

Organically modified sol-gel films doped with infrared dyes: an optical investigation

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Steady-state absorption and emission measurements for an infrared (IR) dye, commercially known as IR1051, have been reported. Measurements in liquid solutions and in hybrid organic/inorganic zirconia-based thin films synthesized with a sol-gel technique have been carried out. The optical properties of films as a function of the densification temperature have also been investigated. The results are discussed in terms of the presence of monomer and dimer species of the dye and of the physical and chemical interactions with the host matrix.

1. Introduction

Thin films prepared by sol-gel technique are of considerable importance because of their potential exploitation in integrated optics for telecommunication. High quality waveguide devices by means of sol-gel methods can be accomplished and fabrication of low-loss waveguides on glass and silicon substrates was recently reported.[1] In particular, organically modified ceramic (ORMOCER)[2] hosts are promising, because they present, with respect to those obtained with the original sol-gel recipes,[3] higher mechanical[4] and optical performance[5,6] with low porosity,[2] no sensitivity to the humidity, and suitability for deposition as thick films via spinning or dipping in a single passage.

Moreover, the low temperature of synthesis of the sol-gel method allows the incorporation of soft dopants, such as organic molecules, without damage for their molecular structure. This opens the possibility to obtain functionalized materials for active components (laser/light sources, modulators) efficiently integrated with optical fibers and external devices. The embedding of molecules in a rigid matrix leads to isolation of the active species that hinders intermolecular interaction and intramolecular rearrangement,[7] protects the active molecule from the environmental attack and/or photofragmentation and increases the life of the material.[8] A careful examination of the physical and chemical interaction between host and guest is therefore a crucial point for obtaining new and more efficient optical materials.

In the last years ORMOCER hosts doped with dye molecules were extensively studied and good results for light amplification were reported with large gain in the visible range.[6,9] In order to extend these studies towards the near-infrared region of interest for fiber optics, we have recently investigated new photoluminescent composite materials based on dye molecules emitting in the range 1.1 - 1.3 μm .[10] In the present work we point out on the effects of the matrix structure on the optical properties of a physically incorporated dye (IR1051) in hybrid matrix. The inorganic network, based on ZrO_2 , is modified by addition of an organic tail brought in by an organosubstituted silico ester, giving rise to a hybrid blend

at molecular level. ZrO_2 instead of SiO_2 or TiO_2 was chosen for its high refractive index and good chemical resistance. Moreover, the low energy phonons of the zirconia glass reduce the probability of nonradiative processes.[11] Finally, the zirconia and zirconia-ormosil undoped films present high transmission coefficient from infrared to about 220 nm.[12]

2. Experimental

The starting solution, for film deposition, was obtained by mixing zirconium(IV)propoxyde, as the inorganic network former, 3-glycidyloxypropyl-trimethoxysilane (GLYMO), as the organic modifier, together with ethanol and acetic acid as stabilizers. Hydrolysis of the solution was promoted by the successive addition of 2-methoxyethanol and of a 50% solution of acetic acid and water. Molar percentage of GLYMO in the films was held in the range 40 - 50 % ($X_{\text{GLY}} = [n_{\text{GLY}} / (n_{\text{GLY}} + n_{\text{Zr}})] \times 100$).

IR1051 dye molecules (purchased by Sigma-Aldrich) were added without further purification to the solution after hydrolysis took place, in a concentration of about 3.0×10^{-4} M. IR1051 is the commercial name for a polymethine dye having the following linear chemical representation: ([6-chloro-2-[2-[3-[(6-chloro-1-ethylbenz[cd]indol-2(1H)-ylidene)ethylidene]-2-phenyl-1-cyclopenten-1-yl]ethenyl]-1-ethylbenz[cd]indolium tetrafluoroborate]) (see Fig. 1).

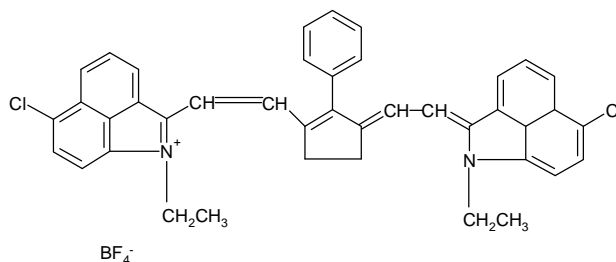


Fig.1: Molecular structure of the IR1051 (Sigma-Aldrich).

The solution used for film synthesis was filtered with membranes of 0.45 μm porosity and deposited by spin coating or by casting on thoroughly cleaned corning glass substrates in a clean room. All films were held at room temperature for 24 hours before measurements. Typical average thickness was in the range 2 - 4 μm depending on the deposition parameters. For the sake of comparison, liquid solutions of IR1051 in methanol were also prepared. Quartz cuvettes with a thickness of 1 mm were used to measure absorption and emission spectra of liquid samples.

A set of IR1051 hybrid films were synthesized by spin coating, using the same deposition parameters (spinning velocity and time), in order to study the effect of the densification on the optical properties. A programmable oven has been used to perform the densification process. The samples, placed into the oven at room temperature, were heated up to the desired densification temperature with a constant rate ($\Delta T/t \approx 14$ $^{\circ}\text{C}/\text{h}$). After 1 hour at the selected temperature the samples were cooled down to room temperature with the same rate. We follow this procedure in order to minimize surface stresses and possible cracks in the film.

Steady-state absorption spectra were recorded with commercial spectrophotometer. Emission spectra were obtained using a standard setup for photoluminescence, excited with a cw Nd:YAG laser ($\lambda=1.064$ μm and average power ≈ 100 mW), dispersed with a 30 cm grating monochromator and detected with a Ge photodiode cooled at liquid nitrogen temperature. Special care was devoted in choosing the geometry of the emission collection to avoid both re-absorption of the emitted light and elastic scattering from exciting laser into the detector.

3. Result and discussion

Liquid solutions with different molar concentration in the range 10^{-3} - 10^{-6} M were prepared to check possible effects related to dye concentration. Fig. 2 shows absorption spectra of IR1051 in methanol solution at room temperature (RT) at four dye concentrations. The most dilute spectrum (1×10^{-6} M) presents two strong peaks at 1045 nm and at 899 nm and a little shoulder at 823 nm.

This spectrum, considering the very low concentration, can be ascribed almost completely to the absorption of the purely IR1051 monomeric species with a very small contribution of dimers. We note that the relative intensity of the shoulder at 823 nm increases with the dye molar concentration. Conversely, emission spectra recorded for different concentration values (not reported) showed no substantial differences in the luminescence line shape.

The presence of an isosbestic point at about 846 nm in the absorption spectra suggests an equilibrium between IR1051 monomer and dimer species.[13] Both of them contribute to the absorption features in a way proportional to their presence in solution. Clear attribution of the spectral components to specific transitions is not possible because the electronic levels of the IR1051 molecule are not known at present. Nevertheless, we

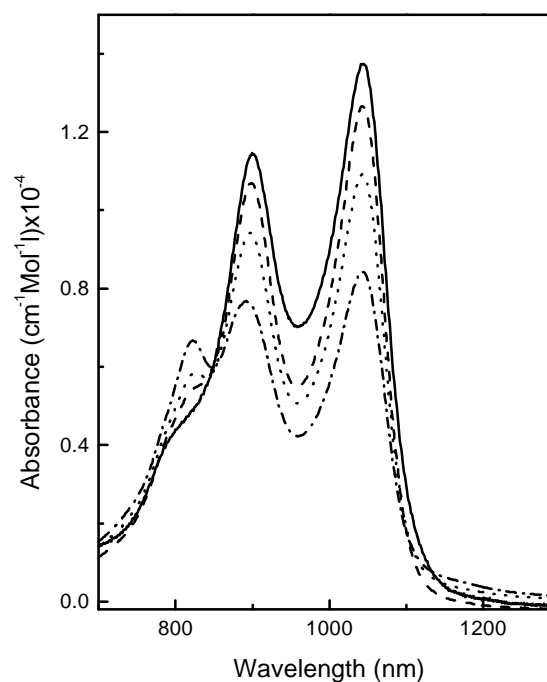


Fig.2: Absorption spectra at room temperature of IR1051 in methanol solution for different concentration: 1×10^{-6} M (solid curve), 5×10^{-5} M (dashed curve), 1×10^{-4} M (dotted curve) and 3×10^{-4} M (dash-dotted curve).

attempt a rough decomposition of the absorption bands in gaussian components. As a result, the monomeric part of the spectra were fit by three bands (centered respectively at 1048, 976 and 899 nm) whose relative amplitudes and widths remain almost constant increasing the concentration. On the other hand, the residual component, peaked at 827 nm, tentatively attributed to the dimers, was fit with a gaussian line-shape constant in energy and width but with an amplitude increasing with the concentration.

On the basis of the molecular exciton theory,[14] the excited state of the dimer splits into two levels, one at higher and one at lower energy with respect to the corresponding monomer excited state. Dimers are classified as H- and J-aggregates according to whether the absorption transition is predominantly allowed to the upper or to lower energy level of the doublet, respectively. The structural configuration of the dimers is a sandwich geometry for H-species and is oblique or coplanar geometry, with an inclined transition dipole, for the J-ones. Due to the above mentioned selection rules, also the emission properties depend strongly on the dimer type: H-aggregates are non fluorescent forms, while J-species show a strong emission. The increase of the absorption structure at 823 nm (high energy side of the monomer peaks) together with the lack of concentration effects in the emission spectra of IR1051, suggest that the dimers are predominantly constituted by H-aggregates.

The normalized steady state absorption and emission spectra of IR1051 in non-densified hybrid films, both for spin and for casting deposition method, are reported in Fig. 3.

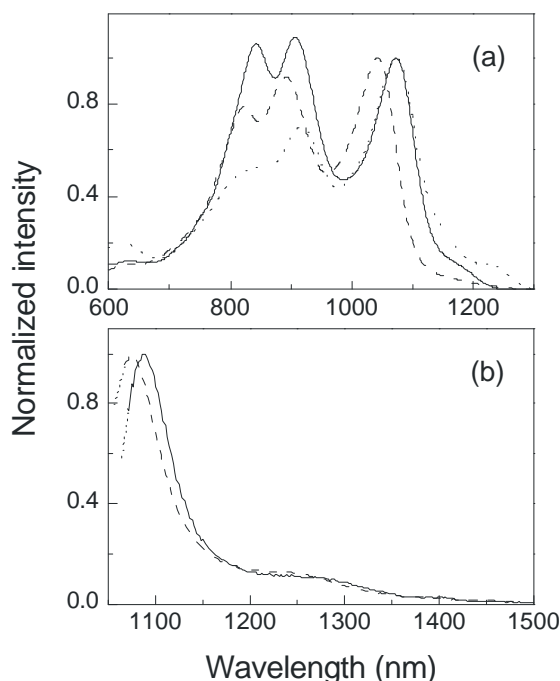


Fig.3: Steady state absorption (a) and emission (b) spectra at room temperature of IR1051 dye molecules. IR1051 in methanol solution 3×10^{-4} M in a 1 mm quartz cuvette (dashed line), in a non-densified hybrid film deposited by spin coating (solid line), and by casting procedure (dotted line).

The spectra obtained in methanol solution (3×10^{-4} M) are also shown. The film thickness was about $4 \mu\text{m}$ for both films. A red shift of the absorption bands for the film spectra (Fig. 3(a)) with respect to liquid solution is observed. The laser-excited emission spectra, corrected for re-absorption process, are shown in Fig. 3(b) for liquid solution and organically modified films (the spectra related to the two films are undistinguishable). Each emission curve was also corrected for the spectral response of the optical apparatus and normalized to the maximum intensity. A red shift of the main emission band of approximately 10 nm was detected for films with respect to solution.

The solvatochromic and local environment effects as well as different polarity and rigidity, experienced from the dye molecules in liquid solvent and in presence of a rigid matrix, can be responsible for the energy shift in the absorption and emission bands. It is well known, in fact, that physical constraints imposed on the molecules, interaction with residual chemicals inside the sol-gel network, increased rigidity and changing in polarity of the surroundings cause both red or blue shift in the absorption and emission bands.[8,15,16] In the present case, the measured red shift in solid samples, compared to solution, suggests that the fluorescent molecules in the hybrid organic/inorganic glasses are basically surrounded by a non-polar environment[2,16] composed predominantly by the organic non-polar groups of the GLYMO.

A noticeable difference in the relative amplitudes of the absorption band components in solution and films can also be observed. In particular, the absorption band related

to the H-aggregates (higher energy side of the spectrum) is strongly enhanced for solid sample obtained by spin coating while is reduced for sample deposited by casting with respect to the solution. We ascribe this behavior to a preferential orientation of the IR1051 dye molecules in the spun film where the molecules tend to place their molecular plane parallel to the film surface.[17] Consequently, the formation probability of the H-aggregates (sandwich geometry) results increased with respect to the solution even if the molecular concentration, in liquid and film, are of the same order (3×10^{-4} M). Immediately after the deposition the film stiffening begins. This process blocks and stabilizes the dimers in their own positions and, as a result, a considerable absorption band related to the H-species can be detected for spun films. On the contrary film stiffening for cast samples stabilizes the molecules in a random distribution, hindering dimerization.

In Fig. 4 the absorption spectra for IR1051 ORMOCER spun films as a function of the densification temperature are shown. In Fig. 4(a) the absorption spectra of the non-densified film and of the samples densified at 60°C and 80°C are reported. It can be noted that the absorption band related to the H-aggregates (843 nm) decreases with the increase of the densification temperature. On the contrary, the absorption bands related to the monomer species increase with respect to the non-densified film. The apparent decrease and the energy shift of the second monomeric absorption band (908 nm) is only an artifact due to the simultaneous decrease of the dimeric band. From

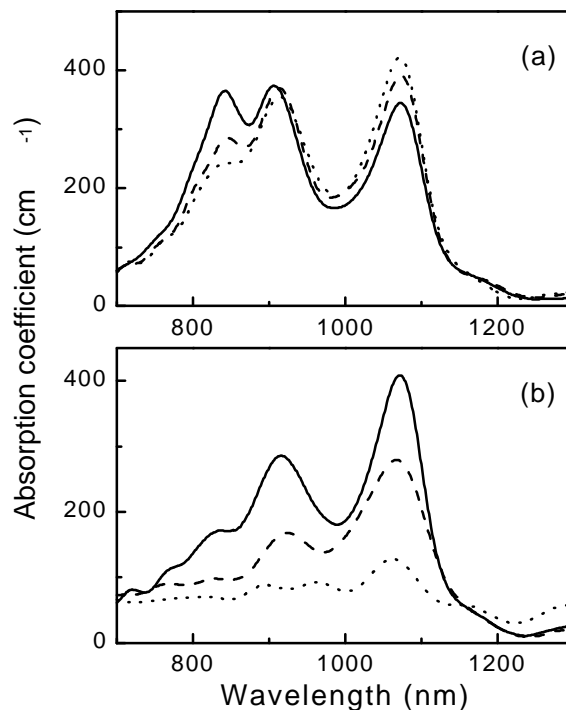


Fig.4: Steady state absorption of IR1051 dye molecules at room temperature in films deposited by spin coating as a function of the densification temperature: (a) untreated (solid line), $T=60^\circ\text{C}$ (dashed line), $T=80^\circ\text{C}$ (dotted line); (b) $T=100^\circ\text{C}$ (solid line), $T=120^\circ\text{C}$ (dashed line), $T=150^\circ\text{C}$ (dotted line).

the above cited fitting procedure in fact the relative amplitudes of the monomeric components remain indeed almost constant changing the densification temperature, while the amplitude of the dimeric band decrease gradually with the increase of the temperature.

In Fig. 4(b) the spectra of the films densified at higher temperatures are shown. For densification temperatures equal or higher than 100 °C the amplitudes of both the dimeric and monomeric bands decrease. Emission measurement of each film as a function of the densification temperature have also been accomplished, showing no difference in the luminescence line shape.

The lowering of the dimeric absorption band with the increase of the densification temperature denotes a decreasing of the total number of H-aggregates. We attribute this result to the reduction of the solvent quantities in the film and to the stiffening of the solid matrix for higher densification temperatures. The presence in the film of solvents and of water in particular, plays an important role in the dimerization process and is fundamental for the dimers formation.[13] Moreover, the increased hardness of the matrix can misalign the couples of molecules constituting the H-dimers contributing to the dimers breaking. These findings can explain the decreasing of the dimeric absorption band and the simultaneous increasing of the monomeric bands for low densification temperatures ($T < 100^{\circ}\text{C}$). For higher treatment temperatures ($T > 100^{\circ}\text{C}$) the IR1051 dye molecules (fusion point 230 °C) begin to damage and therefore a decreasing of the whole absorption spectrum occurs.

4. Conclusions

In conclusion, we reported on the possibility to dope thin solid films, obtained with a sol-gel technique, with an organic dye molecule emitting in the 1.1 - 1.3 μm range. The optical properties of the dye have been extensively studied in solution and in thin solid ORMOCER films, synthesized both by casting and spinning method. The absorption spectra were discussed in term of monomer/dimer model. The effect of the matrix on the molecular distribution was followed at different stages of stiffening, produced by thermal treatments.

Acknowledgments

This research was partially supported by the MURST (cofin98). The authors gratefully acknowledge S.G. Marrone and F. Sarcinelli for the valuable help in sample preparation.

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