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Optical pH Meter by Means of a Porphyrin Monolayer Covalently Assembled on a Molecularly Engineered Silica Surface

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Engineering of inorganic surfaces by covalent bonding of organic molecules represents an interesting approach to the synthesis of hybrid inorganic/organic nanomaterials.[1]

Few works concerning appropriately functionalized porphyrin molecules bound to different substrates have been already reported and, usually, in the perspective of sensors fabrication.[2−5] Some studies regarding optical pH sensors based on thin films containing different dyes have already been reported.[6,7] Among these, only a few papers regard the application of porphyrins as pH sensors and none of them deal with a covalently assembled porphyrin monolayer.[7] In fact, the few reported studies focus on incorporation of porphyrin into sol−gel materials,[7a] protonation of porphyrins in liquid PVC membranes,[7b] electrostatically immobilized porphyrin on the surface of sulfonated polystyrene,[7c] porphyrin-coated platinum electrodes,[7d] and electropolymerized cobalt porphyrin.[7e]

In this context, we focused our interest on the 5,10,15-{*p*-[9-methoxy-3-(oxyethylene)]oxyphenyl}-20-(*p*-hydroxyphenyl) porphyrin (called P), a chromophore (see Scheme 1) that shows a very high molar absorbance coefficient (1.42×10^5 in THF)[8] and a good affinity toward $[H_3O^+]$ (vide infra). The presence of only one hydroxyl group in the peripheral position of the porphyrin allows an univocal covalent linkage to the substrate. Moreover, the presence of the 3-methoxy-3-(oxyethylene) groups, covalently bound in the remaining peripheral positions of the porphyrin, increases its hydrophilic character.

There was, therefore, enough motivation to embark on the fabrication of a P monolayer, covalently assembled on a silica substrate (called P-CAM), and to study its pH sensing behavior for acid solutions.

P was synthesized, by a partial condensation reaction between appropriate quantities of the sodium salt of tetrakis(*p*-hydroxyphenyl)porphyrin and 3-(oxyethylene) methyl ether chloride.[8a] Moreover, it was purified and characterized as already reported.[8a] Its pure sodium salt was obtained by reacting a tetrahydrofuran (THF) porphyrin solution with an equimolar amount of a methanol solution of sodium *tert*-butoxide and removing in a vacuum the *tert*-butylic alcohol formed during the reaction, THF, and methanol. Three successive steps have been expedient (Scheme 1) for the synthesis of the P-CAM.[4a,9] Fused silica (quartz) substrates (i) were first cleaned with “piranha”solution (cH_2SO_4:30% H_2O_2 70:30 v/v) at 80 °C for 1 h and then left to cool to room temperature.[4a,9] They were repeatedly rinsed with double-distilled water and immersed in a H_2O:30% H_2O_2:NH_3 5:1:1 v/v/v mixture at room temperature for 40 min.[4a,9] Then, they were washed with double-distilled water and dried under vacuum immediately before deposition of the coupling agent. All the following sample manipulations have been

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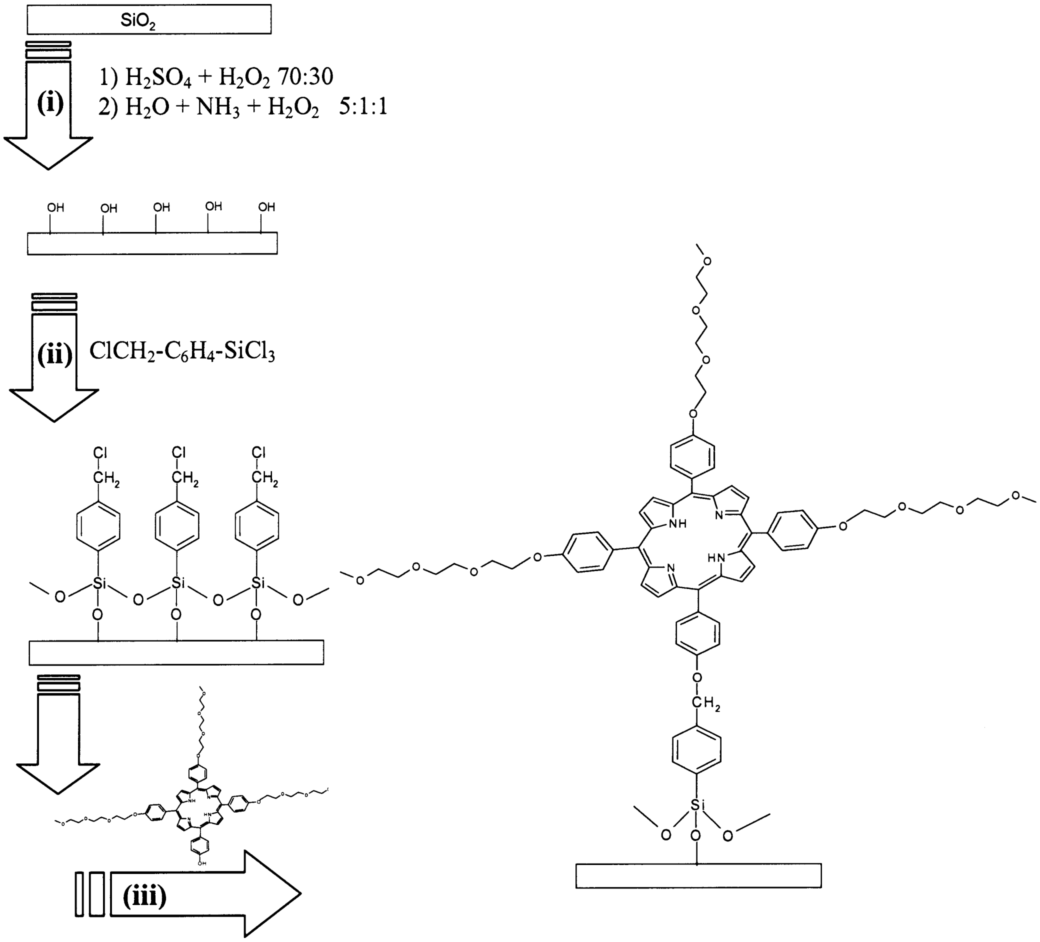
Scheme 1



performed in a glovebox under inert atmosphere. Therefore (ii) freshly cleaned substrates were immersed, at room temperature for 20 min, in a 1:100 (v/v) *n*-heptane solution of the chemisorptive siloxane, trichloro[4-(chloromethyl)-phenyl]silane, to afford a monolayer of the coupling agent (CA).[4a,9] Then, they were washed with copious amount of *n*-pentane and sonicated in acetone for 1 min to remove any physisorbed CA. Moreover, (iii) the silylated substrates were immersed in a 5×10^{-3} M THF solution of the present porphyrin sodium salt and heated to 60°C under stirring for 48 h. Finally, the substrates bearing the covalently bound porphyrin molecules were cooled to room temperature and repeatedly washed with THF to remove any residual unreacted porphyrin.

Angle resolved nitrogen 1s X-ray photoelectron spectra (AR-XPS) of the P-CAM, made at different off-take angles, showed a broad peak at 399.5 eV with a shoulder at lower binding energy (398.2 eV). These features account for the two kinds of nitrogen in the porphyrin core.[4a] The nitrogen atomic concentration also showed a monotonic increase upon decreasing the electron off-take angle from 45° to 5°, as expected for the upper layer nature of the signal.

Atomic force microscopy (AFM) measurements of P-CAMs, performed with a Solver P47 NTD-MDT instrument in semi-contact mode (resonance frequency 150 Hz), showed densely packed features having a “mountain” shape with a 2.38 Å surface mean roughness.

The UV–visible spectrum of the P 6×10^{-5} M THF solution (Figure 1a) shows a characteristic sharp Soret band at 421.5 nm and satellite Q-bands at 517.7, 554.2, 596.2, and 655.5 nm. The UV–visible spectrum of the resulting P-CAM (Figure 1b) is almost coincident, showing high quality signals at 427.2, 519.9, 560.8, 596.1, and 654.7 nm. The calculated[5] value of porphyrin molecules/cm^2 of the P-CAM is 1.91×10^{13}.

Therefore, to verify the possible use of the P-CAM as a pH optical sensor, UV–vis scans in the 375–510 nm range were carried out after a 20 s immersion of the P-CAM in a given HCl solution (pH values between 5 and 1.0), starting from that at pH 6.0 (obtained using high-purity Aldrich H$_2$O only), and drying the P-CAM with a purified N$_2$ gas stream. After every UV–vis measurement, the P-CAM was washed with double-distilled water before the immersion in the more acidic solution.

Figure 2 shows the evolution of the UV–vis absorbance spectra of the P-CAM. It becomes evident that the Soret band at 427.2 nm progressively disappears whereas a new band at 459.1 nm grows up. In particular, after an immersion at pH 1.0, the spectrum is almost dominated by the new band and remains unchanged for more acid solutions. Remarkable, a simple washing procedure and drying under a N$_2$ gas stream totally recovers the starting Soret (dashed line in Figure 2). It is clear that, after having obtained a calibration curve with standard solutions, the percentage of the residual Soret band

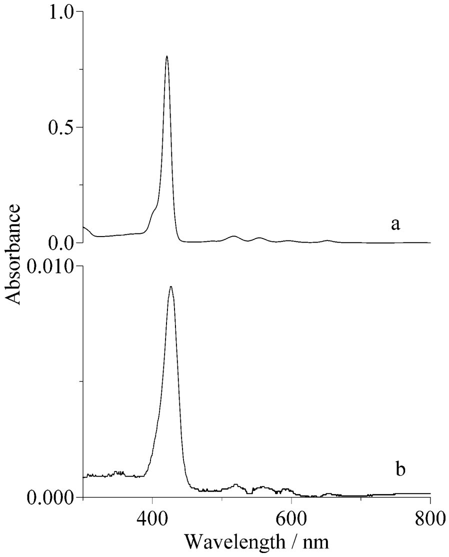


Figure 1. UV−vis spectra of the (a) 6×10^{-5} THF P solution, carried out using 0.1 cm quartz cuvettes and (b) P-CAM.

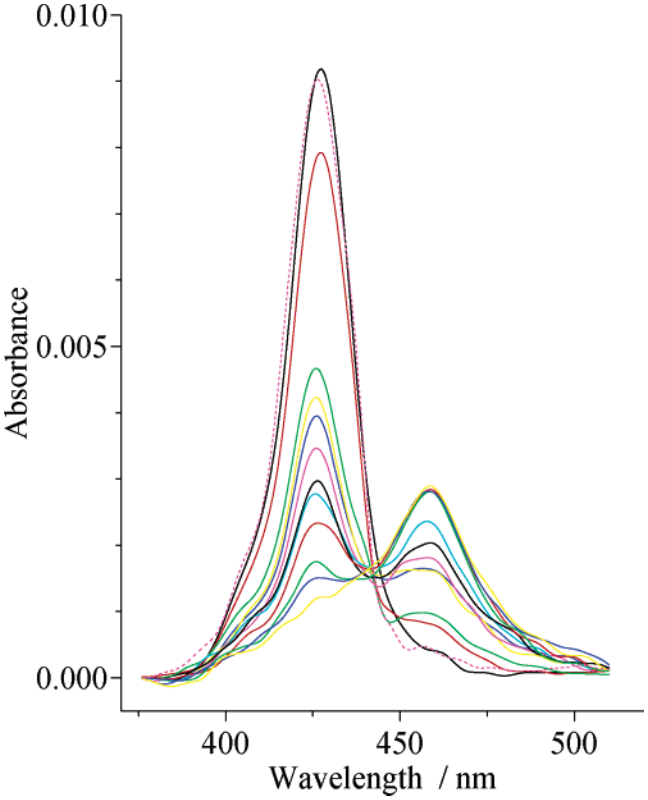


Figure 2. UV−vis spectra of the P-CAM after immersion in solutions at different pH values. Given 100 to the observed Soret absorbance intensity at pH = 6 (obtained with the highest pure Aldrich H_2O), we observed 86%, 51%, 46%, 42%, 38%, 33% 30%, 25%, 20%, 16%, and 12% of residual Soret absorbance (experimental uncertainty ±1%) at pH = 5.0, 4.0, 3.5, 3.4, 3.0, 2.5, 2.3, 2.0, 1.8, 1.2, and 1.0, respectively. The dashed line refers to the spectrum of the P-CAM recovered with a simple washing procedure and drying under a N_2 gas stream.

intensity of the P-CAM, with respect to its initial intensity value, can be used to monitor the pH. Six cycles alternating acid immersion and washing/drying have been performed with no variations of performance. The system, therefore, shows a reliable reversibility. These overall results, according with earlier unique data on a similar system, indicate reversible protonation of the porphyrin.[7a]

The isosbestic behavior of this solid film constituted by a porphyrin monolayer, even though not univocally defined by a single point, is well-represented in Figure 2 since is confined in a very small area. In fact, the moving of the isosbestic point, which goes up and down within a small area, is due to the sample position that has to be centered with respect to the UV−vis light beam each time after the adopted procedure (immersion in a given HCl solution and drying with a purified N_2 gas stream before to record a new spectrum). In addition, the fact that a washing and drying procedure allows us to recover the starting Soret stresses the reversibility of present P-CAM, rules out any decomposition process, and implies the goodness of the isosbestic point.

To collect additional UV−vis results, the P-CAM was placed in water within a cuvette and, without removing it, the solution titrated down in pH. Unfortunately, each spectrum was affected by a large background that changed after every acid addition. Therefore, a background removal procedure was necessary before spectra processing. As a consequence, the isosbestic behavior was similar to that already obtained with the previous procedure. Therefore, further measurements were performed on an aqueous 10^{-5} M solution of the very similar 5,10,15,20-{p-[ω-methoxy-poly(oxyethylene)]phenyl}porphyrin upon varying the pH, and a single isosbestic point was obtained. Moreover, the solution was titrated up and down in pH many times, thus showing a total reversible behavior. This experiment can be considered as a blank test for the P-CAM.

Finally, the P-CAM optical pH sensor behavior was further investigated in the presence of other acids such as H_2SO_4, HNO_3 (at pH = 1, 3, and 5) or CH_3COOH (at pH = 3.5 and 5) to learn about possible anion interferences. No relevant differences were detected. We are aware that further efforts should be devoted to investigate on the interference of other effects (e.g., ionic strength).

In conclusion, a new covalently assembled porphyrin monolayer has been obtained. It has proven to be highly sensitive to acid pH (sensitivity = 0.1 pH unit), and, therefore, represents a well-suited fast and reversible optical acid pH meter. An advantage of the present system with respect to compact multilayer films is the fact that no residual UV−vis signals due to not interacting inner dye layers are observed. On the other hand, porous multilayer films can behave as sponges difficult to be restored after immersion in acid solutions. Conversely, a few seconds washing is enough to restore our starting monolayer system. To our knowledge, this study represents the first case of an acid pH optical solid sensor based on a P-CAM.

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