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Ultrathin chemosensoring films with a photosensitive bis(crown ether) derivative

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The spectral and isotherm changes observed for a new photosensitive bis(crown ether) derivative assigned as optical molecular tweezers (OMT) in mixed monolayers with stearic acid by addition of ammonium and diammonium salts indicated the strongest complex formation between OMT and 1,3-diaminopropane dihydrochloride that may be of particular interest for design of chemosensoring nanomaterials.

The design of ultrathin chemoselective films is a promising direction of supramolecular chemistry having both fundamental and applied importance.[1–3] For example, monolayers of amphiphilic photochromic crown ethers can serve as unique models for the study of self-organization and molecular recognition phenomena, well-known for biological membranes, as well as promising chemosensoring nanomaterials.[4–6] Such nanomaterials[3–5] with high degrees of 2D- or 3D-organization, integrity at the molecular level range, multiple usage, stability and other desirable properties may be realized by the special synthesis of amphiphilic photochromic crown ethers.[7,8]

Here, we report the preparation of monolayers of the photosensitive bis(crown ether) derivative assigned as optical molecular tweezers (OMT) and the investigation of its properties both at the water–air interface and transferred onto transparent plates.

The synthesis of OMT named by IUPAC as 1,1′-[1,4-phenylenedi(methylene)]bis{4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)vinyl]pyridinium}diperchlorate [Figure 1(*a*)] was published recently.[7] For studying the OMT chemosensoring properties 1,ω-diaminoalkane dihydrochlorides [$NH_3^+(CH_2)_nNH_3^+ \cdot 2Cl^-$ (n = 3 or 7)] (Aldrich-Sigma) and tetramethylammonium chloride [NMe_4Cl] (Fluka) were used. For monolayer preparations, measurements of surface pressure – and surface potential – molecular area isotherms, laboratory devices based on the Langmuir principle[4] were used. The mixed monolayers (OMT:stearic acid = 1:2) were transferred onto quartz plates (38×12 mm) by the Langmuir–Blodgett method[4] at a constant surface pressure of 30 mN m^{-1}. The spectral characteristics of OMT were studied using a Cary 4000 UV-VIS and Cary Eclipse Fluorescence spectrophotometers. The data processing was done by the PC programs Trough 2.1 and Cary Scan.

The novel OMT does not form stable monolayers itself but can be stabilized in the mixture with stearic acid (C18) at surfaces of various aqueous solutions (NMe_4Cl, 1,3-diaminopropane and 1,7-diaminoheptane dihydrochlorides) with collapse pressures of 60–66 mN m^{-1} (Figure 2). The area increase in the mixed monolayer (as compared to the pure stearic acid) is

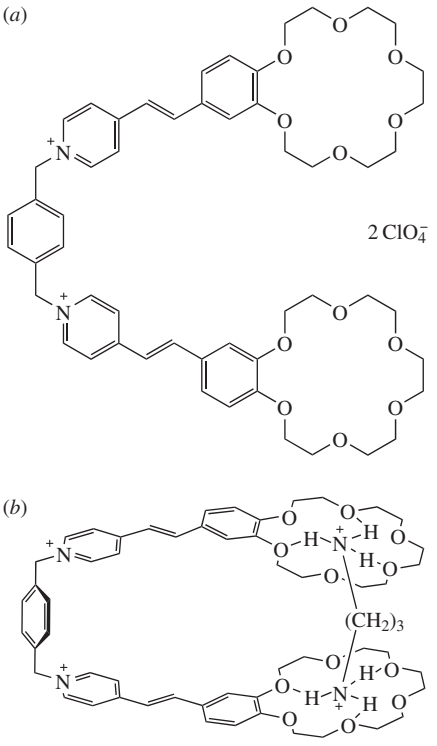

Figure 1 Structure of (*a*) OMT and (*b*) the 1:1 complex between OMT and the 1,3-propanediammonium ion.

directly proportional to the molar fraction of the OMT in the mixture. Taking into account our results on various mixtures, the stoichiometry and various interactions between two molecules of stearic acid and a molecule of OMT, the ratio of OMT to stearic acid of 1:2 in the mixed monolayers was selected for the further study.

The isotherms of stearic acid monolayers on water (not shown here because well-known[9]) and 1,3-diaminopropane dihydrochloride solution (Figure 2, curve *3*) were almost identical and

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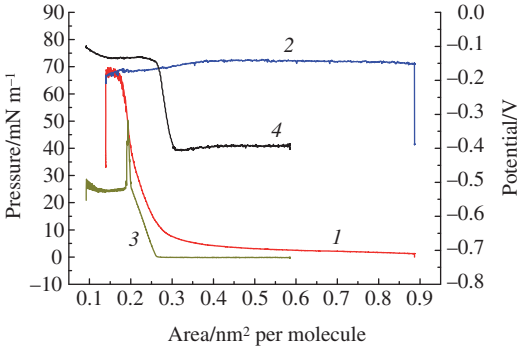

Figure 2 Dependence of (*1*, *3*) surface pressure *vs.* area per stearic acid molecule and (*2*, *4*) surface potential *vs.* area for mixture of (*1*, *2*) OMT:C18 = 1:2 or (*3*, *4*) pure stearic acid at the subphase of 1 mM solution of 1,3-diaminopropane dihydrochloride.

had two steeply sloping 'quasi-linear' regions: 'liquid-condensed' and 'solid-like' with transition point[9] at about 25 mN m^{-1} and collapse pressure[9] at about 55–60 mN m^{-1} with abrupt decrease by further monolayer compression that was typical of pure stearic acid monolayers.[9] The surface pressure–area isotherm for the mixed OMT:C18 monolayers at the surface of 1,3-diaminopropane dihydrochloride solution (Figure 2, curve *1*) had mainly one 'liquid-expanded' region with non-linear gradual sloping, especially at surface pressures till 40 mN m^{-1}, and larger molecular areas (for better comparison the area per stearic acid molecules was applied for all isotherms in Figure 2) that was qualitatively different from the reference isotherm (Figure 2, curve *3*). The relative increases in the molecular area values for these mixed monolayers were 12% for 1,3-diaminopropane dihydrochloride or 4% for NMe_4Cl at the interface of the 1 mM solutions, as compared to distilled water (the area per stearic acid molecule in the mixed monolayer with OMT was 0.25 nm^2) at a constant surface pressure of 10 mN m^{-1}. The relative molecular area increase was about 16% for the mixed monolayers of OMT:C18 = 1:2 (Figure 2, curve *1*) as compared to pure stearic acid on the same 1 mM solution of 1,3-diaminopropane dihydrochloride (Figure 2, curve *3*). Such a pronounced increase in the molecular area can be explained by strong interaction of OMT (in the mixed monolayer) with 1,3-diaminopropane dihydrochloride (from the aqueous subphase), taking into account also a negligible change for the stearic acid monolayer parameters in the presence of 1,3-diaminopropane dihydrochloride.

Even more pronounced changes for monolayer parameters in the presence of OMT were found for surface potential–area isotherms (Figure 2, curves *2* and *4*). The surface potential (ΔV) for the mixed OMT:C18 monolayers at the interfaces of 1,3-diaminopropane dihydrochloride (Figure 2, curve *2*) 'jumped up' upon spreading (by about 0.20–0.24 V) due to the strong positive charges of OMT molecules and remained almost constant by monolayer compression in the whole studied areas range (from 0.85 to 0.20 nm^2 per molecule). The changes in surface potential of the gas–liquid interface after monolayer formation can be expressed by the Helmholz equation:[9] $\Delta V = n\mu(1/\varepsilon_0)$, where n is the number of molecules in the monolayer, μ is the mean change of the effective dipole moment per amphiphilic molecule normal to the interface, ε_0 is the permittivity of the vacuum. Using the identity $n = 1/A$, where A is the mean area per molecule, this equation can be transformed to the form[4] $\mu = A\varepsilon_0\Delta V$ in order to calculate the change of the effective dipole moment per molecule in monolayer, which reflects changes in molecular orientation, as well as interactions of OMT and diamines at the interface. Using such an approach, we found a gradual decrease of almost a factor of 4 for the effective dipole moment values during monolayer area decrease from 0.85 to 0.20 nm^2 per molecule. This effect can be due to the OMT molecules reorientation in the mixed monolayer by interaction with diamines by gradual compression with moving barrier. In contrast, for pure stearic acid monolayers on the same 1 mM solution of 1,3-diaminopropane dihydrochloride the surface potential values (Figure 2, curve *4*) were increasing sharply (by about 0.25 V) only in the narrow areas range (from 0.32 to 0.26 nm^2 per molecule) by monolayer compression just before the pronounced increase in surface pressure (Figure 2, curve *3*) that was typical of pure stearic acid monolayer on distilled water.[9] The observed effects gave the additional evidence of the strong interaction between OMT in the mixed monolayer and 1,3-diaminopropane dihydrochloride [Figure 1(*b*)]. The isotherms of the prepared mixed monolayer were almost the same after expansion and second compression (after 2–3 h) proving the stability of the obtained mixed 'nanofilms'. The complete transfer of these mixed monolayer onto quartz plates by the Langmuir–Blodgett method was found at constant surface pressure of 30 mN m^{-1} in the case of the 1 mM salt solutions.

The major spectral characteristics of OMT in monolayers are the following: a strong absorption (maximum at 398 nm) and fluorescence (maximum emission at 532 nm) for OMT in solution and its mixture with C18 (both at the air–water interface and transferred onto quartz plates). A shift of the absorption maximum to 394 nm and the fluorescence maximum to 542 nm was observed for the mixed OMT:C18 monolayer transferred from the 1 mM solution of 1,7-diaminoheptane dihydrochloride. Moreover, a shift of the absorption maximum to 406 nm and the fluorescence maximum to 540 nm was found for this monolayer transferred from the 1 mM solution of 1,3-diaminopropane dihydrochloride (Figure 3). It is interesting that the shifts of the absorption maximum for these diammonium compounds were in the opposite directions, as compared to the initial absorption maximum (at 398 nm) and the total difference was about 12 nm that can be connected with the formation of the complexes of various types between OMT and particular diamines. These changes were a little bit higher that those observed in the chloroform–methanol (85:15) solution for pure OMT (λ_{max} = = 398 nm) and in the presence of 1,3-diaminopropane dihydrochloride (λ_{max} = 393 nm), but a little bit lower that those changes in acetonitrile solution for pure OMT (λ_{max} = 410 nm, $\varepsilon \approx 68000$) and in the presence of 1,3-diaminopropane dihydrochloride (λ_{max} = = 387 nm, $\varepsilon \approx 64400$). The negligibly small shifts of absorption and fluorescence maxima were found for the mixed OMT:C18 monolayer transferred from the 1 mM solution of tetramethylammonium chloride that can be due to the non-specific interactions between all components at the interfaces. Studying the OMT:C18 spectra directly in Langmuir trough at the surface of various salt solutions and water (data not shown[10]) we found a pronounced decrease in the spectra intensity by monolayer compression (from 1.3 to 0.2 nm^2 per molecule) only in the case of the mixed OMT:C18 monolayer on the 1,3-diaminopropane

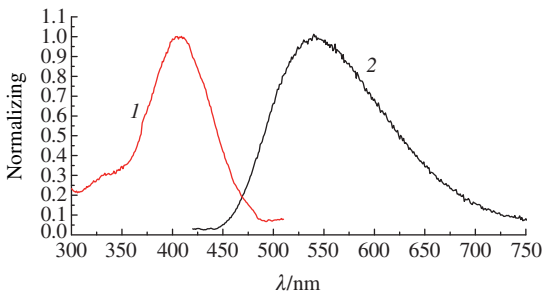

Figure 3 Spectra of (*1*) absorption in comparison to (*2*) fluorescence of mixed monolayer (OMT:C18 = 1:2) transferred from 1 mM solution of 1,3-diaminopropane dihydrochloride.

dihydrochloride solution that proved a reorientation of the hydrophobic parts of the OMT:C18 molecules from almost flat to the vertical conformation with respect to the interface. These data are in agreement with a gradual decrease in the effective dipole moment almost by a factor of 4 during such monolayer compression.

Thus, the maximal changes were found for the mixed OMT:C18 monolayer at the interface or transferred from the 1 mM solution of 1,3-diaminopropane dihydrochloride due to the strong interaction between OMT and this diammonium ion (having the sterically most appropriate spacer for interactions of positively charged ammonium groups with two crown ether rings of OMT) forming a pseudocyclic 1:1 complex [Figure 1(*b*)]. We anticipate that such complex formation between OMT and particular alkanediammonium salts can be promising for design of chemosensoring nanomaterials, capable for optical detection of biogenic diamines in solutions.

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