A Soliton Phenomenon in Langmuir Monolayers of Amphiphilic Bistable Rotaxanes

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Surface pressure–area isotherms, light scattering microscopy, and atomic force microscopy have all been used to provide information about the stabilities and dynamics of Langmuir monolayers composed of amphiphilic bistable [2]rotaxane molecules. Superstructures that have the appearance of localized mobile solitons are formed during the compression of monolayers of the [2]rotaxanes below their collapse pressures. Solitons move solely in a linear trajectory in both directions across the film, perpendicular to the compression direction, without any apparent broadening or change in their shape.

Bistable [2]rotaxanes are a class[1] of mechanically interlocked molecules composed of a dumbbell-shaped component, consisting of a central linear rodlike section terminated by two bulky stoppers at each end of the rod, encircled by a ring component. During the past five years, amphiphilic redox-controllable bistable [2]rotaxanes,[2,3] in which the ring component can be induced to move, on command by some appropriate stimulus, between two nonidentical recognition sites, have been introduced as the active elements in solid-state molecular switch tunnel junction devices[4] for memory and computing applications. Since Langmuir monolayers of the [2]rotaxane molecules form the basis for the fabrication of these molecular electronic devices, efforts are being pursued[5–8] continuously that are aimed at understanding the molecular organization and stabilities of such one-molecule thick films at the air–water interface. As a part of this research, surface pressure–area (π–A) isotherms, light scattering microscopy[9] (LSM), and atomic force microscopy (AFM) have all been employed subsequently to elicit information about the dynamics and stabilities of Langmuir monolayers of both charged[2] and neutral[3] amphiphilic bistable [2]rotaxanes. In this communication, we report the discovery of an unusual two-dimensional (2D) to three-dimensional (3D) transition in which superstructures that have the appearance of localized mobile solitons are formed during the compression of monolayers below their collapse pressures.[10,11]

The structural formulas of the charged[2] [2]rotaxanes **1**[4+] and **2**[4+] and their respective dumbbell precursors **3** and **4**, on which we have focused most of our attention, are shown in Figure 1, along with the structural formula of the neutral[3] [2]rotaxane **5**. The [2]rotaxane **1**[4+] consists of (i) a ring component (dark blue) cyclobis(paraquat-*p*-phenylene) (CBPQT[4+]), (ii) a dumbbell-shaped component that includes two different recognition sites for the CBPQT[4+] ring component, a tetrathiafulvalene (TTF) unit (green), and a 1,5-dioxynaphthalene (DNP) unit (red), sepa-
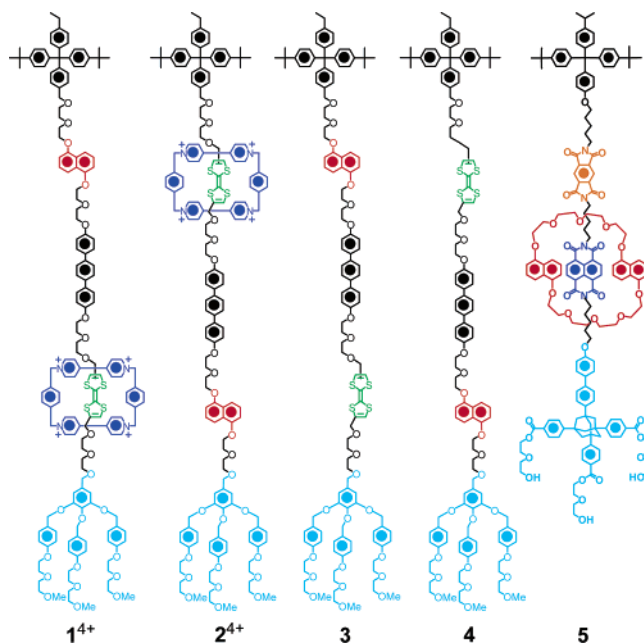

Figure 1. Structural formulas of the charged [2]rotaxanes **1**[4+] and **2**[4+], together with their respective dumbbell precursors **3** and **4**, and the neutral [2]rotaxane **5** which were used in the preparation and analyses of Langmuir films.

rated by a rigid terphenylene spacer (black). A hydrophilic dendritic stopper (light blue, close to the TTF unit) and a hydrophobic tetraarylmethane stopper (black, close to the DNP unit) are incorporated at each end of the dumbbell, thus rendering the molecule amphiphilic and enabling it to form insoluble monolayers at the air–water interface. The [2]rotaxane **2**[4+] is a constitutional isomer of **1**[4+] in which the locations of the TTF and DNP units have been reversed. In both the [2]-rotaxanes **1**[4+] and **2**[4+], the CBPQT[4+] ring is located predominantly on the TTF unit.[2,6,7] The neutral bistable [2]rotaxane **5** incorporates[3] pyromellitic diimide (PmI, orange) and naphtho-diimide (NpI, dark blue) recognition sites in its dumbbell

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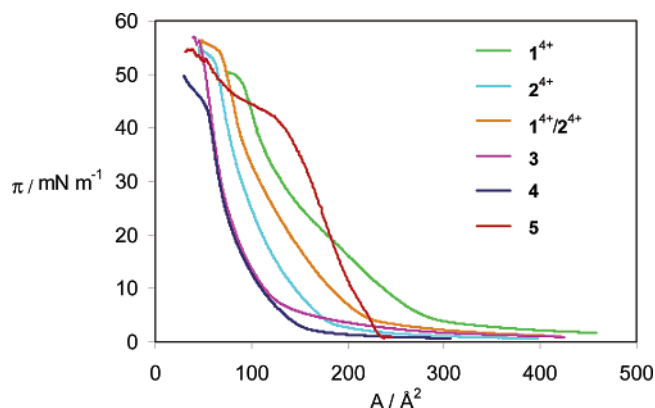‡ Department of Chemistry and Biochemistry.

Figure 2. π-A isotherms of the [2]rotaxanes 1^{4+}, 2^{4+}, mixed (1:1) 1^{4+}/2^{4+} and **5**, and the dumbbell compounds **3** and **4**, obtained by compressing the appropriate monolayers continuously at a rate of 5 mm/min.

component, which is encircled predominantly around the NpI site by the 1,5-dinaphtho[38]crown-10 ring component (red).

Solutions of approximately 0.5–1.5 g/L of the [2]rotaxanes 1^{4+}, 2^{4+}, and **5** and the dumbbell precursors **3** and **4** of the charged rotaxanes in CHCl$_3$ were prepared, spread onto the aqueous subphase (pH = 5.5–6.2, resistivity $\geq$18 MΩ/cm), and allowed to equilibrate for 15–30 min. Surface pressure-area (π–A) isotherms were obtained on a 600 cm^2 Langmuir trough (Nima, model 611) using a paper Wilhelmy plate to measure the surface pressure. π–A Isotherms of the [2]rotaxanes 1^{4+}, 2^{4+}, and **5** and the dumbbell compounds **3** and **4** reveal (Figure 2) a characteristic behavior that can be attributed to their

molecular structural differences. In common with previously measured[5] isotherms of not-too-dissimilar [2]rotaxanes, the isotherms' behavior can be related to the presence of the ring component and its relative location in the [2]rotaxane. Note that the isotherm of 1^{4+} shows a greater projected area than that of 2^{4+} at the same pressure, implying that the presence of the CBPQT^{4+} ring closer to the subphase in 1^{4+} increases the average surface area per molecule. The absence of the CBPQT^{4+} ring in the dumbbells **3** and **4** allows their films to be compressed to smaller areas for the same increase in the surface pressure. All the isotherms were characterized by similar collapse pressures, ranging from 48 up to 55 mN/m. Langmuir films of [2]rotaxanes are reasonably stable at surface pressures below 30 mN/m with a 10% area loss after 1 h. Similar stabilities were observed in previous investigations[5] of related bistable [2]-rotaxanes.

At low pressures, the [2]rotaxane 1^{4+} monolayer exists in the gaseous state. As revealed by synchrotron X-ray reflectometry[7] and molecular dynamics simulations,[12] these flexible molecules adopt very tilted and locally folded conformations in which the widely separated molecules are in contact with the water surface. The folded conformation is presumably a result of the CBPQT^{4+} ring and its associated counterions. At these pressures, LSM images[13] show the presence of a few small bright features (2–3 μm) that are believed to be multilayer islands that are formed by so-called slow collapse.[11]

When the monolayer is compressed to higher densities at compression rates in excess of 5 mm/min, mobile compact bright features become visible in the LSM images. These 3-D features (Figure 3) move solely in a linear trajectory in both directions
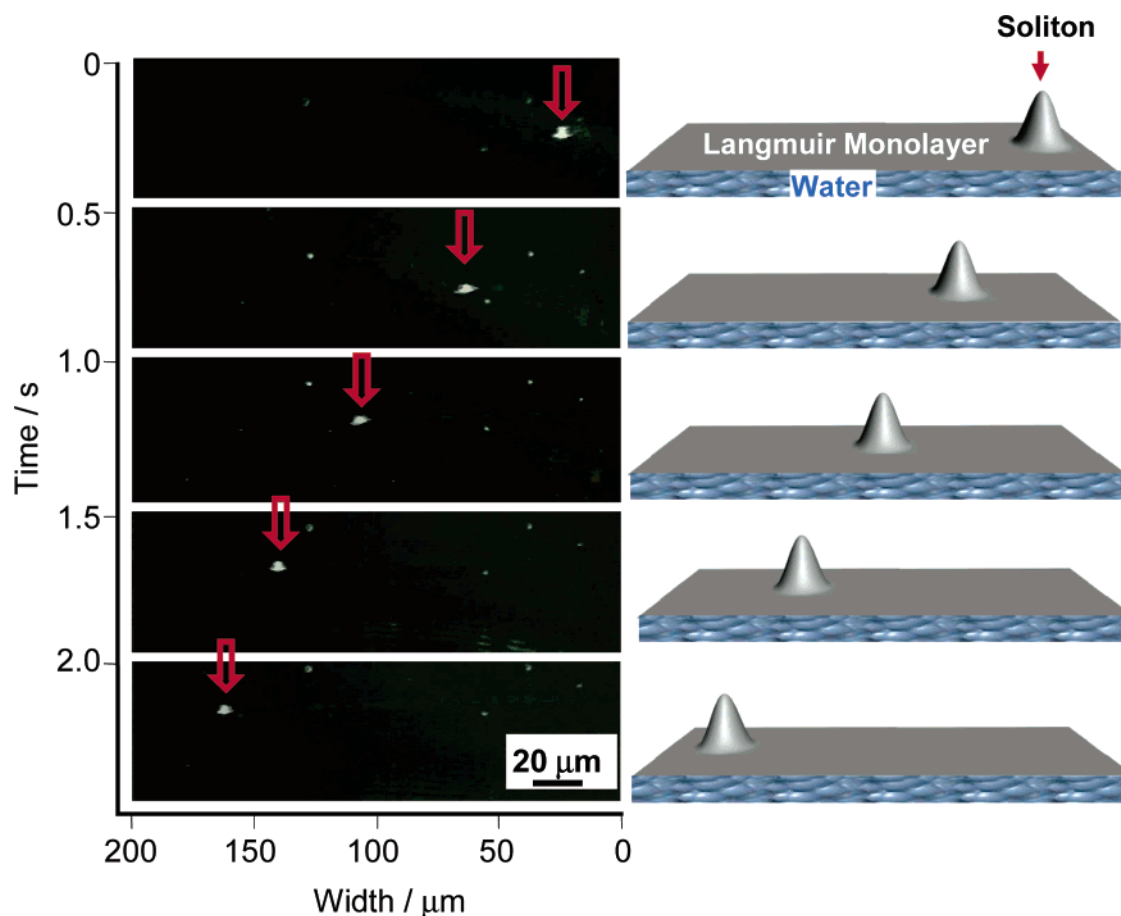

Figure 3. Five consecutive LSM images of a Langmuir film of the [2]rotaxane 1^{4+} compressed at 5 mm/min and a pressure of about 30 mN/m, illustrating the motion of a 10 μm wide soliton (denoted by the arrows) from right to left of the view. The time interval between images is 0.5 s.
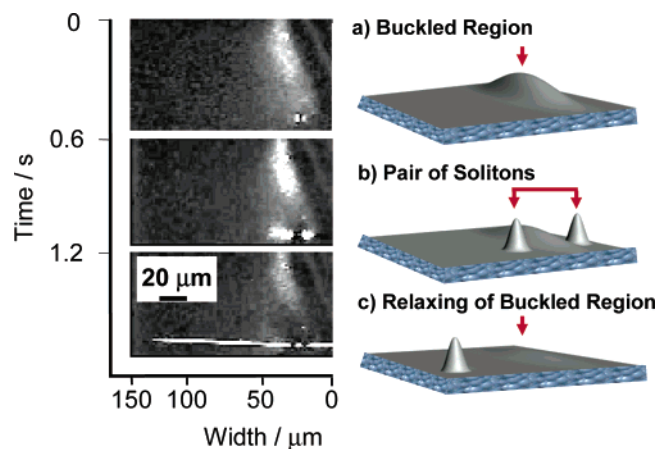
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Figure 4. Three consecutive LSM images of a Langmuir film of the [2]rotaxane $\mathbf{1}^{4+}$ immediately prior to appearance of soliton features, showing (a) a microscale buckled region that grows laterally and (b) gives birth to two solitons moving in opposite directions; (c) Buckled region relaxes upon formation of solitons.

across the film, perpendicular to the compression direction, without any apparent broadening or change in shape. (See the movie available in the Supporting Information.) They travel at speeds of $50-350\ \mu$m/s and their speed is roughly proportional to the compression speed. If the compression is slowed to less than 3 mm/min, the features stop moving and fade away in a few seconds. If the compression is resumed within about a minute, the features arise at the same point and continue to move in the same direction.

The features have similarities to solitary traveling waves or solitons, i.e., localized waves that are formed[14] in a variety of nonlinear systems. Although the term soliton has also been applied to equilibrium stripe patterns caused by electrostatic interactions in charged Langmuir monolayers,[15] the phenomena that we have observed arise only in driven systems. There have been some earlier reports of the generation of soliton-like superstructures in driven 2-D systems. Tabe and Yokoyama[16] describe orientational waves in condensed Langmuir monolayers of an azobenzene derivative that are generated by illumination, which drives a cis−trans photoisomerization. Recently, compact soliton-like waves on the surface of a ferrofluid were generated by the application of a magnetic field.[17] These phenomena, however, differ significantly from those that we have observed in the [2]rotaxane films.

In a few instances we have observed the birth of a pair of counter-propagating solitons. They arise from what appears to be the onset of a large (40 μm wide) buckled region of the film which relaxes (Figure 4) immediately after the solitons appear. (See the movie available in the Supporting Information). The solitons first arise when the molecular area is about 130 Å^2, close to a point at which a $100-1000$-fold increase in the viscosity of monolayers of similar [2]rotaxanes has been observed,[5] and thus coincides with a point at which there is a pressure gradient in the film during compression. This pressure difference can account for the observation that the density of solitons is higher near the barrier. Soliton features can move parallel to one another without interacting, but if they collide they mutually annihilate. Another important aspect of these soliton features is that they can cross slow-collapse islands without losing their velocity and shape, but they are annihilated if they hit 3-D folds ($\sim10-40\ \mu$m wide and up to millimeters long) that appear at pressures of $35-45$ mN/m.[18] Solitons can also be seen to originate from folds.

The solitons leave behind a track composed of two parallel lines, a feature which does not fade when the compression is stopped. When the monolayer is reexpanded, these lines are seen to be closed loops, which open up, become distorted, and eventually break up, as shown in Figure 5a. The behavior upon expansion resembles that previously observed[18] during the unfolding of buckled monolayer films of 2-hydroxy-tetra-cosanoic acid. Contact-mode AFM analysis of the films transferred (Figure 5b) at 10 mN/m to mica reveal (Figure 5c) that the lines are 2 to 4 nm in height (z) and several nanometers[19] in width (x).

Some conclusions about the origin of the superstructures in the present systems can be drawn from the experiments. We have observed solitons only for monolayers of [2]rotaxanes both charged ($\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$) and neutral ($\mathbf{5}$). They are not present in monolayers of the dumbbell precursors $\mathbf{3}$ and $\mathbf{4}$. Thus, the ring is essential although the phenomenon does not appear to be sensitive to the positioning of the ring on the dumbbell component. Electrostatic interactions do not play a significant role: the solitons are observed in [2]rotaxanes with both charged ($\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$) and neutral ($\mathbf{5}$) ring components and they are unaffected by the ionic strength of the subphase. The addition of an oxidant to the subphase also has no effect, showing that the phenomenon is not related to the movement of the ring between recognition sites. The solitons observed for the neutral [2]rotaxane $\mathbf{5}$ move more rapidly ($300-2000\ \mu$m/s) than those for the charged counterparts $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$; otherwise, their behavior is identical. The fact that solitons do not arise in (1:1) mixtures of $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ indicates that the packing of the CBPQT^{4+} rings is important. This observation is in accord with the onset of the solitons occurring at densities for which the
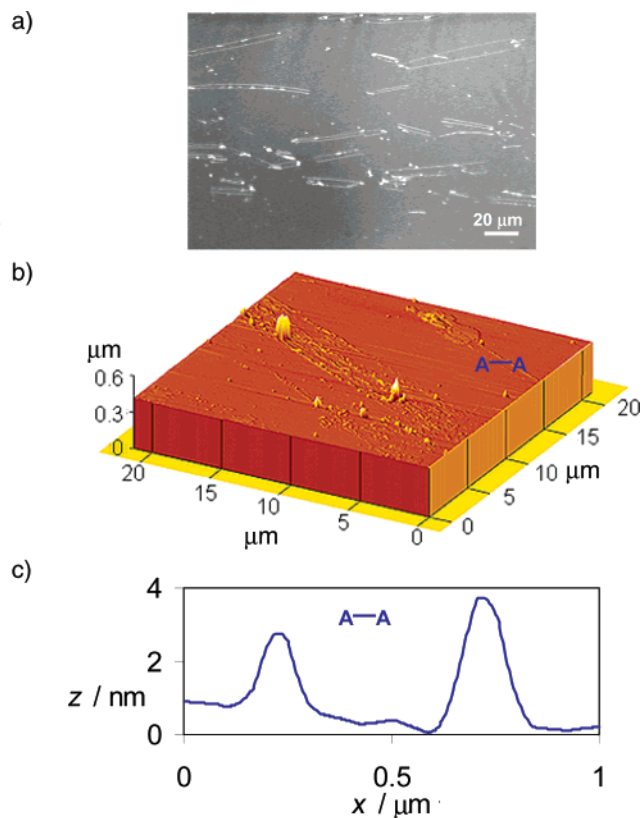

Figure 5. (a) LSM and (b) AFM images of the [2]rotaxane $\mathbf{1}^{4+}$, after compression to about 50 mN/m and reexpansion to 10 mN/m, showing expanded and broken soliton tracks. (c) Height profile along the A−A line in b.

X-ray reflectivity measurements show[7] that the molecules form condensed phases in which they are tilted but in which the $CBPQT^{4+}$ ring is no longer in contact with the aqueous subphase.

While we still lack a complete understanding of the origin of the soliton phenomenon, clues to its origins can be found in several features that have been observed. The fact that the solitons reappear in the same place when the compression is stopped and then restarted indicates that they are related to some underlying feature in the monolayer, likely a defect. Further, the origin of the solitons as a pair of counter-propagating features suggests that they arise from pairs of defects such as five- and seven-fold disclination pairs[20] that separate, the opposite signs of the disclinations, perhaps accounting for the different directions of motion. The existence of disclinations in condensed tilted monolayer films has been established.[21] They are known to produce a buckling of thin films[22] which would account for their detectability by LSM. On the other hand, disclinations are defects in the orientational order in the film and are not coupled directly to the shear stress that arises when the film undergoes compression.

Although our experiments show that the appearance of the solitons in Langmuir monolayers of amphiphilic bistable [2]-rotaxanes is somehow related to the presence of their ring components, the precise nature of the nonlinear behavior that underlies the phenomenon is not known yet. Relatively few monolayer systems have been examined by LSM so it is not possible to say if the solitons can be found[23] for systems other than the [2]rotaxanes.

Supporting Information Available: Movies S1 and S2 of the light scattering microscopy shown in Figures 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The light scattering experimental setup consisted[10,11] of a 100 cm^2 home-built Langmuir trough with a single Teflon barrier mounted on a POLYVAR-MET microscope. A 50 mW solid-state laser ($\lambda = 532$ nm, Enlight Technologies, model MGL-S) was reflected off the air−water interface at an oblique angle. A silicon wafer, mounted on the trough bottom, reflected the transmitted beam out of the field of view, and its polished surface minimized scattering. Laser light scattered from the interface was focused by 20× microscope objective lens coupled to a CCD camera (Dage 772S), which was connected to a TV monitor and a video recording system. Surface pressure was measured with a filter paper Wilhelmy plate and an R&K transducer.

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(23) While the compression and collapse of a larger number of monolayers has been followed by Brewster-angle or fluorescence microscopy, those imaging methods do not have sufficient resolution to observe the small soliton features.