Bistable, redox-controllable [2]rotaxanes (Figure 1) constitute a class of mechanically interlocked supramolecular systems in which a macrocyclic ring is confined to move between two different recognition sites (stations) along a dumbbell-shaped thread. Such rotaxanes have been proposed as central functional elements in a variety of nanoscale devices where the function is derived from differences in the molecular properties of the rotaxanes depending on the relative position between the interlocked molecular components [1].

In solutions of the rotaxanes $R_1^{4+}$ and $R_2^{4+}$, the position of the ring can be switched reversibly back and forth between the two stations. Yet, a central question has remained as to the conservation of this switching behaviour in solid state devices and in condensed media. To address this issue, we have studied the structure of Langmuir monolayers of $R_1^{4+}$ and $R_2^{4+}$ at the air/water interface using specular X-ray reflectometry (XR) at beamline BW1. As a modification to our previously reported investigations [2,3], a rigid p-terphenylene spacer was inserted into the studied rotaxanes (see Figure 1) to obtain a larger spatial separation between the two stations, and hence a better match to the vertical resolution available in the XR experiments.
Chloroform solutions of $\text{R}_1^{4+}$ and $\text{R}_2^{4+}$ were spread as monolayers at the air/water interface, and XR measurements were performed at several points along the compression isotherm. Oxidative switching of the rotaxane molecules was brought about by injection of a solution of $\text{Fe(ClO}_4)_3$ into the water subphase beneath the monolayer [4]. Figure 2 summarizes the XR measurements performed on $\text{R}_1^{4+}$ and $\text{R}_2^{4+}$ and the oxidized species $\text{R}_1^{6+}$ and $\text{R}_2^{6+}$ at a mean molecular area of 230 Å²/molecule.

Figure 2: Specular X-ray reflectivity data.

a,b) The electron density profiles for $\text{R}_1^{4+}$ and $\text{R}_2^{4+}$, respectively, inverted from the reflectivity data for the starting compound (green lines) and the in-situ oxidized compounds $\text{R}_1^{6+}$ and $\text{R}_2^{6+}$ (red lines). The areas above the horizontal dashed lines correspond to the number of electrons in one molecule, while the dotted lines represent the approximate position of the interface to bulk water (defined as $\rho/\rho_{\text{water}} = 1.05$).

c,d) The measured reflectivity data normalized by the Fresnel reflectivity (open circles or squares) and fit to the data (lines) for the profiles shown in (a) and (b).

The combined XR data indicate that for both $\text{R}_1^{4+}$ and $\text{R}_2^{4+}$ the macrocyclic ring shifts from the TTF station to the DNP station upon oxidation, and thus demonstrate that the switching capability of the rotaxane molecules is retained in condensed monolayer films.

References