Molecularly Engineered Silica Surfaces with an Assembled Porphyrin Monolayer as Optical NO_2 Molecular Recognizers

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

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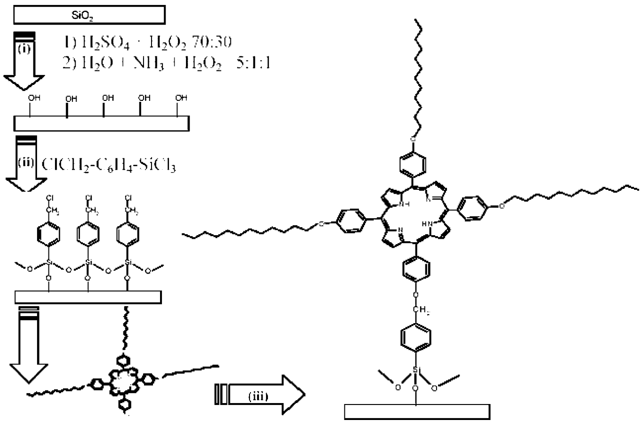
Engineering of inorganic surfaces by covalent bonding of organic molecules represents an interesting approach to the synthesis of hybrid inorganic/organic nanomaterials,[1] in the perspective of fabrication of highly sensitive gas sensors for environmental monitoring.[2]

Both porphyrin and phthalocyanine thin films offer attracting challenges for easy monitoring at the ppm level on the basis of their semiconducting[3] and also optical[4,5] properties.

Few works concerning appropriately functionalized porphyrin molecules bound to different substrates have already been reported.[2,5] In this context, we focused our interest on the 5,10,15-tri-{*p*-dodecanoxyphenyl}-20-(*p*-hydroxyphenyl) porphyrin (called P), a chromophore (see Scheme 1) that shows a very high molar absorbance coefficient (3.3 × 10^5)[6] and a good affinity toward NO_2 (vide infra). The combination of these features makes the porphyrin very efficient as an optical gas sensor. The presence of only one hydroxyl group in the peripheral position of the porphyrin allows a univocal covalent linkage to the substrate. Moreover, the steric hindrance due to the three long aliphatic groups, covalently bounded in the remaining peripheral positions of the porphyrin, could prevent the well-known aggregation due to stacking interactions.[7] There were, therefore, enough motivation to embark on the fabrication of a P monolayer, covalently assembled on silica substrates (called P-AM), and to study its NO_2 optical recognition behavior.

Scheme 1



P was synthesized, by a partial condensation reaction between appropriate quantities of the sodium salt of tetrakis(p-hydroxyphenyl)porphyrin and 1-bromododecane.[6] Moreover, it was purified and characterized as already reported.[6] Its pure sodium salt was obtained by reacting a tetrahydrofurane (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 P-AM. Fused silica (quartz) 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.[8] They were repeatedly rinsed with double-distilled water and immersed in H_2O:30% H_2O_2:NH_3 5:1:1 v/v/v mixture at room temperature for 40 min.[8] 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 performed in a glovebox under an inert atmosphere. Therefore, (ii) freshly cleaned substrates were im-

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* Corresponding authors. E-mail: agulino@dipchi.unict.it (A. Gulino). Fax: ++39-095-580138.

† Università di Catania.

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

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mersed, at room temperature for 30 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).[8] Then, they were washed with copious amounts 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 dimethylformamide (DMF) solution of the present porphyrin sodium salt and heated to 80 °C under stirring for 48 h. Finally, the substrates bearing the covalently bound porphyrin molecules were cooled to room temperature and repeatedly washed with DMF to remove any residual unreacted porphyrin.

Silica substrates have been characterized by static and dynamic water contact angle (ϑ) measurements after every reaction step. Two-microliter water drops were applied on the sample surface and measurements of ϑ have been made on both sides of the two-dimensional projection of the droplet, executing both advancing and receding procedures. Five different sets of measurements have been performed on different surface portions of every substrate to obtain statistically reliable results. Uncoupled substrates showed a ϑ value in the 9−13° range. After cleaning (step i), the ϑ values decreased to 5°, consistent with hydroxylated silica surfaces.[8] The contact angle changed from 5° to 92° after treatment with the CA (step ii), in accordance with the presence of densely packed benzylic chloride surface functionalities.[8] After the final step (iii), the contact angle showed the expected reduction of the hydrophobic character with ϑ falling to 62° upon the porphyrin linkage.

Angle-resolved X-ray photoelectron spectra (XPS) were made at different take-off angles.[9] Nitrogen 1s AR-XP spectra of the P-AM showed a broad peak at 399.7 eV with a shoulder at lower binding energy (398.17 eV). These features account for the two kinds of nitrogen in the free porphyrin base.[10] The nitrogen atomic concentration also showed a monotonic increase upon decreasing the electron take-off angle from 45° to 3°, as expected for the upper layer nature of the signal.

A representative UV−visible spectrum of the resulting P-AM, reported in Figure 1b, shows high-quality signals and finds counterparts in that of the porphyrin THF 5×10^{-6} M solution (Figure 1a). Both spectra show a characteristic sharp Soret band at 425 nm and satellite Q-bands in the 522−654-nm range. The calculated[5f] value of porphyrin molecules/cm^2 of the P-AM is $1.1 \times 10.^{13}$

The NO_2 sensing capability of the porphyrin system was first tested in solution. The UV−vis spectrum (Figure 2) of the THF porphyrin 5×10^{-6} M solution, after 10 s of bubbling of 5 ppm NO_2 in a N_2 gas stream (flow rates = 190 sccm) shows an evident intensity decrease of the Soret and Q-bands parallel to the increase of two additional bands at 452 and 685 nm. This result is in accordance with previously reported data on similar systems and indicates reversible oxidation of the porphyrin.[4d]

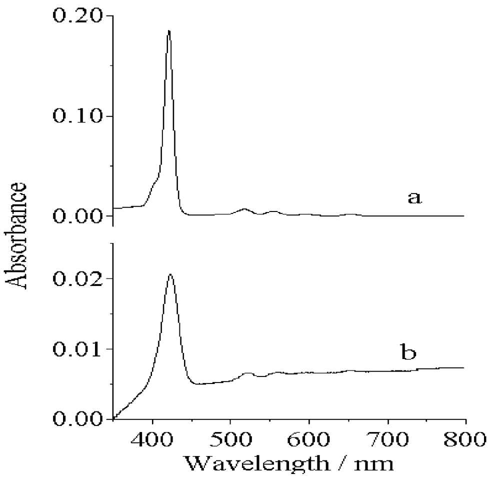

Figure 1. UV−vis spectra of the porphyrin THF solution (a) and P-AM (b).

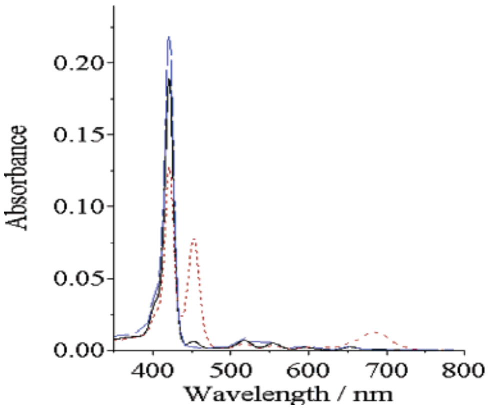

Figure 2. UV−vis spectra of the porphyrin THF solution: solid line refers to the as-dissolved porphyrin in THF; dotted line refers to the solution after bubbling a 5 ppm NO_2/N_2 gas stream for 10 s; dashed line refers to the recovered porphyrin tetrahydrofurane solution.

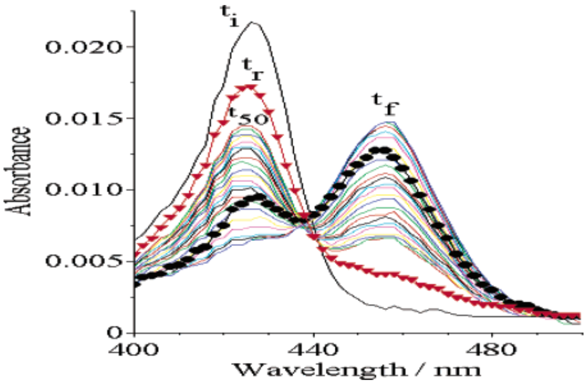

Figure 3. UV−vis spectra of the P-AM during the in situ continuous leaking of 1 ppm NO_2/N_2 gas stream (for clarity, reported spectra are after 0, 4, 12, 20, 28, 36, etc. seconds of exposure). In particular, t_i is the spectrum of the starting P-AM.

Cycles of 50 fast UV−vis scans (scan frequency = 4 s, scan rate 50 nm/s) in the 400−500-nm range of the P-AM were carried out during an in situ continuous leaking of a NO_2/N_2 gas stream at 1 ppm (flow rate =100 sccm). Figure 3 shows the evolution of the UV−vis absorbance spectra of the P-AM upon gas exposure. It becomes evident that the Soret band at 425 nm progressively disappears whereas a new band at 462 nm grows

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upon NO_2. In particular, the Soret band intensity takes 4 s to fall to 50% with respect to its final saturated value (t_{50} in Figure 3). This value (4 s) safely represents the response speed of the present P-AM system and, to the best of our knowledge, is better than those previously reported.[4,5a−b,d] After an exposure of 180 s, the spectrum is fully dominated by the new band at 462 nm (t_f in Figure 3) and remains unchanged for many days. Short heating time (4 s) at 80 °C under a N_2 gas stream recovers about 33% of the Soret (closed circles in Figure 3). The band is almost fully recovered in 60 s (t_r closed triangles in Figure 3).

Four cycles alternating NO_2 exposure and recovery in N_2 under heating have been performed with no variations of performance. The system, therefore, shows a reliable reversibility.

In conclusion, a new assembled porphyrin monolayer has been obtained. It has proven to be highly sensitive to 1 ppm of NO_2 and, therefore, is a well-suited fast and reversible optical NO_2 recognizer. To our knowledge, present data are indicative of better performances than those already reported for porphyrin-based NO_2 sensors.[4,5a−b,d]

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