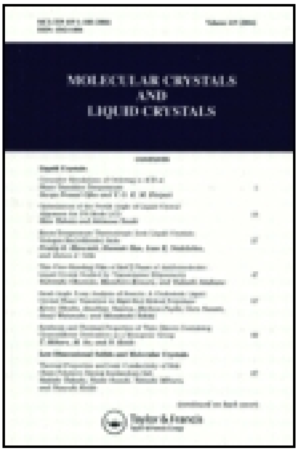

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Molecular Engineering at the Air-Water Interface: Building up Designed Supermolecular Assemblies with Amphiphilic Porphyrins

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MOLECULAR ENGINEERING AT THE AIR-WATER INTERFACE: BUILDING UP DESIGNED SUPERMOLECULAR ASSEMBLIES WITH AMPHIPHILIC PORPHYRINS.

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Abstract. Designed supermolecular assemblies can be built up by the Langmuir-Blodgett technique, through the vectorial control of chemical interactions occurring at the air/water interface between adjacent amphiphilic molecules.

Keywords: molecular engineering, langmuir-blodgett films, two-dimensional network, amphiphilic porphyrins, heterodimeric porphyrins, air-water interface

INTRODUCTION

The building up of two-dimensionnal networks into organized surroundings is of both practical and theoretical importance. For instance, they can be used as selective permeability membranes (1), for biological modeling (2), in microlithographic processes (3) or for the elaboration of materials of high temperature stability.

We describe here a strategy based on "molecular recognition" at the air-water interface between two different tetrasubstituted amphiphilic porphyrins. We are interested in the formation of ionic links (to form a 2D ionic network), through electrostatic attraction at the air-water interface between oppositely charged monomers P_1 and P_2. A precise control of the direction of the ionic links between the molecules is crucial for that goal.

EXPERIMENTAL DETAILS.

The synthesis of the porphyrins P_1 (tetra[p-oxy (2'-docosanoic acid)phenyl] porphyrin), P_2 (tetra-3-docosylpyridiniumporphyrin bromide) and the μ-oxo dimer $(FeP_2)_2O$ as well as the building up of the homolayers and alternated layers and the characterization apparatus are already described (4).

RESULTS AND DISCUSSION.

Homodimerization in pure P_1 and pure P_2 monolayers

As already described by several authors (4-6), the amphiphilic porphyrins P_1 and P_2 exhibit a strong tendency to the homodimerization at the air/water interface. For instance, P_2 spontaneously forms dimers at the air/water interface, which are characterized by their molecular area on the water bath (160 Å^2), the parallel orientation of the macrocycles with respect to the substrate in the resulting LB films (tilt angle 28°), the vertical period of these LB films (d_{001}=48Å) and the dimeric signal observed at g=4 in the ESR spectrum of alternate multilayers built from P_2 and an amphiphilic cyclodextrin CD as a diamagnetic spacer. The following results will show that the strong tendency to dimerization of these amphiphilic porphyrins is strenghtened by their mixing.

Heterodimerization in [$P_1 + P_2$] mixed monolayers

The heterodimerization process which occurs at the air/water interface between the two amphiphilic porphyrins is already described (4). The main results are the following:

All the carboxylic functions (COOH) of MP_1 are ionized into carboxylate anions (COO^-). Each carboxylate of MP_2 is therefore associated with a pyridinium of MP_2, via an ionic bond formed during the compression of the monolayer. This result provides good evidences for the "recognition" mechanism at the air-water interface.

The average angle θ between the plane of the macrocycles and the plane of the substrate is found to be 23° by linear dichroism in the UV-visible region. So, in rough estimate, the macrocycles are found to lie parallel to the surface of the samples in these assemblies. This high anisotropy is confirmed by ESR experiments.

The ESR spectra recorded on the [$CuP_1 + CuP_2$] mixture (where the mixed films are built up as alternated layers with CD) exhibit a well-resolved anisotropic spectrum fully characteristic of a dimeric species of the copper II (7). Moreover, the distinct ESR spectra recorded from homolayers [$CuP_1 + H_2P_2$] or [$H_2P_1 + CuP_2$] unambiguously proves that heterodimerization occurs between P_1 and P_2 and precludes any homodimerization process (P_1-P_1 and P_2-P_2). It also allows us to check the exact location of each porphyrin within the heterodimer. The ESR spectrum of [$CuP_1 + H_2P_2$] films is characteristic of monomeric species of the copper II while the [$H_2P_1 + CuP_2$] one leads to characteristic features of strongly dipolar coupled Cu^{II} (broad signal, disappearance of the hyperfine and superhyperfine patterns compared to the monomer signal). This result is consistent with P_1 lying above P_2 in the monolayer.

Strategy to prevent the heterodimerization

As the heterodimerization undoubtedly occurs at the air/water interface (no shift of the vibration band of the carboxylic functions of P_1 is observed in the infrared spectrum of the mixed spreading solution), it may probably be hindered by any molecule able to fill the volume located just on top of each macrocycle. In other words, we may prevent the molecule P_1 to climb onto P_2 if P_2 is axially complexed by a bulky amphiphilic ligand. This ligand has to be amphiphilic to be located on the "hydrophobic side" of the macrocycle (on the same side as the aliphatic chains), and to be strongly linked and bulky enough to preclude the heterodimerization. This strategy is illustrated in Fig 1.

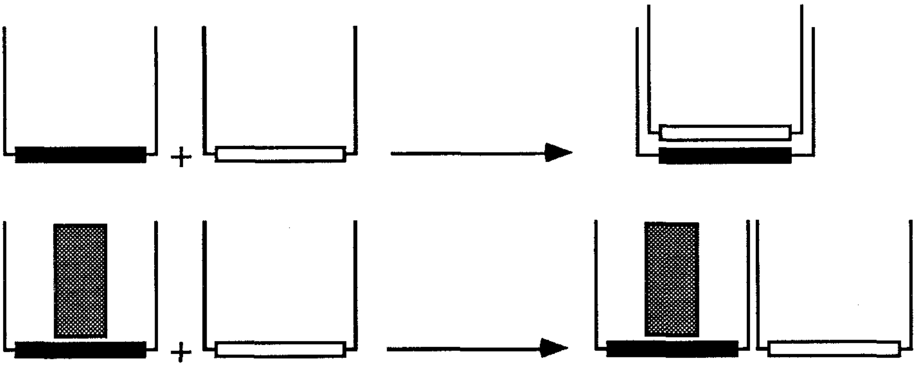

Figure 1: Strategy to preclude the heterodimerization

The merits of this strategy are confirmed by the comparative study of the monolayers built from CoP_2 and CoP_2Im, where Im (N-octadecyl imidazole) is an axial amphiphilic ligand of the cobaltous ion. The latter complex is spontaneously formed at the air/water interface when CoP_2 and Im are mixed in the spreading solution (8). The axial complexation only occurs on the "hydrophobic side" of P_2 because Im bears a long aliphatic chain. The complexation can be checked on the resulting multilayers by studying the oxidation of the complex by dioxygen (8).

Indeed, CoP_2 is not affected by air when CoP_2Im, the cobaltous ion of which is activated by the axial complexation, is quickly oxidized in the air. Fig 2a shows the compression isotherms recorded on these monolayers. As expected, the molecular area is significantly higher for CoP_2Im than CoP_2. Since the orientation of the chains and the macrocycles are the same in both cases, as confirmed by linear dichroism, we can assume that the axial complexation of Co^{II} precludes the homodimerization of CoP_2 at the air/water interface. Indeed, the resulting molecular area (210 $Å^2$) is consistent with a flat lying monomeric porphyrin ring. On the contrary, the molecular area observed for CoP_2 (150$Å^2$) is typical for a dimeric structure at the air/water interface. Similar values are observed on the monolayers built from $(FeP_2)_2O$, P_1 and from the mixture $[P_1+P_2]$.

Ionic network built from axially complexed cobaltous porphyrins

The last result shows that the strategy we built can be successful in preventing the homodimerization of amphiphilic porphyrins at the air/water interface (similar results are obtained for P_1). In order to build up an ionic bidimensional network, it is necessary to apply that strategy to the mixture $[P_1+P_2]$. Fig 2b shows the compression isotherms recorded on the monolayers built from the mixtures $[CoP_1+CoP_2]$ and $[CoP_1Im+CoP_2Im]$. As for CoP_2 alone, the molecular area is higher for the pentavalent than for the tetravalent complex. Moreover, the kinetics of oxidation by air confirms that both cobaltous porphyrins are axially complexed by the imidazole ring in the

[$CoP_1Im+CoP_2Im$] LB films and the infrared spectrum of these multilayers indicates that all the carboxylic functions of P_1 have been ionized into carboxylates. Thus, it seems likely that we have built up an ionic network of coplanar monomeric cobalt porphyrins.

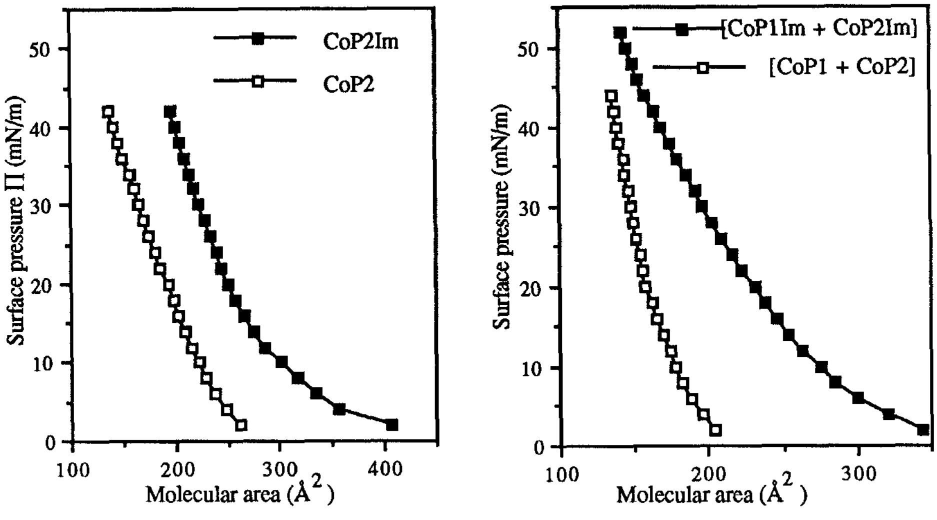

Figure 2: Compression isotherms of different cobalt porphyrins

The last assumption is confirmed by the study of the solubility of these mixed LB films. When the [CoP_1+CoP_2] LB films appear perfectly soluble in chloroform, which is the spreading solvent, the [$CoP_1Im+CoP_2Im$] multilayers are totally insoluble in that solvent. The first result is consistent with the claimed heterodimeric structure of the [CoP_1+CoP_2] films: each heterodimer P_1-P_2 is a neutral supermolecule independent from its neighbours. On the contrary, if each macrocycle is chemically linked to its closest neighbours, insolubility is likely to occur. So, the insolubility of the [$CoP_1Im+CoP_2Im$] films in chloroform is strongly in favour of a "polymeric" structure, built up at the air/water interface by lateral recognition between coplanar monomeric porphyrins.

Linear dichroism in the infrared and visible ranges shows that the ionic network is not as ordered as the [CoP_1+CoP_2] LB films. Indeed, the macrocycles appear significantly tilted from the substrate plane (35°). Moreover, the vertical periodicity of the LB films is less reproducible in the case of the ionic network than in the heterodimer case. So, the ionic network is slightly disordered. This may result from the "fight" occuring at the air/water interface between the heterodimerization and the axial complexation. This problem may be resolved by using more strongly linked axial ligands. The following paragraph will show that the octadecylimidazole ligand may be fruitfully replaced by FeP_2 itself as axial ligand.

Ionic network built up from μ-oxo dimers

Indeed, the cobalt-imidazole axial complexation is achieved at the air/water interface and thus competes with the spontaneous formation of the heterodimer P_1-P_2. It may be more fruitful to build up within the spreading solution very stable axially complexed porphyrins, which are thermodynamically more stable than the heterodimer and not supposed to compete with it within a kinetic formation process at the air/water interface. The μ-oxo dimer of P_2 appears to be a good candidate for that role. Indeed, $(FeP_2)_2O$ forms a stable monolayer on the water bath (collapse pressure: 52 mN.m^{-1}; molecular area 165 Å^2 at 40 mN.m^{-1}) and is easily transferred onto solid substrates. Moreover, linear dichroism in the visible and infrared ranges indicates that the macrocycles are still dimerized after the transfer and lie almost flat on the substrate (tilt angle: 30°). Thus, we can consider the upper macrocycle (located on top of the other at the air/water interface) as a covalently linked axial ligand for the bottom ferric porphyrin. This bulky and stable ligand may then play the same role as Im in the previous case, without having to compete with the heterodimerization process, since the μ-oxo dimer is already formed within the spreading solution, but actually avoiding the formation of the heterodimer by filling the volume located on top of the P_2 macrocycle (Fig 3).

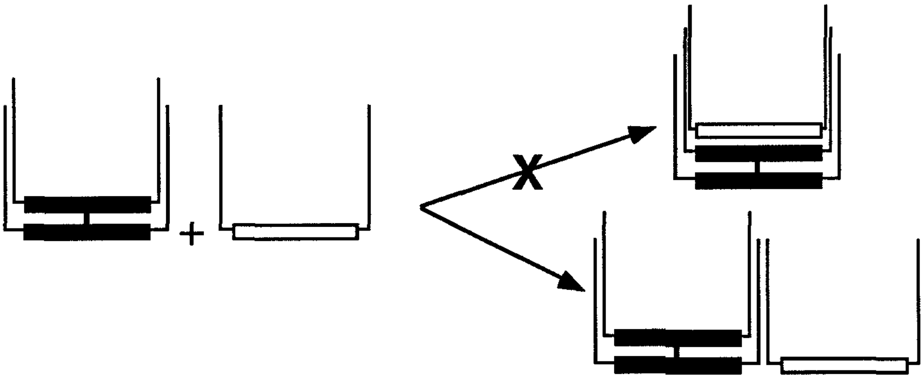

Figure 3: Ionic network built up by using μ-oxo dimers

So, the mixture [$(FeP_2)_2O$ + P_1] has been studied. The monolayer is very stable (collapse pressure 52 mN.m^{-1}) and the average molecular area (210 Å^2) is consistent with a "monomeric" structure (i.e. a structure where $(FeP_2)_2O$ and P_1 are lying side by side within the monolayer instead of forming a "heterotrimer" in which P_1 is lying on top of $(FeP_2)_2O$). This assumption is confirmed by the study of the resulting LB multilayers:

(i) The infrared spectrum indicates that all the carboxylic functions of P_1 have been ionized into carboxylates, even in alternated multilayers wih CD. Thus, each molecule P_1 is chemically linked with $(FeP_2)_2O$.

(ii) Linear dichroism performed in the visible and infrared ranges confirms that all the macrocycles are lying flat on the substrate (tilt angle 25°). The aliphatic chains are slightly tilted from the normal to the substrate (tilt angle 30°). Thus, the $[(FeP_2)_2O + P_1]$ multilayers appear as ordered as the $[P_2 + P_1]$ and more ordered than the pure $(FeP_2)_2O$ and $[CoP_1Im+CoP_2Im]$ ones.

(iii) The vertical period d_{001} equals 47°±1° for the $[(FeP_2)_2O + P_1]$ LB films and 46° for the pure $(FeP_2)_2O$ films. This very slight difference completely rules out the heterotrimeric structure, which would give rise to thicker bilayers.

(iv) The $[(FeP_2)_2O + P_1]$ LB films are totally insoluble in chloroform. As in the case of the $[CoP_1Im+CoP_2Im]$ films, this indicates that a collective consistency has been created within the lamellar structure (more precisely within each monolayer). The ionic network is then an ionic polycondensate built up from lateral recognition between adjacent coplanar macrocycles.

The study of the periodicity within the monolayer is now in progress, by normal incidence transmission X-ray diffraction and atomic force microscopy.

CONCLUSION

The present study shows that combining the versatility of chemical engineering and the power of the Langmuir-Blodgett technique as a tool for building supermolecular assemblies may result in a controlled supermolecular engineering and give rise to well-defined and well-ordered supermolecular assemblies.

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