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Structural Evidence of Mechanical Shuttling in Condensed Monolayers of Bistable Rotaxane Molecules**

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Bistable, redox-controllable [2]rotaxanes constitute a class of artificial molecular machines[1,2] in which a mobile ring is confined to move between two different recognition sites (stations) along a dumbbell-shaped component. Linear motor molecules and nanoelectromechanical actuators[3] can be constructed from such redox-controllable [2]rotaxanes. These latter compounds have also been utilized[4,5] as electromechanical switches in molecular memory devices. In this context, the possibility of relative mechanical motion occurring within such bistable [2]rotaxanes in condensed phases has been questioned[6] and disputed.[7] Such motion has been demonstrated unequivocally in solution,[8] in polymer matrices,[9] and in self-assembled monolayers on gold electrodes[10] to result in the movement of the ring from one primary station to a secondary one and then back again in a stepwise manner. One glaring deficiency, however, has been the lack of structural characterization methods for these switching processes in nanoscale systems that can be applied directly to highly condensed phases on surfaces and at interfaces.

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Herein, we describe the use of surface-sensitive synchrotron X-ray reflectometry[11] (XR) to provide the first direct structural investigation of the redox-controlled switching process in condensed monolayers of amphiphilic, bistable [2]rotaxanes at the air/water interface. We find that efficient shuttling of the ring component in such [2]rotaxanes takes place in the condensed liquidlike monolayers. The ring travels the 37 Å between the two stations of the dumbbell along a path that is largely confined to the plane of the monolayer. This movement causes insignificant changes in the overall monolayer thickness. Our study has focused on exactly the same molecules whose switching within molecular monolayers has recently been characterized,[12] albeit indirectly, by Langmuir π-A isotherms and the Langmuir–Blodgett (LB) technique in combination with X-ray photoelectron spectroscopy (XPS). By contrast, XR has previously been demonstrated to provide direct detailed information about monolayer organization in general[13] and of amphiphilic bistable rotaxanes at the air/water interface in particular.[14] The working principle of XR is illustrated schematically in Figure 1 a. The incident (α_i) and exit (α_f) grazing angles are varied simultaneously ($\alpha_f = \alpha_i$) while the intensity pattern that results from the interference of X-rays reflected from different depths of the sample is recorded. Data inversion[15] yields—on an absolute scale—the out-of-plane electron-density distribution across the water/monolayer/air interface. The density profiles are smeared by the intrinsic roughness (ca. 3 Å (rms)) of the water surface on account of capillary waves.[16] The bistable [2]rotaxanes **R1**$^{4+}$ and **R2**$^{4+}$ (Figure 1 b) consist of a tetracationic ring component (dark blue) encircling a linear dumbbell-shaped component, which contains two different stations for the ring: 1) a tetrathiafulvalene (TTF) unit (green) and 2) a 1,5-dioxynaphthalene (DNP) unit (red). The two recognition sites are separated by a rigid *p*-terphenylene spacer (black). Both molecules are terminated by a hydrophilic (light blue) and a hydrophobic (gray) stopper at opposite ends of the dumbbell component. This constitution renders the molecules amphiphilic and accordingly enables them to form monomolecular (Langmuir) layers when deposited at the air/water interface. The [2]rotaxanes **R1**$^{4+}$ and **R2**$^{4+}$ are constitutional isomers, differing only in the relative positions of the TTF and DNP units with respect to the two stoppers. The ring will therefore move in an opposite direction (up or down) when the TTF unit of **R1**$^{4+}$ and **R2**$^{4+}$ is oxidized, thus allowing critical internal comparisons to be made.

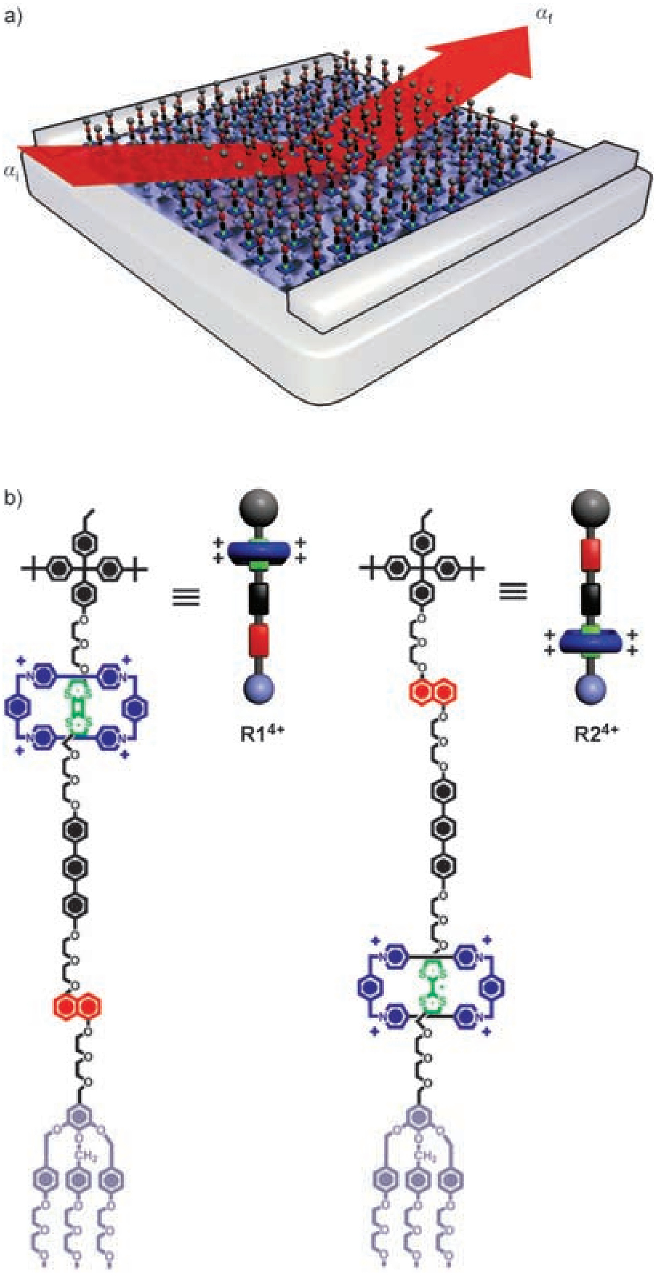

Figure 1. a) A schematic illustration of the working principle in specular X-ray reflectivity measurements of Langmuir monolayers. b) Graphical representations and structural formulas of the amphiphilic, bistable [2]rotaxanes **R1**$^{4+}$ and **R2**$^{4+}$.

Electrochemical switching of the relative position of the ring within these particular bistable [2]rotaxanes is well documented from solution-phase studies,[8,17] and for closely related bistable [2]rotaxanes across a range of different environments.[8c,9,10] In the initial states within each environment, the rotaxane exists in its ground-state co-conformation with the cyclophane encircling the TTF station preferentially by a factor of greater than 9, relative to the DNP station.[18] However, the monocationic TTF$^{\bullet+}$ or dicationic TTF^{2+} species that is produced upon oxidation repels[8–10,17] electrostatically the tetracationic cyclophane and induces the ring to move to the DNP station. In condensed media akin to the Langmuir films characterized here, this switching behavior and the two states associated with the two different locations of the ring have thus far only been observed by indirect methods of structural analysis, such as XPS[12] and electrochemistry.[10] XR investigations, on the other hand, give direct structural information about the electron distribution in thin films, and hence of the two isomeric structures associated with the location of the ring—up or down.

The experimental approach followed in this work, including oxidation of the rotaxane monolayers in situ, is illustrated schematically in Figure 2. Solutions of **R1**$^{4+}$ and **R2**$^{4+}$ in chloroform were spread onto the pure water surface of a

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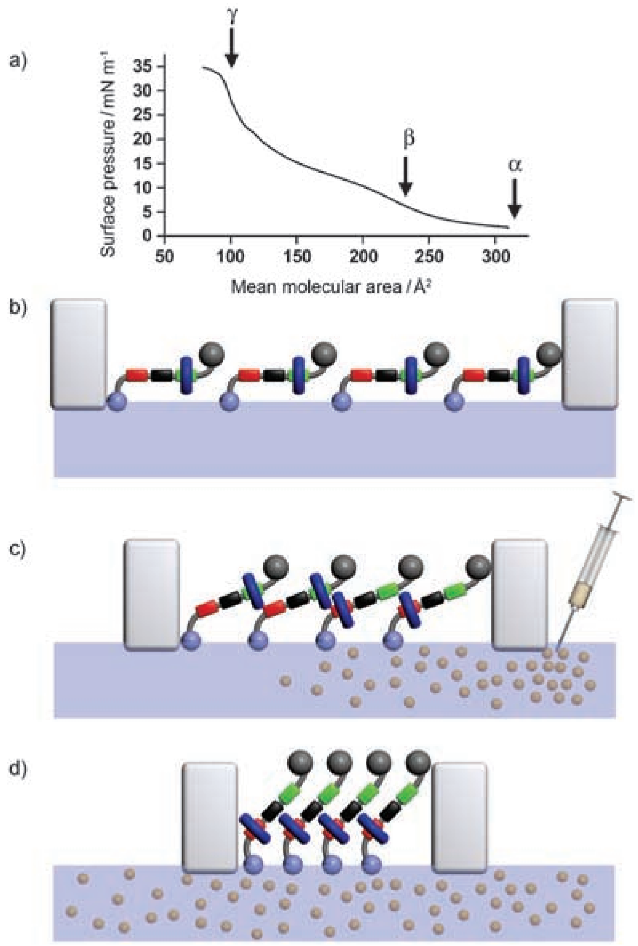

Figure 2. Illustration of the experimental procedure. a) Compression isotherm (surface pressure versus area) for **R2**$^{4+}$. b) A schematic representation of a moderately expanded monolayer of **R1**$^{4+}$ at the air/water interface. c) Injection of the oxidant $Fe(ClO_4)_3$ into the water subphase at various points along the isotherm (α, β, or γ). d) A densely compressed monolayer of the oxidized form of **R1**$^{4+}$.

Langmuir trough, and the resulting monolayers were compressed at a constant rate while the surface pressure was monitored as a function of the mean molecular area (Figure 2a,b). Oxidation of the monolayers was performed[12] in situ by injecting an aqueous solution of the oxidant $Fe(ClO_4)_3$ into the water subphase beneath the Langmuir monolayer to obtain a nominal concentration of 5×10^{-4} M (Figure 2c). The oxidant was injected at decreasing mean molecular areas of 330, 230, or 100 Å^2, as indicated on the compression isotherm (Figure 2a). After injection, one hour was allowed for the oxidant to diffuse to the surface, and the monolayer was typically compressed to a mean molecular area of 100 Å^2 to maximize the electron density changes along the surface normal resulting from the reduced molecular tilting and folding (Figure 2c,d).[19] This area corresponds[12,19] to a very closely packed Langmuir monolayer (Figure 2d). All experiments were performed on a subphase containing 10^{-3}–10^{-4} M $NaClO_4$ to allow efficient ion exchange[12] of PF_6^- with ClO_4^- ions, regardless of the presence of the oxidant. This condition is the only deviation from the procedure described in the literature.[12]

The in-plane structure of the rotaxane monolayers was investigated by grazing-incidence X-ray diffraction.[11] As expected for such flexible molecules that bear a rich array of subunits capable of intra- and intermolecular interactions mediated by noncovalent forces, none of the Langmuir monolayers showed any crystallinity at any of the surface pressures investigated. XR measurements, which probe the out-of-plane structure, as described in Figure 1a, were performed on Langmuir monolayers of the unoxidized rotaxanes, as well as on the oxidized states of the monolayers at several positions (Figure 2a) along the compression isotherm. Figure 3a shows the resulting electron-density profiles for the highly compressed Langmuir monolayers of **R1**$^{4+}$ with the ring up, measured at a mean molecular area of 100 Å^2. The green line represents the monolayer of unoxidized **R1**$^{4+}$ and the red line corresponds to the monolayer of **R1**$^{6+}$, oxidized in situ. The oxidation was performed on a moderately condensed monolayer with a mean molecular area of 230 Å^2 that was subsequently compressed to 100 Å^2. The areas above the horizontal dashed lines represent the total number of electrons in one molecule (including counterions). The horizontal dotted lines correspond to the approximate positions of the interfaces with bulk water and were chosen as the point on the curve where the electron density is 5% larger than that of bulk water. The discrepancy between the dashed and dotted lines in Figure 3 is caused by the inclusion of a small number of water molecules (ca. 10 per rotaxane molecule, see Supporting Information) from the subphase into the hydrophilic parts of the rotaxane monolayer. This water inclusion is less pronounced in highly compressed Langmuir monolayers than in less closely packed monolayers.[14]

Two distinct features emerge from the data analysis shown in Figure 3a: 1) The profiles of **R1**$^{4+}$ and **R1**$^{6+}$ contain two peaks with a vertical separation of approximately 12 Å. These peaks correspond to regions of high electron density within the Langmuir monolayer, and are therefore ascribed (see below) to the locations of the two stations along the rod segments of the dumbbell components in the two bistable [2]rotaxanes. This assignment is corroborated[20] by recent molecular dynamic simulations of similar systems.[14] 2) The relative densities of the two peaks associated with **R1**$^{4+}$ and **R2**$^{4+}$ change significantly upon oxidation of the monolayers. Hence, a shift of the electron distribution towards the water surface (namely, down) is observed in oxidized monolayers of **R1**$^{6+}$ relative to the unoxidized case. This shift is in agreement with a vertical change in the position of the ring upon oxidation from the "upper" station (TTF) to the "lower" station (DNP), analogous to the movement known[8,17,18] to take place in solution. The shaded areas between the red and green curves represent the net number of electrons that change vertical position upon oxidation. Since the movement of the ring is compensated by reorganization of the local environment, the effective number of electrons changing places upon oxidation is relatively small. We notice, however, that the shift in electron density is symmetrical around the intersection point, which shows that the switching is a local

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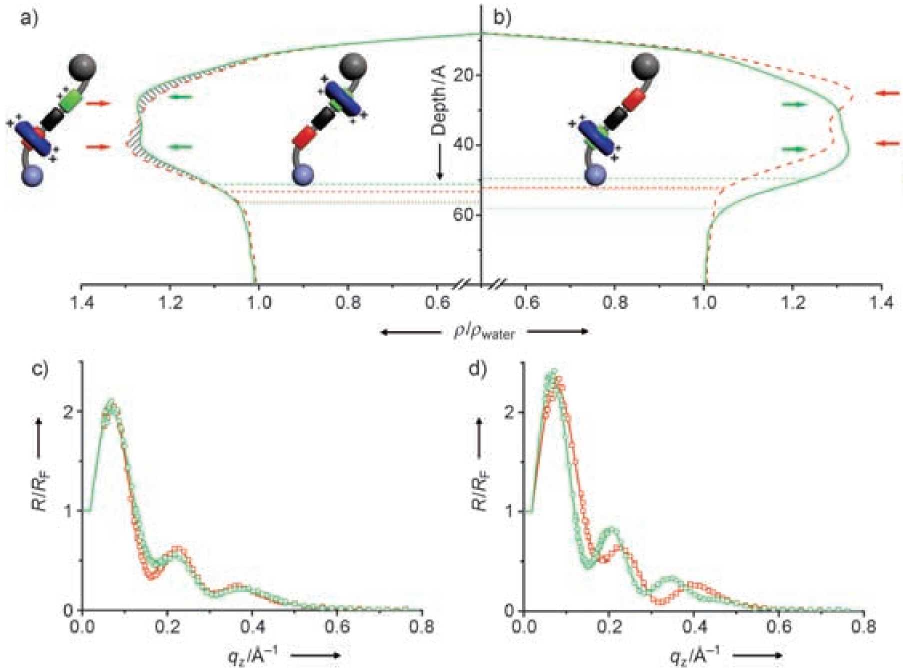

Figure 3. X-ray reflectivity measurements. a,b) Electron-density profiles for **R1**$^{4+}$ and **R2**$^{4+}$, respectively, inverted from the reflectivity data for the tetracationic starting compounds (green lines) and the hexacationic compounds **R1**$^{6+}$ and **R2**$^{6+}$ oxidized in situ (red lines). The areas above the horizontal dashed lines correspond to the numbers of electrons in one molecule, while the dotted lines represent the approximate position of the interface to bulk water. c,d) The measured reflectivities R (open circles or squares; normalized to the Fresnel reflectivity of bare water, R_F) and the best fits to the data (solid lines) corresponding to the $\rho(z)$ curves in (a) and (b) for **R1**$^{4+}$ and **R2**$^{4+}$, respectively. The green lines and circles correspond to the starting compounds and the red lines and squares correspond to the oxidized compounds. The data was obtained at beamline BW1 at the DESY synchrotron facility in Hamburg, Germany.

reorganization that does not change the overall hydration state of the rotaxane. If nearly all of the rings are located initially on the TTF station—as documented for solution-phase experiments[8,17,18]—then this symmetry also indicates that almost all of the rings move from the upper to the lower station upon oxidation because a fractional displacement (for example, 50 %) would otherwise lead to a smearing of the two peaks, which is not observed. The 12-Å vertical shift is less than the expected distance between the two stations in a fully stretched and vertically aligned rotaxane. Molecular modeling studies[12] indicate that this distance is 37 Å. This value implies that at a mean molecular area of 100 Å^2 within the Langmuir monolayer, the rotaxane molecules are tilted and locally folded,[19] even in these very compressed Langmuir monolayers.[21] Similar attenuation of the distance traveled out of the plane was observed in the XPS data of Langmuir monolayers transferred onto SiO$_2$ substrates.[12] Consequently, the movement of the ring must have a significant component in the plane of the Langmuir film. Further evidence of folding and tilting comes from observations of the total monolayer thicknesses, which fall in the range 50–55 Å (Figure 3) and are notably smaller than the thickness (ca. 80 Å) expected for a monolayer of fully extended and nontilted rotaxanes. The electron-density profiles of **R1**$^{4+}$, measured for both low and moderately compressed Langmuir monolayers, show that the molecules are folded and tilted to an even greater extent with respect to the normal of the water surface, as illustrated schematically in Figure 2b,c. This observation is consistent with our previous investigations[14] of similar amphiphilic, bistable [2]rotaxanes. The local folding of molecular segments along the rod can be considered to be a consequence of the large differences between the cross-sectional areas of different segments along the fully stretched rod. To fill space, the slimmer segments must fold and tilt, which, in turn, gives rise to a fluidlike, disordered local environment within the monolayer. This property allows the ring to be displaced in a fluidlike environment without any significant changes[20] in the overall thickness of the film, as is clearly illustrated by the density profiles in Figure 3a. This latter observation indicates that switching would also be possible in films sandwiched between two solid surfaces, as for example, in crossbar memory devices.[4,5]

In a control experiment, monolayers of the constitutionally isomeric **R2**$^{4+}$ were examined by using identical experimental procedures. The monolayers of **R2**$^{4+}$ show (Figure 3b) the opposite effect upon oxidation to that observed for **R1**$^{4+}$, that is, the peak in the electron distribution shifts upwards. This result, therefore, supports the notion that the observed shift in electron density is caused by a net movement of the ring component relative to the dumbbell (in the case of **R2**$^{4+/6+}$, from the lower TTF to the upper DNP station) and is not a consequence of the movement of water or counterions. It is evident from Figure 3b that the unoxidized monolayers of **R2**$^{4+}$ contained more water molecules than was observed for **R1**$^{4+}$. This condition may be related to the proximity of the tetracationic ring to the water surface.

Analogous XR measurements for **R1**$^{4+}$ and **R2**$^{4+}$ were performed at different mean molecular areas. Similar trends were observed at 230 Å^{2}mol^{-1} (Figure 4), albeit with less distinct changes in the electron density, presumably on account of a larger in-plane component of the movement—that is, the amphiphilic bistable rotaxanes have ample room to lie down at the interface. Attempts to perform the entire oxidation at a mean molecular area of 100 Å^{2}mol^{-1} did not result in any changes in the electron density profiles, an observation which indicates that the oxidant is unable to react with the TTF unit in these extremely dense monolayers, or that ring movement is inhibited.[21]

In summary, X-ray reflectivity data have provided direct structural evidence for the molecular motion of the ring

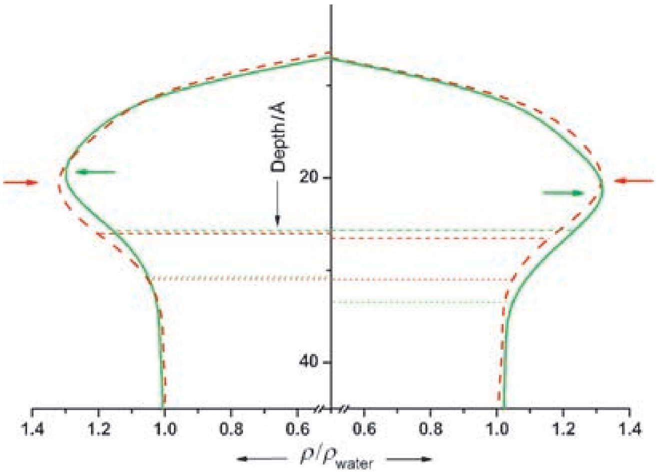

Figure 4. Electron-density profiles for **R1**$^{4+}$ (left) and **R2**$^{4+}$ (right), both measured at a mean molecular area of 230 Å^2. The profiles are inverted from the reflectivity data for the starting compounds (green lines) and the oxidized compounds (red lines). Oxidation was performed in situ at a mean molecular area of 230 Å^2. The areas above the horizontal dashed lines correspond to the numbers of electrons in one molecule, whereas the dotted lines represent the approximate position of the interface to bulk water. A comparison of these density profiles with the profiles measured at mean molecular area of 100 Å^2 (see Figure 3) shows that the ring motion contains a large in-plane component.

component of amphiphilic bistable [2]rotaxanes in condensed, oriented monolayers during redox-controlled switching.

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[18] Quantitative measurements of the preference of the ring for the TTF station are based on solution studies of model, degenerate rotaxanes bearing either two TTF or two DNP stations, each with the *p*-terphenylene spacer used in **R1**$^{4+}$ and **R2**$^{4+}$. The barriers to shuttling measured for the two degenerate rotaxanes are 17–18 kcal mol^{-1} and 15 kcal mol^{-1}, respectively. The difference of 2–3 kcal mol^{-1} is related to the energy difference between the preferences of the cyclophane for the TTF station over the DNP station, which leads to ratios of 96:4–99.3:0.7; see: S. Kang, S. A. Vignon, H.-R. Tseng; J. F. Stoddart, *Chem. Eur. J.* **2004**, *10*, 2555–2564. In order to reflect these thermodynamic differences, we have introduced the term ground-state co-conformation for the translational isomer with the cyclophane residing at the TTF station and metastable state co-conformation when it is at the DNP station; see references 8c and 9 for more details.

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[21] The XPS data recorded on LB films of **R1**$^{4+}$ oxidized at a mean molecular area of approximately 150 Å^2 per molecule indicate, although indirectly, that oxidation and movement are still favored at these densities; see reference 12 for more details. Films at densities of approximately 150 Å^2 per molecule were also used to prepare molecular memory devices, see reference [4].

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