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Sol−Gel Hybrid Silica Thin Films Doped with 2-(5-Amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide as Optical Chemical Sensors

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The metal(II) coordinating anion 2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide ($C_{11}N_7H_2^-$, L′, $\lambda_{\max} = 549$ nm, $\epsilon_{\max} = 35\,000$ M^{-1} cm^{-1}) has been incorporated as dispersed monomer at a fairly high concentration ($c \approx 0.06$ M) in a thin film (thickness < 1 μm) of a two-component (poly(methyl methacrylate)/SiO_2) glass. L′ in the film reacts specifically with Hg^{2+}, as mercury(II) acetate, in water, forming the corresponding monochelated pyrrolizinato complex, >HgL ($\lambda_{\max} = 670$ nm). A color change from violet to blue occurs along with this transformation. The >HgL-doped film releases L′ in the matrix after interaction with small molecules, such as CN^- in water or NH_3 in the gas phase, generating the associated reversal color change to violet. These systems have been investigated for future adaptation as optical chemical sensors.

Introduction

The title anion (L′), which some of us synthesized for the first time,[1] is a planar, intensely colored molecule ($\lambda_{\max} = 549$ nm, $\epsilon_{\max} = 35\,000$ M^{-1} cm^{-1}), very soluble and stable as the sodium salt both in water and in oxygenated organic solvents.[2] Interestingly, after interaction with a variety of transition-metal(II) cations, M (M = Fe,[3c] Co,[3c], Ni,[3b] Cu,[3a,d] Zn,[3f] Pd,[3e,g] Hg[3h]), it isomerizes rapidly and quantitatively to the pyrrolizinide anion (L) affording the corresponding bischelated (ML_2) or monochelated (>ML) metal complexes, depending on M and/or the reaction conditions (Scheme 1).

A color change from violet to blue or blue-green, varying M ($\lambda_{\max} = 623$ or 732 nm, for Fe or Pd, respectively) occurs along with this transformation. In addition, the reaction can be quantitatively reversed in solution, simply by adding a M-coordinating donor ligand (S) stronger than L (e.g., S = CN^-, NH_3), so that L is displaced from M as a consequence of the formation of [MS] and, since it is not stable as metal-free anion,[3] promptly isomerizes to L′ generating the reversal color change to violet. Following these observations, the system may be considered as a novel photometric reagent for the construction of optical chemical sensors, provided that it is incorporated into a suitable matrix, either as L′ for sensing free metal cations in water or as >ML (or ML_2) for sensing donor ligand (S) stronger than L, in both water and air. It is widely recognized that the sol−gel porous glass is the almost ideal material for such a matrix. The feasibility of this support was demonstrated by Avnir and co-workers, who were the first to prepare and to study dye-doped sol−gel inorganic oxide glasses.[4] The list of organic doped sol gels for detection purposes has been constantly expanding during the past 5 years, ranging from monoliths[5] to thin films[6] for sensing metal cations,[5c,g,j,6a] H^+,[5d,j,6a,e,g] anions,[5e,j,6c] neutral species,[5f,i,j,6b,d] O_2,[5b] CO,[5e] NO[5e] in water and CO,[5h,6f] O_2,[5h] NH_3[5l,6h] in the gas phase. It

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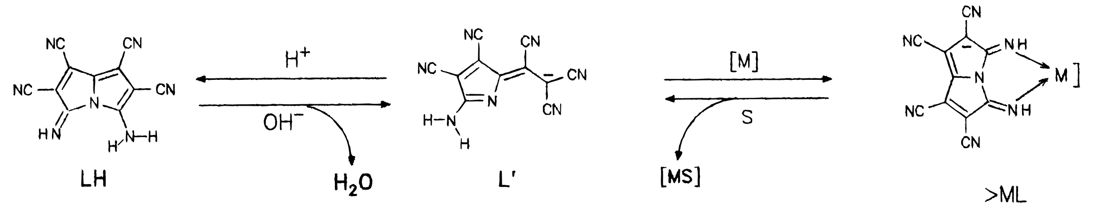
Scheme 1



must be emphasized that the thin film would be the most desirable configuration for the sensor matrix, whenever the dye to be incorporated is very soluble in the matrix material without being leached out of it by water. Then, a fast response time coupled with a high sensitivity for the sensor are attained even when it will be used in aqueous solutions. We therefore sought to incorporate L′ into a sol–gel silica thin film in order to fully exploit its eventual sensing properties. According to the literature information,[7] we polymerized the tetraethyl orthosilicate (TEOS) in a H_2O/HCl/EtOH/NaL′ solution under carefully controlled pH to avoid the formation of LH after protonation of L′ (Scheme 1), which would cause a phase separation being LH completely insoluble in water.[8] We partially succeeded in the objective: L′ was incorporated in the silica network, but soon after the film deposition, it started to fade ending colorless within a few hours. The reason for this lies in the reduced stability of L′ toward the EtOH/H_2O/HCl mixture, impregnating the sol–gel film, as it can be proved with control experiments in homogeneous solution. In fact, L′, while indefinitely stable in EtOH/H_2O under neutral conditions, decomposes and discolors over time (hours) at pH as low as 2.4. Probably, the acid-catalyzed ethanolysis of the −CN groups occurs, according to the well-known behavior of polycyano aromatic compounds in acidic ethanol.[9] At this point, in order to select a hosting matrix where L′ is stable enough, we discarded pure silica for the reasons discussed above and turned to organic hybrid silica matrixes of class I.[10] Among the many matrixes of this type described in the literature, PMMA/SiO_2 (PMMA = poly(methyl methacrylate)) was found to be suitable for our purposes. Thus, as reported in the current paper, L′ could be incorporated into a PMMA/SiO_2 matrix; it is stable in the matrix and reacts selectively with Hg^{2+} in water, forming a monochelated mercury complex [>HgL]. The >HgL-doped film can be used for sensing outer species such as CN^- in water or NH_3 in air.

Experimental Section

Instrumentation. Optical spectra were recorded on a Cary 5 and IR spectra on a Digilab 40A FT-IR spectrometer. Fluorescence spectra of the films were measured using a Perkin-Elmer MPF-44B instrument; the glass slide supporting the film was oriented around 45° with respect to the exciting and the monitored beams, to avoid reflection of the exciting light into the slit of the monochromator. XPS measurements were carried out on a VG ESCALAB MK II spectrometer located at the Servizio ESCA del CNR, Area della Ricerca di Roma; the binding energies (eV), $4d_{5/2}$ for Hg^{2+} (360.6) and $2p_{3/2}$ for Cu^{2+} (932.9), were referenced to the C_{1s} pump-oil hydrocarbon peak (285.0); the atomic ratios were evaluated according to the procedure proposed by Wagner.[11] Scanning electron microscopy (SEM) images, with a 2×10^4 magnification, were recorded on a JEOL SM6100 instrument at 20 kV. Atomic force microscope (AFM) images were taken in contact mode with a Digital Instrument (typical forces, 10^{-8}–10^{-9} N; cantilever and H_p in silicon nitride). The N_2 adsorption isotherm, on the powdered gel obtained from the same precursor solution used for depositing the L′-doped films, was obtained in the volumetric mode using a homemade glass line. A homemade dip-coating apparatus, based on a scheme kindly supplied by Montenero (Chemistry Department, University of Parma), was used. Film thicknesses were measured by an Alpha-Step 2000 stylus profilometer of Tencor Instruments with a resolution of ±100 Å.

Materials. NaL′·$x$$H_2O$ was prepared after lyophilization of a water solution obtained on metathesis of $As(C_6H_5)_4$·L′ with $B(C_6H_5)_4$·Na according to our procedure.[1b] TEOS (98%) and PMMA (powder; M_w 101 000; d 1.20) were from Aldrich. Tetrahydrofuran (THF) was dried and freshly distilled before use. Mercury acetate, $HgAc_2$, was crystallized from THF.

Preparation of Doped Thin Films. A PMMA/TEOS/HCl/THF stock solution was prepared according to the work of Landry et al.[12b] by mixing PMMA (4.4 g), TEOS (7.2 mL), and HCl (0.15 M, 2.2 mL) in THF (55 mL). After stirring for 12 h, the dye-doped solution (deep violet) was prepared by adding the appropriate amount of NaL′ (M_W 255.2) to a known volume of the stock solution so as to attain the required molarity (C_i) in the coating solution, PMMA/TEOS/HCl/THF/NaL′, which was immediately used for dip-coating. Precleaned (washed with detergent in an ultrasonic bath, then with chromic acid, rinsed with distilled water, and dried) microscope slides (5 mm × 30 mm) were used as support. The withdrawal rate was 0.5 cm/s. The samples were left in air for 3 h at room temperature and then equilibrated in a KOH aqueous solution (pH 8.0) for about 1 h, until their absorbance stopped increasing or fluorescence disappeared.

Film Thickness Measurements. The reported values are the average thickness obtained on three measurements made on different points ≈1.5 mm away from the drying front of the dip-coated film. In this zone the thickness was constant within 10%. In a more central zone of the film, the uniformity degree of thickness was tested by reflectivity measurements in the visible region (on an L′-free film dip-coated on silicon); from the interference patterns the variation of the thickness was estimated to be within 3%; the average refractive index (1.50) of the film was also calculated.

Determination of Absolute Concentration of L′ in the Film. The central vertical part (1.67×2.00 cm^2) of an L′-doped film (thickness 1.515 μm, C_i 4.6×10^{-3}), resulting from cutting off the edges that showed small irregular zones, was dissolved in dimethylformammide (DMF, 5 mL). The measured absorbance was compared with that of a standard

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solution (a DMF solution of an authentic sample of NaL′ at a comparable concentration). The concentration of L′ in the film (moles of L′ per liter of coating) was calculated. It was 4.5×10^{-2} M.

Optical Spectra Measurements. The glass slide supporting the film was inserted vertically across the light beam into a 10-mm square quartz cuvette, containing a water solution (3 mL) of the analyte ($HgAc_2$ or $CuCl_2$ or KCN); the experiment with NH_3 in the gas phase was carried out similarly but with the placement of a few drops of the aqueous ammonia solution on the inside bottom of the stoppered cuvette, without bathing the film. The NH_3 concentration (M) in the gas phase was calculated from a graphic extrapolation of the appropriate tabulated constants of aqueous ammonia solutions.[13] In all the experiments an uncoated glass slide was placed in the reference compartment; the absorbances were measured relatively to the baseline absorbance at 800 nm. For the construction of the CN^- calibration curve, five >HgL-doped films were prepared under identical conditions from the same batch.

IR Measurements. The transmission IR spectrum of L′ in $PMMA/SiO_2$ films, dip-coated on a silicon slide (0.5 mm thick and "mirrorlike" polished sides both), was obtained from the ratio of the spectrum of the sample and a reference, i.e. NaL′/$PMMA/SiO_2$ and $PMMA/SiO_2$ film, respectively, as described previously.[14]

Results and Discussion

Incorporation of L′ into a $PMMA/SiO_2$ Matrix. After the initial unsuccessful efforts to incorporate L′ into pure silica for the reasons explained above, we tried a two-component hybrid glass, $PMMA/SiO_2$, as the hosting matrix. This material, when properly prepared,[12] is suitable for our purposes, being as transparent as SiO_2, and able to impart a satisfactory stability to L′. Landry et al.[12b] claimed to obtain optically clear homogeneous thick films (thickness $\approx$ 100 μm) by horizontal coating TEOS/PMMA/HCl/THF solutions on a Kapton support at 30 °C temperature. The reported preparation gave us also good-quality L′-doped thin films (thickness < 1 μm) by dip coating on a glass support after a minor modification of the selected recipy (PMMA-53A-30)[12b] consisting in using a larger TEOS/PMMA molar ratio than the one given, in order to improve the adhesion of the film to the support. The films were hard and of high clarity; their SEM images show homogeneous, uniform, and crack-free surfaces (Figure 4A). The use of THF as cosolvent was of primary importance to the successful preparation of homogeneous films: both NaL′ and HL,[8] which eventually is formed after protonation of L′, are very soluble in this solvent, so that no phase separation occurs during the formation of the film even without controlling the pH. NaL′ was added to the starting solution in the required amount (6×10^{-3} M) to give the maximum possible concentration as dispersed monomers in the resultant film (0.06 M). Thus, the concentration of L′ in the film is 10-fold higher than in the coating solution. Correspondingly, the volume reduces about 90% on film formation, in agreement with the estimated volume percentage of volatiles removed (93%, if the polymerization of TEOS were complete). A withdrawal rate of the dip-coating was chosen such as to give a film of optical density about 0.25 from a single dip of a freshly prepared coating solution 0.006 M in L′ or of 0.6−0.7 μm thickness. The film was then air dried (for 3 h at room temperature after deposition) with the result it is selectively permeable to metal cations in water without releasing L′ out of the matrix. The final film contains a significant amount of LH formed after protonation of L′. LH is easily identified and discriminated from L′ because it is fluorescent ($\lambda_{em} = 640$ nm, $\lambda_{ex} = 480$ nm) like in dilute THF solution, while L′ is not fluorescent at all.[8] Moreover, the presence of a certain amount of LH in the matrix causes a broadening and an overall intensity reduction of the visible optical band of the film. Conversely, such band would be significantly narrower and more intense, since the absorption maximum of LH is red-shifted with an associated low extinction coefficient in comparison to that of L′ (LH: $\lambda_{max} = 580$ nm, $\epsilon_{max} = 20\,000$ M^{-1} cm^{-1}).[8] To overcome this problem, at last the film was soaked in a buffered aqueous solution (pH 8.0) until the fluorescence disappeared and the absorption band increased and reached a steady profile, indicating the occurred quantitative transformation: $LH + OH^- \rightarrow L'$ (Scheme 1). Finally it was of interest to ascertain whether L′ is incorporated into the matrix completely as discrete molecules or partly aggregated. In this regard we recall that L′ shows some propensity to self-aggregate through intermolecular hydrogen bonding between the amino hydrogen on one hand and the nitrile nitrogen atoms on the other. In fact, even if it is monomer in water solution, from molecular weight measurements[2] at a concentration as high as 10^{-2} M, and follows Beer's law down to 10^{-5} M, in the solid state as tetraphenylarsonium salt, it gives rise to segregated anion stacks or anion dimers depending on the extension of the intermolecular hydrogen-bonding network.[1c] In the present case we infer that discrete noninteracting L′ anions are embedded into the matrix on the basis of the following observations. The molar extinction coefficient of L′ in the matrix (ϵ') vs wavelength has been calculated after normalizing the optical spectrum of an L′-doped film to the concentration of L′ in this film and to its thickness. On comparison of ϵ' with the corresponding value of L′ in water solution (ϵ, $C = 0.5 \times 10^{-3}$ M) a very close resemblance results (Figure 1), and therefore L′ is in the same situation in the two media, that is a noninteracting monomer. Incidentally we note that the maximum of ϵ' is slightly red-shifted (6 nm) compared to ϵ, indicating the slightly less polar nature of the hybrid silica with respect to water. Further support to the existence of L′ in the matrix as dispersed monomer comes from the evidence that Beer's law holds in this phase, ruling out any aggregation equilibrium for L′. Three different films were prepared from coating solutions with different L′ concentrations (C_i); the thickness (s) and maximum absorbance (A) of each film were measured. The data reported in Table 1 show that the absorbance ratios are equal to the ones of the corresponding products sC_i within a deviation (maximum 7%, between samples 1 and 2) lower than the thickness approximation (10%, see Experimental Section). More importantly, L′ is not leached out of the film by water since the absorbance of the L′-doped film remained constant when immersed in water even for long times.

Structural Characterization of the Film. In view of the utilization of the L′-doped film (**A**) and others

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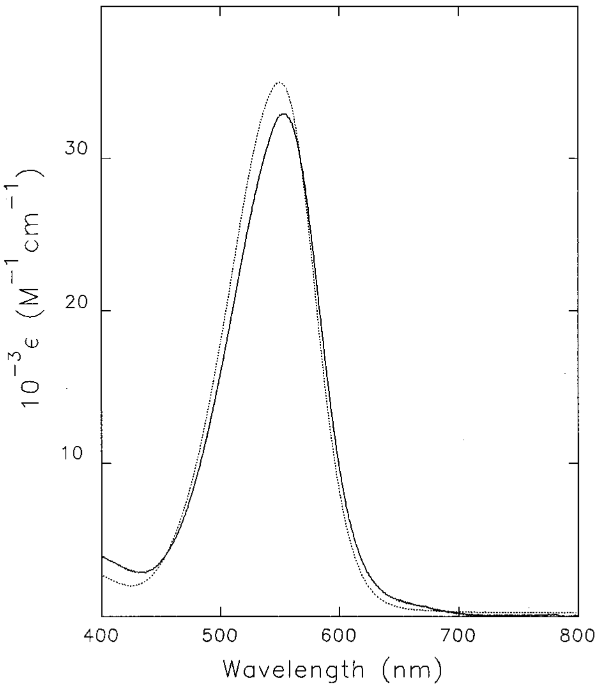

Figure 1. Optical spectra of NaL′ in a PMMA/SiO$_2$ film (—) and in water (- - -).

Table 1. Thickness (*S*),[a] Absorbance (*A*),[b] and Film Solution Concentration (*C*$_i$) of Dip-Coated L′-Doped Films

sample	*S* (μm)	*A*	*C*$_i$ (M)
1	0.72	0.314	0.006
2	0.80	0.270	0.005
3	0.99	0.270	0.004

[a] Average value; mean deviation, 10%. [b] At 555 nm.

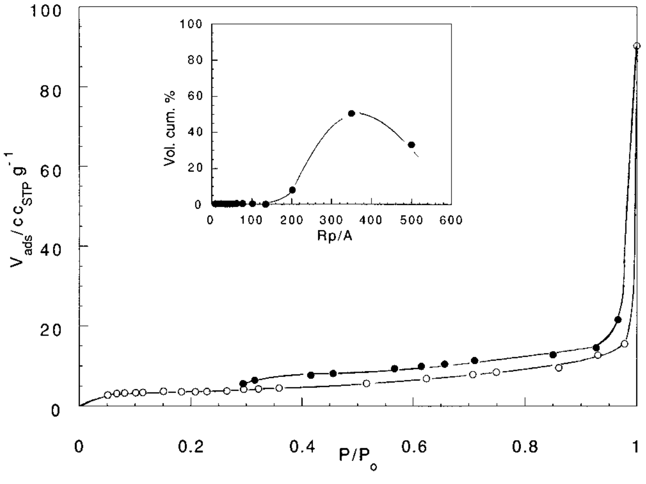

Figure 2. Nitrogen absorption isotherm at liquid nitrogen temperature on PMMA/SiO$_2$/NaL′ composite (sol−gel powder) and pore size distribution (inset).

similar to **A** (vide infra) as chemical sensors for detecting ionic species in water, we undertaken several chemicophysical measurements on the sol−gel composite material either as powdered monolithic pieces or as film, in order to gain insight into the sensing mechanism in operation. Nitrogen absorption (BET) on the powder (Figure 2) shows type IV isotherm with closed hysteresis, suggesting the presence of mesopores.[15] A low (less than 5%) nitrogen uptake occurs at relative pressures up to 0.2, indicating the absence of micropores, as expected for this kind of materials.[16] The cumulative pore volume distribution, according to Brunauer,[17] gives an average pore radius of 350 Å. Other calculated parameters are the following: specific surface area (12.5 m^2/g), mesopores area (11.1 m^2/g), and mesopores volume (0.075 cm^3/g). The AFM image of the A film (Figure 3) is in qualitative agreement with the porosity measurements on the powder, just reported. In particular, the surface is quite rough (average roughness: $R_a = 1.2$ nm, calculated on a 2×2 μm^2 area) characterized by the presence of wide craters. For instance, the line scan of the arrowhead-indicated crater in the figure gave values of 55 and 240 Å for the vertical and horizontal distance, respectively. All these findings suggest that L′ in the film is not entrapped in small cavities but homogeneously dispersed throughout the matrix and so totally accessible from outer species diffusing into the film, as it will be shown by the completeness of the reaction with Hg^{2+} in water, described in the following section. Moreover, from the SEM images of the air-dried films (Figure 4) prior (**A**) and after (**B**) soaking in water containing HgAc$_2$ (10^{-3} M), we can postulate that the film is swollen by water. The two samples have different morphology. Clearly, the fractured surface of **B** is an indication of the shrinkage effect consequent upon the swelling process due to water absorption. Within this picture, the absence of leaching of L′ out of the matrix by water is not easily understandable, recalling that NaL′ is very soluble in water. Presumably, hydrogen bonding of L′ with the matrix material, eventually stronger than that with water, is responsible for this behavior. To test this possibility, we compare the IR spectra of L′ in the film and of NaL′·xH$_2$O in anhydrous KBr. The valuable information lies in the amino stretching band,[1c] falling around 3300 cm^{-1} (Figure 5): the similar shape of the two bands and the associated red-shift ($\approx$37 cm^{-1}, for the most intense peak) in the former compared to the latter sample indicate that the −NH$_2$ group of L′ is engaged in hydrogen bonding with oxygen atoms and that the hydrogen bonding in question is stronger in the matrix.

Formation of the Mercury Complex in the Film. The L′-doped film (**A**), after 4 h from the deposition, when immersed in a Hg^{2+}-containing water solution (3 mL, 10^{-3} M as HgAc$_2$) undergoes a slow color change from violet to blue, due to the formation of the mercury complex (>HgL, Scheme 1) in the hybrid silica. Longer than 1 day exposure to the air at room temperature of the **A** film makes it much less reactive. The spectral dynamics (Figure 6) are characterized by the raising of an absorbance spectrum to an asymptotic profile with the maximum at 670 nm and an isosbestic point at 600 nm. The final spectrum does not show the presence of any amount of L′. These findings indicate that (i) the conversion of L′ to >HgL is quantitative, (ii) >HgL is stable in the matrix even in contact with free Hg^{2+}, and (iii) no one of the two species are leached out of the matrix by water. Concerning the molecular structure of the mercury complex, presently the ratio of Hg to L

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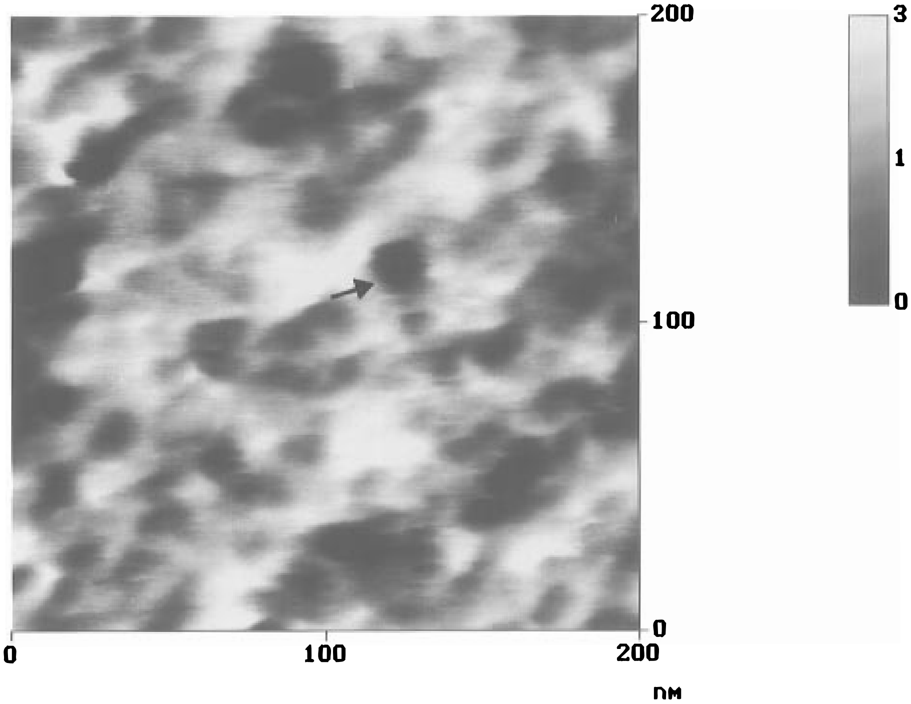

Figure 3. AFM image of L′-doped film.

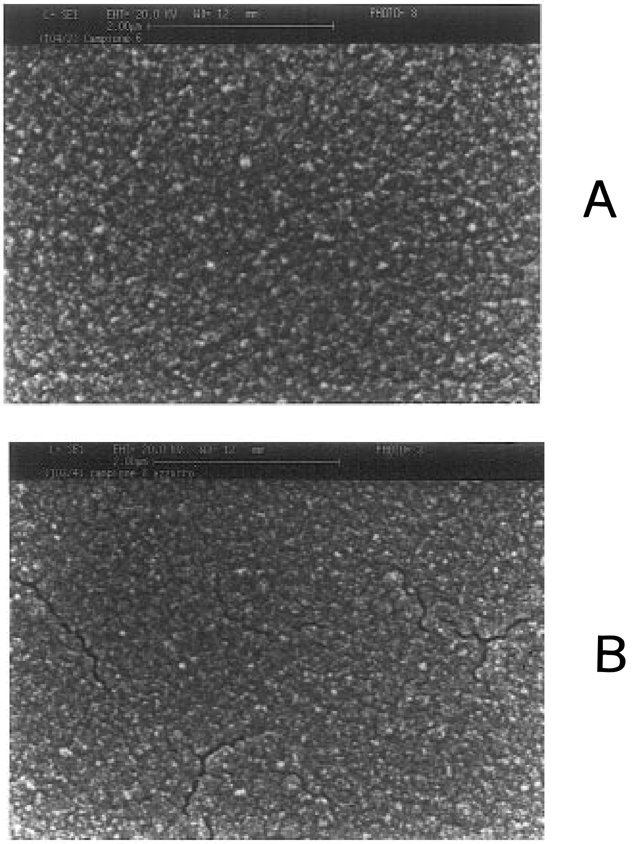

Figure 4. SEM image of L′-doped film (**A**) and >HgL-doped film (**B**).

can be assessed with some confidence (Hg/L = 1.0), as being based on the comparison (Figure 7) of the band profile of its optical spectrum (λ_{max} = 670 nm; half-height width, hhw, 84 nm) with the one of the solution optical spectrum of an authentic sample of a monochelated pyrrolizinato−Hg(II) complex (i.e., H_3CHgL, prepared from LH and H_3CHgAc in anhydrous THF:[3h] λ_{max} = 663 nm, hhw = 40 nm). The alternative bischelated complex can be excluded because the expected optical spectrum would display two maxima of comparable intensity, similar to those exhibited by the optical spectrum of an authentic sample in a noncoordinating solvent (i.e., HgL_2[3h] in 1-chloronaphthalene: λ_{max} = 674 and 603 nm; hhw = 130 nm). The stability of >HgL in the matrix toward water is also remarkable, considering that it is formed and it is stable in the matrix permeated by water while trace amounts of water dissociate it in homogeneous organic solutions.[3h] For further comparison we studied the same reaction occurring in the film

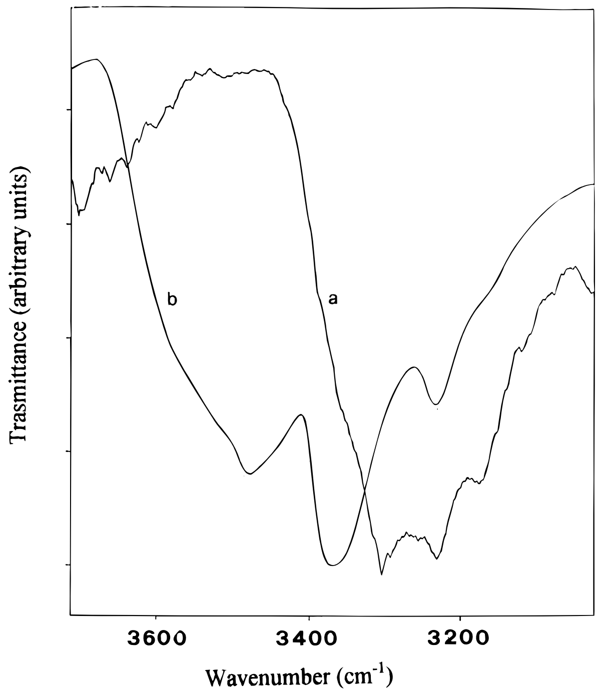

Figure 5. IR absorption spectrum of L′ in the PMMA/SiO_2 film (a) and of $NaL' \cdot xH_2O$ (b, KBr pellet) in the 3300 cm^{-1} region.

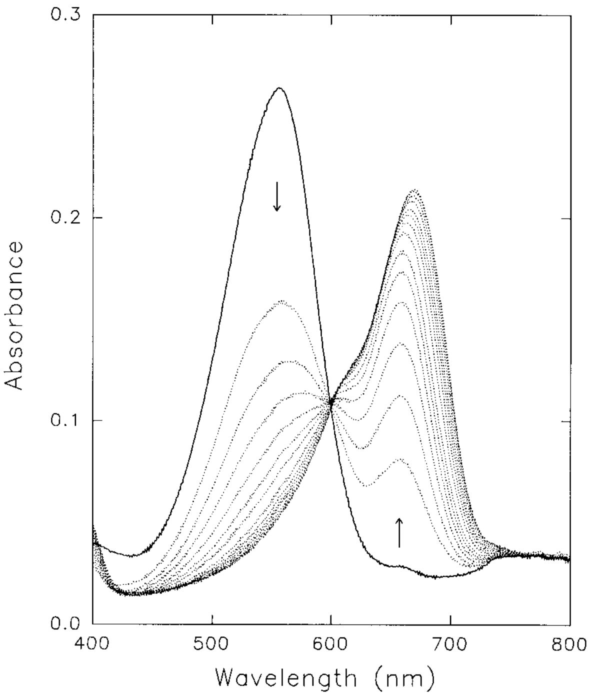

Figure 6. Spectral changes with time (every 30 min) undergone by a NaL′/PMMA/SiO$_2$ film (after 3 h from the preparation) immersed in a water solution containing HgAc$_2$ (10^{-3} M). Arrows indicate the direction of the spectral changes.

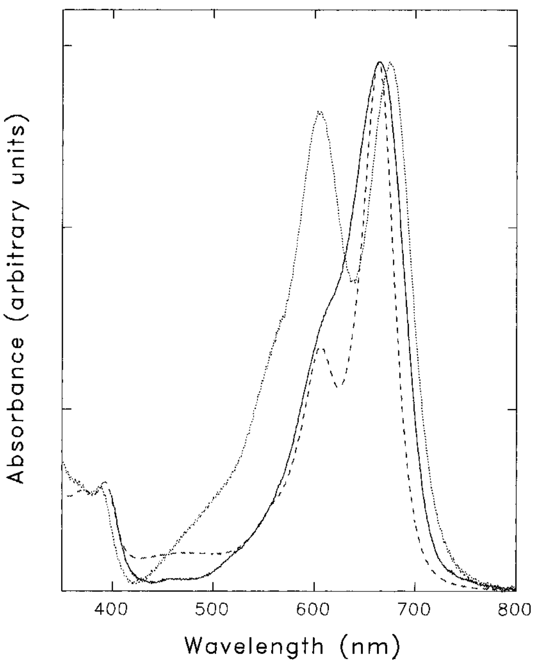

Figure 7. Optical spectra of: a PMMA/SiO$_2$ L′-doped film after equilibration in HgAc$_2$ containing water solution (—); HgL$_2$ (···) and CH$_3$HgL (- - -) in solution of 1-chloronaphthalene. Solution spectra have been normalized to the film spectrum.

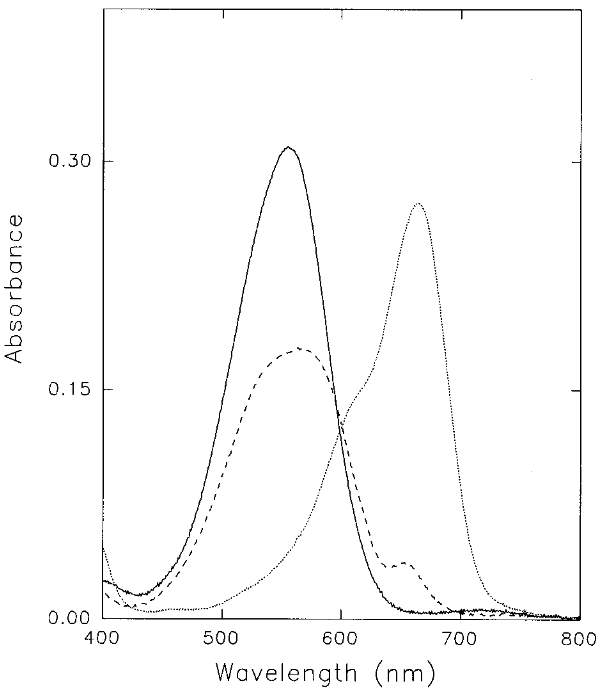

Figure 8. Optical spectra of a NaL′/PMMA/SiO$_2$ film after exposure for 16 h to Hg^{2+} (···) and Cu^{2+} (- - -) in water solution (10^{-3} M) and prior to exposition (—).

(NaL′ + HgAc$_2$ in excess to the stoichiometric amount), spectrophotometrically in homogeneous water solution. The optical spectrum (not reported here) of a clear dilute water solution resulting from miximg NaL′ and HgAc$_2$ (1:3) is very broad (hhw = 172 nm),[3h] indicating the presence of more than one mercury complex species. Thus, we conclude that the reaction in question is much more complicated in water than in the film. Finally, a somewhat unexpected result is that Hg^{2+} shows an enhanced affinity toward L′ in the matrix. As shown in Figure 8, the reaction with Cu^{2+}, monitored by the absorbance increase at 655 nm, proceeds to a little extent while within the same time interval (16 h) the reaction with Hg^{2+}, at the same molar concentration, goes to completion. Furthermore, when the film is immersed in a water solution equimolar in the two cations (0.5×10^{-3} M), mostly Hg^{2+} reacts. In homogeneous solution the reverse is usually observed: for instance, the copper complex is formed more easily than the mercury complex, as proved by the occurrence of the metathesis in anhydrous THF: $\mathrm{HgL_2 + Cu^{2+} \rightarrow CuL_2 + Hg^{2+}}$.[3h] It is therefore likely that the matrix material is the cause of the observed selectivity. To test this possibility, an undoped **A** film was soaked in an equimolar (0.5×10^{-3} M) water solution of M(II) (M = Hg and Cu) for a long enough time (16 h) and then analyzed by ESCA for the metallic species adsorbed and/or exchanged on the film surface. XPS data indicated that the mercury laoding factor is 4 times as large as the copper one, in accordance to the expected selective interaction between M(II) and the matrix.

Sensing Properties of >HgL in the Film. The >HgL-doped film (**B**), formed as described previously, is reactive toward S species (Scheme 1) even after long exposure to the air (at least for 1 month), showing it to be a sensor for them, eventually recyclable, as described in the following sections.

(a) Reaction with CN$^-$ in Water. When film **B**, specifically the one coming from the experiment described in Figure 6, is contacted with a CN$^-$-containing water solution, the colorimetric reaction (L → L′) occurs in the matrix as the result of coordination of CN$^-$ to >HgL. From the associated absorbance changes with time (Figure 9), compared to those of Figure 6, the following are obvious: (i) the reaction is clean and quantitative, for the 100% recovery of the former initial spectrum; (ii) neither >HgL nor L′ are leached out of

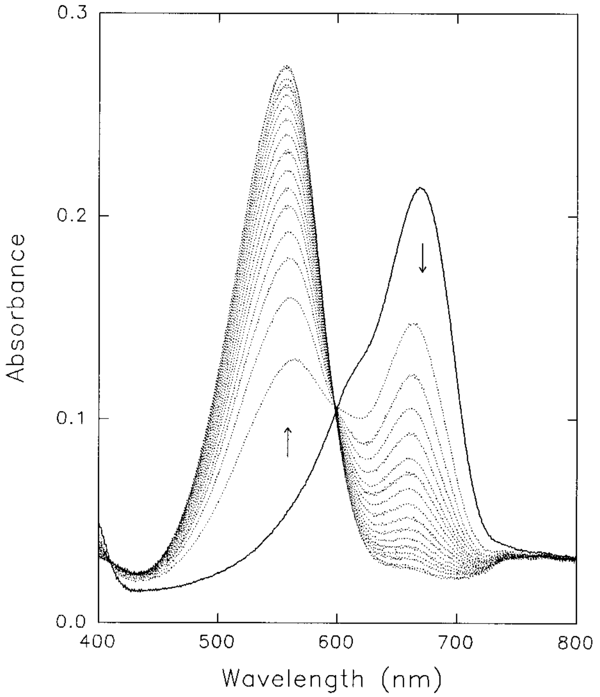

Figure 9. Spectral changes with time (every 1 min) undergone by the >HgL/PMMA/SiO_2 film, resulting at the end of the experiment described in Figure 6 and then stored in air for 4 weeks, immersed in a water solution containing KCN (1.25×10^{-3} M). Arrows indicate the direction of the spectral changes.

Table 2. Fractional Change in Absorbance of A^a or B^b Film at the Most Sensitive Wavelength (Φ), Corresponding Response Time (*t*), and Analyte Concentration in Solution (*C*)

analyte	Φ_{555nm}	Φ_{670nm}	*t* (min)	*C* (M)
Hg^{2+}	0.40		30	1.0×10^{-3}
CN^-		0.40	5	1.25×10^{-3}
NH_3		0.48	5	1.9×10^{-4}

[a] For Hg^{2+} determination. [b] For CN^- and NH_3 determination.

the matrix, for the persistence of the isosbestic point at 600 nm; (iii) the reaction is much faster than that which occurred in the former experiment, as the time interval necessary to give the same response ($\Phi = 0.4$) is correspondingly 6-fold shorter at a comparable analyte concentration (Table 2). Surprisingly enough, film **A** is not regenerated in this manner; as a matter of fact the resultant film from the latter experiment does not react with Hg^{2+} any more even after prolonged exposure. This probably indicates that neither the CN^--containing mercury complex is washed out of the matrix by water, but it remains there in close proximity to L′, preventing other free Hg^{2+} to react with L′. Coming back to the section-heading reaction, it was of interest to calibrate the response of the film to changes of CN^- concentration. Thus, five films were examined as reported in the Experimental Section. The fractional absorbance changes, $(A_0 - A_t)/A_0$ (Φ), at the most sensitive wavelength (670 nm), were measured and plotted against the initial CN^- concentrations in the bulk solutions. A simple linear relationship was found, $\Phi = Kc$ (1) (Figure 10). A least-squares fitting of the data, the origin included as an experimental point based on the absence of leaching ($\Phi = 0$ with $c = 0$), produced a *y* intercept of -0.0037, $k = 1.427$ M^{-1}, and a correlation index of 0.9908. These findings are consistent with a diffusion-controlled mechanism[18] operating for the reaction in the matrix when the leaching of the doping dyes out of the matrix is totally absent. In this case the general hyperbolic law, $A_0/A_t = 1 + Kc$ (2), holds; from (2), after simple manipulations, the equation $\Phi =$

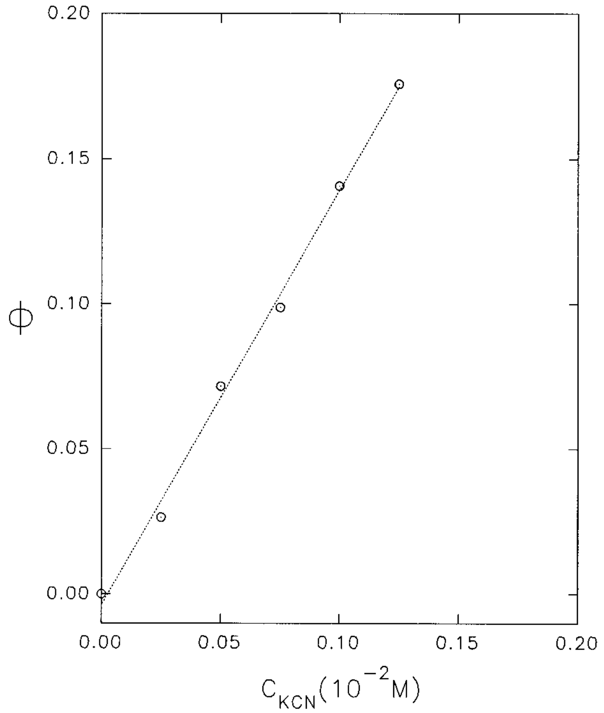

Figure 10. Response of B films to CN^- concentration in water (C). $\Phi = (A_0 - A_t)/A_0$ was measured after 2 min at the most sensitive wavelength (670 nm), relative to the baseline absorbance at 800 nm. Five identical B films were used. The linear fitting (- - -) gave $\Phi = 1.427C - 0.0037$.

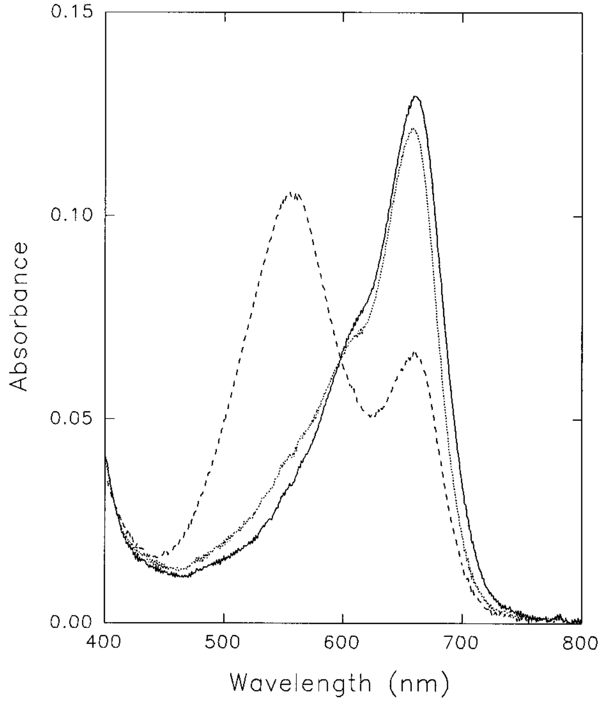

Figure 11. Optical spectra of a B film (stored in air for 4 weeks) after 5 min exposure to NH_3 (1.9×10^{-4} M) in the gas phase (- - -) and then immersed in water for 2 h (···) and prior to exposition (—).

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(18) Mills, A.; Chang, Q. *Analyst* **1992**, *117*, 1461.

$Kc/(1 + Kc)$ (3) can be derived, for which a good approximation is (1) provided that $1 + Kc = 1$ (4). In the current case the approximation (4) is obviously valid, with c 0.01−0.0001 and K almost unitary.

(b) Reaction with NH_3 in Air. Film B is also suitable to detect NH_3 in the atmosphere. Ammonia coordinates to >HgL, causing a color change from blue to violet for the releasing of L′ in the film (Figure 11). It is interesting to note (Table 2) that the reaction with ammonia is faster than that with CN^- in water, i.e., the response time interval is the same for a lower analyte concentration (Table 2), in accordance with the different diffusional behavior of gases with respect to liquids. On comparison with the latter experiment, another notable difference is that in this case the starting film (B) can be regenerated and eventually reused, simply by washing the film with water after exposure to ammonia. The return to the initial spectrum was complete within 2 h (Figure 11). However, a significant degradation in repeated cycling was observed (≈40%, after five cycles). Water removes NH_3 from the ammonia-containing mercury complex and then from the matrix, leaving free Hg^{2+} in the matrix, which makes L′, close to it, undergo the usual isomerization to L.

Conclusions

L′ can be incorporated into a thin film of PMMA/SiO_2 at a fairly high concentration, as discrete molecules totally accessible to outer species diffusing into the film. It is stable in the matrix and is not leached out by water. The matrix material deeply modifies the metal-coordinating properties of L′ making it a specific ligand for Hg^{2+} in water. In turn, the mercury complex (>HgL) in the film can be used for sensing species whose affinity for Hg^{2+} is stronger than that of L. Presently, the rapid loss of reactivity of L-doped film toward Hg^{2+} in water, in contrast with the long-term activity of the analogous >HgL-doped film toward CN^- in water, is not understood. The route to avoid this drawback and to improve other specific properties of the system for a successful practical exploitation as chemical sensor is currently being investigated.

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