

Experiment report for

Proposal Code A25-2-964

Proposal Title Structural and compositional characterization of 2D MOFs grown on silica

The goal of this proposal is to characterize thin films of a 2D MOF of formula $[Ln_xLn'_{(1-x)}(MeCOO)(PhCOO)_2]$ grafted on a p-doped silicon wafer using a silane.

The capabilities of SpLine Beamline afford the possibility of performing grazing incidence X ray diffraction (GIXRD) as well as compositional characterization of the film by means of XPS/HAXPES and XRF.

During the experiment we found several problems: mainly the MOF samples would suffer irreversible radiation damage when GIXRD experiments were performed open to air. This resulted in the destruction of several of the important samples. In order to mitigate this risk several other samples has been shipped to ESRF. Mainly, a luminescent Eu complex on the same functionalized silica wafers.

The HAXPES/GIXRD setup at BM-25 allow us to work under UHV and thus obtain some data.

From the data obtained:

-The 2D MOF seems to be present on the surface as randomly oriented crystallites (manuscript in preparation).

-The Eu-SYML complex is grafted on the surface in ordered regions that cover a large area of the substrate. Results have been reported in *Inorg. Chem. Front.*, 2022, 9, 4160, DOI: 10.1039/d2qi00995a

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Towards large area surface functionalization with luminescent and magnetic lanthanoid complexes†

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Homogeneous surface deposition of molecules over a large area of the substrate is difficult to achieve but extremely important for proposed applications of magnetic molecules in data storage, information processing or molecular spintronics. In this paper we report a simple method for large area surface functionalization with the aim of grafting complex molecules in an organized manner. A proof of concept is given by grafting the complexes $[Ln_2(SYML)_3(H_2O)]$ (**1** Ln = Eu(III), **2** Ln = Dy(III)) on the functionalized Si(100) and using a combination of techniques, including luminescence to track the process. We obtain a homogenous coverage of Si(100) wafers (from 0.5 cm × 0.5 cm to 1 cm × 1 cm) with complexes **1** and **2**. Time of flight secondary ion mass spectroscopy (ToF-SIMS) confirms the presence of the expected molecular fragments on the surface. Grazing incidence X-Ray diffraction (GIXRD) measurements show preferred orientations and ordered domains of the molecules. The magnetic properties and anisotropy of the monolayer of grafted molecules are examined by X-Ray magnetic circular dichroism (XMCD), showing a fraction of molecules with a preferred orientation of their easy axis of magnetization at 30° with respect to the surface-normal.

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