



Experiment title: Orientation induced and surface pressure controlled redox-isomerism of lanthanide bis-phthalocyaninates at air/water interface in situ confirmed by XANES

Experiment number:
SC-5145

Beamline: ID10	Date of experiment: from: 25.01.2022 to: 31.01.2022	Date of report: 29.04.2022
Shifts: 18	Local contact(s): Oleg Kononov	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

*Selektor S.L. ¹

*Raitman O.A. ²

*Raytman E.V. ²

Shokurov A.V. ¹

Repchenko Yu.L. ³

Arakcheev A. ^{1,2}

¹ Frumkin Institute of Physical Chemistry RAS

² Mendeleev University of Chemical Technology Department of Physical Chemistry

³ NRC Kurchatov Institute NBIC – Centre

Report:

In the framework of the project, simultaneous in situ measurements by UV-visible reflection-absorption spectroscopy, GID and XANES were carried out to investigate Langmuir monolayers of sandwich bis-phthalocyaninates of lanthanides (Fig. 1), which exhibit the ability for surface pressure-controlled redox isomerization in such planar supramolecular systems (i.e., changes in the oxidation number of the metal center due to reversible intramolecular electron transfer between it and the macromolecule ligand).

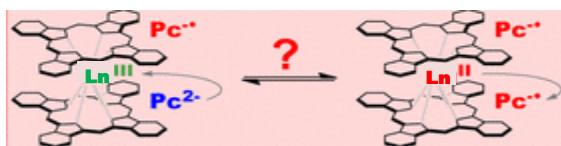


Figure 1

The measurements have demonstrated that it is possible in situ to register XANES spectra at the air/water interface with high resolution even for dilute monolayers containing one atom in question per 4 nm². It was found that for all the studied lanthanides (Eu, Sm, Yb, Tm) the locations of absorption edges in the Ln³⁺ state for Ln-bisphthalocyanate monolayers coincide

with the values we have obtained in the same experiment for solid powder samples of standards. The L2 and L3 lines were examined for Eu atom, and L3 lines were tested for all other studied lanthanides.

For all compounds the spectral measurements were carried out for just formed monolayers and upon its 2D compression-expansion. In spite of the fact that during each experiment for all monolayers under study UV-Vis absorption spectra characteristic of the complexes containing Ln²⁺ were recorded, the position of the absorption edges in all obtained XANES spectra corresponded to the trivalent states of the lanthanide ions. However, when we have tracked the evolution of the absorption spectra during the XANES spectra measurement, we have discovered that once the absorption edge is reached the UV-Vis spectra undergo the changes, indicating the Eu[(BuO)₈Pc]₂ redox-isomer transformation (Fig. 2).

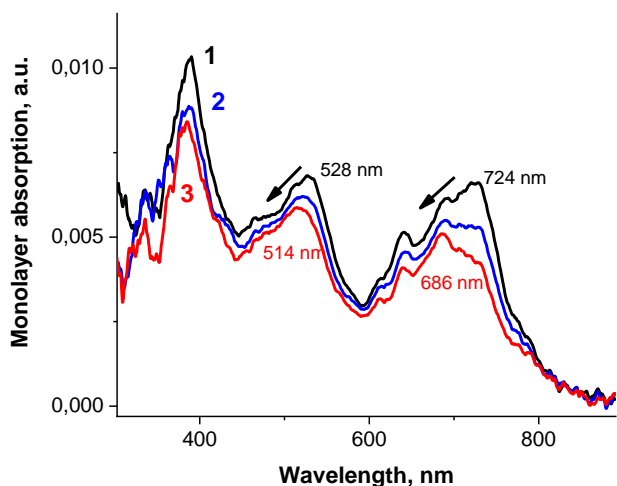


Figure 2 – Evolution of UV-Vis spectra of $\text{Eu}[(\text{BuO})_8\text{Pc}]_2$ monolayer upon XANES measurements, black arrows indicate the direction of spectrum changes upon crossing the absorption edge

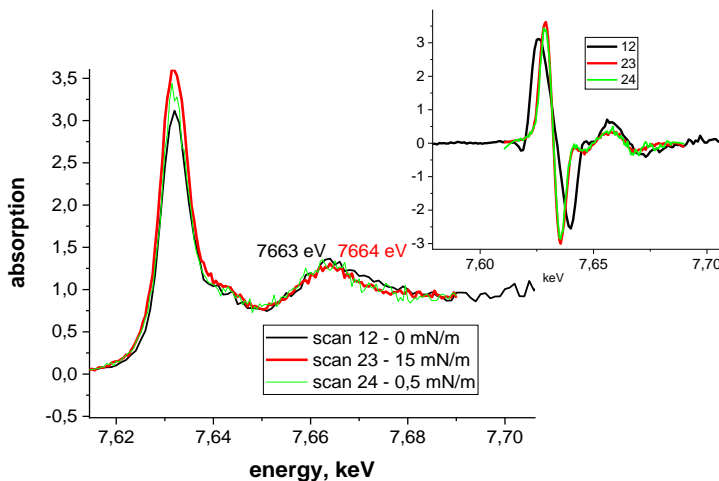


Figure 3 - XANES spectra of the $\text{Eu}[(\text{BuO})_8\text{Pc}]_2$ monolayer at different surface pressures corresponding to Eu^{2+} (0 mN/m, scan 12) and Eu^{3+} (15 mN/m, scan 23) according in situ UV-Vis spectra. The inset shows the differential curves.

At the same time, a comparative analysis of XANES spectra recorded at different surface pressures shows that for an uncompressed monolayer, in which the europium atom is presumably in the 2-valent state, the white line is much wider than for a monolayer at 15 mN/m, at which UV-Vis spectra indicate the transition $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ (Fig. 3). The right side of the XANES spectrum on scan 12 (0 mN/m) also differs from the spectra of the compressed monolayer. These differences, apparently, can be related to the "traces" of the redox-isomer transformation of the complex and require a detailed analysis. Such behavior of the monolayer may be explained by the rapid redox-isomer transformation of the complex on the water surface under the action of X-ray irradiation at energies corresponding to the absorption edge of the metal center. The fact that earlier we were able to register XANES spectra for the Eu^{2+} in the same monolayer transferred to a silicon substrate [doi.org/10.1021/acs.langmuir.9b03403] suggests that the observed high conversion rate is due to the radiolysis of water under X-Ray irradiation.

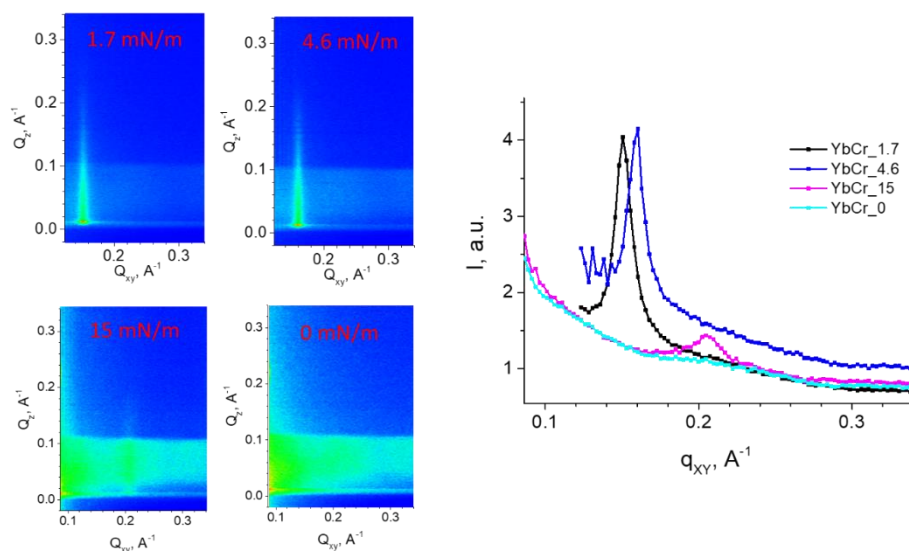


Figure 4. In-plane GID patterns for $\text{Yb}[(15\text{Cr}5)_4]\text{Pc}$ monolayer at different surface pressure values: 1.7 mN/m, 4.6 mN/m, 15 mN/m and after complete release. Curves show the corresponding in-plane scans of the low q_z region, the Bragg rod positions at various surface pressures

and 39.5 Å correspondingly), the further compression of the monolayer led to the decrease of the d-spacing up to 30.5 Å. Final decompression of the led to complete disappearance of the Bragg rod. Therefore, the obtained d-spacing can be attributed to the in-plane packing of the discotic bisphthalocyanate molecules. The changes of these values upon compression possibly corresponds to the tilt of the phthalocyanine decks to the surface plane, and the concomitant decrease of the interdeck distance in the complexes when Yb^{2+} transforms to Yb^{3+} upon monolayer compression up to 15 mN/m.

In addition, according to the experimental plan, GID measurements were carried out simultaneously with the registration of changes in the complexes' monolayer spectra during its 2D compression-expansion. The most interesting results were obtained for the crown-substituted ytterbium bisphthalocyanate. The in situ XRD experiment with a Langmuir monolayers showed a distinct Bragg rod on the compressed $\text{Yb}[(15\text{Cr}5)_4]\text{Pc}$ monolayer. While at low surface pressure values (1.7 mN/m and 4.6 mN/m) the d-spacing was quite large (41.7 Å