ESRF	**Experiment title:** Selective Capture of Heavy Metal Ions by Bioinspired Polymers Detected by Element-Specific Localization with Grazing Incidence X-ray Fluorescence	**Experiment number:** SC5193
Beamline: ID10	**Date of experiment:** from: September 1, 2021 to: September 7, 2021	**Date of report:**
Shifts: 18	**Local contact(s):** Oleg V. Konovalov	*Received at ESRF:*

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Report:

To remove toxic heavy metal ions from ground water and river, many developing countries plant trees, which is called "phytoremediation". *Phytochelatin* in plants (PC, Fig. 1A) is an oligomer of gluthathione, which captures heavy metal ions with a high sensitivity ($K_D \sim 10^{-17}$ M) and keep them in vacuoles. Inspired by the molecular design of PC, we have synthesized polymers possessing –SH and –COOH side chains (Fig. 1B).

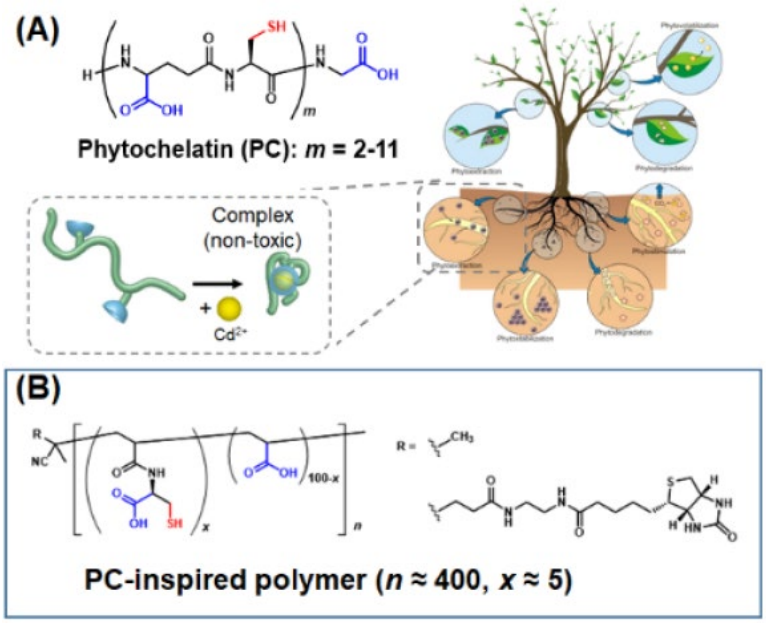

Figure 1. (A) Removal of heavy metal ions by plant phytochelatin (www.intechopen.com). (B) PC-inspired polymers synthesized for this study.

The proposed experiment aims to unravel the mechanism how bio-inspired polymers capture Cd^{2+} by simultaneous X-ray reflectivity (XRR) and grazing incidence X-ray fluorescence (GIXF) techniques. The experiments were performed at ID10 beam line using 13 keV beam, from September 1 to September 7, 2021. A lipid monolayer functionalized with the PC-inspired polyacrylic acid with cystein side chains (molar fraction of

cystein: 5 mol%) was deposited on a Langmuir film balance. After the solvent evaporation and film compression, simultaneous XRR/GIXF measurements were performed.

XRR curves measured on the subphase in the absence and presence of 1 mM $CdCl_2$ are presented in Figs. 2A and 2B. Note that the Cd^{2+}-free and Cd^{2+}-loaded buffers contain100 mM NaCl and 10 mM Hepes. As shown in the figures, polymer-functionalized lipid monolayers exhibited clear minima irrespective of the presence of Cd^{2+}. A clear shift of the minimum position indicates that the polymer brushes become compact by the binding of Cd^{2+} ions, which is in good agreement with our high energy XRR measured at the solid/liquid interface [Ref 1].

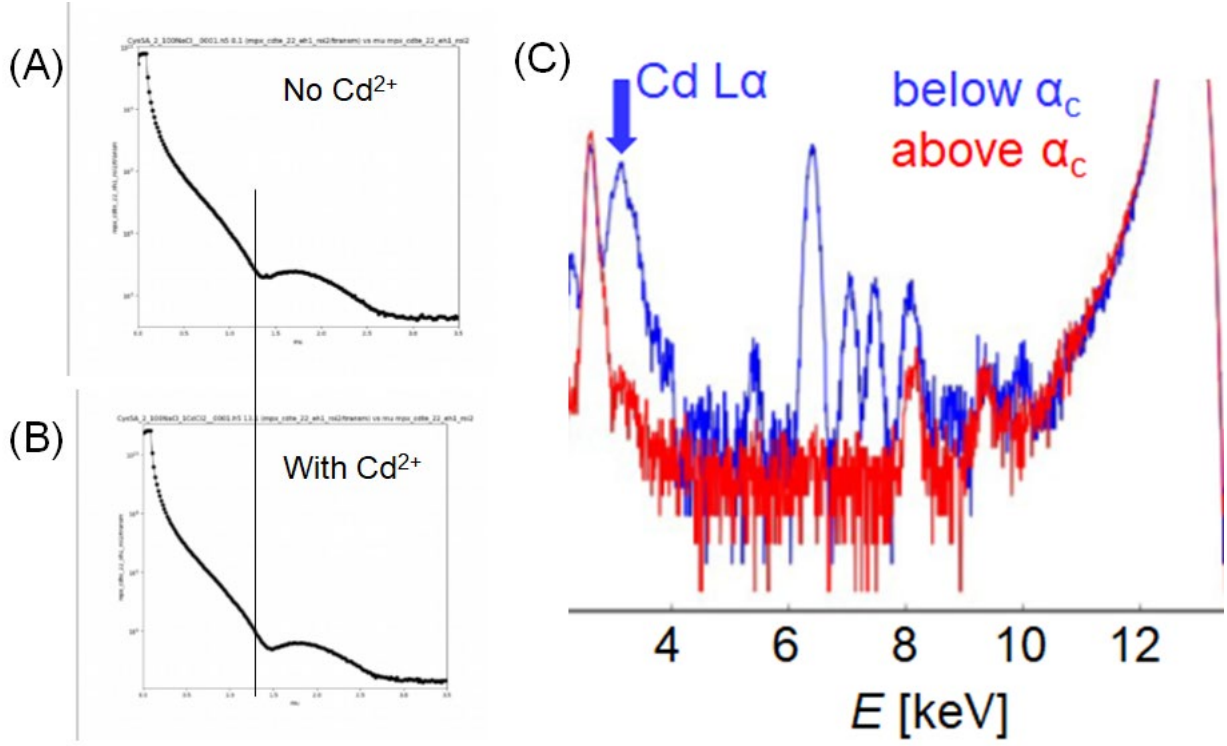

Figure 2. XRR curves measured in the absence (A) and presence (B) of 1 mM Cd^{2+}. (C) GIXF spectra measured in the presence of 1 mM Cd^{2+} below (blue) and above (red) of the crictial angle of total reflection.

In Fig. 2C, the GIXF spectra measured below (blue) and above the critical angle of incidence for total reflection were presented. The data measured below the critical angle of incidence clearly exhibited a prominent peak corresponding to Cd Lα line, indicating that the condensation of Cd^{2+} ions even in the presence of 100 mM NaCl. Our recent in-house results (QCM-D) indeed suggested the polymer chain compaction occured only in the coexistence of –SH and –COOH groups, whose onset was found as low as [Cd^{2+}] = 0.01 mM [Ref 2].

[1] F. Weissenfeld, L. Wesenberg, M. Nakahata, M. Müller*, M. Tanaka*, ***arXiv*** (2022). (doi.org/10.48550/arXiv.2203.1479).
[2] A. Yamamoto*, K. Hayashi, A. Sumiya, F. Weissenfeld, S. Hinatsu, W. Abuillan, M. Tanaka*, ***Front. Soft. Matter***, **2**, 959542 (2022).