Characterization, Optical Recognition Behavior, Sensitivity, and Selectivity of Silica Surfaces Functionalized with a Porphyrin Monolayer

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The optical gas recognition capability of a covalently self-assembled monolayer of 5,10,15-tri-{*p*-dodecanoxyphenyl}-20-(*p*-hydroxyphenyl) porphyrin molecules on silica substrates was studied. The following analytes have been investigated: NO_2, CO, CH_4, H_2, NH_3, HCl, $CHCl_3$, C_2H_5OH, CH_3OH, pyridine, tetrahydrofurane, triethylamine, and dimethylformamide. The self-assembled porphyrin monolayer appears highly sensitive to 1 ppm of NO_2 in both anhydrous and humid conditions. The selectivity of the self-assembled porphyrin monolayer with respect to other analytes was also examined and present data show that the presence of CO, CH_4, H_2, and NH_3 does not influence its UV−vis spectrum. Many common solvents slowly affect the position of the Soret band. The presence of HCl vapors results in a broad band extending over the entire 440−500 nm range while the starting Soret disappears. UV−vis measurements on a *n*-hexane $1.0 \cdot 10^{-5}$ solution of the 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine, that does not contain phenyl substituents in the meso positions, show no changes in the optical spectrum upon NO_2 interaction. It emerges that aromatic substituents in the meso positions play a crucial role in determining the optical sensing properties.

Introduction

The appeal of reversible gas detection at low concentration levels has become fundamental in the perspective of fabrication of highly sensitive gas sensors for environment monitoring.[1]

There is an increasing technological interest in the synthesis of hybrid inorganic/organic nanomaterials by covalent bonding of organic molecules on suitable inorganic surfaces in the perspective of fabrication of devices showing specific molecular properties.[2−6]

In this context, the 5,10,15-tri-(*p*-dodecanoxyphenyl)-20-(*p*-hydroxyphenyl) porphyrin[7a,b] (Figure 1) shows a good affinity toward NO_2[6] and suitable steric hindrance[8] for a very efficient optical gas-sensor. In addition, selectivity is important as well as sensitivity in gas sensing. Therefore, there is enough motivation for an extensive investigation on the optical recognition behavior of gas analytes by a covalently self-assembled monolayer of this porphyrin on silica substrates. Moreover, the origin of optical NO_2-sensing properties of porphyrins has been investigated.

Experimental Details

Aldrich grade reagents and solvents, packed under nitrogen, were used throughout all present syntheses. The sodium salt of the 5,10,15-tri-(*p*-dodecanoxyphenyl)-20-(*p*-hydroxyphenyl) porphyrin (H_2TPP3R) was synthesized and characterized as already reported.[6,7a,b]

Fused silica (quartz) substrates were cleaned by immersion in “piranha” solution (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.[6,9] Subsequently, substrates were repeatedly rinsed with double distilled water and immersed in an H_2O/30% H_2O_2/NH_3 5:1:1 v/v/v mixture at room temperature for 40 min. Then, they were washed with double distilled water and dried under vacuum immediately before coupling agent deposition. All the successive sample manipulations were performed

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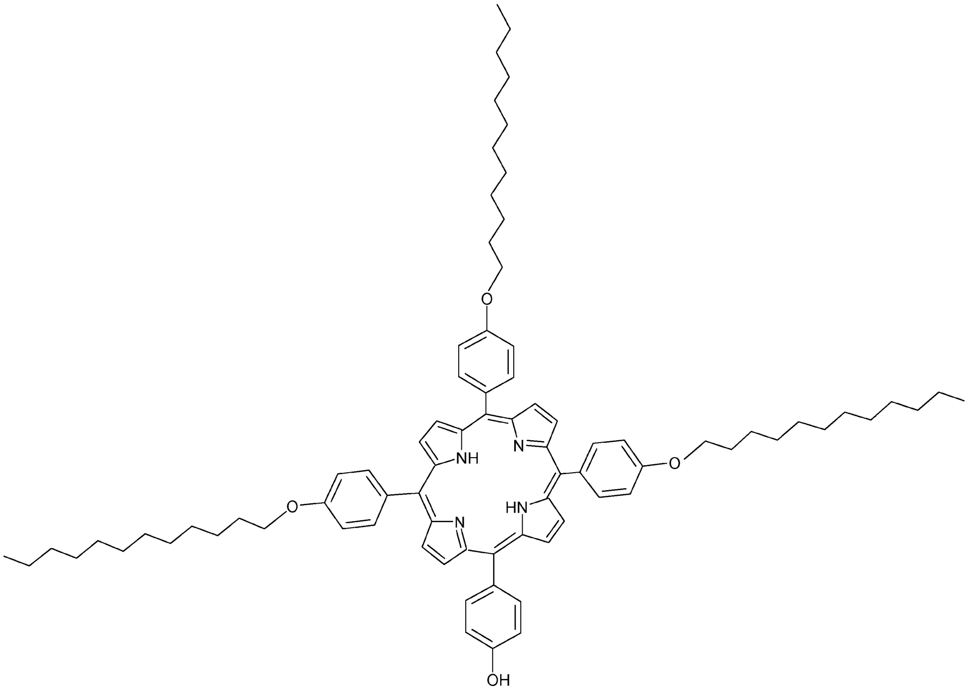

Figure 1. Schematic drawing of the 5,10,15-tri-(*p*-dodecanoxyphenyl)-20-(*p*-hydroxyphenyl) porphyrin (H_2TPP3R).

in a glovebox under N_2 atmosphere. In particular, freshly cleaned substrates were immersed, at room temperature for 30 min, in a 1:100 (v/v) *n*-heptane solution of the chemisorptive siloxane, trichloro[4-(chloromethyl)phenyl]silane, 4-$ClCH_2C_6H_4SiCl_3$, to afford a monolayer of the coupling agent (CA). Then, they were washed with copious amounts of pentane, sonicated in acetone for 1 min to remove any physisorbed CA, immersed in a $5 \cdot 10^{-4}$ M dimethylformamide (DMF) solution of the porphyrin sodium salt and heated to 80 °C under stirring for 48 h. Finally, the substrates bearing the covalently self-assembled porphyrin molecules (P−SAM) were cooled to room temperature and repeatedly washed with DMF to remove any residual unreacted porphyrin.

Angle-resolved X-ray photoelectron spectra (AR-XPS) were made at different takeoff angles (45°, 10°, 3°) with a PHI 5600 Multi Technique System (base pressure of the main chamber $2 \cdot 10^{-10}$ Torr). A freshly prepared P−SAM was quickly transferred from the glovebox under N_2 atmosphere to the XPS main chamber. Resolution, corrections for satellite contributions, procedures to account for steady-state charging effects, and background removal have already been described elsewhere.[10] Experimental uncertainty in binding energies lies within ± 0.45 eV.

UV−visible measurements were performed using a UV−Vis-1601 Shimadzu spectrophotometer. Hexane solution spectra were carried out using 0.1-cm quartz cuvettes. UV−vis scans (in the 400−500 nm range, scan frequency = 4 s, scan rate 50 nm/sec) were performed on the P−SAM during an in situ continuous leaking of 1 ppm NO_2 in a N_2 gas stream (flow rate =100 sccm). Experimental uncertainty in the P−SAM spectra lies within ± 1 nm.

Both static and dynamic contact angle (ϑ) measurements were performed at room temperature in air with a Kernco goniometer. Water drops (2 μL) were applied on the sample surface and measurements of ϑ were made on both sides of the two-dimensional projection of the droplet. Five different measurements were performed on different surface portions of every substrate in order to have statistically reliable results. Both advancing and receding procedures were adopted.

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(8) (a) 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 bound to the remaining peripheral positions of the porphyrin, could prevent the well-known aggregation due to stacking interactions; (b) Micali, N.; Villari, V.; Mineo, P.; Vitalini, D.; Scamporrino, E.; Crupi, V.; Majolino, D.; Migliardo, P.; Venuti, V. *J. Phys.l Chem. B* **2003**, *107*, 5095.

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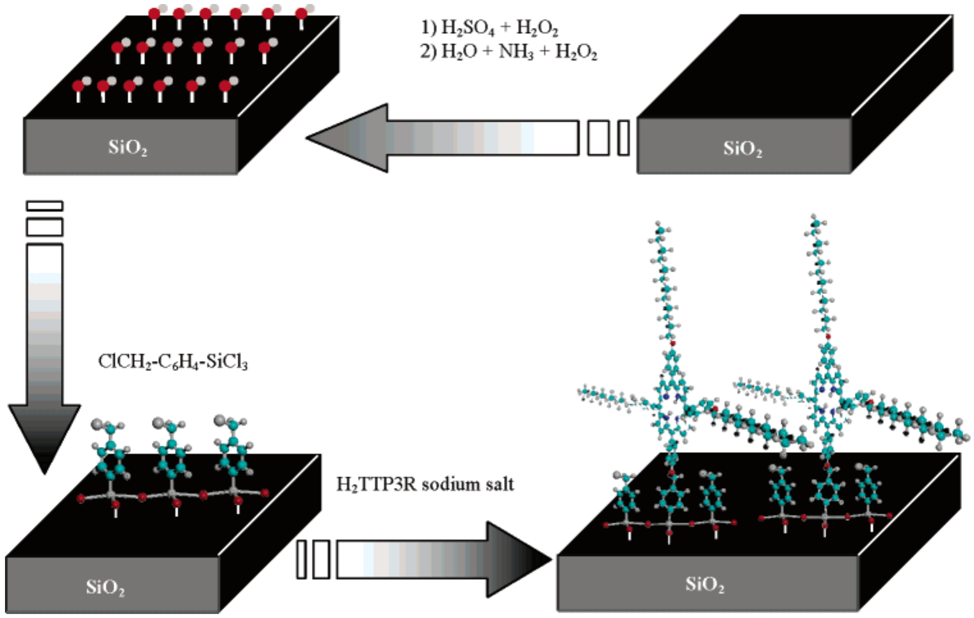
Scheme 1



Results and Discussion

The porphyrin self-assembled monolayer on silica substrates (P–SAM) was prepared by three successive steps according to Scheme 1: (*i*) Silica surfaces were first cleaned and hydroxylated; (*ii*) then, under rigorously inert atmosphere, were treated with the chemisorptive siloxane to afford a monolayer of the coupling agent; (*iii*) the porphyrin was covalently linked to the silylated substrates.[6,9]

The modification of the substrate surfaces, after every reaction step, was monitored by water contact angle (ϑ) measurements. The starting uncoupled silica substrates showed a $\vartheta = 10°$ mean value. After cleaning (step *i*) the ϑ values decreased to 5°, due to the hydroxylated silica surfaces.[6,9] The static contact angle changed from 5 to 79° (maximum dynamic advancing angle = 88° and minimum dynamic receding angle = 60°), after treatment with the CA (step *ii*), according with the presence of densely packed benzylic chloride surfaces.[6,9] Finally, after step (iii), ϑ showed the expected reduction of the hydrophobic character falling to 62° (maximum dynamic advancing angle = 65° and minimum dynamic receding angle = 56°), upon the porphyrin linkage.

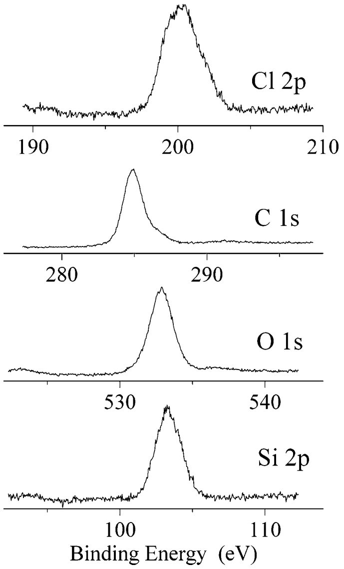


Figure 2. Al Kα excited XPS of silica substrates after the coupling agent deposition, step (*ii*), in the C 1s, Cl 2p, Si 2p, and O 1s energy regions. Structures due to satellite radiation have been subtracted from the spectra.

Figure 2 shows XP spectra of silica substrates after the CA deposition (step (*ii*), Scheme 1). The C 1s peak and unresolved Cl 2p doublet are at 284.9 and 200.3 eV binding energies, respectively. Their intensities, making due allowance for the relevant atomic sensitivity factors,[11] exactly match the theoretical C/Cl atomic concentration ratio (7:1) (C = 49.4% and Cl = 7.2%). This result is tuned well with a complete cross-linking of the siloxane moieties on the silica surfaces. Moreover, the C 1s peak shows a shoulder at higher binding energy 286.3 eV, the intensity of which is about $^1/_6$ that of the main peak. This observation is nicely tuned with the theoretical C benzylic/C aromatic functionalities ratio (1:6). Both Si 2p at 103.3 eV and O 1s at 533.0 eV peaks show symmetric shapes, thus precluding any further speculation.

Nitrogen 1s AR-XP spectra (Figure 3) of the P–SAM show a broad peak at 399.7 that accounts for the nitrogen in the free porphyrin.[12] The nitrogen atomic concentration also shows a monotonic increase upon decreasing the electron takeoff angle from 0.73% (at 45°), 0.95% (at 10°) to 1.54% (at 3°), as expected for the upper layer nature of the signal.

Both UV–visible spectra of the P–SAM (Figure 4a) and of the porphyrin *n*-hexane $5 \cdot 10^{-6}$ M solution (reported for comparison in Figure 4b) show a characteristic sharp Soret band at 424 (P–SAM) and 421 nm (hexane solution) and satellite Q-bands in the 500–650 nm range. The calculated[5f] number of porphyrin molecules/cm^2 of the P–SAM is $1.1 \cdot 10^{13}$.

In situ continuous leaking of NO_2 (1 ppm) in N_2 (flow rate =100 sccm) on the P–SAM causes the progressive

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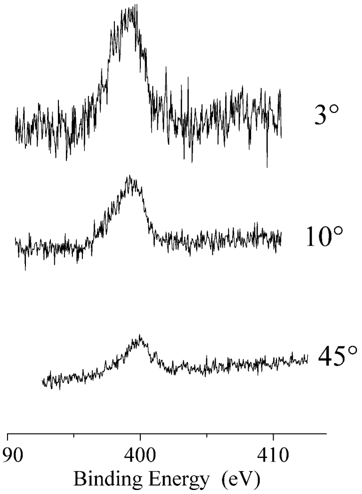

Figure 3. Al Kα excited AR-XPS of a P−SAM on a silica surface measured in the N 1s energy region, at different electron takeoff angles (45°, 10°, 3°). Structures due to satellite radiation have been subtracted from the spectra.

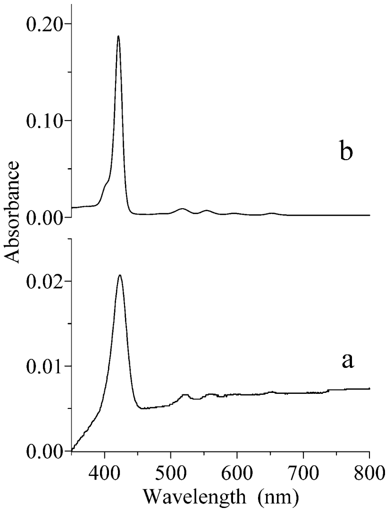

Figure 4. UV-vis spectra: (a) P−SAM; (b) H_2TPP3R *n*-hexane solution.

disappearance of the Soret band at 424 nm which parallels the growth of a new band at 458 nm (Figure 5a). The half-life time of the Soret is 4 s (t_{50} in Figure 5a). This t_{50} value safely represents the response speed of the present P−SAM.[4,5a−b,d] As noticed previously,[6] 180 s exposure results in a spectrum dominated by the new band at 458 nm (t_f in Figure 5a) that remains unchanged for many days. Short heating (4 s) at 80 °C under N_2 gas stream recovers about 33% of the Soret band (closed circles in Figure 5a) that is almost fully recovered in 60 s (t_r closed triangles in Figure 5a). This behavior is similar to that already observed in the porphyrin solution (Figure 5b) and can be rationalized in terms of Lewis acid−base interaction.[6] In fact, porphyrins are electron-rich systems and NO_2 is a fairly strong oxidizing agent.

Figure 5c shows the time dependence of the Soret and new (at 458 nm) band intensities upon switching the 1 ppm NO_2 in a N_2 gas stream. There is evidence of a direct (new band) and inverse (Soret) dependence of band intensities versus the time of NO_2 exposure. Moreover, the system shows a reliable reversibility tested by alternating five cycles of NO_2 exposure and recovery in N_2 under heating.

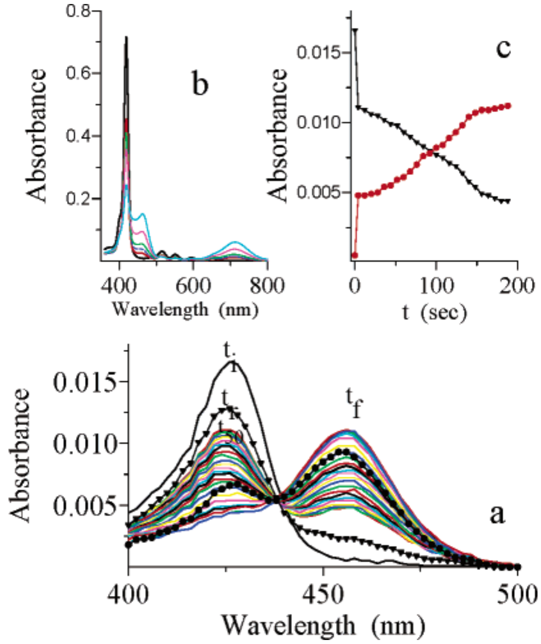

Figure 5. (a) UV−vis spectra of the P−SAM at the initial time (t_i); during the in situ continuous leaking of 1 ppm NO_2 in a N_2 gas stream (t_{50} and t_f), and after the recovering of the Soret band (t_r). (b) Selected UV−vis spectra of a *n*-hexane $1.5 \cdot 10^{-5}$ M H_2TPP3R solution after 120, 150, 210, 270, 330 s bubbling of 10 ppm NO_2 in a N_2 gas stream (flow rates = 200 sccm). This behavior indicates an intensity decrease of both Soret and Q-bands and an increase of two additional bands at 462 and 714 nm. The original absorbance spectrum was recovered by removing the solvent and subsequent redissolution of H_2TPP3R. (c) Exposure time (sec) dependence of the Soret P−SAM and new (at 458 nm) band intensities upon switching the NO_2 (1 ppm)/N_2 gas stream.

One of the major drawbacks when gas sensors are used for environment monitoring is represented by the eventual interaction of the investigated gas analyte with air humidity.

To test the influence of humidity on the behavior of the P−SAM, a similar experiment (cycles of 50 fast UV−vis scans in the 400−500 nm range) was carried out using the same 1 ppm NO_2/N_2 gas stream, saturated, in this case, with H_2O vapors allowing the nitrogen to bubble within H_2O. Inspection of Figure 6 shows that, similarly to the previous case, the Soret band at 424 nm progressively disappears, whereas two additional bands at 448 and 463 nm grow upon NO_2 exposure. In this case, the Soret band intensity takes 72 s to fall to 50% with respect to its final saturated value (t_{50} in Figure 6). After an exposure of 92 s, the spectrum is fully dominated by the new band at 463 nm (t_{100} in Figure 6). Already reported measurements on multilayer films show residual Soret signals due to inner porphyrin layers not interacting with NO_2 molecules.[4] Presently, we have observed a significant broadening of the new band at 463 nm because of the overlap with the 448 nm band upon $NO_2/N_2/H_2O$ exposure. This response may be due to a competitive porphyrin protonation, (due to acid vapors, $H_2O + 2NO_2 = HNO_2 + HNO_3$), that also causes a red shift of the Soret band. To better rationalize this behavior, we performed further UV−vis spectra of porphyrin solutions in different conditions. Figure 7a shows the UV−vis spectrum of an aqueous $2 \cdot 10^{-5}$ M solution of the similar, water soluble, 5,10,15,20-tetrakis{*p*-[*ω*-methoxy-poly(oxyethylene)]phenyl}-porphyrin at pH = 3.5. In addition to the Soret, there is a new band at 448 nm that unambiguously is due to the portion

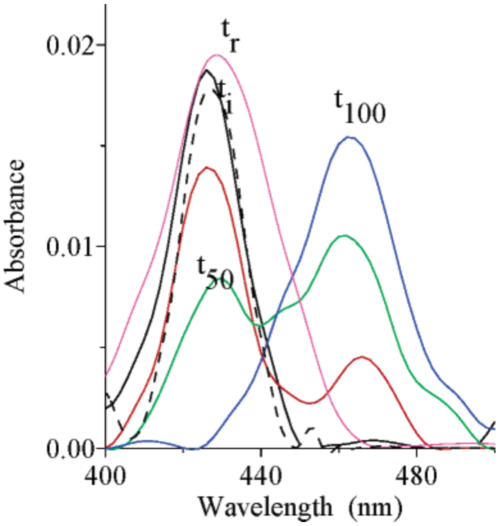

Figure 6. UV-vis spectra of the P−SAM at the initial time (t_i solid line); during the in situ continuous leaking of 1 ppm NO_2 in a N_2 gas stream saturated with H_2O vapors (t_{50} and t_{100}); after the partial recovering (t_r) and total recovering (t_i dashed line) of the Soret band.

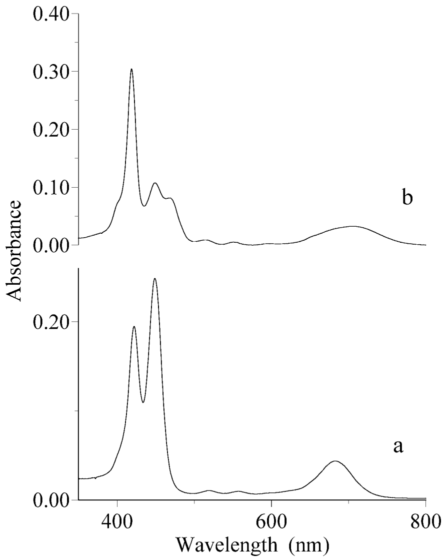

Figure 7. (a) UV−vis spectrum of an aqueous $2 \cdot 10^{-5}$ M solution of the water soluble, 5,10,15,20-tetrakis{*p*-[*ω*-methoxy-poly(oxyethylene)]phenyl}-porphyrin at pH = 3.5; (b) UV−vis spectrum of the $1.5 \cdot 10^{-5}$ M *n*-hexane solution of the 5,10,15,20-tetrakis-(*p*-dodecanoxyphenyl) porphyrin after 5 s leaking of NO_2 (5 ppm) in N_2 followed by 5 s of CH_3COOH in N_2 vapors.

of protonated porphyrin.[7c] Moreover, Figure 7b shows a $1.5 \cdot 10^{-5}$ M *n*-hexane solution of the 5,10,15,20-tetrakis-(*p*-dodecanoxyphenyl) porphyrin after 5 s leaking of NO_2 (5 ppm) in N_2 followed by 5 s of CH_3COOH vapors in N_2. Three bands are evident: the initial Soret at 418 nm, the additional band at 448 nm, already present in the porphyrin water solution at pH = 3.5 and, finally, the band due to the NO_2 interaction at 467 nm.

Therefore, we are confident that the concomitant observation of these two bands, in UV−vis spectra of the P−SAM under (1 ppm) $NO_2/N_2/H_2O$ gas stream, are due to the copresence of the protonated porphyrin (new band at 448 nm), not suited for interaction with NO_2, and of the oxidized porphyrin that has interacted with NO_2 molecules.

The present study does not really concern kinetic measurements. Nevertheless, on a qualitative basis, we note that the observed t_{50} = 72 s value (larger than 4 s observed in the case of anhydrous NO_2) and t_{100} = 92 s value (shorter than 180 s in the case of anhydrous NO_2) are due to the competing interaction of both NO_2 and acid vapors with the P−SAM. It can be noticed that the heating at 80 °C under N_2 gas stream partially recovers the Soret band that, however, remains really broad (t_r in Figure 6) even after prolonged heating. This behavior is the consequence of the fact that the heating procedure at 80 °C removes the interacted NO_2 molecules but is not capable of restoring the starting unprotonated porphyrin. The initial shape of the Soret band was almost recovered upon heating at 80 °C under vacuum (dashed line in Figure 6).

Alternating cycles of $NO_2/N_2/H_2O$ exposure and recovery in N_2 under heating without vacuum increase the portion of protonated porphyrin (not available to interact with NO_2), thus hampering the performances, and the band at 448 nm dominates the spectrum. By contrast, the heating treatment under vacuum after every cycle fully recovers the starting porphyrin UV−vis spectrum.

Previously reported studies concerning gas-sensing of porphyrin-based materials have also been aimed to test their ability to detect other chemical species as NH_3, C_2H_5OH, CO, CH_4, NO_2/air, Cl_2, HCl, O_2, 2-propanol, triethylamine, limonene, cyclohexene, 1,2-diaminocyclohexane, and so on.[3c,d,f,4h,i,l,5b,d]

Therefore, the selectivity of the present P−SAM was tested by further UV−vis measurement using CO/N_2, CH_4/N_2, and H_2/N_2 gas streams at different concentrations, starting from a few ppm to pure CO, CH_4, and H_2. In all these cases, no optical evidences have been detected and the spectrum remains unchanged. Therefore, analogous measurements were performed using $CO/NO_2/N_2$, $CH_4/NO_2/N_2$, and $H_2/NO_2/N_2$ gas streams (NO_2 =1 ppm; CO, CH_4, and H_2 in the 10−100 ppm range). Results are similar to those obtained using NO_2 (1 ppm) in N_2. Similarly, the presence of $CHCl_3$, C_2H_5OH, CH_3OH, pyridine (Pyr), THF, triethylamine (TEA), and DMF pure vapors only moves the Soret band at 423, 419, 419, 426, 421, 421, and 423 nm, respectively (Figure 8a).

Moreover, NH_3 vapors do not significantly affect the optical spectrum of the P−SAM that remains almost unchanged. By contrast, the presence of HCl vapors instantaneously results in a rather broad band extending over the entire 440−500 nm range (Figure 8b). This experiment was followed by reaction with dry NO_2. Unfortunately, HCl vapors caused complete protonation of the porphyrin and no further evidence of NO_2 interaction was observed in the spectrum. This behavior was not unexpected. In fact, in a simple localized bonding model, the porphyrin·NO_2 adduct can be depicted as an interaction involving unprotonated porphyrin nitrogens with oxygens of NO_2. Since HCl vapors instantaneously cause complete pronotation of porphyrin nitrogens no further interactions are possible with NO_2.

Finally, we analyzed already reported experimental data regarding optical sensing properties of porphyrin-based materials and observed that in all cases the adopted porphyrin molecules contain phenyl groups in the meso positions.[4,5] Therefore, we performed identical UV−vis measurements on an *n*-hexane $1.0 \cdot 10^{-5}$ solution of the 2,3,7,8,12,13,17,18-

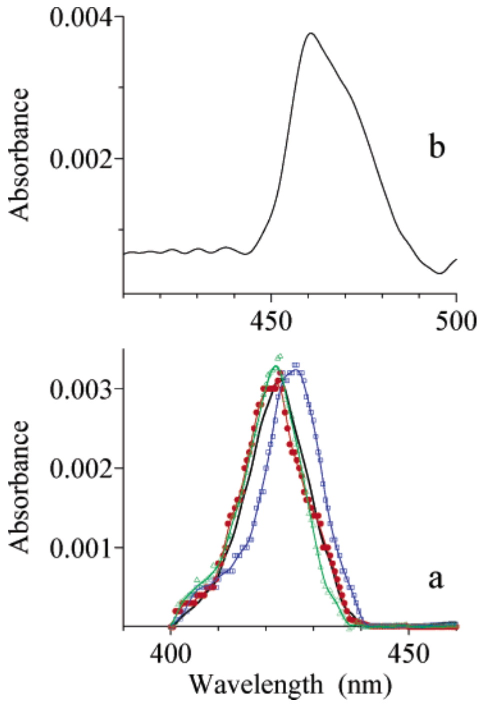

Figure 8. Selected UV−vis spectra of the starting P−SAM (solid line) and in the presence of the following pure vapors: (a) C_2H_5OH (closed circles), Pyr (open squares), and THF (open triangles); (b) HCl vapors.

octaethyl-21H,23H-porphine (Aldrich reagent), that does not contain any substituent in the meso positions. In particular, UV−vis scans were recorded after 0, 5, 20, 120, 180, 240, and 300 s bubbling of 10 ppm NO_2 in a N_2 gas stream (flow rates = 200 sccm). No changes in the optical spectra were observed, thus indicating that aromatic substituents in the meso positions play a crucial role in determining the Soret energy shift upon NO_2 interaction. It could be the case that interaction of NO_2 with the nitrogen core of meso-substituted porphyrins brings about a porphyrin geometrical distortion that modifies the phenyl participation to the aromatic porphyrin ring and, therefore, the relative positions of the uppermost energy levels thus causing energy shifts of the Soret band. This behavior agree well with results of time-dependent density function theory, TDDFT, calculations which show that some geometrical distortions, by themselves, do not induce any energy shift in the electronic absorption spectra, therefore, in the singlet B (Soret) states, of “simple” porphyrin ($(P)H_2$).[13]

Conclusions

In conclusion, the assembled porphyrin monolayer is highly sensitive to 1 ppm of NO_2, and, therefore, represents a well-suited fast and reversible optical NO_2 recognizer. The presence of both NO_2 and humidity causes an overlap between three bands at 424, 448, and 463 nm corresponding to the Soret of the starting, protonated, and NO_2-oxidized porphyrin molecules, respectively. In this case, heating at 80 °C under vacuum recovers the starting porphyrin spectrum. The presence of CO, CH_4, H_2, and NH_3 does not influence the optical spectrum of the P−SAM whereas some common solvents slowly affect the position of the Soret band. The presence of HCl vapors heavily modifies the optical spectrum that shows a broad band in the 440−500 nm range. UV−vis measurements performed on a solution of a porphyrin that does not contain any substituent in the meso positions show no changes in the optical spectrum upon NO_2 interaction. From this behavior and from the analysis of other experimental literature data, we observe that aromatic substituents in the meso positions play a crucial role in determining the Soret energy shift upon NO_2 interaction. To the best of our knowledge, this observation was not already reported.

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