Spectroscopic and Microscopic Characterization and Behavior of an Optical pH Meter Based on a Functional Hybrid Monolayer Molecular System: Porphyrin Molecules Covalently Assembled on a Molecularly Engineered Silica Surface

Antonino Gulino,*,† Placido Mineo,‡ Emilio Scamporrino,*,† Daniele Vitalini,‡ and Ignazio Fragalà*,†

Dipartimento di Scienze Chimiche, Università di Catania and I.N.S.T.M. UdR of Catania and Istituto di Chimica e Tecnologia dei Polimeri-CNR Catania, Viale Andrea Doria 6, 95125 Catania, Italy

Received January 13, 2006. Revised Manuscript Received February 21, 2006

A covalently assembled monolayer of 5,10,15-tri{*p*-[9-methoxy-tri(ethyleneoxy)]phenyl}$_{20}$(*p*-hydroxyphenyl)porphyrin molecules on a silica substrate was fabricated and characterized by X-ray photoelectron spectra, AFM images, and UV−vis measurements. In addition, its [H_3O^+] optical sensing behavior was studied and compared to that of the parent water-soluble star polymer 5,10,15,20-tetrakis{*p*-[ω-methoxypoly(ethyleneoxy)]phenyl}porphyrin having ~40 repetitive units in each of the poly(oxyethylene) branches. Upon immersion in increasingly acidic solutions, the UV−vis absorbance spectra of the porphyrin-assembled monolayer show the gradual disappearance of the Soret band at 427.2 nm and the progressive increase of a new band at 459.1 nm. In strongly acidic solutions (pH 1.0), the spectrum is substantially dominated by the new band and remains unchanged even with more acidic solutions. The simple washing with water and drying under a N_2 gas stream totally recovers the starting Soret signal. The presence of Mn(II), Co(II), Ni(II), Cd(II), or Pb(II) ions in water solution does not interfere with the behavior of the present optical acid pH meter. In contrast, the presence of Hg(II), Cu(II), or Zn(II) ions changes the pH-metering performance due to formation of metal−porphyrin complexes as revealed by UV−vis and MALDI-TOF measurements of metal-containing solutions of the similar 5,10,15,20-tetrakis{*p*-[ω-methoxypoly(ethyleneoxy)]phenyl}porphyrin with ~17 repetitive units in each poly(oxyethylene) branch.

Introduction

pH monitoring has important applications in many different fields ranging from environment monitoring (waste, river and seawaters, acid rain) to biological, medical, analytical, and industrial chemistry.[1] Many pH-metering systems have already been proposed mostly based on electrochemical measurements.[1] Optical techniques are particularly appealing since they can be combined with optic fibers for remote sensing. Such methods require indicators exhibiting pH-dependent variations in absorption or emission and a suitable matrix material to allow immobilization of the indicator.

As a part of ongoing studies on the synthesis of hybrid inorganic/organic nanomaterials via the engineering of inorganic surfaces by covalent bonding of organic molecules,[2] we recently reported earlier results on the first fabrication of an optical acid pH meter based on a porphyrin (P1) monolayer covalently assembled (CAM) on a molecularly engineered silica surface (called P1−CAM).[2b]

In this context, it is worthy remembering that porphyrin molecules have been mainly involved in molecular recognition applications.[3−7] Moreover, some optical pH sensors based on thin films containing different dyes have already

---

* Corresponding author. Fax: ++39-095-580138. E-mail: agulino@dipchi.unict.it.

† Università di Catania and I.N.S.T.M. UdR of Catania.

‡ Istituto di Chimica e Tecnologia dei Polimeri-CNR Catania.

(1) (a) Irgolic, K. J.; Martell, A. E. *Environmental Inorganic Chemistry*; VCH Publishers: Deerfield Beach, FL, 1985. (b) Stumm, V.; Morgan, J. J. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*; Wiley: New York, 1981.

(2) (a) Gulino, A.; Condorelli, G. G.; Mineo, P.; Fragalà, I. *Nanotechnology* **2005**, *16*, 2170. (b) Gulino, A.; Mineo, G. P.; Bazzano, S.; Vitalini, D.; Fragalà, I. *Chem. Mater*. **2005**, *17*, 4043. (c) Gulino, A.; Bazzano, S.; Condorelli, G. G.; Giuffrida, S.; Mineo, P.; Satriano, C.; Scamporrino, E.; Ventimiglia, G.; Vitalini, D.; Fragalà, I. *Chem. Mater*. **2005**, *17*, 1079. (d) Gulino, A.; Bazzano, S.; Mineo, P.; Scamporrino, E.; Vitalini, D.; Fragalà, I. *Chem. Mater*. **2005**, *17*, 521. (e) Gulino, A.; Mineo, P.; Scamporrino, E.; Vitalini, D.; Fragalà, I. *Chem. Mater*. **2004**, *16*, 1838.

(3) (a) Liu, Z.; Yasseri, A. A.; Loewe, R. S.; Lysenko, A. B.; Malinovskii, V. L.; Zhao, Q.; Surthi, S.; Li, Q.; Misra, V.; Lindsey, J. S.; Bocian, D. F. *J. Org. Chem*. **2004**, *69*, 5568. (b) Yamada, H.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Ahn, T. K.; Kim, S. K.; Kim, D.; Fukuzumi, S. *J. Am. Chem. Soc*. **2003**, *125*, 9129. (c) Van der Boom, T.; Evmenenko, G.; Dutta, P.; Wasielewski, M. R. *Chem. Mater*. **2003**, *15*, 4068. (d) Facchetti, A.; Abbotto, A.; Beverina, L.; Vand der boom, M. E.; Dutta, P.; Evmenenko, G.; Pagani, G. A.; Marks, T. J. *Chem. Mater*. **2003**, *15*, 1064. (e) Samori, P.; Francke, V.; Enkelmann, V.; Muellen, K.; Rabe, J. P. *Chem. Mater*. **2003**, *15*, 1032. (f) Fendler, J. H. *Chem. Mater*. **2001**, *13*, 3196. (g) Gomez-Romero, P. *Adv. Mater*. **2001**, *13*, 163. (h) Xia, C.; Advincula, R. C. *Chem. Mater*. **2001**, *13*, 1682.

(4) (a) Kappler, J.; Weimar, U.; Gopel, W. In *Advanced Gas Sensing*; Doll, T., Ed.; Kluwer Academic: Norwell, MA, 2003; p 55. (b) Massari, A. M.; Gurney, R. W.; Wightman, M. D.; Huang, C.-H. K.; Nguyen, S. T.; Hupp, J. T. *Polyhedron* **2003**, *22*, 3065. (c) Rodriguez-Mendez, M. L.; Gorbunova, Y.; de Saya, J. A. *Langmuir* **2002**, *18*, 9560. (d) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed*. **2001**, *40*, 3118. (e) Lu, X.; Winnik, M. A. *Chem. Mater*. **2001**, *13*, 3449. (f) Nickel, A. M. L.; Seker, F.; Ziemer, B. P.; Ellis, A. B. *Chem. Mater*. **2001**, *13*, 1391.

(5) (a) In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2003. (b) Tepore, A.; Serra, A.; Arnold, D. P.; Manno, D.; Micocci, G.; Genga, A.; Valli, L. *Langmuir* **2001**, *17*, 8139.

10.1021/cm060086g CCC: $33.50

been reported.[8,9] Among these, few papers regard the application of porphyrins as pH sensors and none of them deals with a covalently assembled porphyrin monolayer.[8,9] In fact, the few reported studies focus on incorporation of porphyrin into sol−gel materials,[9a] protonation of porphyrins in liquid PVC membranes,[9b] electrostatically immobilized porphyrin on the surface of sulfonated polystyrene,[9c] porphyrin-coated platinum electrodes,[9d] and electropolymerized cobalt porphyrin.[9e]

In this paper we focus on the 5,10,15-tri{*p*-[9-methoxy-tri(ethyleneoxy)]phenyl}$_{20}$(*p*-hydroxyphenyl)porphyrin (hereafter P1). This chromophore (see Figure 1a) shows a very high molar absorbance coefficient (1.42 × 10^5 in THF), a good affinity toward [H_3O^+] (vide infra), and some hydrophilic character due to the three 9-methoxy-tri(ethyleneoxy) chains covalently bounded in the peripheral positions of the porphyrin.[10,11] Therefore, we extend our preliminary results and report on the full characterization of this P1−CAM system and on pH-sensing capabilities in metal-cation-containing solutions.

Experimental Details

The porphyrins were synthesized by condensation reactions between appropriate quantities of the sodium salt of 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrin and either $CH_3-(O-CH_2-CH_2)_3-Cl$ (in the case of P1)[10] or a poly(oxyethylene)methyl ether chloride [$CH_3(OCH_2CH_2)_nCl$] having a narrow polydispersity (∼1.07) and an average molecular weight (M_w) of 750 (for P3) or 2000 (for P2) Da (with ∼17 or ∼40 repetitive units, respectively, in the chain).[10] These compounds were purified and characterized as already reported.[10] The pure sodium salt of P1 was obtained by reacting a tetrahydrofuran (THF) porphyrin solution with a stoichiometric amount (relative to the four −OH groups) of a methanol solution of sodium-*tert*-butoxide and removing in a vacuum THF, methanol, and *tert*-butylic alcohol formed during the reaction.

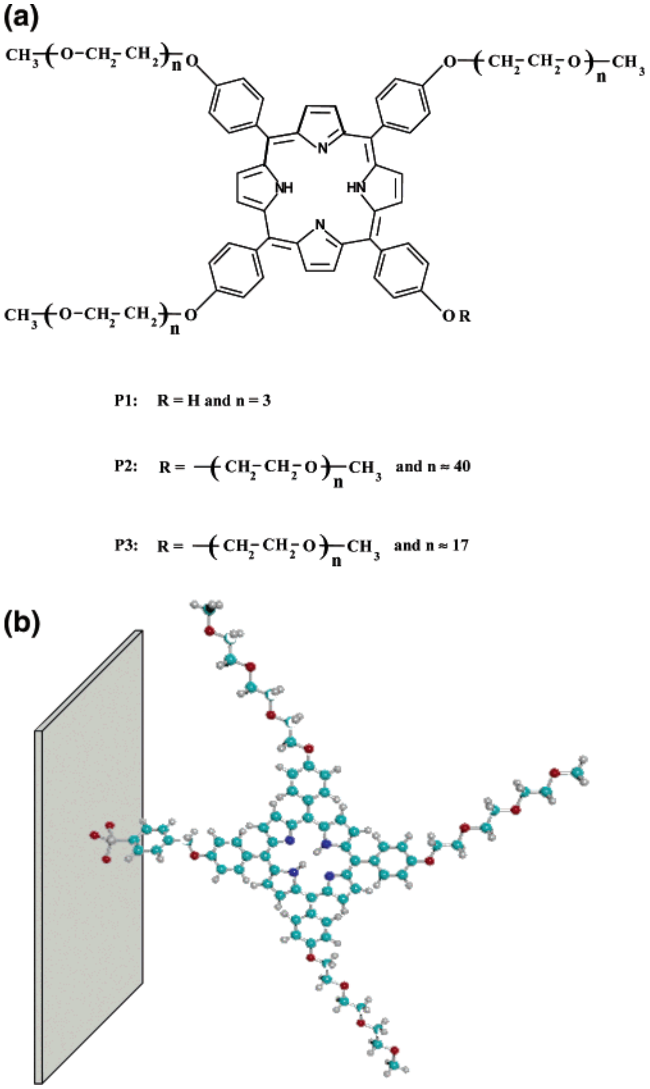

Figure 1. Schematic drawing of (a) 5,10,15-tri{*p*-[9-methoxy-poly-(ethyleneoxy)]phenyl}$_{20}$(*p*-hydroxyphenyl)porphyrin (P1) and tetrakis porphyrin derivatives P2 and P3. (b) P1−CAM system.

Three successive steps were adopted for the synthesis of the P1−CAM (Figure 1b).[2,12] Fused silica substrates (i) were first cleaned with "piranha"solution (c H_2SO_4:30% H_2O_2 70:30 (v/v)) at 80 °C for 1 h and then left to cool to room temperature.[2,12] 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.[2,12] Then they were washed with double-distilled water and dried under vacuum immediately before deposition of the coupling agent. All the following sample manipulations were performed in a glovebox under inert N_2 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).[2,12] Then they were washed with a 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 P1 sodium salt and heated to 60 °C under stirring for 48 h. Finally, the substrates

---

(6) (a) Pedrosa, J. M.; Dooling, C. M.; Richardson, T. H.; Hyde, R. K.; Hunter, C. A.; Martin, M. T.; Camacho, L. *J. Mater. Chem.* **2002**, *12*, 2659. (b) Suzuchi, Y.; Nishide, H.; Tsuchida, E. *Macromolecules* **2000**, *33*, 2530. (c) Amao, Y.; Asai, K.; Miyakawa, K.; Okura. I. *J. Porphyrins Phthalocyanins* **2000**, *4*, 19. (d) Dooling, C. M.; Worsfold, O.; Richardson, T. H.; Tregonning, R.; Vysotsky, M. O.; Hunter, C. A.; Kato, K.; Shinbo, K.; Kaneko, F. *J. Mater. Chem.* **2001**, *11*, 392.

(7) (a) Paolesse, R.; Monti, D.; La Monica, L.; Venanzi, M.; Froiio, A.; Nardis, S.; Di Natale, C.; Martinelli, E.; D'Amico, A. *Chem. Eur. J.* **2002**, *8*, 2476. (b) Amao, Y.; Asai, K.; Okura. I. *J. Porphyrins Phthalocyanins* **2000**, *4*, 179. (c) Redman, J. E.; Sanders, J. K. M. *Org. Lett.* **2000**, *2*, 4141. (d) Ashkenasy, G.; Ivanisevic, A.; Cohen, R.; Felder, C. E.; Cahen, D.; Ellis, A. B.; Shanzer, A. *J. Am. Chem. Soc.* **2000**, *122*, 1116. (e) Offord, D. A.; Sachs, S. B.; Ennis, M. S.; Eberspacher, T. A.; Griffin, J. H.; Chidsey, C. E. D.; Collman, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 4478. (f) Li, D. Q.; Swanson, B. I.; Robinson, J. M.; Hoffbauer, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 6975.

(8) (a) Wirnsberger, G. S.; Brian, J.; Stucky, G. D. *Chem. Commun*. **2001**, *1*, 119. (b) Blair, S.; Lowe, M. P.; Mathieu, C. E.; Parker, D.; Senanayake, P. K.; Kataky, R. *Inorg. Chem*. **2001**, *40*, 5860. (c) Lee, S.-H.; Kumar, J.; Tripathy, S. K. *Langmuir* **2000**, *16*, 10482. (d) Koncki, R.; Wolfbeis, O. S. *Anal. Chem*. **1998**, *70*, 2544. (e) Shi, Y.; Seliskar, C. J. *Chem. Mater*. **1997**, *9*, 821.

(9) (a) Delmarre, D.; Meallet-Renault, R.; Bied-Charreton, C.; Pasternack, R. F. *Anal. Chim. Acta* **1999**, *401*, 125. (b) Papkovsky, D. B.; Ponomarev, G. V.; Wolfbeis, O. S. *J. Photochem. Photobiol., A: Chem.* **1997**, *104*, 151. (c) Igarashi, S.; Kenji, Y.; Yotsuyanagi, T. *Anal. Sci*. **1994**, *10*, 821. (d) Yuan, R.; Chai, Y.; Shen, G.; Yu, R. *Talanta* **1993**, *40*, 1255. (e) Blair, T. L.; Allen, J. R.; Daunert, S.; Bachas, L. G. *Anal. Chem*. **1993**, *65*, 2155.

(10) Mineo, P.; Scamporrino, E.; Vitalini, D. *Macromol. Rapid Commun.* **2002**, *23*, 681.

(11) Micali, N.; Villari, V.; Mineo, P.; Vitalini, D.; Scamporrino, E.; Crupi, V.; Majolino, D.; Migliardo, P.; Venuti, V. *J. Phys. Chem. B* **2003**, *107*, 5095.

(12) Lin, W.; Lin, W.; Wong, G. K.; Marks, T. J. *J. Am. Chem. Soc*. **1996**, *118*, 8034.

bearing the covalently bound porphyrin molecules were cooled to room temperature and repeatedly washed with THF to remove any residual unreacted porphyrin.

Molecular monolayer characterization has been carried out with small-spot X-ray photoelectron spectroscopy. This technique is ideal since it allows high vertical resolution and gives information on the bonding states of the grafted molecules. In particular, X-ray photoelectron spectra (XPS) were measured at a 90° takeoff angle, relative to the surface plane, with a PHI 5600 Multi Technique System (base pressure of the main chamber 2×10^{-10} Torr) which offers good control of the electron off-take angle.[2a,13−14] The spectrometer is equipped with a dual-anode X-ray source, a spherical capacitor analyzer (SCA) with a mean diameter of 279.4 mm, and an electrostatic lens system Omni Focus III. The nominal analyzer resolution was set to 400 meV. Samples were mounted on Mo stubs. Spectra were excited with Al Kα radiation. Structure due to satellite radiation has been subtracted from the spectra before data processing. The XPS peak intensities were obtained after Shirley background removal.[15] Procedures to account for steady-state charging effect have been described elsewhere.[13,14] Freshly prepared samples were quickly transferred from the glovebox under N_2 atmosphere to the XPS main chamber. Experimental uncertainties in binding energies lie within ±0.5 eV.

Morphological characterizations were performed by atomic force microscopy (AFM) measurements with a Solver P47 NTD-MDT instrument in semi-contact mode (resonance frequency 150 Hz). The noise level before and after each experiment was 0.01 nm.[2c]

UV−vis measurements were performed using a UV−Vis-1601 Shimadzu spectrophotometer. Experimental uncertainty lies within ±0.5 nm. UV−vis scans in the 375−510 nm range were carried out after a 20 s immersion of the P1−CAM in a given HCl solution (pH values between 5 and 1.0, starting from a solution at pH 6.0 obtained using high-purity Aldrich H_2O) at 25 °C and drying the quartz surface with a purified N_2 stream. HCl solutions at different pH values (5.0−1.0 range) were prepared and tested by a pH meter (Metrohm model 691) equipped with a combined glass electrode (Metrohm model 6.0202.100).

MALDI-TOF mass spectra were measured by a Voyager DE-STR instrument (PerSeptive Biosystem) using a delay extraction procedure (25 kV applied after 2600 ns with a potential gradient of 454.54 V/mm and a wire voltage of 250 V) and detection in linear mode.[16] The instrument was equipped with a nitrogen laser (emission at 337 nm for 3 ns, 50 Hz) and a flash AD converter (time base 2 ns). *trans*-3-Indoleacrylic acid was used as a matrix. For MALDI measurements the water metal/porphyrin solutions were dried by a nitrogen flow and successively under vacuum at 40 °C. The residue was then dissolved in CH_2Cl_2, mixed with the matrix, and loaded in the sample plate. The mass spectrometer calibration was performed as already reported.[17] Spectra were corrected for the offset and baseline.[18] Because of the isotopic composition, molecular species were detected in the mass spectra as clusters of peaks. To simplify their assignments, m/z values reported in the spectra and in the text are referred to the peak of each cluster corresponding to the ion containing the most abundant isotope of each element.

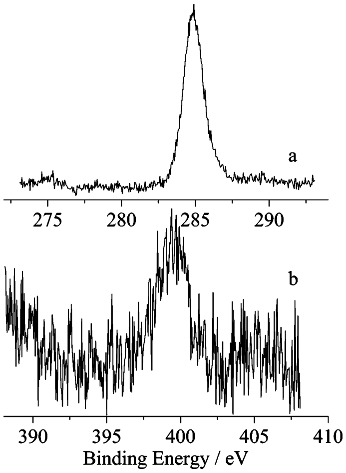

Figure 2. Al Kα excited XPS of the P1−CAM, at a 90° photoelectron takeoff angle, in the (a) C 1s and (b) N 1s energy regions. Structures due to satellite radiation have been subtracted from the spectra.

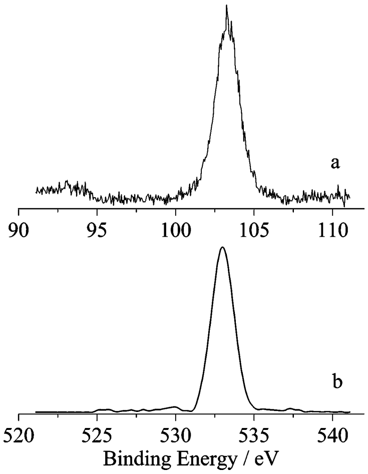

Figure 3. Al Kα excited XPS of the P1−CAM, at a 90° photoelectron takeoff angle, in the (a) Si 2p and (b) O 1s energy regions. Structures due to satellite radiation have been subtracted from the spectra.

Results and Discussion

Normal emission core-level photoelectron spectra of the P1−CAM are shown in Figures 2 and 3. The C 1s peak (Figure 2a) lies at 284.8 eV binding energy (BE). The N 1s signal (Figure 2b) consists of a broad peak at 399.8 eV with a lower binding energy (398.1 eV) shoulder. These features account for the two kinds of nitrogen in the free porphyrin base.[2b,6a] The Si 2p signal at 103.3 eV (Figure 3a) shows a symmetric shape with a BE typical of SiO_2 substrates, which does not require any further discussion. The O 1s peak (Figure 3b) lies at 532.9 eV. O 1s BEs for ether linkages are expected at values similar to that due to the silica substrate.[19−21]

AFM measurements of P1−CAMs (Figure 4) show densely packed features having a "mountain" shape with a 2.38 Å surface mean roughness.

---

(13) Gulino, A.; La Delfa, S.; Fragalà, I.; Egdell, R. G. *Chem. Mater*. **1996**, *8* 1287.

(14) Gulino, A.; Condorelli, G. G.; Fragalà, I.; Egdell, R. G. *Appl. Surf. Sci.* **1995**, *90*, 289.

(15) Repoux, M. *Surf. Interface Anal*. **1992**, *18* 567.

(16) (a) Scamporrino, E.; Vitalini, D.; Mineo, P. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 2511. (b) Mineo, P.; Scamporrino, E.; Vitalini, D.; Alicata, R.; Bazzano, S. *Rapid Commun. Mass Spectrom*. **2005**, *19*, 2773.

(17) Scamporrino, E.; Vitalini, D.; Mineo, P. *Macromolecules* **1996**, *29*, 5520.

(18) Scamporrino, E.; Vitalini, D.; Mineo, P. *Macromolecules* **1997**, *30*, 5285.

(19) Briggs, D.; Beamson, G. *Anal. Chem*. **1993**, *65*, 1517.

(20) Briggs, D.; Beamson, G. *Anal. Chem*. **1992**, *64*, 1729.

(21) Lopez, G. P.; Castner, D. G.; Ratner, B. D. *Surf. Interface Anal*. **1991**, *17*, 267.

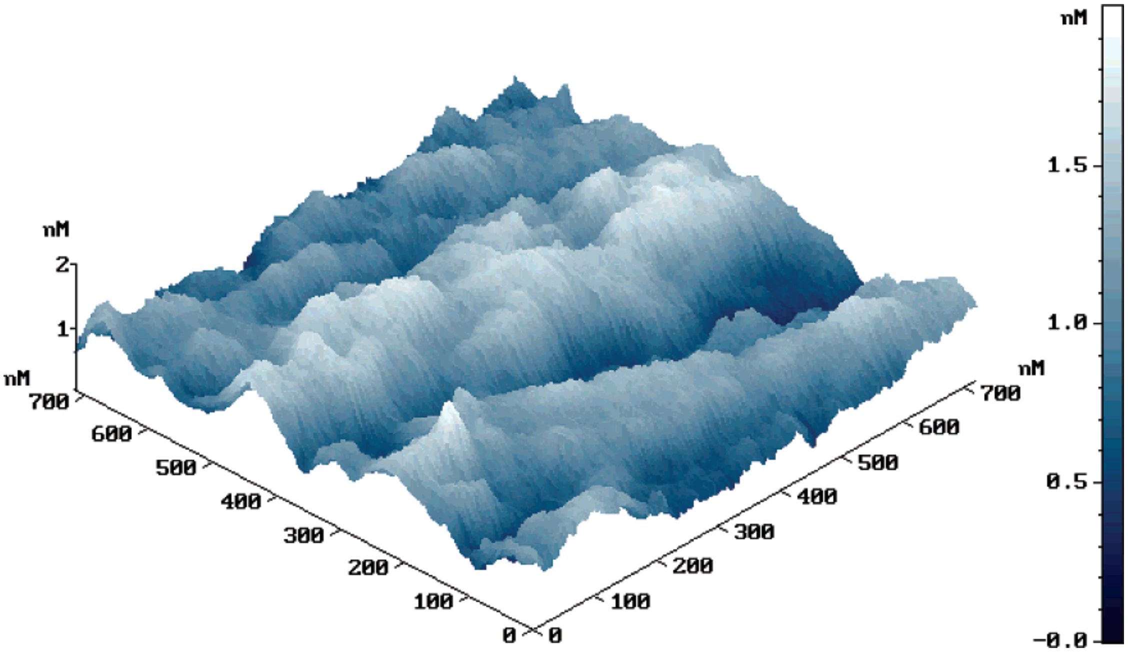

Figure 4. Typical AFM image of the representative P1−CAM.

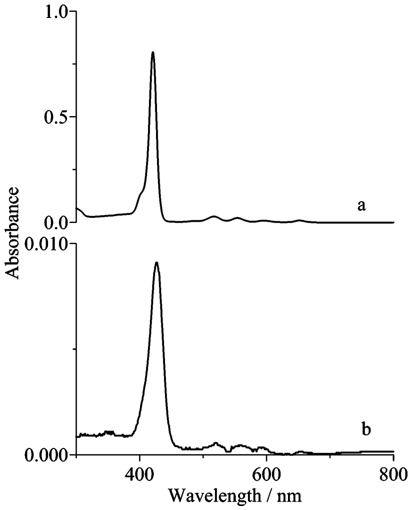

Figure 5. UV−vis spectra of (a) 6 × 10^{-5} THF P1 solution (carried out using 0.1 cm quartz cuvettes) and (b) P1−CAM.

The UV−vis spectrum of the P1 6 × 10^{-5} M THF solution (Figure 5a) 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. Analogously, the UV−vis spectrum of the resulting P1−CAM (Figure 5b) shows high-quality signals at 427.2, 519.9, 560.8, 596.1, and 654.7 nm. Using the Beer−Lambert law, $A = \epsilon lc$, where A is the absorbance and ϵ, l, and c are the extinction coefficient, thickness of film, and concentration of the film, respectively, one can calculate the surface coverage, $d_{\mathrm{surf}} = A\epsilon^{-1}$.[7f] The calculated[7f] density of porphyrin, molecules/cm^2, in various synthesized P1−CAM is in the 1.67 × 10^{12} to 1.95 × 10^{13} range. Thus, the present covalently bound porphyrin monolayer is densely packed.

The optical (UV−vis) pH-sensing capability of the porphyrin was first tested in solution as a blank reference. In fact, P1 does not dissolve in H_2O; therefore, UV−vis spectra of two aqueous 5 × 10^{-5} and 4 × 10^{-8} M solutions of the close parent water-soluble porphyrin derivative, namely, the 5,10,15,20-tetrakis{*p*-[*ω*-methoxy-poly(ethyleneoxy)]phenyl}-porphyrin (hereafter called P2), were measured upon varying the pH with HCl. P2 is a star polymer with four poly(oxyethylene) branches, each constituted of ∼40 oxyethylene repetitive units with an average molecular mass of about 2000 Da.

The UV−vis spectra show a Soret band at 421.7 nm and satellite Q-bands at 521.1, 559.8, 599.5, and 652.5 nm (Figures 6). The fwhms of the starting Soret signals are 26.6 and 14.8 nm for the 5 × 10^{-5} M (Figure 6a) and 4 × 10^{-8} M (Figure 6b) solutions, respectively. The broadening of the Soret band, upon increasing the porphyrin solution concentration, is clearly related to some intermolecular self-aggregation phenomenon and causes a sizable dependence of the molar extinction coefficient upon the solution concentration. Thus, the ϵ value is 2.52 × 10^5 in the 5 × 10^{-5} M solution and slightly larger (3.38 × 10^5) in the 4 × 10^{-8} M solution.

Laser scattering experiments with water solutions (≥1 × 10^{-4} M) of porphyrin derivatives with poly(oxyethylene) branches in the 8−120 repetitive units range have shown that fractal aggregation occurs only for porphyrins with branches of ∼8 repetitive units.[11] Nevertheless, FT-IR measurements on present star polymers pointed to the presence of some dimeric J- and H-form aggregates for ≥1 × 10^{-4} M water solutions even for the derivative with branches of ∼17 repetitive units.[22,23] In addition, small angle neutron scattering (SANS) experiments have shown that shorter poly(oxyethylene) branches favor self-aggregation of star polymers.[22] From all these observations it, therefore, turns out that this phenomenon is scarcely present in the 5 × 10^{-5} M P2 solution while it can be considered absent in the 4 × 10^{-8} M solution.

---

(22) Crupi, V.; Giordano, R.; Majolino, D.; Migliardo, P.; Venuti, V.; Micali, N.; Villari, V.; Mineo, P.; Vitalini, D.; Scamporrino, E. *Mol. Phys.* **2003**, *101*, 1517.

(23) Crupi, V.; Majolino, D.; Migliardo, P.; Venuti, V.; Micali, N.; Villari, V.; Mineo, P.; Vitalini, D.; Scamporrino, E. *J. Mol. Struct.* **2003**, *651−653*, 675.

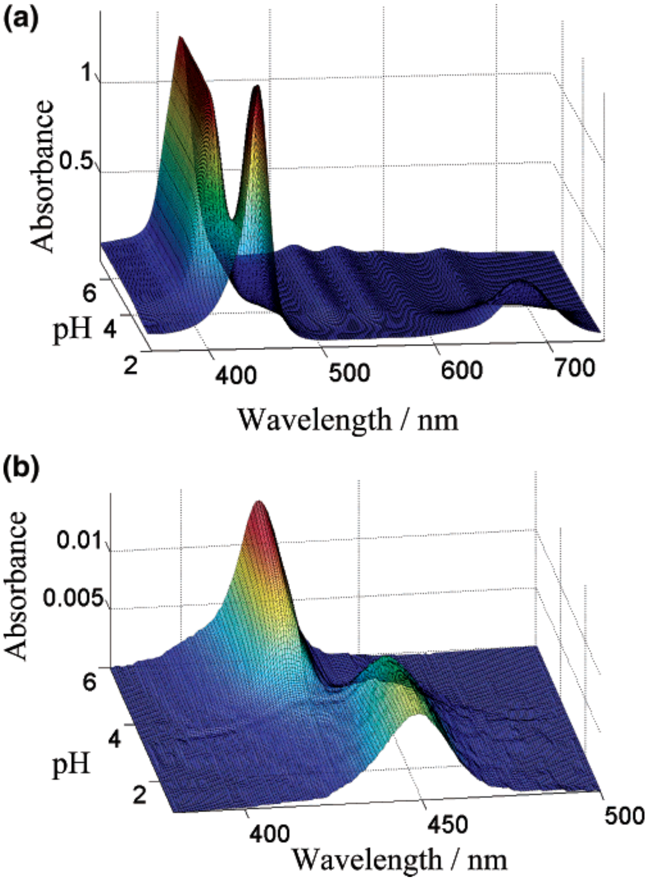

Figure 6. Three-dimensional UV−vis spectra of the aqueous solutions of (a) 5 × 10^{-5} (scan range 325−800 nm; 0.1 cm quartz cuvettes) and (b) 4 × 10^{-8} M (scan range 375−500 nm) P2 upon decreasing the pH value from 6.0 to 1.0.

Titration experiments with HCl suggest that the Soret band at 421.7 nm suffers a red shift in acidic conditions. Thus, UV−vis spectra show that the Soret and Q-bands are less intense upon decreasing the pH of solutions (Figures 6) while two additional bands at 448.8 and 683.9 nm (the latter outside the range of Figure 6b) increase. Both the intensity ratio between the 448.8 and 421.7 nm bands and the residual percent of Soret band intensity (relative to the initial intensity value at pH 6 obtained with the highest pure Aldrich H_2O) depend on pH values and can be used as pH indicators. Thus, residual absorbances of 86%, 74%, 39%, 22%, 15%, 12%, 8%, 6%, and 2% can be measured at pH = 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, and 1.0, respectively. These results refer to the 4 × 10^{-8} M solution. Even more interesting, there is evidence of a total reversibility upon adding NaOH. No variations of the Soret intensity have been observed for basic pH values. This overall result agrees well with the almost unique report on a similar system and points to a reversible protonation of the porphyrin.[9a]

In the more concentrated 5 × 10^{-5} M solution, where some aggregation could occur, repulsive interactions between positively charged molecules after protonation of nitrogen sites of porphyrin result in a molecular dis-aggregation.[11,22−23] This observation is tuned well with the increased intensity of the new Soret band, upon decreasing the pH value, beyond that observed in the reference solution at pH 6 (Figure 6a).

In this respect the possible use of the P1−CAM as a pH optical sensor has been tested. Therefore, UV−vis spectra have been measured after immersion (20 s) in acid solutions (pH 6.0−1.0) and drying with a purified N_2 stream. After every measurement, the system was washed with double-distilled water before immersion in more acidic solutions. The inset in Figure 7 shows the changes of the UV−vis absorbance spectra of the P1−CAM.

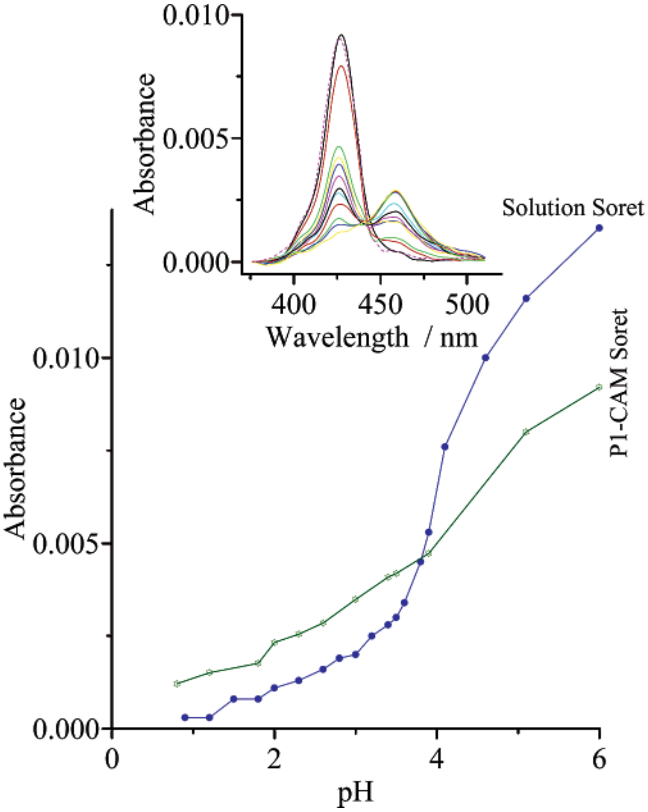

Figure 7. Soret band intensity trends, for a set of measurements, for both P2 4 × 10^{-8} M solution and P1−CAM. Inset: UV−vis spectra of the P1−CAM (scan range 375−510 nm) after immersion in solutions at different pH values and drying. The dashed line refers to the spectrum of the P1−CAM recovered with a simple washing procedure and drying under a N_2 gas stream.

It becomes evident that the Soret band at 427.2 nm progressively disappears, whereas a new band at 459.1 nm grows in. In particular, at pH 1.0, the spectrum is almost dominated by the new band and remains unchanged for more acidic solutions. Remarkable enough, a simple washing procedure (20 s) and drying under a N_2 gas stream totally recovers the starting Soret band (dashed line in the inset of Figure 7).

Figure 7 shows the intensity of the Soret band vs pH for both P2 solution and P1−CAM. It is clear that, once calibrated against standard solutions, the residual (relative to the pH 6 reference) Soret band intensity of the P1−CAM can be used to monitor the pH. Thus, residual absorbances of 86%, 51%, 46%, 42%, 38%, 33%, 30%, 25%, 20%, 16%, and 12% have been measured 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. Moreover, the system shows a reliable reversibility during iteration of several acid immersion and washing/drying cycles.

The P1−CAM optical pH sensor behavior has been further investigated with 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 detect possible anion interferences. No relevant changes have been detected.

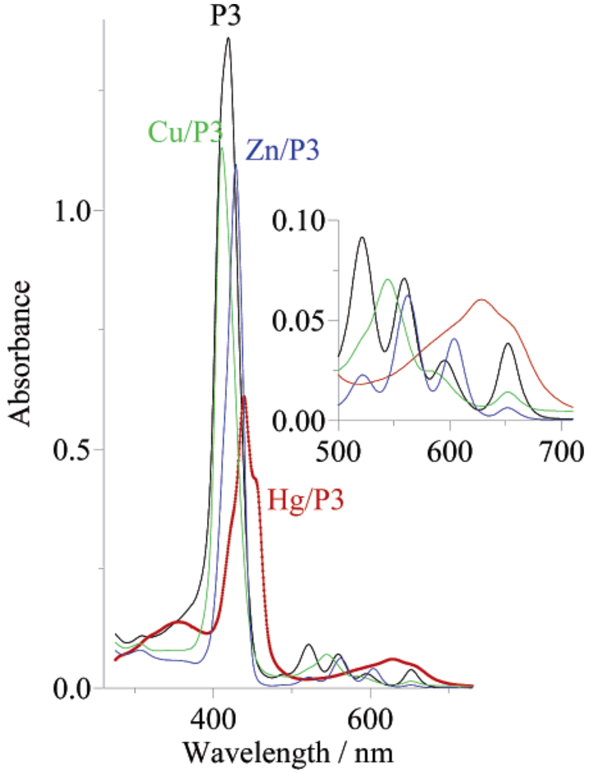

Figure 8. UV−vis spectra of the P3 (1×10^{-5} M solution, black line) solution obtained mixing equal volumes of P3 (1×10^{-5} M) and Hg^{2+} (1×10^{-4} M) solutions (red line), P3 (1×10^{-5} M) and Cu^{2+} (1×10^{-4} M) solutions (green line), and f P3 (1×10^{-5} M) and Zn^{2+} (1×10^{-4} M) solutions (blue line). Inset: expanded scale of the Q-band region.

Similarly, possible interferences due to metal ions have been investigated. Therefore, some blank tests have been performed using a soluble 5,10,15,20-tetrakis{*p*-[*ω*-methoxypoly(ethyleneoxy)]phenyl}porphyrin (called P3), where each of the four poly(oxyethylene) branches has $M_w \approx 750$ Da, corresponding to ∼17 repetitive units. The choice of P3 (instead of P2) has been suggested by the lower molecular weight that favors a better mass resolution, inversely proportional to the time-of-flight, in MALDI-TOF experiments.

Note that the fwhm of the P3 Soret band (32.7 nm) is only slightly broader than that of P2 (26.6 nm) in 1×10^{-5} M water solutions. Therefore, we feel confident that molecular aggregations are similar in both cases, thus rendering transferable the related results.

In particular, identical volumes of 1×10^{-5} M P3 and 1×10^{-4} M metal nitrate or acetate (Aldrich reagents) aqueous solutions have been admixed at room temperature to obtain a porphyrin/metal ion 1:10 molar ratio.

In the case of Mn(II), Co(II), Ni(II), Cd(II), or Pb(II), no significant differences have been found in the P3 absorbance spectrum.[24] Moreover, the UV−vis spectra upon decreasing the pH are identical to those of the P2 system reported in Figure 6a. This indicates that P3 behaves as P2 and its pH response is not influenced by the presence of the mentioned cations.

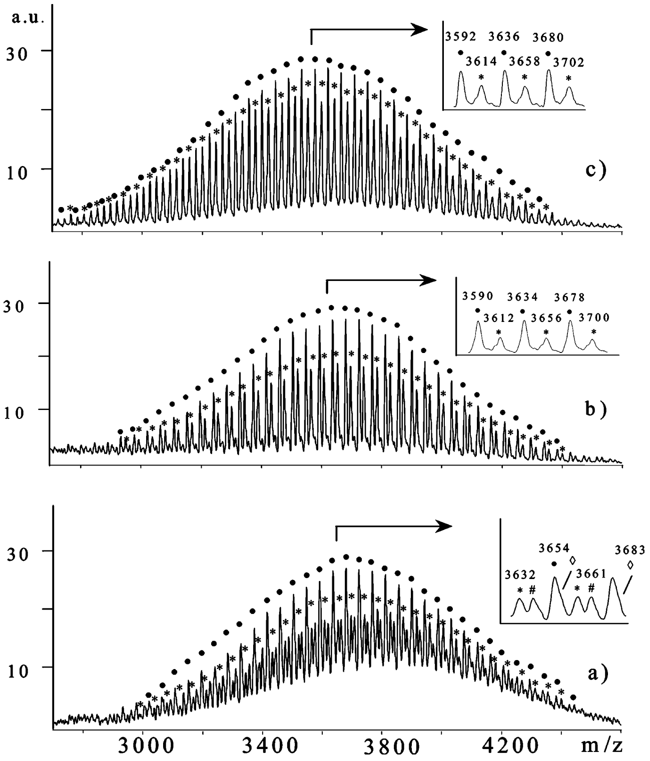

Figure 9. MALDI-TOF spectra of the species contained in (a) Hg^{2+}-containing P3 water solution, (b) Cu^{2+}-containing P3 water solution, and (c) Zn^{2+}-containing P3 water solution.

By contrast, dramatic changes of the UV−vis spectrum of the P3 water solution in the presence of Hg(II) ions (Figure 8, red line) have been observed. In particular, the Soret band red shifts at 438.3 nm and shows two shoulders at 421.7 and 452.5 nm. Moreover, only one broad Q-band is now evident. All these features point to the contemporary presence of the metal-free porphyrin and, at least, two Hg−porphyrin species. This hypothesis was further confirmed by positive MALDI-TOF mass spectra. Thus, in the case of the mentioned P3/$Hg(Ac)_2$ water solution (Figure 9a), the MALDI-TOF mass spectrum consists of two couples of peaks series. The first includes peaks at *m*/*z* 2928 + *n*44 and 2950 + *n*44 (where $n = 44-80$) corresponding to the AcHg−P3 (M_n) molecular ions (in which the AcHg fragment substitutes for one H in the porphyrin core), detected as M_nH^+ (∗) and M_nNa^+ (●), respectively. The second represented by peaks at *m*/*z* 2957 + *n*44 and 2979 + *n*44 corresponding to Hg−P3 (M_n) molecular ions (where Hg substitutes for both H atoms in the porphyrin core), detected as M_nH^+ (#) and M_nNa^+ (◇), respectively. Unfortunately, signals corresponding to $[P3]Na^+$ and $[AcHgP3]H^+$ species overlap.

The UV−vis features, in terms of both number of Q-bands and shift of the Soret band (Figure 8), all agree well with theoretical and experimental data already reported for metalloporphyrins.[25] Thus, while the porphyrin free base shows four clear visible Q-bands, metalloporphyrins show two of them. Therefore, in the present HgP3 complex the broad envelope centered at 627 nm accounts for the contemporary presence of some metal-free porphyrin and the two Q-bands of the two Hg−porphyrin species: AcHg−P3 and Hg−P3. The extra band observed at 355.6 nm strongly parallels that

---

(24) Formation constant of metal−porphyrin complexes are rather large because of the macrocyclic effect. Nevertheless, rather low reaction kinetics can be observed at room temperature for many cations. Therefore, the behavior observed in the case of Mn(II), Co(II), Ni(II), Cd(II), or Pb(II) should be due to this second reason.

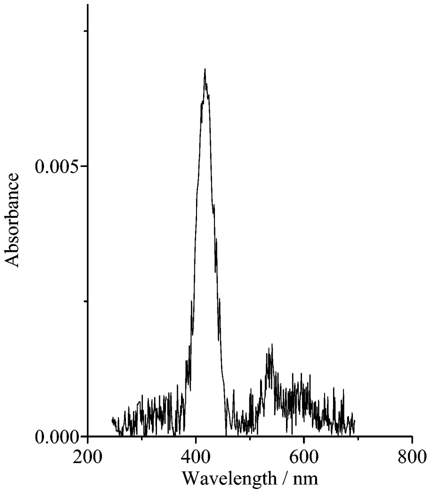

Figure 10. UV−vis spectrum of the P1−CAM after 30 min immersion in a 1×10^{-4} M $Cu(NO_3)_2$ water solution.

calculated by Petke et al.[26] using ab initio SCF-MO on MgP and confirmed Gouterman et al. on Zn(TFPP).[25a]

A similar behavior has been observed in the case of either Cu(II) or Zn(II) solutions. In the Cu(II) case, the UV−vis (Figure 8, green line) shows a blue-shifted Soret band at 409.8 nm[25] and some changes in the Q-band region (Figure 8). These data indicate the formation of a Cu−porphyrin complex, in agreement with MALDI results which show (Figure 9b) a couple of peaks at m/z 2732 + n44 and 2754 + n44 ($n = 44-80$ range), corresponding to Cu/P3 (M_n) molecular ions (in which a Cu atom substitutes for both two porphyrin core H atoms), detected as M_nH^+ (∗) and M_nNa^+ (●), respectively.

Finally, the Zn(II)-containing solution shows a red shift of the Soret band at 427.5 nm associated to some variations in the Q-band region (Figure 8, blue line). Its MALDI spectrum (Figure 9c) consists of two peaks at m/z 2734 + n44 and 2756 + n44 ($n = 44-80$ range), corresponding to Zn/P3 (M_n) molecular ions, detected as M_nH^+ (∗) and M_nNa^+ (●), respectively (unfortunately, m/z values of [Zn/P3]-H^+ species are coincident with those of $[P3]Na^+$).

There is, therefore, evidence that the P1−SAM performance could be hampered in the presence of Hg(II), Cu(II), and Zn(II) ions because of the formation of porphyrin complexes that are "poisoning" for the pH optical response. Moreover, in the acid pH range presently investigated no metal-ion displacement is observed.

Therefore, the optical pH-sensing behavior of the P1−CAM was further tested in Mn(II), Co(II), Ni(II), Cd(II), or Pb(II) solutions below pH 6. As expected, no UV−vis differences have been observed relative to metal-free acidic solutions. By contrast, 30 min exposure of the P1−CAM to a 1×10^{-4} M Cu^{2+} water solution (Figure 10) results in a blue-shifted Soret band at 416.6 nm (427.2 nm in the original P1−CAM) and signals at 539 and 595 nm in the Q-band region. All these features agree well with those observed for the Cu (II)/P3 solution (Figure 8) and are again well tuned with the formation of a Cu/(P1−CAM) complex. Therefore, as expected, the presence of Cu^{2+} ions hampers the P1−CAM optical pH-meter performance.

Conclusion

A novel covalently assembled porphyrin monolayer P1−CAM has been obtained and characterized by UV−vis, AFM, and XPS measurements. It has proven to be highly sensitive to variation of pH values below 6 with a sensitivity of 0.1 pH units. This renders the system a well-suited, fast, and reversible optical pH meter (in the 1−6 pH range). The presence of Mn(II), Co(II), Ni(II), Cd(II), or Pb(II) ions in water solution does not interfere with the sensing capability, while the presence of Hg(II), Cu(II), or Zn(II) ions hampers the P1−CAM performance because of metal−porphyrin complex formation. Dilute P2 solutions are also of interest in pH sensing. Further studies are in progress to probe the influence of other metal ions as well as other chemicals.

Acknowledgment. The authors thank the Ministero Istruzione Università e Ricerca (MIUR, Roma-PRIN 2003 and -FIRB 2005) and CNR-Rome for financial support. Mr. Ivan Bykov (Lomonosov Moscow State University, Russia) is fully acknowledged for his assistance during AFM measurements.

Supporting Information Available: UV−vis spectra of the solution obtained mixing P3 with Hg^{2+}, Cu^{2+}, and Zn^{2+} solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

CM060086G

---

(25) (a) Ryeng, H.; Ghosh, A. *J. Am. Chem. Soc.* **2002**, *124*, 8099. (b) Wertsching, A. K.; Koch, A. S.; DiMagno, S. G. *J. Am. Chem. Soc.* **2001**, *123*, 3932. (c) Parusel, A. B. J.; Ghosh, A. *J. Phys. Chem. A* **2000**, *104*, 2504. (d) Hashimoto, T.; Choe, Y.-K.; Nakano, H.; Hirao, K. *J. Phys. Chem. A* **1999**, *103*, 1894. (e) Shelnutt, J. A.; Ortiz, V. *J. Phys. Chem*. **1985**, *89*, 4733. (f) Wang, M.-Y. R.; Hoffman, B. M. *J. Am. Chem.* Soc. **1984**, *106*, 4235. (g) Spellane, P. J.; Gouterman, M.; Antigas, A.; Kim, S.; Liu, Y. C. *Inorg. Chem*. **1980**, *19*, 386. (h) Goutermann, M. *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3. (i) Spangler, D.; Maggiora, G. M.; Shipman, L. L.; Christoffersen, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 7470.

(26) Petke, J. D.; Maggiora, G. M.; Shipman, L. L.; Christoffersen, R. E. *J. Mol. Spectrosc*. **1978**, *71*, 64.