	3.9(4)	2.2(2)	3.6(4)	4.4(4)
$\langle J_z \rangle$	5.8(6)	3.4(3)	4.5(5)	5.5(5)
m_J	7.7(8)	4.5(4)	5.4(6)	6.5(6)

- $Dy(p\text{-}HOB)_2$: higher moments at GI, $\langle J_z \rangle = {}^{11}/_{2}$
- $Er(p\text{-}HOB)_2$: higher moments at NI, $\langle J_z \rangle = {}^{11}/_{2}$

Dy^{+3}

$\langle J_z \rangle = {}^{11}/_{2}$

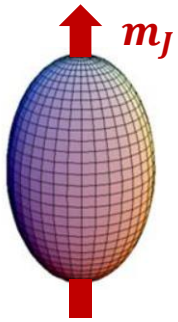
oblate charge density



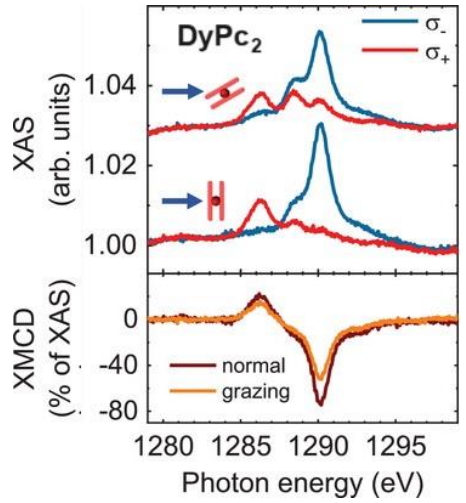
Er^{+3}

$\langle J_z \rangle = {}^{11}/_{2}$

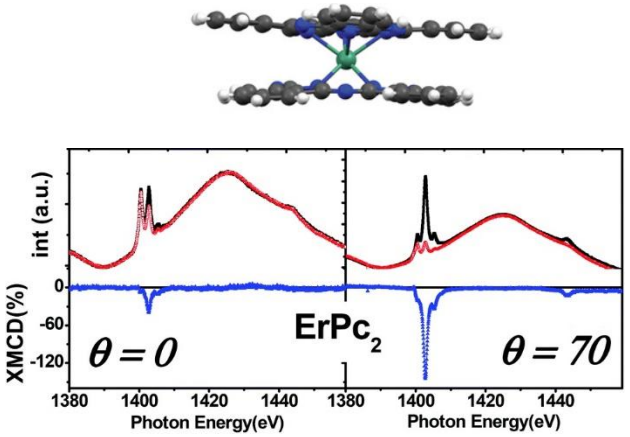
prolate charge density



Magnetism of sandwich complexes: comparation with literature

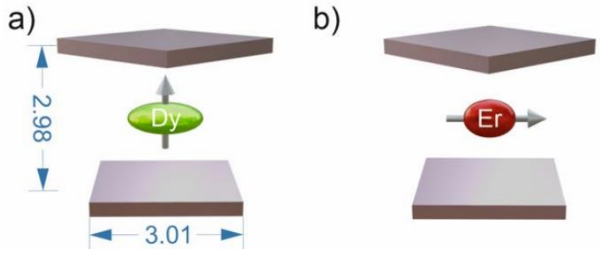


M. Studniarek et al., *Adv. Sci.* **2019**, 6, 1901736



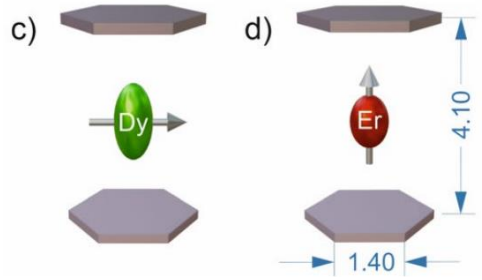
V. Corradini et al., *Nanoscale* **2018**, 10, 277

$LnPc_2$

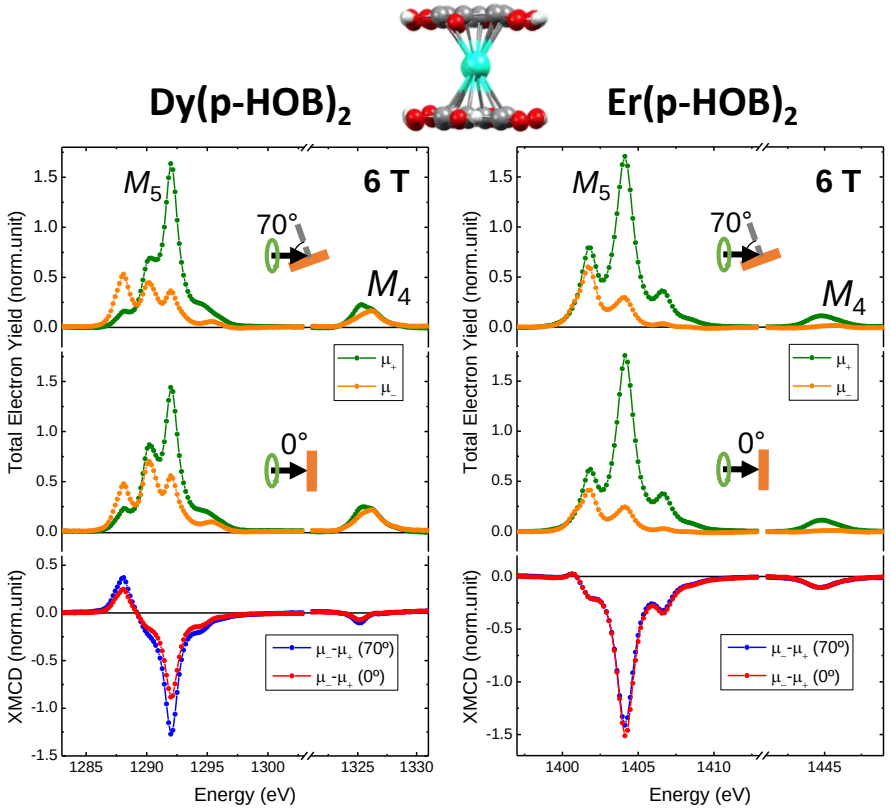


Sandwich structure compressing the lanthanide atoms

$Ln(p\text{-}HOB)_2$



More elongated crystal field, higher separation between the two layers



Magnetic properties are determined by the elongated crystal field

Summary

- Unprecedented lanthanide-directed organometallic architectures designed by on-surface chemistry
  - Lanthanide atoms sandwiched between two partially deprotonated hydroxybenzene molecules

- By metal-exchange (Dy/Er):
  - Structural integrity preserved
  - Similar electronic properties
  - Drastic modification of the magnetic properties

- Our results open avenues for the development of organometallic chemistry on surfaces and envision the capability to tailor the magnetic properties of such complexes on surfaces, while preserving the structural integrity by lanthanide exchange.

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Shanmugasibi K. Mathialagan, Sofia O. Parreiras, Maria Tenorio, Lenka Černa, Daniel Moreno, Beatriz Muñiz-Cano, Cristina Navío, Manuel Valvidares, Miguel A. Valbuena, José I. Urgel, Pierluigi Gargiani, Rodolfo Miranda, Julio Camarero, José I. Martínez, José M. Gallego, and David Écija**

Thanks for your attention!

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