Cavitand-, fullerene-, and porphyrin-containing Langmuir films: preparation of mechanically and optically active monolayers

Doctoral Thesis

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Cavitand-, Fullerene-, and Porphyrin-containing *Langmuir* Films: Preparation of Mechanically and Optically Active Monolayers

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Abstract

The *Langmuir* technique is one of the most common methods for preparing two-dimensional molecular assemblies. In this method, a solution of an amphiphilic compound in a low-boiling solvent, usually immiscible with water, is spread on a water subphase. After the solvent has evaporated, the amphiphilic molecules form a monolayer in which their hydrophilic heads interact with the water subphase and the hydrophobic tails are directed away from it. Compression of the monolayer on the water subphase leads to a reduction of the area available per molecule (A), thus causing an increase in surface pressure (π). The resulting π–A isotherm (surface pressure as a function of the molecular area at constant temperature) provides information on the molecular packing within the monolayer, the orientation of the headgroups, the molecular area requirement, and possible interactions with molecules or ions dissolved in the aqueous subphase. The monolayer formed at the air-water interface can be transferred onto a solid support (*Langmuir–Blodgett* deposition). Due to the ease in assembling amphiphiles into a variety of thin films with defined composition, structure, and thickness, the *Langmuir* and *Langmuir–Blodgett* (LB) techniques have allowed the development of novel functional materials by many scientists.

In the first part of *Chapter 1*, the reader is introduced to the concept of self–assembly along with its applications in the fields of self–assembled monolayers (SAMs) and molecular recognition. This section is concluded with a description of significant examples of self–assembled monolayers comprising resorcin[4]arene-based cavitands, fullerenes, and porphyrins. The second part of *Chapter 1* consists of a comprehensive description of the *Langmuir* and *Langmuir–Blodgett* techniques as well as of *Brewster* angle microscopy (BAM) as one of the most common methods to analyze the morphology of the *Langmuir* films formed at the air-water interface.

The discussion of the research carried out in the context of the present thesis starts with *Chapter 2*. After an introductory general account on the resorcin[4]arene-based cavitands, their conformational properties are discussed along with the discovery of pH-promoted *vase-kite* switching which we investigated at the air-water interface. Amphiphilic cavitand **11** and velcrand **16** which, at room temperature, prefer the *vase* and *kite* conformation, respectively, were spread on water to demonstrate that the *Langmuir* technique allows a distinction between the two geometries at the air-water interface.

11, R = [structure: O, O⁻]

vase

16, R = [structure: O, O⁻]

kite
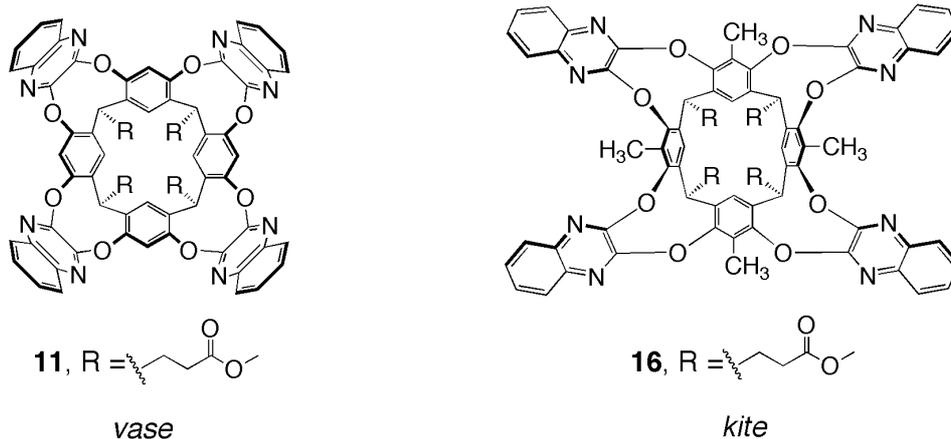
The molecular area requirement obtained by extrapolating the linear part of the π–A isotherm of cavitand **11** is 125 Å^2 which well reproduces the theoretical value expected for the *vase* conformation (120 Å^2). In case of cavitand **16**, the obtained value is 140 Å^2, about half of the area calculated for the *kite* conformation (290 Å^2). This value suggests that **16** undergoes dimerization, leading to the formation of velcraplexes at the air-water interface. The conformational switching was investigated by spreading cavitand **11** on a water subphase containing trifluoroacetic acid (TFA). Evidence for successful conformational control was obtained by variations in the limiting molecular area which increases (from 125 Å^2 to 223 Å^2) by increasing the concentration of TFA in the aqueous subphase. The spreading behavior of **11** was further investigated after addition of Zn(OAc)$_2$ to the water subphase which led to the discovery of a new Zn(II)-promoted conformational switching. Molecular modeling calculation and ^{1}H-NMR spectroscopic investigations supported the formation of a stoichiometric *kite*-cavitand·2 Zn(II) complex with each metal ion coordinating to two neighboring quinoxaline nitrogen atoms. The last part of *Chapter 2* describes investigations on the influence of the length of the polyethylene glycol chain on the monolayer packing of cavitands **12** and **13**.

12, R = [structure]

13, R = [structure]
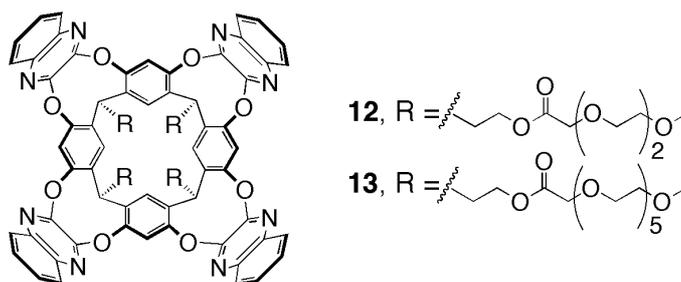
In particular, cavitand **13** with five glycol units in each of the four hydrophilic "legs", required a larger area per molecule at low pressure than cavitand **12**, having only two such units per "leg". The different acyl groups also explain the behavior of monolayers in experiments with high concentrations: No phase transition was observed with cavitand **12**, at high concentration, whereas in the case of cavitand **13**, two transitions were detected. Five glycolic units better approximate the limit case of PEG2000+ (notation referred to a PEG polymer derivatized with a hydrophobic headgroup), the *Langmuir* films of which display both transitions.

Chapter 3 starts with a general account of buckminsterfullerene and its main electronic and spectroscopic properties along with its incorporation into *Langmuir* monolayers. The second part of this *Chapter* is an investigation of the spreading behavior of fullerene-ionophore conjugates **35** and **36** on pure water and on aqueous subphases containing the metal ions Li^+, Na^+, K^+, Cs^+, and Ca^{2+}.
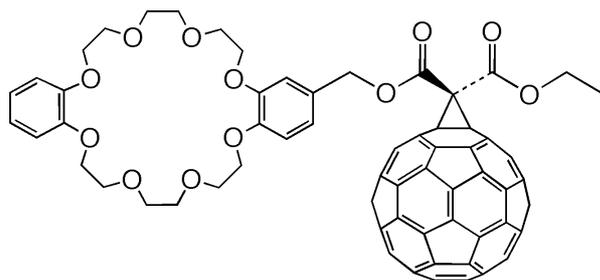
35
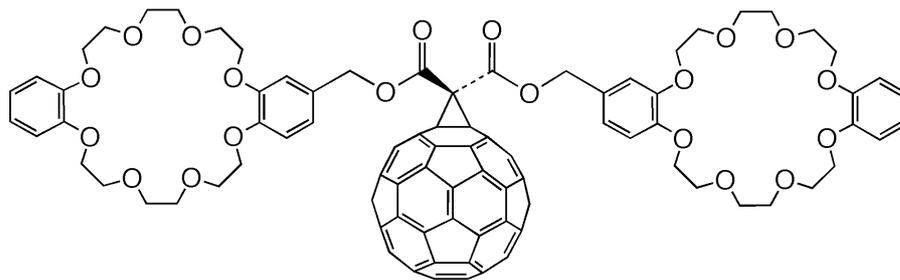
36

The presence of the dibenzo [24]crown-8 ether unit(s) in **35** and **36** leads to an improvement of the spreading behavior as compared to pristine C_{60} (60 $Å^2$ (**35**) and 75 $Å^2$ (**36**)). The areas per molecule are larger than in the case of unmodified buckminsterfullerene, even though they are still smaller than the theoretical value expected for the carbon cage (86 $Å^2$). The limiting molecular areas increase on subphases containing alkali metal chlorides or

CaCl$_2$, particularly in the cases of KCl and CsCl, due to the complexation of the cations by the crown ether moieties. The binding event leads to a conformational change of the crown ether, which adopts a more extended conformation and becomes more hydrophilic which provides a better anchoring on the subphase. The larger variation of the area per molecule observed upon addition of Cs$^+$ ions is due to the greater stability of the corresponding complex (logK = 3.78 in MeOH).

In collaboration with *Dr. Jean-Louis Gallani* (*CNRS, Strasbourg*), the spreading behavior of porphyrin-(dibenzo[24]crown-8) conjugates **42** and **43**, and of porphyrin-[60]fullerene-(dibenzo[24]crown-8) conjugate **44** was investigated in detailed *Langmuir* studies performed in order to investigate their spreading behavior (*Chapter 4*).
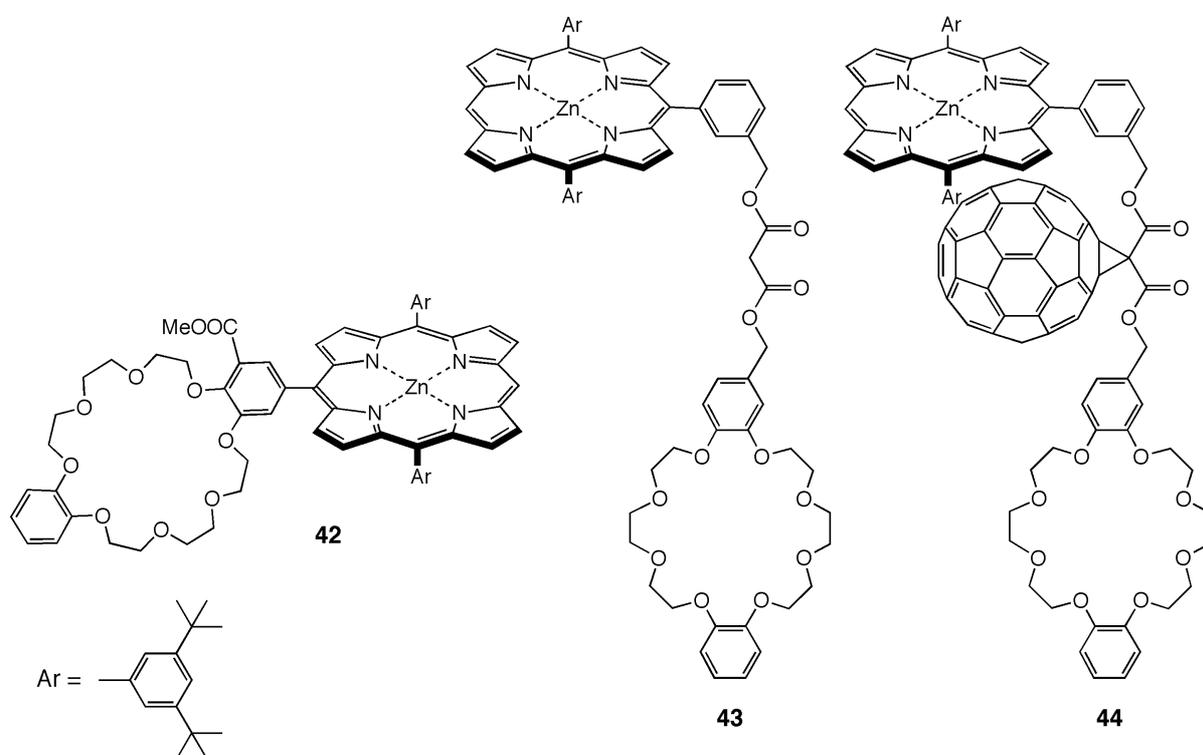
The three porphyrin derivatives show different behavior within the monolayers. In particular, conjugates **42** and **44** form more rigid monolayers than **43** and their spreading behavior is strongly affected by the presence of K$^+$ and Cs$^+$ ions in the water subphase. In the case of compound **42**, the isotherms show a phase transition corresponding to an orientational change of the porphyrin during the compression. At low pressure, the porphyrin unit of **42** lies horizontal on the water subphase and its area requirement becomes predominant when compared to the crown ether moiety. Under compression, the molecules

approach each other and the porphyrin-porphyrin stacking causes the tetrapyrrolic system to change orientation from parallel to normal with respect to the water surface. At higher pressure, the molecular area of the crown ether predominates and the complexation of metal ions becomes more important than in the case of derivative **43**. In fact, in conjugate **43**, the porphyrin does not dramatically change orientation and it stays nearly horizontal during the entire compression of the monolayer. It should be mentioned that the area occupied by a horizontal porphyrin ring is larger than the area of the crown ether both in the absence and in the presence of an alkali metal ion. Moreover, a flexible linker such as the malonate unit between the hydrophobic and the hydrophilic part of **43**, gives more degrees of freedom to the molecule and, consequently, the corresponding monolayers are less rigid than those of derivative **42**. The UV-VIS absorption spectra of LB multilayers of derivatives **42** show significant red-shifts of the *Soret* and *Q*-bands, confirming extensive porphyrin-pophyrin stacking. Conjugate **44** shows a strong influence of alkali ions in the water subphase on its spreading behavior, even if the porphyrin is locked atop the fullerene in horizontal, tangential position. The different behavior of **44** and **43** may be related to the fact that the fullerene moiety increases the hydrophobic character of the molecule. Therefore, the complexation of alkali metal ions by the crown ether moiety becomes important to reestablish a better balance between the hydrophobic and the hydrophilic part of **44**, thus leading to a better anchoring of the molecule on the aqueous subphase. An even more pronounced red-shift of the *Soret* and *Q*-bands was observed for conjugate **44** compared to **43** as consequence of the well-known attractive interactions between the fullerene moiety and the porphyrin. In accord with the low transfer ratios and the poor quality of the LB multilayers, the absorption intensity for all derivatives decreases with increasing numbers of depositions, showing that previously deposited molecules are lost in subsequent dipping cycles. Upon depositing further layers, no additional red-shifting of the *Soret* band was observed, suggesting that the exciton interactions are a consequence of intermolecular interactions occurring within the layers rather than between the layers.

The last part of this thesis, *Chapter 5*, consists of a comprehensive descriptions of the attempts toward the synthesis of the [60]fullerene-sandwiching macrocyclic bis(metallo porphyrin) and porphyrin-crown ether.