ADVANCED MATERIALS

DOI: 10.1002/adma.200502265

Towards Organization of Molecular Machines at Interfaces: Langmuir Films and Langmuir–Blodgett Multilayers of an Acid–Base Switchable Rotaxane**

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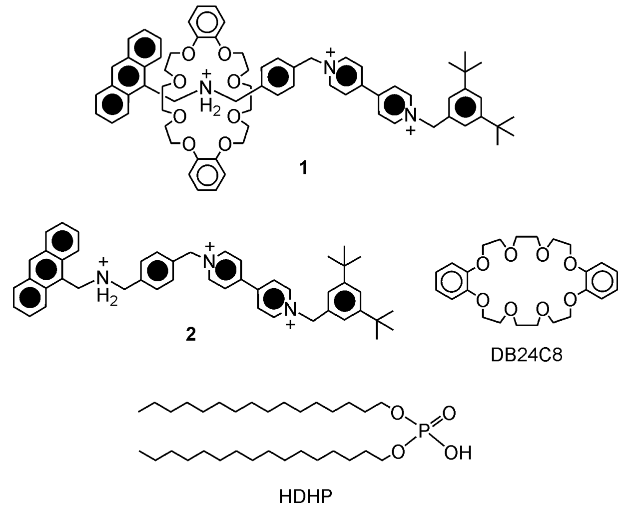
The design and synthesis of nanoscale species capable of performing controllable mechanical movements, that is, molecular machines,[1–3] is a topic of growing interest. Appealing examples of chemical compounds that have movable component parts are suitably designed catenanes, rotaxanes, and pseudorotaxanes.[4] In the past few years, several prototypes of artificial molecular machines based on these types of interlocked systems have been synthesized and subsequently investigated in the solution phase.[1–3] However, it is reasonable that, before functional supramolecular assemblies can find applications as nanoscale machines, they have to be interfaced with the macroscopic world by ordering them in some way. The next generation of molecular machines will need to be organized at interfaces,[5] deposited on surfaces,[6] or immobilized into membranes[7] or porous materials[8] so that they can behave coherently and can be addressed on the nanometer scale. Indeed, the preparation of modified electrodes[9] represents one of the most promising ways to achieve this goal. Solid-state electronic devices containing functional rotaxanes and catenanes are also being developed.[10]

In this context we investigated, for the first time, the organization of a non-amphiphilic tricationic switchable rotaxane and its dumbbell-shaped component into Langmuir films and Langmuir–Blodgett (LB) multilayers by using a cospreading strategy. The Langmuir films have been characterized by surface pressure–area (Π–A) isotherms, and subsequently transferred onto indium tin oxide (ITO) or CaF_2 supports to form LB multilayers, which were then studied by infrared (IR) and UV-vis spectroscopy, and voltammetric techniques. We found that the LB films exhibit a reversible switching behavior when exposed cyclically to bases and acids, and therefore are capable of transducing a chemical input signal into an electrical output signal, although we could not relate such a switching behavior to ring shuttling. The structures of the rotaxane **1**, its dumbbell-shaped and ring components **2**, dibenzo[24]crown-8 (DB24C8), and the anchor lipid hydrogen dihexadecylphosphate (HDHP) are represented in Scheme 1.

The rotaxane **1**, whose dumbbell-shaped component **2** comprises[11] two different recognition sites—namely, a dialkylammonium center and a 4,4′-bipyridinium unit—and an anthracene unit as one of the stoppers, was selected for this study because of its capability to function[12,13] as an acid–base-controllable molecular shuttle (Scheme 2). In a CH_3CN solution



Scheme 1. Structural formulas of the compounds examined.

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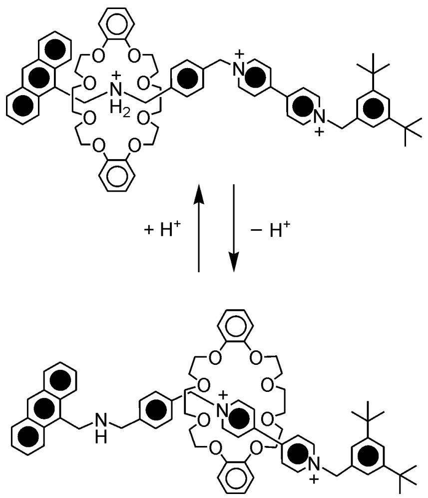
[**] This work was supported by the Italian MIUR (Supramolecular Devices Project), the University of Bologna (Funds for Selected Research Topics), and the Ministerio de Ciencia y Tecnología (MCT project BQU2002-01091). The European Union is gratefully acknowledged for a Marie-Curie Fellowship (to M. C.-L.) and for support under the auspices of the Molecular-Level Devices and Machines Network (HPRN-CT-2000-00029) and the BIOMACH project (NMP2-CT-2003-505487). The authors thank Profs. V. Balzani and M. Venturi for useful discussions.



Scheme 2. The reversible shuttling motion of the DB24C8 ring between the two recognition sites in the rotaxane **1**, controlled by addition of acid and base (CH_3CN solution, room temperature).

the DB24C8 ring exhibits 100 % selectivity for the dialkylammonium recognition site, hence the rotaxane exists as only one of the two possible translational isomers. Deprotonation of the ammonium center by addition of a base causes complete displacement of the ring component to the bipyridinium unit. Reprotonation by addition of acid directs the DB24C8 macrocycle back on the dialkylammonium site. This shuttling process is fully reversible, relies on the chemical energy supplied by the acid–base reaction, and can be monitored by ^{1}H NMR spectroscopy, UV/vis spectroscopic methods, and electrochemical measurements.[12] It is worth noting that a molecular machine operating on chemical-energy inputs requires the addition of fresh reactants ('fuels') at every step of its working cycle, with the concomitant accumulation of waste products that eventually compromise the operation of the machine, unless they are removed from the system.[14] In principle, incorporation of molecular machines into heterogeneous assemblies such as LB films would facilitate the supply of chemical fuels and the removal of waste products, simply by renewing the solution in contact with the surface.

A cospreading technique,[15] in which an organic solution containing a non-amphiphilic adsorbate and an amphiphilic anchor in a well-defined molar ratio spread at an air/water interface, was successfully tested[16] for positively charged macrocycles and catenanes. This strategy is quite convenient because it allows the preparation of thin films by using the LB technique without chemical modification of the target molecules to confer them an amphiphilic character. The hexafluorophosphate salts of **1** and **2** were mixed with the amphiphilic anion DHP$^-$, which was formed upon deprotonation of HDHP when such compounds were spread at the air/water interface. A solution containing **1** or **2** and 12 equivalents of the amphiphilic species HDHP was used as the spreading solution. The monolayer of DHP$^-$ anions obtained in this way is underlaid by the positively charged molecules **1** or **2**, which are electrostatically anchored to the phospholipid anions. Because of the small amount of sample available, a systematic study[16a] of the influence of a number of HDHP molecules per molecule of rotaxane could not be carried out. Therefore, a great excess of the amphiphilic species was employed to ensure that a stable monolayer was formed. Π–A isotherms (Fig. 1a) indicate the formation of stable monolayers of both rotaxane **1** and its dumbbell-shaped component **2** mixed with HDHP, and show that the presence of molecules **1** or **2** induces large changes in the isotherm compared to that of pure HDHP. Different behavior is observed at low and high surface pressures for both compounds. While at lower surface pressures the areas per molecule of the mixtures of HDHP and **1** or **2** are larger than those of pure HDHP, at higher surface pressure they tend to values very close to those of pure HDHP. These results suggest that at low surface pressures the interactions between the DHP$^-$ anions and the cationic species **1** or **2** modify the packing of the DHP$^-$ molecules. Compression of the monolayer leads to the expulsion of molecules **1** or **2**, giving rise to similar areas as that found for pure HDHP. On the other hand, the isotherms of the mixtures of

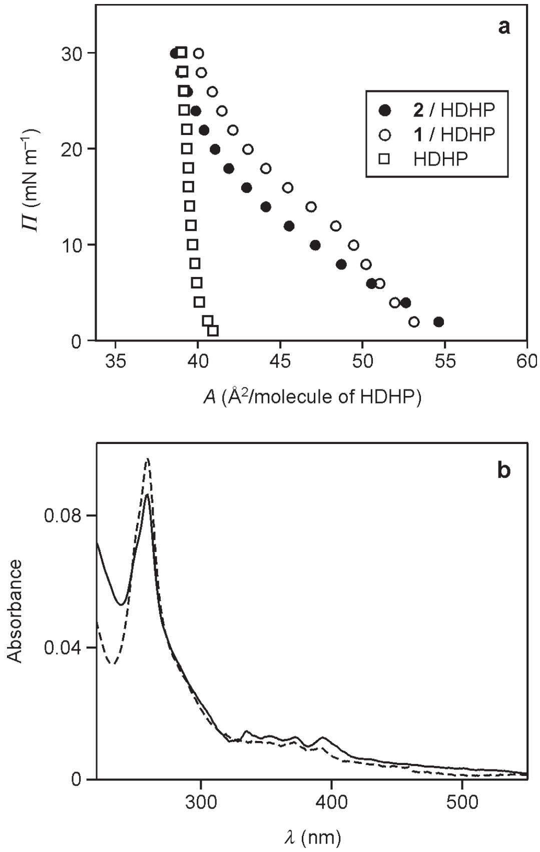


Figure 1. a) Π–A isotherms at 20 °C of HDHP mixtures with the rotaxane **1** and its dumbbell-shaped component **2**, and of pure HDHP. b) UV-vis spectra, at room temperature, of LB films consisting of 20 monolayers of **1**/HDHP (solid line) and **2**/HDHP (dashed line) deposited on each side of a CaF_2 slide.

HDHP with **1** or **2** are different. These small differences can be explained by the presence of the DB24C8 macrocycle in the rotaxane, which may modify the interaction of such species with the HDHP molecules, and the lateral interactions between the molecules cospread with HDHP.

The IR spectra of CaF_2 slides covered on each side with 20 monolayers of the compounds show bands at 2919 and 2850 cm^{-1}, associated with the CH bands of HDHP, and a band centered at 1507 cm^{-1} that can be related[17] to vibration modes of the aromatic CH groups of **1** and **2**. Such a band exhibits no clear dichroism, indicating an isotropic distribution of these molecules. In contrast, the IR bands associated with the alkyl chains of the amphiphile are dichroic. The tilt angle of the HDHP molecules can be easily assessed and has a value of 15°, very close to the tilt angle of a LB film of pure HDHP. The UV-vis absorption spectra of the LB films (Fig. 1b) show the absorption bands typical[12,13] of the anthracene unit of **1** and **2**, namely, an intense band around 255 nm and a weaker and structured band in the 320–400 nm region. The absorbance increases linearly as the number of monolayers is increased, indicating that the Langmuir film is transferred in a regular manner. Since IR linear dichroism measurements have shown that molecules **1** or **2** present a isotropic distribution within the LB films, one can estimate the number of molecules of **1** or **2** trapped within the LB film from the absorbance values of the intense band at 260 nm (in CH_3CN solution, $\varepsilon = 100\,000$ L mol^{-1} cm^{-1} for **1** and 135 000 L mol^{-1} cm^{-1} for **2**).[12,13] As the number of monolayers is known, a concentration of 2.2×10^{-11} and 2.0×10^{-11} mol cm^{-2} per monolayer can be calculated for **1** and **2**, respectively. The number of molecules per unit surface area and the mean area per molecule within each monolayer are therefore 1.3×10^{-3} molecules Å^{-1} and 770 Å^2 in the case of **1**, and 1.2×10^{-3} molecules Å^{-1} and 830 Å^2 in the case of **2**. Considering that the cross sections of rotaxane **1** and its dumbbell-shaped species **2**, determined from molecular modeling, are 295 and 226 Å^2, respectively, only a relatively small fraction (around 30 %) of the surface of the monolayer is occupied by such molecules. These calculations suggest that **1** and **2** are not closely packed within the LB film. On the other hand, it is possible to establish the number of HDHP molecules, assuming that they are in a closely packed state and that the area per molecule is 40 Å^2 at the surface pressure of the transfer, as suggested by the Π–A isotherms. By comparing such a value with the number of molecules of **1** or **2** calculated from UV-vis absorption spectra, we can estimate a ratio of 19:1 between HDHP and molecules **1** or **2** within the LB film. Since the spreading solution contains 12 HDHP molecules per each species **1** or **2**, there must be a partial dissolution of the rotaxane and of the dumbbell-shaped component from the monolayer into the subphase. This phenomenon is related to the low, but not negligible solubility of **1** and **2** in water, because of their insufficiently pronounced hydrophobic character.

Cyclic voltammetric experiments, carried out in a 0.1 mol L^{-1} KCl aqueous solution by using ITO plates coated with six monolayers of **1**/HDHP or ten monolayers of **2**/HDHP as working electrodes, show two quasireversible reduction processes, clearly attributed to the bipyridinium unit (Figs. 2a,b). The halfwave potential values are –0.47 and –0.80 V versus a saturated calomel electrode (SCE) for the rotaxane **1**/HDHP, and –0.41 and –0.76 V versus SCE for the dumbbell-shaped component **2**/HDHP. Both processes are shifted to more negative values compared to those found[12] in a CH_3CN solution (–0.35 and –0.78 V vs. SCE for **1** and **2**, respectively), i.e., reduction of the bipyridinium unit becomes more difficult when the compounds are incorporated in LB multilayers. Moreover, the halfwave potential values for the LB film of **1**/HDHP are more negative with respect to those of **2**/HDHP, suggesting a slightly different multilayer organization for these two compounds. The current intensity of the voltammetric waves decreases upon repeated scanning; this observation indicates that multilayers of the reduced rotaxane and dumbbell-shaped component are not stable. The current intensity grows proportionally with the number of monolayers of the LB films of both compounds, confirming that the transfer is homogeneous. This homogeneity was also deduced from UV-vis absorption spectra, suggesting that reduction–oxidation of the molecules of the external monolayers is possible despite the presence of the insulating lipid layers. A possible explanation for this finding is the presence of defects within the LB film. Another effect observed is that the peak-to-peak separation increases and the reduction potential shifts to more

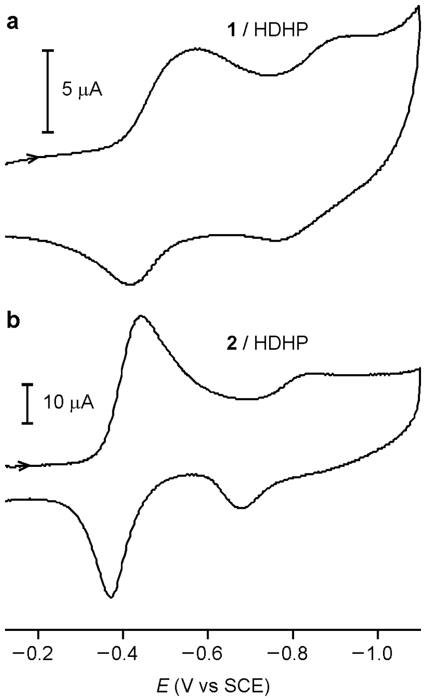


Figure 2. Cyclic voltammetry of LB films of a) six monolayers of the rotaxane **1**/HDHP and b) ten monolayers of its dumbbell-shaped component **2**/HDHP deposited onto ITO plates (room temperature, H_2O, 0.1 mol L^{-1} KCl, scan rate: 100 mV s^{-1}).

negative values upon increasing the number of monolayers. Such behavior has already been observed in other similar lamellar systems and has been correlated[18] with partial hindrance to the diffusion of the charged species through the multilayers, caused by the increasing number of long-chain surfactant layers.

To investigate the possibility of acid–base switching of the rotaxane **1** and dumbbell **2** in the LB films with HDHP, ITO plates covered with 6–20 monolayers of such compounds were subjected to immersion in an aqueous solution at pH 11 and 1, and examined by UV-vis absorption spectroscopy and cyclic voltammetry. These treatments caused no modification in the absorption spectra, and only slight changes ($\Delta E < 30$ mV) in the halfwave potential values for the reduction of the bipyridinium unit. We then exposed the LB films deposited on ITO to NH_3 and HCl vapors, and studied their spectroscopic and voltammetric behavior again. LB Films of both **1**/HDHP and **2**/HDHP showed no change in their absorption spectra or cyclic voltammograms upon exposure to gaseous ammonia. However, the halfwave potential values for the reduction of the bipyridinium unit shifted to less negative potential values ($\Delta E =$ ca. +70 mV) when both LB films of **1**/HDHP and **2**/HDHP were left in contact with the HCl vapors. Subsequent exposure of the films to NH_3 gas produced opposite variations in the redox potential values. No evident change was detected in the UV-vis absorption bands of the anthracene unit in any case. These observations indicate that the reactants in the gas phase can penetrate easily into the LB multilayers, and that the films undergo a reversible acid–base-controlled process. The reversibility of the process was checked for up to two acid–base cycles, as shown in Figure 3.

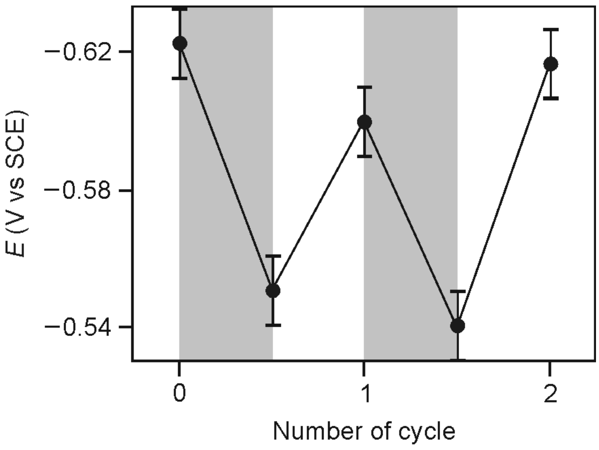


Figure 3. Changes in the potential value of the cathodic wave, corresponding to the first reduction of the bipyridium unit in LB films of 20 monolayers of **1**/HDHP, upon treatment with gaseous HCl (shaded areas) and NH_3 (white areas).

It should be noted that the investigated LB films were prepared with compounds **1** and **2** in their protonated form. Therefore, we expected to observe spectroscopic and/or voltammetric changes upon deprotonation of the ammonium sites, that is, upon addition of a base. As a matter of fact, the first addition of base to the LB films did not produce any change in the properties, whereas the addition of an acid caused changes in the redox potentials; these changes were reversed after the subsequent addition of a base. This behavior suggests that the ammonium centers of molecules **1** and **2** lose their proton during the preparation of the films.

In the case of the LB multilayers of rotaxane **1**/HDHP, the acid–base switching behavior could originate from i) protonation–deprotonation of the amine unit of the rotaxane, ii) shuttling of the macrocyclic component from one recognition site of the dumbbell component to the other, or iii) protonation–deprotonation of HDHP. In the latter case, the shift in the redox potentials should arise from the rearrangement of the film induced by protonation–deprotonation of the amphiphilic anions. This possibility, however, was excluded by investigation of the redox properties of LB multilayers prepared by cospreading the model compound 1,1′-dibenzyl-4,4′-bipyridinium—which does not contain acid or basic sites—and 12 equivalents of HDHP in a $CHCl_3/CH_3CN$ solution. No change in the reduction potential of the bipyridinium unit was observed when the thin films were consecutively exposed to gaseous HCl and NH_3. The fact that the same switching behavior is exhibited by LB films containing the dumbbell-shaped component **2**, in which process (ii) above cannot occur, suggests that both LB films of **1**/HDHP and **2**/HDHP undergo a similar reversible rearrangement process induced by consecutive treatment with acids and bases. One of the main reasons for the rearrangement is likely to be the change in the overall electric charge of the rotaxane and dumbbell molecules, which can be related to the protonation–deprotonation of the ammonium site. Since the solution studies have show[12,13] that the acid–base controlled ring displacement of rotaxane **1** is not accompanied by strong absorption spectral changes, our results do not rule out the occurrence of the shuttling process in the thin films. However, it seems reasonable that such a process can take place in a LB multilayer since we have found that **1** and **2** are not closely packed within the films. Indeed, mechanical molecular switching for rotaxanes and catenanes embedded in condensed environments,[19] including Langmuir films and LB multilayers,[20] has been recently observed.

In summary, we have prepared monolayers of a non-amphiphilic tricationic switchable rotaxane and its dumbbell component by cospreading with the amphiphilic anion DHP^- at the air/water interface of a Langmuir trough. The monolayers were transferred onto solid supports for spectroscopic and electrochemical investigations. Reversible switching of the potential values for the reduction processes of the bipyridinium unit of **1** and **2** upon cyclic exposure of the films to vapors of HCl and NH_3 was observed. Comparison of the behavior of the rotaxane- and dumbbell-containing multilayers suggests that the switching process is related mainly to a rearrangement of the films upon protonation–deprotonation of **1** and **2**, although the occurrence of a ring shuttling motion in the case of the films of rotaxane **1** cannot be excluded. Nonetheless, since the examined thin films provide a reversible electrical output signal in response to acid–base input stimuli, they may be useful for sensing purposes. This work has shown that functional molecular systems can be easily organized at the air/water interface and subsequently transferred onto surfaces where they can be addressed optically[21] or electrically,[22] in an attempt to produce solid-supported artificial molecular devices and machines.

Experimental

Hexafluorophosphate salts **1** and **2** were obtained from previous investigations [12]. HDHP was purchased from Aldrich and used as received. NH_3 and HCl were purchased from Merck. CaF_2 and ITO glass slides were obtained from ICMC (Le Mée-sur-Seine, France) and cleaned by sequential sonication in acetone and distilled water prior to each experiment.

Spreading solutions were prepared by adding 12 equivalents of HDHP dissolved in $CHCl_3$ (HPLC-grade Prolabo) to a solution of **1** or **2** in CH_3CN (HPLC-grade Prolabo). The final composition of the solvent mixture was $CHCl_3/CH_3CN$ 8:1 (*v*/*v*). An appropriate amount of a solution containing **1** or **2** and HDHP was carefully spread onto pure water, and the spreading solvent was allowed to evaporate for 10 min prior to compression. The Langmuir monolayers were compressed at 20 ± 1 °C by using a step-by-step procedure. The Y-type LB films were obtained by a vertical lifting method with a transfer ratio close to unity, at a surface pressure of 30 mN m^{-1} with a dipping speed of 1 cm min^{-1}. After each cycle, the substrate was allowed to dry for 2 min in a nitrogen flow. The films were transferred onto optically polished calcium fluoride slides for IR and UV-vis absorption spectra and onto ITO-coated glass slides for electrochemical measurements. The contact with NaOH (pH 11) and HCl (pH 1) solutions was performed by leaving the LB films inside the solution for 30 min. Exposure of the films to NH_3 and HCl vapors was performed by leaving the LB films in contact with the gases for 5 min in the case of HCl and 30 min in the case of NH_3. After treatment with HCl and NH_3 the plates were purged with a flow of Ar gas. All of the spectroscopic and electrochemical experiments were performed at room temperature (ca. 25 °C).

Molecular modeling was carried out both by inspection of a physical CPK model and molecular mechanics calculations. The latter were performed by employing the MM3 force field as implemented in the Tinker 4.0 package (Copyright 1990–2003 Dr. J. W. Ponder, Biochemistry and Molecular Biophysics, Washington University School of Medicine, St. Louis, MO).

The LB experiments were carried out with a laboratory-made trough [23]. Surface pressure was measured with a Pt Wilhelmy plate. A millipore purification system produced water with a resistivity higher than 18 MΩ cm for all experiments. IR spectra were recorded on a FTIR 750 Nicolet spectrometer. UV-vis absorption and luminescence spectra were recorded with a Perkin–Elmer λ6 spectrophotometer and a Perkin Elmer LS50 spectrofluorimeter, respectively. Electrochemical measurements were carried out with an Autolab 30 multipurpose equipment interfaced to a PC. ITO-coated glass slides (ca. 1 cm × 4 cm) with deposited LB films were used as the working electrodes. The reference electrode was a SCE (Amel), while the counter electrode was a Pt wire separated from the solution by a fine ceramic frit. The electrolytic medium was H_2O (milli Q, 18.2 MΩ cm) containing 0.1 mol L^{-1} KCl. The experimental error on the potential values was ±10 mV.

Received: October 21, 2005
Final version: December 2, 2005

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