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Sensing Behavior of Tetrakis(4-sulfonatophenyl)porphyrin Thin Films

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The search for responsive materials has recently received much attention for their potential applicability in developing various kind of sensors.[1,2] In this respect porphyrins and related macrocycles, together with their metal derivatives, have been widely investigated for their ability to interact with many different chemical species, reporting the binding through changes of their favorable photophysical properties.[3] Deposition of layers of such compounds can be achieved through a variety of techniques, such as layer-by-layer electrostatic adsorption,[4] self-assembling monolayers on gold or other substrates,[2,5] Langmuir−Blodgett or Langmuir−Schaefer techniques,[6] and self-organizing supramolecular structures.[7] Well-organized ringlike[8] or globular structures[9] have been reported by solvent evaporation, and nanorods have been obtained from self-aggregation of water soluble porphyrins.[10]

Quite recently, we have demonstrated the possibility of growing discrete microsized porphyrin crystals on a silica surface from a dichloromethane solution of tetra(4-pyridyl)-porphyrin by irradiation with UV light. This method takes advantage of the photogeneration of HCl at the interface between silica and the solvent and of the lower solubility of the resulting protonated porphyrin with respect to the neutral parent compound.[11]

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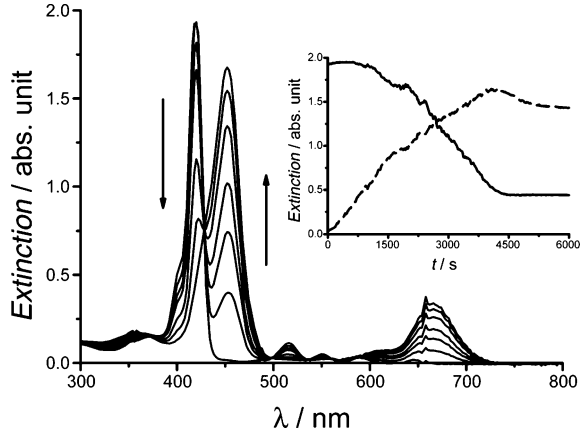

Figure 1. UV−vis spectral changes occurring upon pulsed irradiation with a deuterium lamp of a CH_2Cl_2 solution of TPPS (~4 μM). Irradiation time, 0.3 s; delay between pulses, 15 s; total irradiation time, 6000 s. Inset: changes observed at 420 nm (solid line) and 451 nm (dashed).

The water soluble tetrakis(4-sulfonatophenyl)porphyrin (TPPS) has been largely investigated because of its tendency to form a variety of aggregated species under acidic conditions and in the presence of specific templating reagents.[12,13] Here we report on the formation of homogeneous thin films of the title porphyrin by using the same irradiation technique. The deposited samples exhibit extinction and fluorescence emission features which are strongly dependent upon the addition of basic or acidic vapors, being deeply affected by the nature of the counterion.

The deposition of the porphyrin has been achieved by pulsed irradiation of a diluted solution of the tetrabutylammonium salt of TPPS in CH_2Cl_2 (~3−4 μM) by using a deuterium lamp (see Supporting Information). The Soret band at 420 nm gradually decreases in intensity, whereas a new feature increases at about 451 nm (Figure 1). The Q bands of the TPPS porphyrin at 516, 551, 591, and 646 nm exhibit a red shift, and at the end of the process only two are clearly detectable at 610 and 660 nm. When the extinction at 420 nm reaches a plateau (inset of Figure 1), the silica cell evidences a green round spot on the side exposed to the incoming UV light beam.

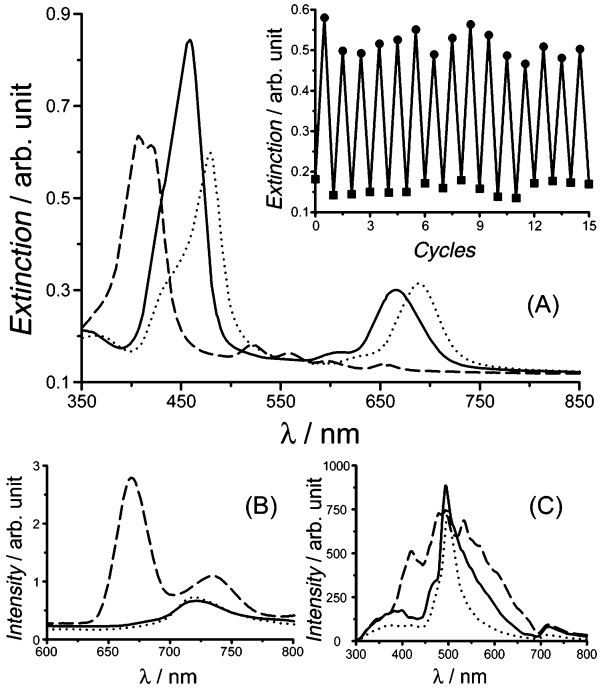

Figure 2. Extinction (A), fluorescence (B), and RLS (C) spectra of the TPPS film deposited on quartz (solid lines), after adding NEt_3 vapors (dashed) and after adding HCl vapors (dotted). Inset: extinction at 410 nm as a function of base−acid addition cycles.

Interestingly, when the same experiment is performed by stirring the solution, even if the spectral changes are similar to the unstirred case, no deposition has been observed (see Supporting Information) because of the dispersion of the protonated porphyrin in the solution.

The spectroscopic features of the TPPS spot are reported in Figure 2. The UV/vis extinction spectra exhibit a series of bands which are very similar to those observed in solution. The presence of two Q bands indicates that the deposited porphyrin is diprotonated at the nitrogen core. The fluorescence emission of the sample is weak and located at 720 nm. Resonance light scattering (RLS)[14] profiles of this sample reveal a quite sharp peak at ~500 nm, reminiscent of J-type aggregates in which neighbor porphyrins are interacting in an edge-to-edge geometrical arrangement.[15] An analysis of the spots through SEM microscopy revealed a quite homogeneous distribution of porphyrin throughout the sample (see Supporting Information).

When the TPPS thin film is exposed to vapors of triethylamine, the color of the spot turns instantaneously to pale pink. Consequently, all the spectral features undergo dramatic changes: (i) the Soret band displays a hypsochromic shift, with two components at 400 and 414 nm, respectively; (ii) the Q bands also move to higher energies and become four, pointing to the free base nature of the porphyrin in this sample; (iii) the fluorescence emission spectra evidence two bands at 668 and 733 nm, respectively, together with a consistent increase in the relative emission intensities with respect to the untreated sample; and (iv) the RLS profile is

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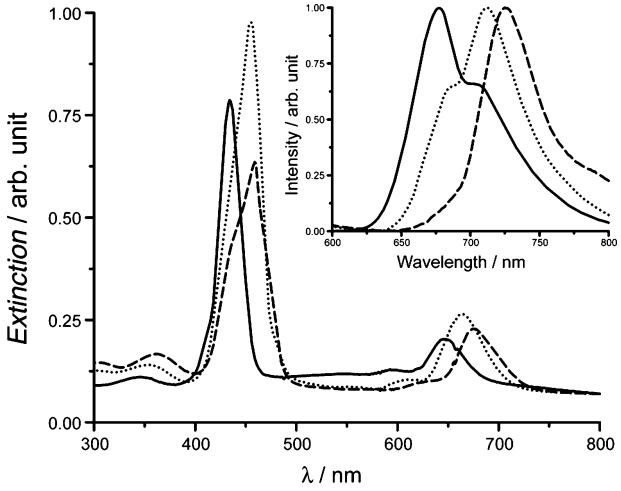

Figure 3. Extinction and fluorescence (inset) spectra of the TPPS film after the addition of HCl (dashed) and CF_3COOH (solid) vapors. The features of the starting film (dotted) are reported for comparison.

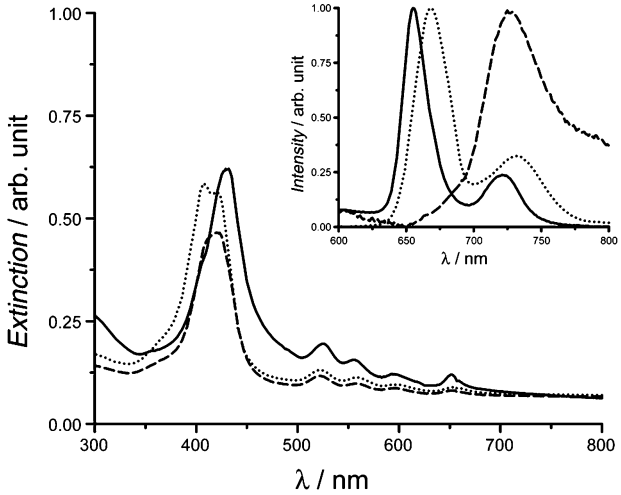

Figure 4. Extinction and fluorescence (inset) spectra of the TPPS film after the first addition of various base vapors: NH_3 (dashed); NEt_3 (dotted); and pyridine (solid).

dominated by an unstructured feature which peaks at 500 nm. These latter spectroscopic properties suggest, at least under these experimental conditions, the formation of the free base porphyrin together with dimers or small oligomers. On treating the TPPS film with HCl vapors, the green color of the sample can been restored and the system switches reversibly between the two species upon repetitive cycling with base and acid vapors (inset of Figure 2). After prolonged treatment, the Soret band of the acidic deposit shifts to 480 nm and the Q bands (630 and 690 nm) are also bathochromically shifted with respect to the starting species. On the basis of the spectral evidence, we can tentatively assign this latter species to a J-type aggregate, very similar to those already reported in the literature in aqueous solutions.[13]

The large difference between these two studied cases prompted us to investigate the possibility of using the TPPS thin film as a sensor for different acids and bases. Figures 3 and 4 report a comparison of the UV/vis extinction and fluorescence emission spectra upon treating the sample with some acids (hydrochloric and trifluoroacetic acid) and bases (triethylamine, pyridine, and ammonia). The different spectroscopic features observed in the presence of the various reagents point to a certain degree of selectivity of the system. Furthermore, a good reversibility has been observed in the case of the ammonia/HCl couple, while a certain extent of poisoning is evident with pyridine.

Further experiments have proved that thin film of TPPS can be obtained by UV-induced photodecomposition of other halogenated solvents. Using dibromomethane, we were able to obtain samples that evidence a split Soret band (425 and 490 nm) and two Q bands at 660 and 715 nm. The almost complete quenching of fluorescence emission and the strong and narrow peak in the RLS profiles point to extended J-aggregated porphyrins (see Supporting Information).

The possibility of tuning the photophysical and optical properties of the sample by deposition from different solvents[16] and its sensing characteristics, together with the previously reported micropatterning capability of the proposed method,[11] seem to be promising for the development of solid-state sensors.

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Supporting Information Available: Experimental methods, UV/vis extinction spectra, RLS profiles, and SEM (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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