Photoresponsive multilayer films by assembling cationic amphiphilic cyclodextrins and anionic porphyrins at the air/water interface

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Densely packed hybrid monolayers of amphiphilic cyclo-dextrins incorporating hydrophilic porphyrins are formed at the air/water interface through electrostatic interaction and can be transferred onto quartz substrates by Langmuir–Schäfer deposition. The resulting multilayers exhibit a good response to light excitation as proven by fluorescence emission, triplet–triplet absorption and singlet oxygen photogeneration.

Organization of porphyrins onto solid substrates and their activation by light have been subjects of strong interest in recent years, not only for a better understanding of life-related processes but also for designing optoelectronic and photonic molecular devices.[1] The Langmuir–Blodgett (LB) technique is one of the most elegant methods to control both packing and molecular orientation in two dimensions.[2] However, the achievement of ordered, photoresponsive LB films is difficult in the cases of simple porphyrins. In fact, their strong tendency for aggregation often precludes a well-defined molecular assembly and promotes effective self-quenching and excitonic interaction among porphyrins in close proximity.[3] Nevertheless, incorporation of diluent molecules, such as ionic and non-ionic surfactants, into LB films is demonstrated to be a viable strategy for obtaining stable multilayers which respond to light stimuli.[4]

Cyclodextrins (CDs) are water soluble cyclic oligosaccharides which have been extremely appealing to investigators in both pure and applied fields for a long time.[5] The appropriate modification of the upper, the lower or both rims of the CD macrocycles can lead to a variety of amphiphilic CDs capable of forming organized assemblies such as monolayers, micelles, vesicles and nanoparticles.[6]

Recently some of us have shown that the cationic amphiphilic CD 1 (Fig. 1) entangles the hydrophilic porphyrin 5,10,15,20-tetrakis(4-sulfonatophenyl)-21H,23H-porphyrin (TPPS) mainly by coulombic interactions, producing photoactivatable nanoparticles.[7] Beside, Liu and coworkers have elegantly demonstrated that porphyrin-containing multilayers can be achieved exploiting interfacial electrostatic interactions between typical cationic amphiphiles and TPPS dissolved in the water subphase.[8] These investigations inspired the present contribution in which we report, for the first time, the fabrication of multilayer films of amphiphilic cyclodextrins incorporating hydrophilic porphyrins and responsive to light excitation. On the basis of the above observations we have explored the possibility for the cationic CD 2 (more amphiphilic than 1 but bearing identical cationic polar heads)[9] to form monolayers at the water/air interface and to trap TPPS molecules via electrostatic binding, encouraging their transfer onto quartz slides by Langmuir–Schäfer (LS) deposition. We envisage that in view of its tubular molecular shape, CD 2 may also exert some control over the intra- and interlayer communication of the TPPS units suppressing self-quenching phenomena and, consequently, increasing the efficiency of the response to light.

Fig. 2A reports the surface pressure vs. area (π–A) isotherms of a monolayer of 1 spread on the water subphase in the absence and in the presence of 10 μM TPPS at pH 6. These results together with the Brewster Angle Microscopy (BAM) analysis (see inset Fig. 2A) are consistent with the formation of stable and homogeneous monolayers in both cases. A comparison between the two isotherms shows clear differences in the slopes, the collapse pressure of the monolayer and the limiting molecular area values. These findings provide good evidence for an electrostatic interaction between the oppositely charged 2 and TPPS occurring at the air/water interface, according to the results by Liu and coworkers in the case of cationic amphiphiles monolayers on TPPS subphase.[8]

The interfacial interaction is additionally confirmed by reflection spectroscopy. This technique is well-suited for investigating the behavior of chromophores on the water surface because only those at the interface contribute to the enhanced reflection.[10] As illustrated in Fig. 2B, an absorption in the typical Soret region of TPPS is promptly notable immediately after spreading 2 on the
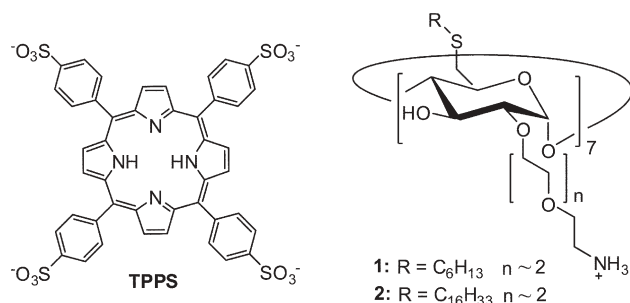
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Fig. 1 The chemical structure of the TPPS and the amphiphilic CDs 1 and 2.
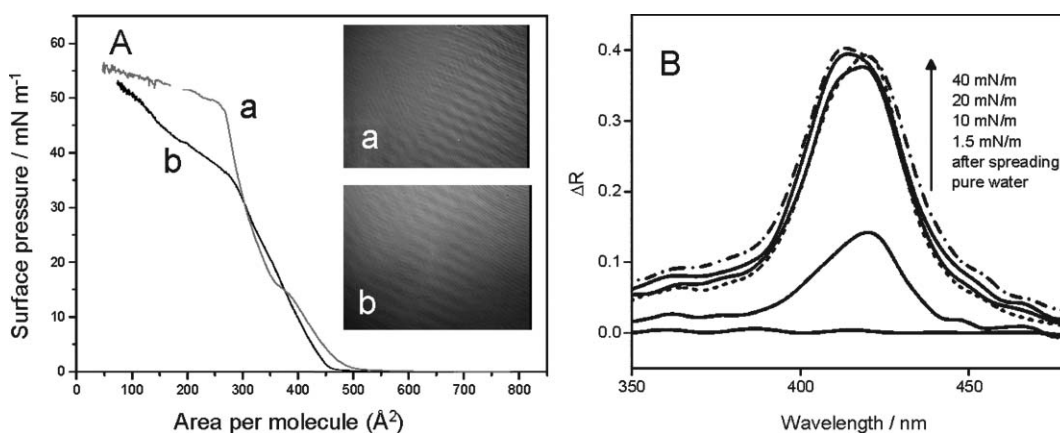
1: R = C₆H₁₃ n ~ 2
2: R = C₁₆H₃₃ n ~ 2

Fig. 2 (A) Surface pressure–area isotherms of **2** on the subphases of (a) pure water and (b) **TPPS** water solution at pH 6 at 20 °C. The inset shows representative BAM images of the corresponding floating layers observed at the pressures of (a) 35 and (b) 49 mN m^{-1}, width of images = 430 µm. (B) Absolute reflection spectra from **2** floating film on the surface of a water solution of **TPPS** at different fixed surface pressures after equilibrium.

water surface. Reflection enhancements, as result of the average surface density growth, associated with changes of the spectral profile are noted upon compression. In particular, the pressure increase leads to the appearance of a new component at *ca.* 410 nm in the Soret region besides that at *ca.* 420 nm observed in the case of the spread solution.

Hybrid monolayers **2/TPPS** could be transferred onto quartz substrates by the LS method (horizontal lifting).[11] In this approach, hydrophobized quartz slides were lowered horizontally until their contacted the floating film on the water surface and then withdrawn from the subphase. Following this procedure, a different number of layers were transferred on the substrate at the surface pressure of 30 mN m^{-1}. The presence of the **TPPS** absorption in the films (Fig. 3) clearly indicates a successful transfer procedure according to the formation of hybrid **2/TPPS** multilayers. It should be noted that the absorption spectrum is virtually identical to that observed in the reflection mode after compression, suggesting that the transferring procedure does not affect the molecular arrangement of the complex **2/TPPS**. Atomic force microscopy (AFM) measurements performed on 1 and 5 layer films deposited on hydrophobized SiO$_2$ substrates
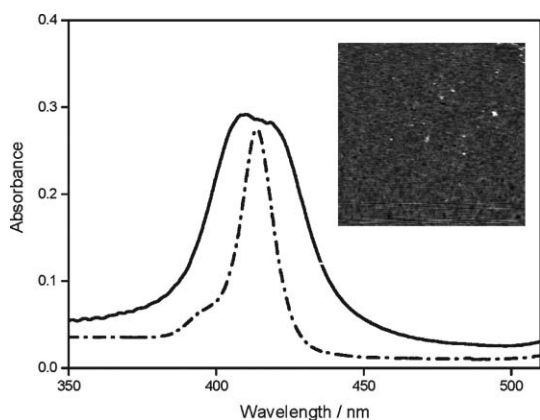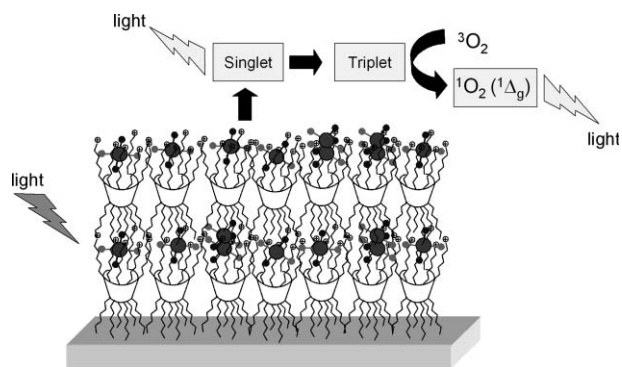

Fig. 3 Absorption spectra of a 30 layer hybrid **2/TPPS** LS film (solid line) and, for comparison, **TPPS** in water solution (dotted line). The inset shows a representative AFM image of **2/TPPS** transferred onto hydrophobized silicon (1 layer), width of image = 1 µm.

(see inset Fig. 3) reveal the formation of densely packed films, characterized by excellent homogeneity. The section analysis allows estimation of film thicknesses of *ca.* 3 and 15 nm, in the cases of 1 and 5 layers, respectively, pointing out a good reproducibility of the transfer process.

A comparison of the **TPPS** absorption in the films with that observed in water solution allows insights to be gained into the probable organization of the porphyrin within the amphiphilic network. As illustrated in Fig. 3 the two components of the Soret absorption in the LS film appearing at *ca.* 410 and 420 nm, are blue- and red-shifted compared with the single absorption maximum of **TPPS** in water peaking at 414 nm.[12] These spectral differences reflect quite well those exhibited by **TPPS** in the presence of the cationic surfactant cetyltrimethylammonium bromide, in aqueous solution.[13] In particular, Periasamy and coworkers[13] have shown that **TPPS** can form H-aggregates (*head to head*), characterized by a blue-shifted absorption, in equilibrium with the micellized monomer, characterized by a red-shifted absorption. We believe that a similar scenario may apply in our case. Actually, by considering both the size and tubular shape of **2**, it might be conceived that single molecules of **TPPS** can be incorporated mainly in the monomeric form at low pressure. Increase of the surface pressure leads also to the formation of some H-aggregates according to the appearance of the blue-shifted component in the reflection spectra (see Fig. 2B). The absence of any significant Cotton effect in the Soret region rules out the inclusion of **TPPS** in the proximity of the CD cavity suggesting that the porphyrins may be reasonably located in a microenvironment close to the cationic periphery of **2** (Scheme 1).

Fluorescence and laser flash photolysis measurements were carried out in order to explore the features of the excited singlet and triplet states, respectively, of **TPPS** generated upon light excitation in the multilayers.

Fig. 4 shows that the LS films exhibit the characteristic structured fluorescence of **TPPS**.[12] A quantitative comparison with an optically matched water solution of **TPPS** using the same experimental conditions shows that the fluorescence quantum yield of the **2/TPPS** hybrids is only *ca.* 4-fold smaller than that of the porphyrin in solution. It is also worth noting that the position of the two emission bands is independent of the excitation energy

Scheme 1 Schematic representation for the potential arrangement of the hybrid **2/TPPS** multilayer LS films.
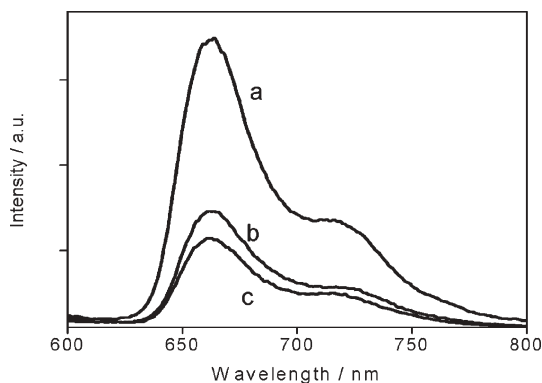

Fig. 4 Fluorescence spectra of a 30 layer hybrid **2/TPPS** LS film recorded at different excitation wavelengths: (a) 420 nm, (b) 530 nm, (c) 550 nm.

Fig. 5 (A) Transient absorption spectra observed 1 (●), 20 (△) and 40 (■) μs after 532 nm laser excitation of a 30 layer hybrid **2/TPPS** LS film. $E_{532} \approx 8$ mJ pulse^{-1}. The inset shows the decay profile at 420 nm. (B) Representative decay kinetic of $^1O_2(^1\Delta g)$ monitored at 1270 nm.

suggesting the presence of a single population of fluorophores in the film. This good fluorescence response indicates a remarkable suppression of the inter- and intralayer self-quenching effects, and accounts for a predominance of fluorescent **TPPS** monomers over the non-emitting H-aggregates.[14]

Fig. 5a shows the transient spectra recorded after 532 nm laser pulse excitation. All spectra are characterized by a bleaching in the region corresponding to the Soret absorption but no positive signal is observed concurrently. The recovery kinetic profile (see inset Fig. 5A) is fitted fairly well by a mono-exponential analysis affording a first-order rate constant $k = 8.3 \times 10^4$ s^{-1} indicating, also in this case, a homogeneous distribution of the chromophores within the film. The laser intensity dependence of the bleaching intensity (data not shown) clearly indicates that a monophotonic process is involved in the generation of this signal. Despite the fact that the typical triplet–triplet positive absorption of **TPPS**, expected at *ca.* 440 nm,[12] is not detected, we believe that the bleaching is strictly related to the population of the triplet state. The reason for the lack of such a signal can be attributed to the combination of broadening and red-shift of the Soret ground state absorption in the film. These effects preclude the observation of the positive signal due to the dominant ground state molar absorption coefficient of **TPPS** over that of its excited triplet state in the spectral region of interest. A comparison with an optically matched solution of **TPPS** in water solution under the same experimental conditions allows estimation that the quantum efficiency for the population of the triplet in the films is *ca.* 4-fold
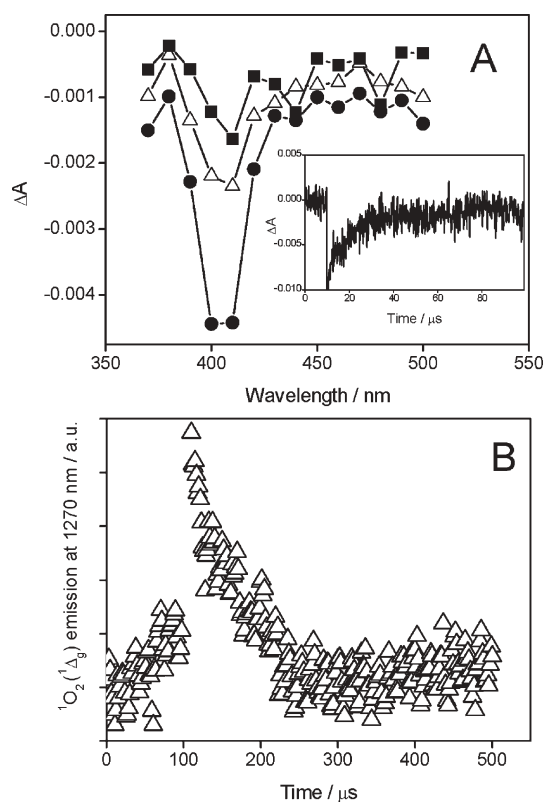
less than in solution. Unambiguous evidence for the population of the excited triplet state is provided by the photosensitization of singlet oxygen, directly monitored by time-resolved near infrared luminescence. As shown in Fig. 5B, the characteristic singlet oxygen, $^1O_2(^1\Delta g)$, luminescence at 1270 nm decaying in the microsecond time scale[15] is observed upon 532 nm laser excitation of the film as result of the energy transfer from the lowest excited triplet state of **TPPS** to molecular oxygen.

In summary, we have shown that homogeneous multilayer films based on amphiphilic CDs entrapping hydrophilic porphyrins can be fabricated exploiting interfacial coulombic interactions between the two components. As illustrated in Scheme 1, despite the presence of photochemically "*silent*" H-aggregates, these LS films exhibit a good response to light excitation. The peculiar shape of the amphiphilic **2** seems to play a role in this concern, entrapping a satisfactory amount of **TPPS** as a monomer and exerting protection against self-quenching and/or annihilation processes. It should finally be stressed that the CD cavity is not involved in the binding with **TPPS** and therefore can be available for incorporation of additional guest molecules. This further advantage contributes to making the present architectures intriguing platforms for the fabrication of more complex supramolecular assemblies on two-dimensional surfaces in which electron/energy transfer processes from suitable guests incorporated within the cavity to the entangled porphyrin and/or *vice versa* could be activated by photons of appropriate energy. This topic is currently under investigation in our laboratories and the results will be reported in due course.

Acknowledgements

Notes and references

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