

Near-Infrared Dyes Encapsulated in Sol–Gel Matrices

Francisco del Monte and David Levy*

Instituto de Ciencia de Materiales, CSIC, Serrano 115, 28006 Madrid, Spain

Received June 21, 1994. Revised Manuscript Received September 23, 1994[⊗]

Near-infrared dye oxazine-1 was introduced into gel glasses by the sol–gel method from TEOS and TMOS. The fluorescence properties of oxazine-1 were preserved in these matrices. The entrapment of 1,1',3,3',3',3'-hexamethylindotrycarbocyanine iodide (HITC) into gel glasses required dye protection from chemical degradation and was obtained from TMOS by producing high-density matrices upon prolonged aging of H₂O/TMOS = 1 (molar ratio). Alternative strategies to protect HITC inside gel glasses were achieved by using a combination of sol–gel techniques with poly(methyl methacrylate) (PMMA) for the formation of mixed matrices of silica gel–PMMA glasses, or by copolymerization of TMOS with titanium tetraethoxide (TEOT) for the formation of gel glasses with a mixed TiO₂–SiO₂ composition, or by encapsulation of HITC with the aid of surface-active agents (SAA). The fluorescence and IR spectral behavior of the doped materials at different reaction conditions were studied.

1. Introduction

Organic dyes have gained a recognized role in commercial devices since the development of new functional optic materials. Improvements of near-infrared (near-IR) dyes (700–1000 nm)¹ have led to applications well beyond optical recording technology: high-density optical data storage, thermal writing displays, laser printer and laser filter, infrared photography, medical applications, and persistent (non)photochemical hole burning² as multiwavelength optical memory.^{3,4} Near-IR dyes attract increasing interest in photodynamic therapy due to the fact that tissue penetration using near-IR dyes is optimal in the near-IR spectral region (~760 nm).

At this time, a major obstacle in the development of optical devices is the lack of suitable materials¹ which have the required chemical and photochemical stability, optical properties and can also be made into usable forms such as thin films and bulk pieces. This limitation makes the sol–gel process^{5–8} a very attractive possibility with the ability to incorporate organic materials in inorganic matrices at low temperatures, in the form of monolithic glasses or thin films, and opens the way to many possible applications, such as in optics^{9–15} and electrooptics.^{16–18}

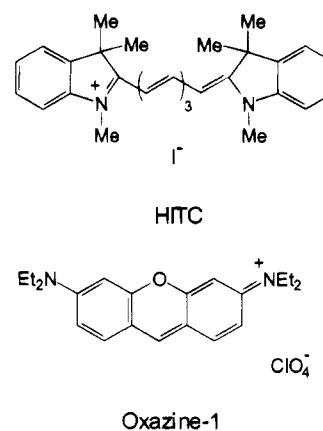


Figure 1. Molecular structure of near-IR dyes.

In general, a sol–gel process^{5,6} begins with the formation of a colloidal suspension of the reaction products called a sol, usually from metal alkoxide monomers through hydrolysis and polycondensation reactions, at room temperature. The sol undergoes a transition to a soft porous wet gel, which eventually becomes a solid porous aggregate of extremely small particles known as xerogel. Using organosilicon compounds under certain reaction conditions, the xerogel may eventually become a porous transparent silica gel glass. Gel glass matrices may show excellent optical properties; it seemed worthy, therefore, to find out whether these matrices might be used to produce near-IR dye-doped gel glasses.

Lebeau et al.¹⁹ have first reported recently on the optical properties of the polymethine dye HITC (Figure 1) when is incorporated inside silica-based gel (using 4-(dimethylamino)pyridine, DMAP, as a catalyst) or aluminum, titanium, and zirconium oxo polymers pre-

* Abstract published in *Advance ACS Abstracts*, December 15, 1994.

(1) Fabian, J.; Nakazumi, H.; Matsuoka, M. *Chem. Rev.* **1992**, *92*, 1197.

(2) Nakatsuka, H.; Inouye, K.; Uemura, S.; Yano, R. *Chem. Phys. Lett.* **1990**, *171*, 245.

(3) Schellenberg, F. M.; Lenth, W.; Bjorklund, G. C. *Appl. Opt.* **1986**, *25*, 3207.

(4) Itoh, U.; Tani, T. *Appl. Opt.* **1988**, *27*, 739.

(5) Brinker, C. J.; Scherer, G. W. *Sol Gel Science*; Academic Press: San Diego, 1990.

(6) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.

(7) Ulrich, D. R. *J. Non-Cryst. Solids* **1988**, *100*, 174.

(8) Yamane, M.; Aso, S.; Sakaino, T. *J. Mater. Sci.* **1978**, *13*, 865.

(9) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956.

(10) Tani, T.; Namikawa, H.; Arai, K.; Makishima, A. *J. Appl. Phys.* **1985**, *58*, 3559.

(11) Dunn, B.; Knobbe, E.; MacKiernan, J. M.; Pouxviel, J. C.; Zink, J. I. *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 331.

(12) MacKiernan, J.; Pouxviel, J. C.; Dunn, B.; Zink, J. I. *J. Phys. Chem.* **1989**, *93*, 2129.

(13) Pope, E. J. A.; Mackenzie, J. D. Proceedings of the 21st University Conference on Ceramic Science, Pennsylvania State University, July 1985; Plenum: New York, 1986.

(14) Levy, D.; Avnir, D. *J. Phys. Chem.* **1988**, *92*, 4734.

(15) Levy, D.; Einhorn, S.; Avnir, D. *J. Non-Cryst. Solids* **1989**, *113*, 137.

(16) Levy, D. *J. Non-Cryst Solids* **1992**, *147–148*, 508.

(17) Levy, D.; Serna, C. J.; Otón, J. M. *Mater. Lett.* **1991**, *10*, 470.

(18) Otón, J. M.; Serrano, A.; Serna, C. J.; Levy, D. *Liq. Cryst.* **1991**, *10*, 733.

(19) Lebeau, B.; Herlet, N.; Livage, J.; Sanchez, C. *Chem. Phys. Lett.* **1993**, *206*, 15.

pared without catalyst, and inside hybrid siloxane-metal oxo coatings. Some of these matrices suffered from the disadvantage of color degradation due to dye-low chemical stability (aluminum, titanium, and zirconium oxo polymers degraded within a week, and degradation was observed in the sol state of hybrid organic-inorganic matrices), but improved stability was reached when using DMAP in silica gels.

In this paper, we report on the spectral behavior and chemical stability of oxazine-1 and HITC (Figure 1) doped gel glasses. The chosen molecular structure of these dyes is illustrative of the oxazine and cyanine near-IR laser dyes. The oxazine-1 dye was selected from the other laser dyes,^{16,20} whose emission in solid matrices are in the VIS spectrum (400–700 nm),^{21–24} because its emission is in the range of near-IR (650–800 nm). Up to our knowledge, from the oxazine dyes entrapped in inorganic matrices,^{20–23} this is the first time in which the near-IR dye oxazine-1 is introduced in sol-gel glasses. In addition, we overcome the poor stability of HITC in TMOS gel glasses by the prolonged aging of the gel from water-to-monomer ratio = 1, or by the copolymerization of TEOT with TMOS, or with the aid of an organic SSA. An alternative strategy to improve HITC chemical stability is by using a modification of the techniques proposed by Pope and Mackenzie²⁵ or by Reisfeld et al.²⁶ in which a combination of the sol-gel techniques with organic polymers (by mixing dissolved PMMA in the starting solution) allows the preparation of transparent optical materials of excellent optical and mechanical quality. Here, we also discuss on the chemical stability and fluorescence properties of HITC gel glasses which vary widely depending on conditions during gel formation and may be tightly controlled with the chemical composition of the starting mixture.

The purpose of this work is the encapsulation of near-IR dyes in sol-gel matrices, for which we investigated the preparation and photophysical properties of a wide variety of oxazine-1 and HITC doped gel glasses using different reaction conditions that allow high chemical stability of the dye in the final material.

2. Experimental Section

2.1. Preparation of Near-IR Doped Gel Glasses. Four types of matrices were used in this study. The first was silica gel prepared from TEOS or TMOS. The second was a mixed organic-inorganic gel formed from a mixture of PMMA and SiO₂. The third was an inorganic composite formed using TEOT as the comonomer in the hydrolysis-condensation of TMOS, and the fourth matrix was prepared using Triton X-100. The samples in this study were kept in the dark.

TEOS Gel Glasses. For all the starting solution in the preparation of sol 1 and sols 7–20, the quantity of tetraethoxysilane (TEOS, Fluka) was fixed at 9.1 mmol, and H₂O and ethanol were added in the corresponding molar ratios shown in Table 1. To the resulting solution, 0.4 mL of oxazine-1

Table 1

sample	monomer	dye	$r_{w/m}$	$r_{s/m}$	t_h^d
sol 1	TEOS	oxazine-1	4	3.5 ^a	0
sol 2	TMOS	oxazine-1	4	2.9 ^a	0
sol 3 ^f	TMOS	HITC	1	1.7 ^a	0
sol 4 ^e	TMOS	HITC	1	1.7 ^a	0
sol 5 ^e	TMOS	HITC	4	2.9 ^a	0
sol 6 ^e	TMOS	HITC	10	5.6 ^a	0
sol 7	TEOS	HITC	1	2.0 ^a	0
sol 8	TEOS	HITC	1	2.0 ^a	1.5
sol 9	TEOS	HITC	1	3.1 ^b	1.5
sol 10	TEOS	HITC	4	3.5 ^a	0
sol 11	TEOS	HITC	4	3.5 ^a	1.5
sol 12	TEOS	HITC	4	6.3 ^b	0
sol 13	TEOS	HITC	4	6.3 ^b	1.5
sol 14	TEOS	HITC	4	6.3 ^b	2.5
sol 15	TEOS	HITC	4	6.3 ^b	7
sol 16	TEOS	HITC	4	7 ^b	0
sol 17	TEOS	HITC	10	7.6 ^a	1.5
sol 18	TEOS	HITC	10	12.3 ^b	1.5
sol 19	TEOS	HITC	1	1 ^c	0
sol 20	TEOS	HITC	4	1.5 ^c	0

^a Solvent amount added to the starting solution to avoid phase separation. ^b Solvent amount added to the starting solution is in excess. ^c Solvent amount added to the starting solution causes phase separation. ^d Prehydrolysis time at which the dye is added to the reacting solution (always before gel formation). ^e $t_{\text{aging}} = 7-10$ days. ^f $t_{\text{aging}} = 45$ days.

(Kodak, 3×10^{-4} M in ethanol) or 0.2 mL of HITC-iodide (Aldrich, 2.3×10^{-4} M in ethanol) was added. The HITC was incorporated to the reacting solution after different prehydrolysis times (from $t_h = 0$ to $t_h = 7$ h of reaction), while the oxazine-1 was added at $t_h = 0$. The polymerization was carried out at room temperature in glass bottles covered with aluminum foil. After gelation occurred, the aluminum foil was perforated to allow the slow evaporation of the solvents until the formation of dried xerogels.

TMOS Gel Glasses. For all the starting solution in the preparation of sols 2–6, the quantity of tetramethoxysilane (TMOS, Fluka) was fixed at 9.1 mmol, and H₂O and methanol were added in the corresponding molar ratios shown in Table 1. To the resulting solution, 0.2 mL of oxazine-1 (3×10^{-4} M in methanol, sol 2) or 0.2 mL of HITC (2.3×10^{-4} M in methanol, sols 3–6) were added without prehydrolysis. The sols (except sol 2) were allowed to age as shown in Table 1. Drying was carried out as with the TEOS gels.

Silica Gel-PMMA Glasses. Mixed matrices were prepared by adding to the starting solution of TMOS gel glasses 1–8 wt % (wt PMMA/wt gel glass $\times 100$) of PMMA with composition of $r_{w/m} = 4$ or 1–50 wt % with $r_{w/m} = 1$. PMMA was previously dissolved in 2.25 mL of TMOS and 2.65 mL of methanol. After 20 h, 0.5 mL of 2.2×10^{-4} M HITC solution and water were added, and the solution was left to stir for 2 h. Drying was carried out as with the TMOS gels.

Silica Gel-TiO₂ Glasses. A two-step polymerization process was initiated by 2 h of prehydrolysis of the starting solution of TMOS ($r_{w/m} = 1$). Copolymerization was then performed by slow dropping 1 mL of 0.21 M of TEOT (molar ratio of TMOS/TEOT ≈ 43) in ethanol to the prehydrolyzed solution. Drying was carried out as with the TMOS gels.

Silica Gel-Triton X-100 Glasses. Several amounts of Triton X-100 (Aldrich, 4–16 wt %, wt Triton X-100/wt gel glass $\times 100$) were added to the starting solution with $r_{w/m} = 1$ or $r_{w/m} = 4$ following the standard procedure as with the TMOS gels.

Adsorption of HITC in Commercial SiO₂. Samples consisting of HITC adsorbed on silica (Carlo Erba) were used to study the chemical stability of HITC and were prepared as follows: 2 mL of HITC solution (6.86×10^{-4} M in methanol) was allowed to adsorb for a week on a flask containing 0.5 g of SiO₂, while stirring at room temperature.

2.2. Spectroscopic Measurements. Fluorometric measurements at 25 °C were performed on a 48000s (T-Optics) spectrofluorometer from SLM-Aminco. The apparatus is configured to a software-controlled computer. A front-surface sample holder for thin-film solid samples was built for data collection and oriented at 60° to light excitation to minimize scattered light on the cooled wide-band rf housing for the R928

(20) Dunn, B.; Zink, J. I. *J. Mater. Chem.* **1991**, *1*, 903.

(21) Gvishi, R.; Reisfeld, R. *J. Non-Cryst. Solids* **1991**, *128*, 69.

(22) Kobayashi, Y.; Imai, Y.; Kurokawa, Y. *J. Mater. Sci. Lett.* **1988**, *7*, 1148.

(23) Kobayashi, Y.; Imai, Y.; Kurokawa, Y. *J. Non-Cryst. Solids* **1988**, *105*, 198.

(24) Avnir, D.; Kaufman, V.; Reisfeld, R. *J. Non-Cryst. Solids* **1985**, *74*, 395.

(25) Pope, E. J. A.; Mackenzie, J. D. *MRS Bull.* **1987**, *12*, 29.

(26) Reisfeld, R.; Brusilovsky, D.; Eyal, M.; Miron, E.; Burshtein, Z.; Ivri, J. *Chem. Phys. Lett.* **1989**, *160*, 43.

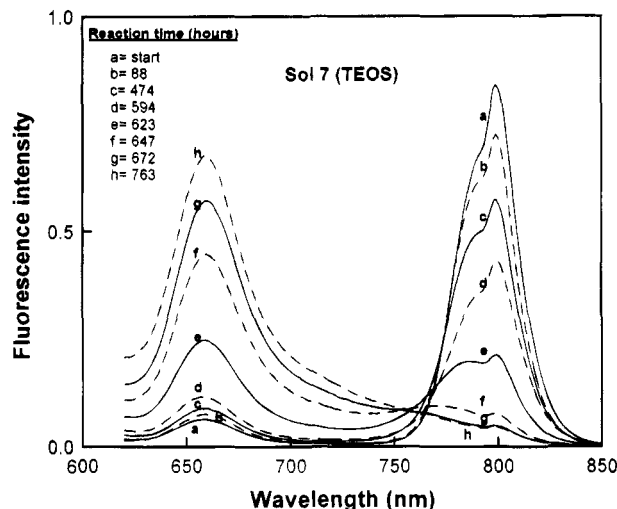


Figure 2. Fluorescence degradation of HITC during the sol-gel transition of sol 7 (TEOS, $\lambda_{\text{excitation}} = 590$ nm).

tube. Appropriate filters were used to eliminate Rayleigh and Raman scatter from the emission. Emission spectra were corrected for the wavelength dependence of the 450-W xenon arc excitation but not for the wavelength dependence of the detection system. Reference samples for these studies consisted of gel glasses which do not contain the dopant and were not fluorescent. Relative fluorescence intensity (I_F) is referred to the ratio of the HITC orange band (650 nm) to the red band (800 nm).

Absorption measurements of HITC doped gel glasses were performed on a Varian 2300 spectrophotometer. Spectral changes during HITC degradation were observed, which showed a similar pattern as emission results as in Figure 2.

The infrared spectra were carried in a Nicolet FT-IR spectrophotometer Model 20SXC and the ^1H NMR measurements were made in a Varian Gemini 200 MHz (liquid) or Bruker MSL 400 MHz (solids). The morphology of the microstructures was examined with a scanning/transmission electron microscope (SEM, Zeiss, DSM-950 and TEM, Phillips 300). The specific surface area (S_A) of samples treated at 60 °C for 24 h was measured using the BET method with nitrogen gas using a Carlo Erba Model Sorptomatic 1800.

2.3. Chemical Degradation of HITC. Dye chemical stability was assessed in gel glasses by measuring the fluorescence emission spectra as a function of time. Whereas samples in this study were kept in the dark, the degradation of HITC is from chemical sources. The dye concentration of 10^{-4} M was selected after a previous study in the range of 10^{-4} – 10^{-6} M, which indicated that HITC concentration is not related to the HITC stability behavior. Since the chemical mechanism of degradation of HITC in solution or solid matrices has not been investigated, we have made attempts to recognize in the gel glass the degraded HITC product by spectroscopic techniques, such as ^1H NMR spectroscopy and IR spectroscopy, but HITC or degraded products were not detectable due to the low HITC concentration in the matrix. To further obtain information on the degradation product, experiments made in acidic solution have revealed that such fluorescence behavior of the degraded HITC, e.g., spectra in Figure 2, is similar to that found after degradation of HITC in TEOS (pure monomer) or in gel glasses. In addition, the UV shift (~ 150 nm, Figure 2) observed after degradation in the fluorescence spectra is an evidence that the mechanism of chemical HITC degradation is related to the rupture of the conjugated π -system,¹ which takes place in the polymethine dye. The degradation product of HITC in TEOS as well in acidic solution have been examined by ^1H NMR spectroscopy. In both systems, while the ethylenic signals (~ 6.3 , ~ 6.5 , ~ 7.7 , and ~ 7.9 ppm) disappeared, new bands assigned to the formation of $-\text{CH}_2$ groups (~ 1.8 to ~ 2 ppm) were detected. These results are consistent with that of the UV shift in the fluorescence and showed that in both solutions, the mechanism

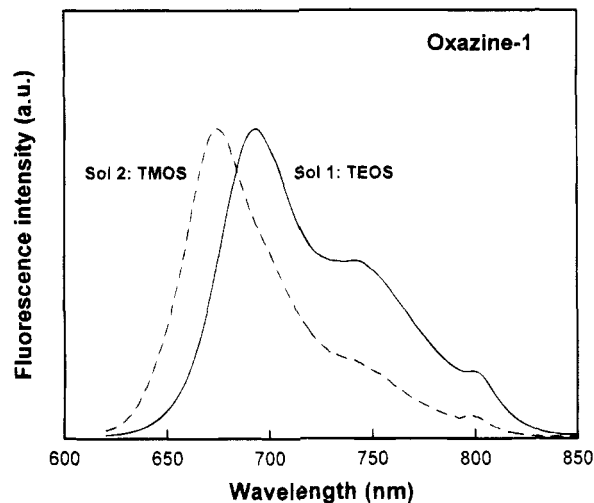


Figure 3. Fluorescence spectra of oxazine-1 doped gel glasses from TMOS (---) and TEOS (—).

involving such as drastic changes is due to the loss of π -conjugation from the polymethine dye.

An attempt was made to enhance the stability of HITC-doped gel glasses with diethanolamine (DEA) used as a base catalyst in a composition similar to sol 5, but the degradation of HITC was observed within 2–3 days.

3. Results and Discussion

3.1. Stability of Near-IR-Doped Gel Glasses.

While the fluorescence of oxazine-1 is stable into gel glasses, several reaction conditions such as the nature of the monomer, the water-to-monomer ratio and solvent-to-monomer ratio, and the time in which the HITC dye was added to the starting solution were found to play an important role in the improvement of the HITC fluorescence properties in gel glasses.

SiO₂ Gel Glasses. Oxazine-1-doped gel glasses prepared from TEOS and from TMOS (sol 1 and sol 2) yield stable fluorescence and no signal loss is observed over 11 months. The fluorescence spectra of these materials are presented in Figure 3. The spectra of TMOS and TEOS gel glasses exhibit the near-IR emission centered at ~ 675 nm and ~ 695 , 745 nm, respectively.

HITC-doped gel glasses prepared from TMOS (sol 3) showed longer chemical stability (over 7 months, Figure 4a) than these prepared from TEOS with different starting compositions, in which HITC degradation was observed within 1–25 days (sols 7–20). Stabilization of HITC in TMOS gel glasses was achieved by prolonged aging of sol 3, $r_{w/m} = 1$: $t_{\text{aging}} = 45$ days. Under these conditions, SEM image of this sample (Figure 5a) shows that such prolonged aging allows to high-density gels with very homogeneous microstructure. This silica gel is formed under conditions where the condensation rate is low and the forming structure can reasonably freely shrink in response to solvent removal, which causes a further shrinkage of the structure with a low specific (BET) surface area (not measurable in our apparatus) of $S_A < 10$ m²/g, and no detectable porosity by TEM (Figure 5b). Upon shrinkage, the decrease in solvent content in the matrix is large, and HITC aggregation became observed as a result of the increase of the HITC concentration during the final steps of the gel formation. The appearance of the strong absorption band at 660 nm in Figure 4e is a clear indication of the dimerization enhancement on such dense matrix.²⁷

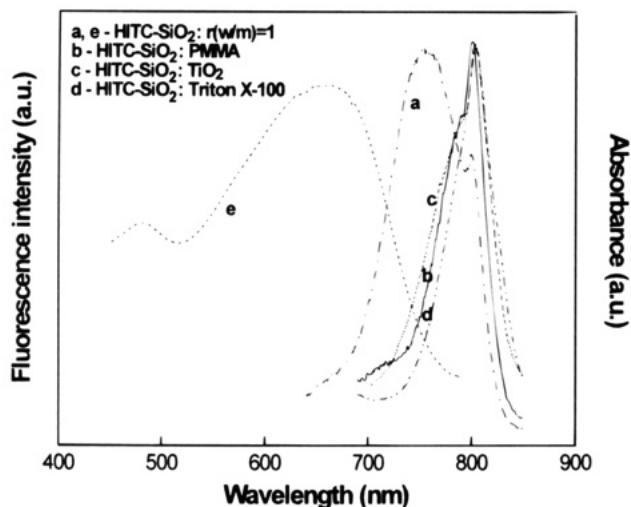


Figure 4. Fluorescence spectrum of HITC-doped gel glass from sol 3 aged to $t_{\text{aging}} = 45$ days, $r_{w/m} = 1$, sample after 7 months (a), when using PMMA in the preparation, after 10 months (b), TiO_2 - SiO_2 gel glass, after 4 months (c), prepared with Triton X-100 of $r_{w/m} = 1$ or $r_{w/m} = 4$ compositions, after 5 months (d), absorbance spectra, same sample as "a" (e).

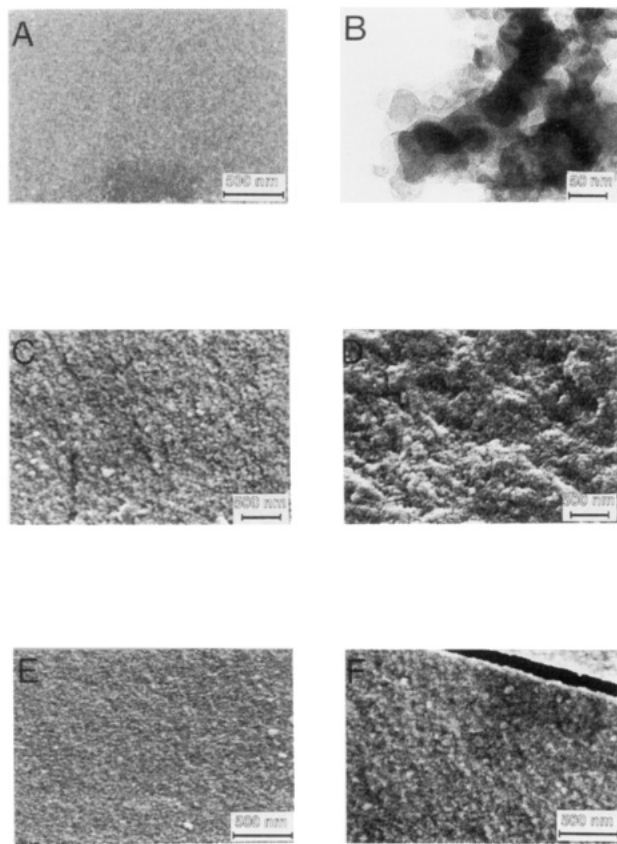


Figure 5. SEM (a) and TEM (b) photographs of microstructures of gel glasses prepared from sol 3 aged to $t_{\text{aging}} = 45$ days, $r_{w/m} = 1$; SEM photograph of microstructure of gel glasses aged to $t_{\text{aging}} = 7$ -10 days, $r_{w/m} = 1$ (c); SEM photograph of microstructure of gel glasses aged to $t_{\text{aging}} = 7$ -10 days with $r_{w/m} = 4$ (d); SEM photograph of microstructure of gel-PMMA glasses (e); mixed TiO_2 - SiO_2 composition (f).

Taking into consideration the fact that we used $r_{w/m} = 1$ with $t_{\text{aging}} = 45$ days, a significant part of nonreacted alkoxy groups which are in the surrounding environ-

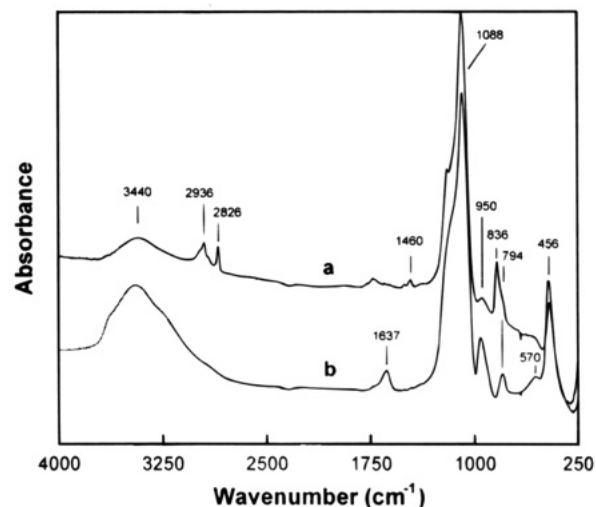


Figure 6. Infrared spectra of gel glasses: sol 4 before degradation, 1000 h (a); sol 4 after degradation, 1150 h (b). The spectra of gel glasses from sol 3 after 7 month, and the spectra of TiO_2 - SiO_2 after 5 months are similar to "a".

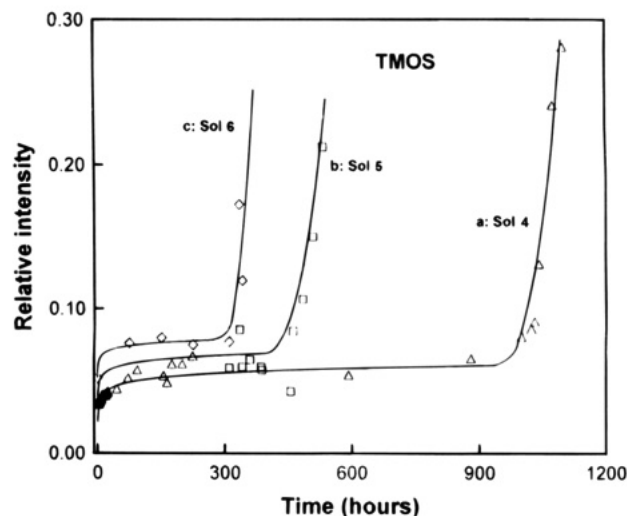


Figure 7. Stability behavior of HITC in gel glasses prepared from TMOS, $t_{\text{aging}} = 7$ -10 days: $r_{w/m} = 1$ (a), $r_{w/m} = 4$ (b), and $r_{w/m} = 10$ (c).

ment of the HITC molecules, remain in the formed dense gel matrix as shown in Figure 6a (see below). As a result, HITC degradation is ineffective and the occurrence of stabilization is governed by the presence of nonreacted methoxy groups on the matrix surface. Consequently, due to shrinkage the gel glasses showed a great resistance to posterior hydrolysis of these groups by readsorption of water when the gels were exposed to air, allowing very stable HITC gel glasses. Such as properties, make these gel glasses better for the protection of organic dopants that are moisture and air sensitive (see section 3.2). In all cases studied in this work, the presence of oxygen during the preparation does not affect the stability of HITC gel glasses, e.g., in doped gel glasses prepared from sol 3, PMMA, TiO_2 , or Triton X-100.

When the aging time is within 7-10 days, a decrease in chemical stability of TMOS gel glasses is observed. Degradation of HITC occurs during the gel to xerogel transition in sol 4 with $r_{w/m} = 1$ (1100-1150 h, Figure 7a), while in samples with higher water to monomer ratios, sol 5 and sol 6 with $r_{w/m} = 4$ and $r_{w/m} = 10$, HITC degraded within 300-500 h (Figure 7b,c). As revealed

by these experiments, the degradation of HITC, which occurs in the gel stage, is not related to the presence of the TMOS monomer in the starting solution as in the case of TEOS samples (dissolution of HITC in TMOS does not degrade HITC). In TMOS samples, HITC degradation is related to the step of the gel-to-xerogel formation which is associated to the expected local chemical changes which are known to occur during aging in the nature of the gel.⁶ SEM image of the surface (Figure 5c) revealed a slight roughness in $r_{w/m} = 1$ aged for $t_{aging} = 7-10$ days (sol 4) than in gels prepared with $t_{aging} = 45$ days (Figure 5a,b), which is much more increased in gels with $r_{w/m} = 4$ with $S_A = 485 \text{ m}^2/\text{g}$ (Figure 5d, sol 5). Thus, in sol 4 hydrolysis of nonreacted methoxy groups takes place by posterior adsorption of water when the gels were exposed to air, allowing degradation of HITC. The evidence that hydration of the methoxy groups to silanols is the main cause that allows HITC degradation is supported by the catalyst effect observed on the degradation of HITC (less than 2 h) prepared from sol 4 when introduced in water.

While the variations performed on the composition of the starting solution for the preparation of stable HITC-doped gel glasses from TEOS and TMOS (produced without additives) have led only to one way of gel glass preparation that avoid HITC degradation, we also found alternative methods that prevented HITC chemical degradation. The chemical modifications were oriented to avoid the formation or/and exposure of silanol groups to the HITC-entrapped molecule.

PMMA Gel Glasses. SEM analysis in Figure 5e has revealed a good dispersion of PMMA throughout the silica gel. By adding PMMA, the microstructure of the silica gel becomes much more homogeneous and results in a dense material. Such a dense material avoids readsorption of water when the sample is exposed to air. Consequently, the hydrolysis of the unhydrolyzed methoxy groups on the surface is reduced. Thus, the use of PMMA, is capable of producing directly the stabilization of the HITC molecule. The fluorescence of the gel glass is invariable, and no signal loss is observed over 10 months (Figure 4b). This is due to the chemical compatibility and protection against chemical degradation provided to the HITC by the PMMA encapsulation. This is specially important to inhibit air, moisture and surface reactions with HITC, which occurs in purely inorganic gel glasses mentioned previously.

When examining the optical transparency of the gel glasses, it was found that addition of small quantities of PMMA ($r_{w/m} = 4$: 1–8% or $r_{w/m} = 1$: 1–3%) to the starting solution allows preparing transparent silica gel–PMMA composites. A large amount of PMMA (12–20%) results in HITC-stable gel glasses, but observed is a reduction in optical transparency due to the phase separation and polymer precipitation observed once the gelation begins. Over 20% of PMMA, produces heterogeneous opaque material and the PMMA becomes ineffective, specially in gel glasses made with $r_{w/m} = 4$.

TiO₂–SiO₂ and Triton X-100–SiO₂ Gel Glasses. A different way of chemical stabilization of HITC in inorganic matrices has been achieved by preparing gel glasses with a mixed TiO₂–SiO₂ composition.^{28,29} As

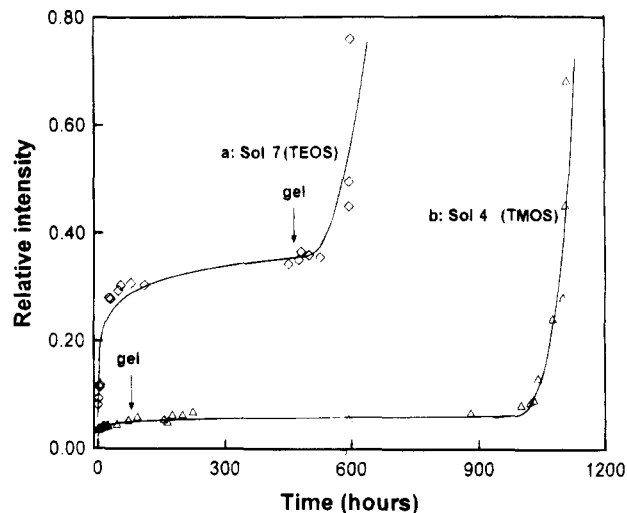


Figure 8. Evolution of the ratio I_F of the HITC red (800 nm) and orange (650 nm) intensities during the gelation and drying of sol 7 (a) and sol 4 (b).

presented in Figure 5f, by employing a low content of TEOT as copolymerizable monomer in the hydrolysis–condensation of TMOS ($r_{w/m} = 1$) results in homogeneous microstructure of less shrinkage than this observed with PMMA gel glasses in Figure 5e. As demonstrated by IR analysis (same spectra as in Figure 6a), such as shrinkage retarded the hydrolysis of alkoxy groups when exposed to air, and reduced the formation of new silanol groups in the pores of the matrix. Alkoxy groups on the surface provided a high chemical stability to HITC molecules in the gel glass (Figure 4c).

In the presence of SSA such as Triton X-100, a high chemical stability of HITC was found in samples prepared from $r_{w/m} = 1$ and $r_{w/m} = 4$. The stability behavior is similar as the expected by the effect of HITC encapsulation since SSA can be used to reduce the reactivity of hydrolyzed surfaces of the samples. The stable fluorescence after 5 months in these matrices are shown in Figure 4d. In this case, both compositions in the starting solution $r_{w/m} = 1$ and $r_{w/m} = 4$ can be used in the preparation of stable HITC gel glasses, since demonstrated is the effectiveness of Triton X-100 in avoiding chemical reactions between silanol groups and HITC.

3.2. Fluorescence and IR Behavior of HITC-Doped Gel Glasses. HITC fluorescence degradation was observed in the steady-state spectra of Figure 2 of the reacting TEOS, when using $r_{w/m} = 1$ (sol 7, Table 1). The decrease of the near-IR fluorescence at $\lambda_{max} \approx 800 \text{ nm}$ is paralleled to the increase of a new band that appears at $\lambda_{max} \approx 650 \text{ nm}$ which is ascribed to the degraded HITC product. The variations in the fluorescence relative intensity, I_F , are shown in Figure 8a. It was observed that dissolving HITC in TEOS (without addition of water) allows fast degradation of HITC (<7 h), which shows a similar degradation pattern to HITC in Figure 2. During HITC degradation an orange coloration of the original blue solution was observed, which suggested that the formation of I₂ molecules by a reduction/oxidation process is one step of the degradation mechanism. This process allows the dissociation of the ion pair I–HITC, thus producing the change in the coloration.

Since it becomes obvious that HITC degradation will be facilitated when TEOS is present, it is essential to

(28) Yoldas, B. E. *J. Non-Cryst. Solids* **1980**, 38–39, 81.

(29) Brinker, C. J.; Harrington, N. S. *Solar Energy Mater.* **1981**, 5, 159.

decrease the TEOS content in the starting solution, which could be imposed by the reactivity of TEOS (e.g., the $r_{w/m}$ and $r_{s/m}$ molar ratios) in the sol-gel reaction.^{5,6,30-32}

First, we made experiments to test the effect of various TEOS prehydrolysis time (t_h , before dye addition) on HITC chemical stability (sols 12-15, Figure 9a). The results revealed that the faster degradation of the red band at $\lambda_{max} \approx 800$ nm corresponds to sol 12 with $t_h = 0$, and the better stability to $t_h = 1.5, 2.5,$ and 7 h (Figure 9a).

To study the effect of water content on HITC chemical stability, TEOS solutions with $r_{w/m} = 1, 4,$ and 10 were prepared. The results show that sols with higher water-to-monomer ratio (sols 11 and 17 in Figure 9b) have higher HITC chemical stability. These results confirmed that in the preparation, the fast decrease of TEOS content in the solution shall retard HITC degradation.

In the study of the ethanol content in the starting solution (Figure 9c) with $r_{w/m} = 4$ (sols 10, 12, 16, and 20), we observed that an increase in the ethanol-to-monomer ratio from $r_{s/m} = 1.5$ to $r_{s/m} = 7$ results in improved HITC stability (sol 16: $I_F \approx 0.20$). Similar I_F 's were found in sols 9, 13, and 18 in which the variation of the $r_{w/m}$ do not cause any change in the fluorescence. On the other hand, a very low ethanol concentration such as in sols 19 and 20 should be avoided (sol 19: degradation < 24 h, $I_F \approx 2.6$, not shown).

TMOS gel glasses ($r_{w/m} = 1$, sol 4) showed a different pattern of behavior as observed in Figure 8b. The HITC fluorescence remain stable during the sol-gel transition as long as 1000 h without the appearance of the HITC degraded band at $\lambda_{max} \approx 650$ nm (Figure 10). HITC degradation in sol 4 starts at an advanced stage of the wet-gel to the dry-xerogel transition (Figure 10, 1150 h). Since HITC stability is clearly associated to the composition of the starting solution, which is one of the most important factors controlling the structure of the gel, ^{6,31,33,34} we analyzed in detail the infrared spectra of the gel glasses prepared from sols 3-6 to clarify the important role of the structure of the gel glass on the dye stability. After degradation, large differences in surface composition of the gel glasses were found in Figure 6b (sol 4), which is also representative of sols 5 and 6 after HITC degradation (800 h). These spectra showed typically absorption bands that are ascribed to the Si-O-Si asymmetric bond stretching (1088 and 794 cm^{-1}) and bending (456 cm^{-1}) vibrations.³⁵ The bands at 950 cm^{-1} and the shoulder at 570 cm^{-1} are ascribed to terminal Si-O⁻ groups. The bands at 3440 cm^{-1} (broad) and 1637 cm^{-1} were due to the adsorbed H₂O molecules on the surface. No traces of C-H bonds ($1460, 836$ cm^{-1}) were observed due to solvents or uncompleted reaction of the monomer. In the stable gel glasses, a low intensity of the Si-OH band at 950 and 3440 cm^{-1} was found in Figure 6a, as well as peaks

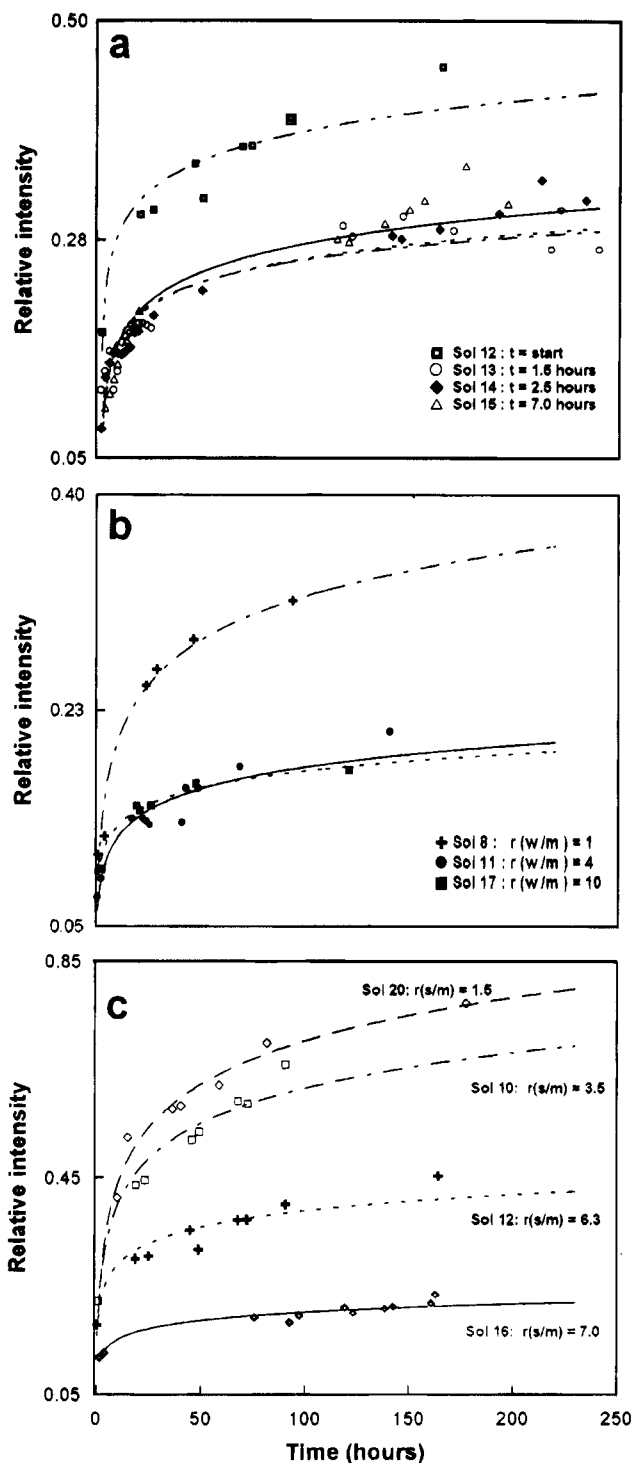


Figure 9. Evolution of the I_F versus time for various prehydrolysis times at which HITC is added to the reacting solution (a); different H₂O/TEOS molar ratios in the starting solution (b); different ethanol/TEOS molar ratios in the starting solution (c).

ascribed to unhydrolyzed Si-O-R groups³⁵ ($2936-2826, 836$ cm^{-1}), but these are also observed the Si-O-Si bands. Therefore, the unhydrolyzed alkoxy groups observed in the gel glasses from $r_{w/m} = 1$ (sols 3 and 4 before degradation) avoid HITC degradation, and were also observed in the IR spectra of the PMMA-SiO₂ and TiO₂-SiO₂ gel glasses. On the other hand, complete

(30) Sakka, S.; Kamiya, K. *J. Non-Cryst. Solids* **1980**, *42*, 403.

(31) Scherer, G. W. *Yogyo-Kyokai-Shi* **1987**, *95*, 21.

(32) Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Ashley, C. S. *J. Non-Cryst. Solids* **1982**, *48*, 47.

(33) Hu, Y.; Chung, Y. J.; Mackenzie, J. D. *J. Mater. Sci.* **1993**, *28*, 6549.

(34) Sakka, S.; Aoki, K.; Kozuka, H.; Yamaguchi, J. *J. Mater. Sci.* **1993**, *28*, 4607.

(35) Ocaña, M.; Fornés, V.; Serna, C. J. *J. Non-Cryst. Solids* **1989**, *107*, 187.

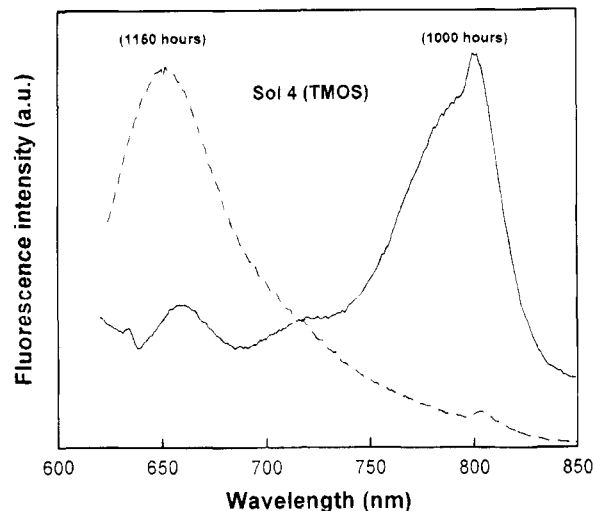


Figure 10. Fluorescence spectra of HITC gel glass from sol 4 after 1000 h (—), and 1150 h (---) of reaction ($\lambda_{\text{excitation}} = 590$ nm).

hydrolysis of alkoxy groups in $r_{w/m} = 4-10$ (sols 5 and 6) and sol 4 after 1150 h allows fast and irreversible HITC degradation. In this case HITC molecules are located on a surface with open porosity, which can be easily hydrolyzed. Additional evidence supporting that fully hydrolyzed surfaces (silanol groups) produce HITC degradation was obtained from HITC adsorbed in commercial SiO_2 , in which upon adsorption degradation takes place after 2–3 days. Under this situation, the IR (Figure 6) and the fluorescence (Figure 11) spectra of HITC adsorbed on the SiO_2 showed similar characteristics that these found in the degraded sols 4–6. After following the analysis (see Experimental Section) of HITC in acid solution, the proposed mechanism for dye degradation is related to an acid catalyst effect of the silanol groups with the residual water, which causes the hydroxylation of the conjugated π -system.

4. Conclusions

Encapsulation on near-IR dyes with stable fluorescence has been achieved with oxazine-1 in TMOS and TEOS gel glasses. HITC gel glasses prepared from TMOS required a protected environment provided by a high content of unhydrolyzed alkoxy groups on the

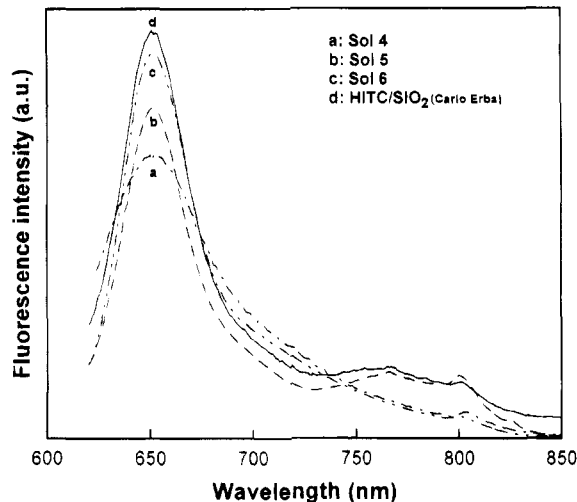


Figure 11. Fluorescence spectra after degradation of HITC gel glasses from sol 4 after 1150 h (a); sol 5, 550 h (b); sol 6, 400 h (c); and SiO_2 after HITC adsorption and evacuation of the ethanol (d).

matrix surface. To avoid posterior hydrolysis of these groups and further degradation of HITC, a high density in the gel glass is also required. From all the preparations, $r_{w/m} = 1$ (TMOS) and $t_{\text{aging}} = 45$ days are the best conditions to prepare chemically stable HITC gel glasses. In the case of HITC gel glasses prepared from TEOS, the poor stability of HITC is due to the partial chemical degradation of HITC by the monomer in the starting solution and completed by the surface of the trapping matrix. Alternatives to this preparation are organic-inorganic hybrid matrices of silica gel-PMMA glasses, or inorganic gel glasses with a mixed TiO_2 - SiO_2 composition, or encapsulation of HITC with the aid of surface-active agents. It is concluded that chemical stabilization of HITC involves removing the concentration of surface silanols which is the primary cause of the HITC degradation in gel glasses.

Acknowledgment. We thank CAM (Comunidad Autónoma de Madrid) for a SLM-Aminco spectrofluorometer. We thank to Dr. T. Carreño and Dr. M. Ocaña for helpful discussion on SEM, TEM, and IR analysis, and to Carlos Alonso for technical support.

CM940310E