

## Hybrid Materials for Solid-State Dye Laser Applications

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The quest for a solid-state tunable dye laser can be satisfied by sol–gel prepared organic–inorganic hybrids. A photostability study of porous silica–Rhodamine 6G hybrids prepared via a sol–gel method is presented. The dye molecules can be incorporated into the silica matrix by forming weak or covalent bonds (hybrids of classes I and II, respectively). New class II samples and traditional class I materials prepared by the pre-doping method were synthesized. Samples were characterized by photoluminescence measurements to compare the emission properties and the photostability of the samples. The decay of the fluorescence signal as the cumulative excitation energy increases is reported and interpreted by hypothesizing that the dye molecules can be hosted in different surroundings within the porous glass matrix. The reported photoluminescence and photobleaching features indicate the class II samples as good candidates for solid-state dye lasers.

### I. Introduction

The incorporation of dye molecules into solid matrixes is an attractive and widely investigated basis to prepare dye-doped solid-state devices.<sup>1–3</sup> Among the possible applications, the large oscillator strength and the broad tunability of organic dye molecules combined with the advantages offered by the solid host with respect to liquid solutions indicate that these materials are good candidates for solid-state dye laser applications.<sup>4–6</sup> Indeed, as compared to liquid solutions, the solid matrix offers a larger mechanical and thermal stability, reduces the risks of environmental and operator hazards, and allows, in principle, achievement of larger concentrations of the dye, avoiding or, at least, reducing the formation of aggregates responsible for the quenching of the luminescence.<sup>1</sup> In the past few decades, solid-state active media were prepared by introducing dye molecules into solid matrixes of organic, inorganic, or hybrid nature.<sup>1,4,7–14</sup> Among the investigated possibilities, the embedding of dye molecules into silica glass prepared via sol–gel methods can offer the highest physical and chemical performances.<sup>1,15–25</sup> Two different approaches can be followed to prepare dye-doped silica glasses: the impregnation or post-doping method, where the selected dye is incorporated into the sol–gel prepared porous silica by imbibition,<sup>18,26,27</sup> and the pre-doping method, where the dye molecule is introduced at the sol stage of the sol–gel procedure.<sup>1,18,19,23,25</sup> The latter can easily be achieved because the sol–gel method is a room-temperature synthesis and the organic molecules do not suffer thermal degradation. The main advantages of the pre-doping method with respect to the post-doping one are the homogeneous distribution of the dye molecules because of the mixing of the components at a molecular level, the possibility of introducing larger amounts of dye avoiding or reducing the fluorescence quenching because of dye aggregation, and the elimination, or reduction, of leaching. The interaction between dye and silica

matrix can be accomplished by electrostatic or covalent bonding: in the first case the samples are classified as class I materials; in the second they are classified as class II. The latter, due to the immobilization of the dye molecules, are expected to resolve the leaching and bleaching effects reported for class I samples.<sup>1,25</sup> Samples prepared via standard pre- and post-doping methods belong to class I; samples prepared via pre-doping method by properly engineering (i.e., grafting) the dye molecule belong to class II. However, the main drawback to the realization of a solid-state dye laser remains the limited photostability of the confined dye inside the solid matrix, the consequently fast degradation of the dye molecules, and their luminescent properties.<sup>11,12,28–31</sup> In this respect, the presence of the covalent bond introduces in the dye molecule a series of recombination channels through which it can dissipate the energy excess and therefore the accumulated heat from the excitation wavelength during the pumping process.<sup>28,32</sup> The aim of this work is to compare the photoluminescence and photostability properties of class I and II samples. Because of its high quantum yield in fluorescence in the 500–600 nm range, Rhodamine 6G (Rh6G) has been one of the most frequently used dye molecules and is the one of choice in the present work. The presence of leaching and bleaching effects in the prepared samples and the influence of different chemical treatments were investigated. The photobleaching effect is interpreted by hypothesizing that the dye molecules can be hosted in different surroundings within the porous glass matrix. The reported analysis indicates that the class II samples are good candidates for solid-state laser applications.

### II. Samples and Experimental Setup

**(a) Samples.** Three sets of sol–gel prepared samples were investigated: two different sets of type I samples and one kind of type II. The first set of type I samples was prepared with chloride Rhodamine salt; the second set was prepared with perchlorate Rhodamine salt.

Type I samples were synthesized adding dye molecules at the sol stage, according to the following recipe: 0.125 mol of

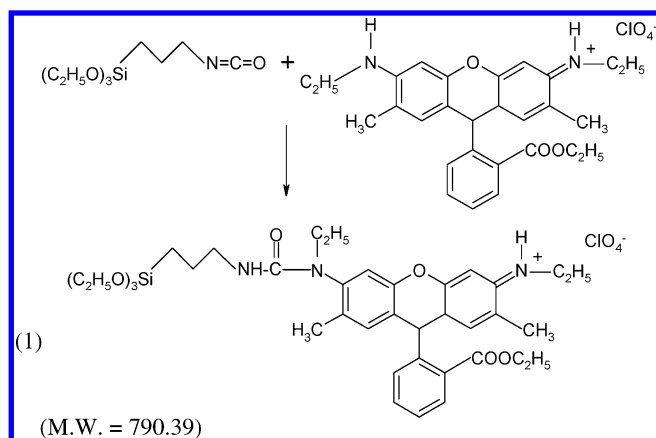
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TEOS was added to 50 mL of an aqueous solution of 0.01 N HCl and mixed with 12.5 mL of ethanol as a cosolvent. The mixture was stirred for 15 min, and then ethanol was removed by distillation at 35 °C by a rotating evaporator to obtain 45 mL of "sol". Then, the chloride or perchlorate Rhodamine salt dissolved in methanol at the desired concentration was added to the sol, together with 0.05 N  $\text{NH}_4\text{OH}$  to increase the pH from 2 to 4.2. Gelation occurred in about 2–3 h. Gels were aged for at least 1 day in the mold and dried at room conditions for about 1 month. By contrast, samples subjected to thermal treatment (indicated with the index "T") were dried at 65 °C.

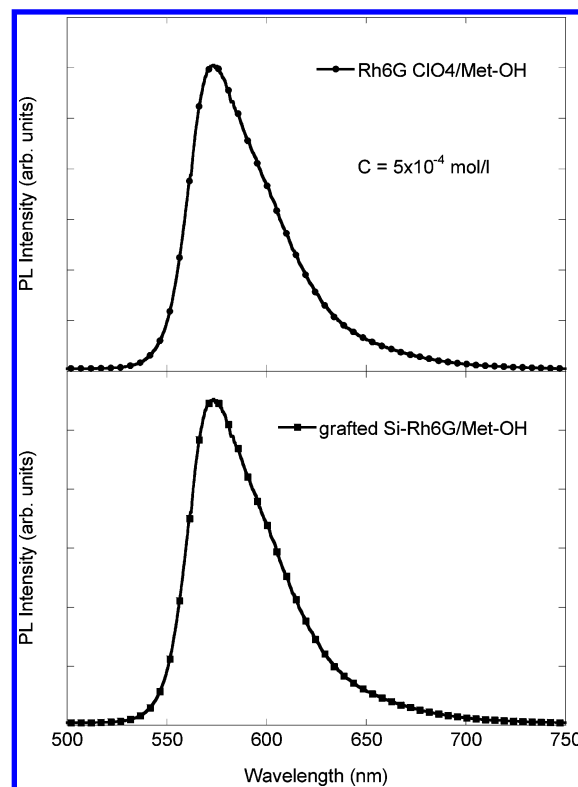
Type II hybrids were prepared by a two-step process, by using perchlorate salts. In the first step a grafted Rhodamine perchlorate was prepared as follows: 0.3 g of Rhodamine perchlorate was dissolved in 12 mL of acetonitrile; then 0.15 g (with an excess of 5% to take into account reactivity with the moisture in the atmosphere) of 3-isocyanatepropyltriethoxysilane was added to the solution. The mixture was stirred for 24 h at room temperature. At the end the solvents were evaporated at 60 °C. The obtained powder was successively dried at 60 °C under vacuum for at least 1 h. The following reaction took place:



In the second step, the hybrid synthesis was performed as described for type I hybrids. Two kinds of samples were produced: (i) as prepared; (ii) washed. As-prepared samples were extracted and directly dried under room conditions for about 1 month. Washed samples (indicated with the index "W") were extracted and washed in distilled water three times for at least 1 day each time to eliminate some not-grafted Rh6G. Then, they were dried under room conditions for about 1 month.

The molar concentration of the dye in the gels was estimated as the ratio between the molar amount of Rh6G in 15 mL of sol and the geometric volume of the dried xerogels, which was measured for each sample by means of a micrometer calliper because of the different shrinkages. The final molar concentration of the samples ranged between  $1.6 \times 10^{-3}$  and  $1.4 \times 10^{-4}$  mol/L. A 10% error is allowed.

**(b) Measurements.** Steady-state photoluminescence spectra were obtained with the 363.8 nm line of an argon ion laser (INNOVA 90C-4) and detected with a photonic multichannel spectrum analyzer (Hamamtsu PMA-11). Photostability measurements were performed by means of a high power pulsed laser. The excitation was provided by the third harmonic (355 nm) of a Nd:YAG pulsed laser (Spectra Physics Quanta Ray Pro270) with a temporal pulse width at half-maximum of 10 ns at 30 Hz repetition rate. Photoluminescence (PL) photostability spectra were recorded by focusing the PL emission onto the entrance slit of a triple grating spectrograph (ARC SpectraPro-275). Light signal detection was achieved through an



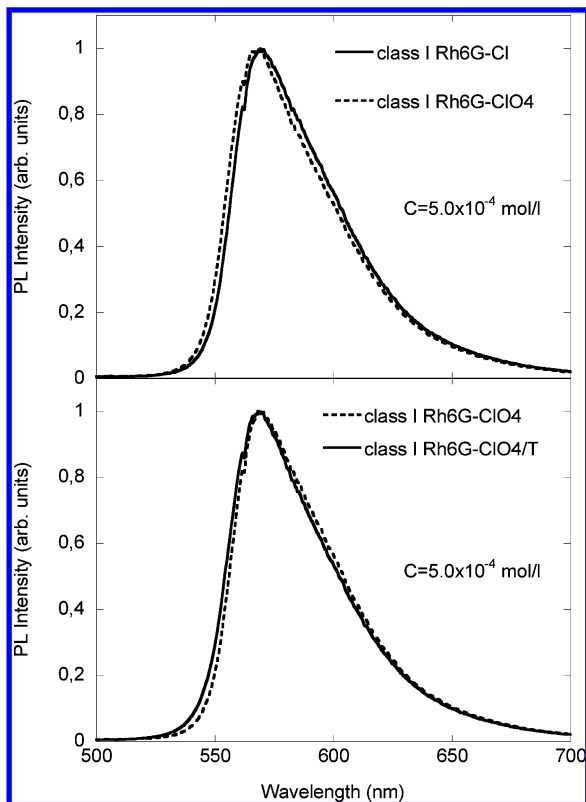
**Figure 1.** Normalized PL spectra of Rh6G molecule and Si-Rh6G grafted molecule in methanolic solution (Rh6G concentration  $5 \times 10^{-4}$  mol/L).

intensified photodiode array (EG&G Model 1420). For both experimental setups, spectral resolution was 1 nm. All spectra have been corrected for the spectral response of the optical systems. Steady-state PL and PL photostability measurements were carried out in front face configuration to minimize reabsorption effects.<sup>33</sup>

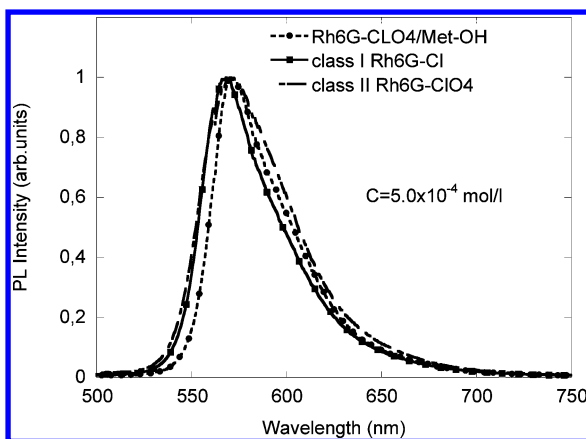
Absorbance measurements were performed in transmittance configuration upon film samples prepared via spin-coating method. A nondoped silica film was assumed as reference. Sample thickness was estimated to be about 2  $\mu\text{m}$ .

### III. Results and Discussion

The sol-gel synthesis of samples of class I succeeded for both salts of Rh6G; however, class II samples were prepared with perchlorate salt because reaction 1 with chloride was difficult to perform. All class I samples showed leaching effects when subjected to washing procedure. As regards class II samples, small leaching phenomena were observed for the samples with the largest concentration of dye molecules ( $1.1$  and  $1.6 \times 10^{-3}$  mol/L). The completion of reaction 1 was verified by Fourier transform infrared measurements (not reported here). The disappearance of the band of the isocyanate group ( $\nu_{\text{as}} = 2275 \text{ cm}^{-1}$  and  $\nu_{\text{sim}} = 1380 \text{ cm}^{-1}$ ) and the observation of a band at about  $3380 \text{ cm}^{-1}$  typical of the NH group of a ureic derivative ( $-\text{HNCONH}-$ ) allowed the assessment that the reaction succeeded. In addition, it was verified that the absorption properties of the Rh6G molecule were not modified by the reaction with the 3-isocyanatepropyltriethoxysilane. This is expected since the characteristic UV-vis absorbance of chromophore is due to the particular  $\pi$  electron delocalized structure by means of the three conjugated benzene rings. Figure 1 shows the photoluminescence spectra of both the Rh6G molecule and the Si-Rh6G grafted molecule in methanolic solution (Rh6G concentration  $5 \times 10^{-4}$  mol/L).



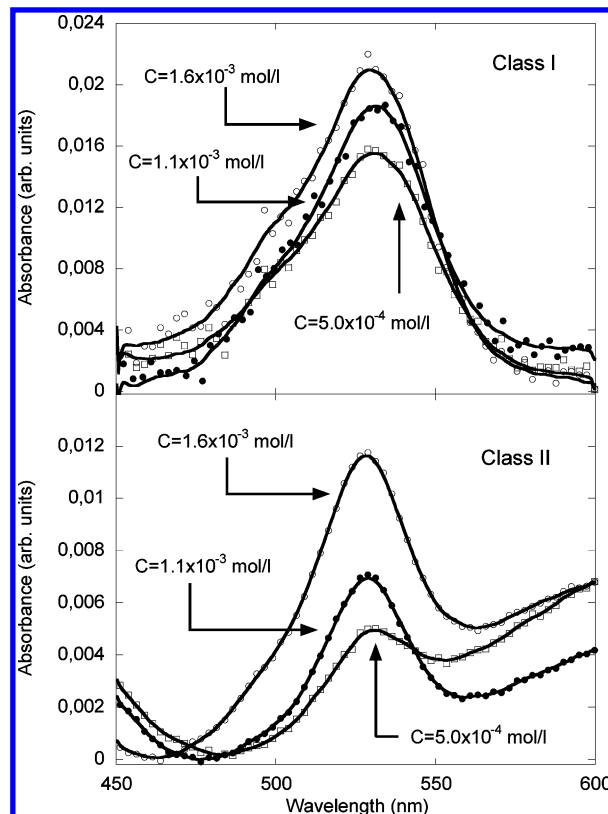
**Figure 2.** Normalized PL spectra of class I samples (Rh6G concentration  $5 \times 10^{-4}$  mol/L).



**Figure 3.** Normalized PL spectra of class I and class II samples compared to Rh6G methanolic solution (Rh6G concentration  $5 \times 10^{-4}$  mol/L).

Spectra were arbitrarily normalized to their maximum. The photoluminescence of both solutions of Rh6G is characterized by an emission peak at 574 nm, in agreement with the data reported in the literature.<sup>5</sup> We conclude that the grafting procedure does not change the optical properties of the dye. The comparison of the different types of class I samples (Rh6G concentration  $5 \times 10^{-4}$  mol/L) is reported in Figure 2: the photoluminescence properties do not change in samples prepared from the perchlorate or chloride precursors, nor by drying the samples at 65 °C in order to speed up the evaporation of the residual solvent; similar results also hold for samples with different concentrations (not reported here for the sake of brevity).

When compared to the PL band of the dye in solution (Figure 3), the spectrum shown by the prepared hybrid samples displays a blue shift of the peak position for hybrids of class I and an

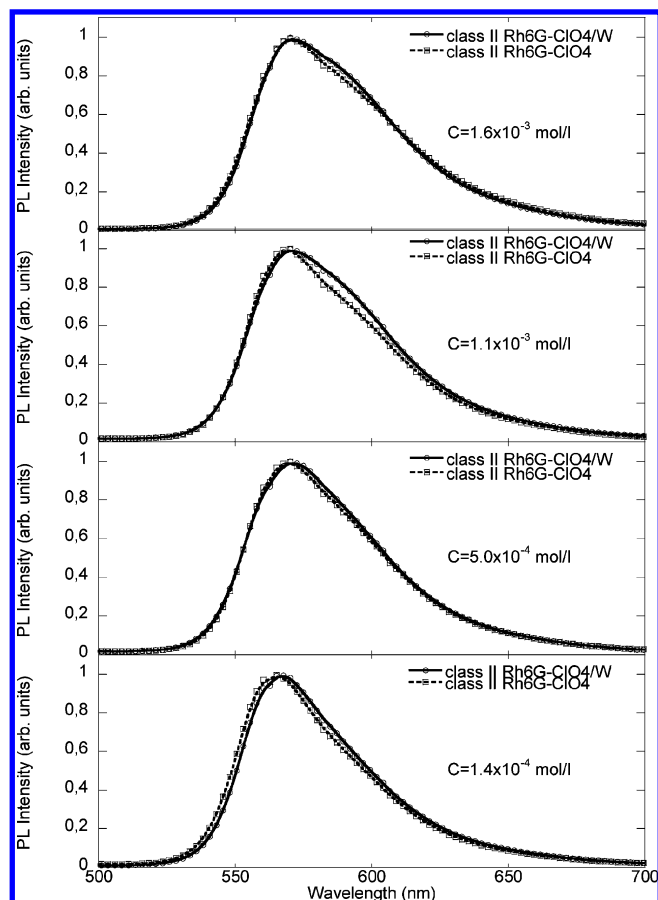


**Figure 4.** Absorbance spectra of class I and II film samples.

enlargement of the PL width for both class I and II specimens. These effects have been already reported for dye molecules hosted in porous glass materials and are related to surface polarity effect and restriction on the mobility of the molecules.<sup>1,34–36</sup> It is interesting to note that class II samples present a PL band larger at larger wavelength with respect to class I samples.

The absorbance spectra of the class I and II samples are reported in Figure 4 and display the typical band around 530 nm related to the monomer dye molecules. As the concentration increases, the absorbance increases for both classes, as expected. Concerning the shoulder about 500 nm, its contribution is larger in class I samples and a heuristic deconvolution of the spectra with two Gaussian bands indicates that it increases with respect to the main absorbance peak at the highest concentration investigated. In class II samples the contribution at 500 nm is barely visible in samples with the largest dye concentration. Since the shoulder around 500 nm is related to both the vibronic replica of the main absorbance peak and the absorbance of dimer molecules,<sup>21,37</sup> we may conclude that, at least in the film samples, no aggregates are formed in class II samples while the formation of aggregates is inferred for class I samples at the largest concentration. However, it is worth underlining that differences in the formation of aggregate species in film and bulk samples can be expected because of the different amounts of specific surface area (SSA): because of fast gelation, film samples are more compacted and the tendency to form aggregates should be reduced. Further investigations are in progress at the moment to elucidate this aspect.

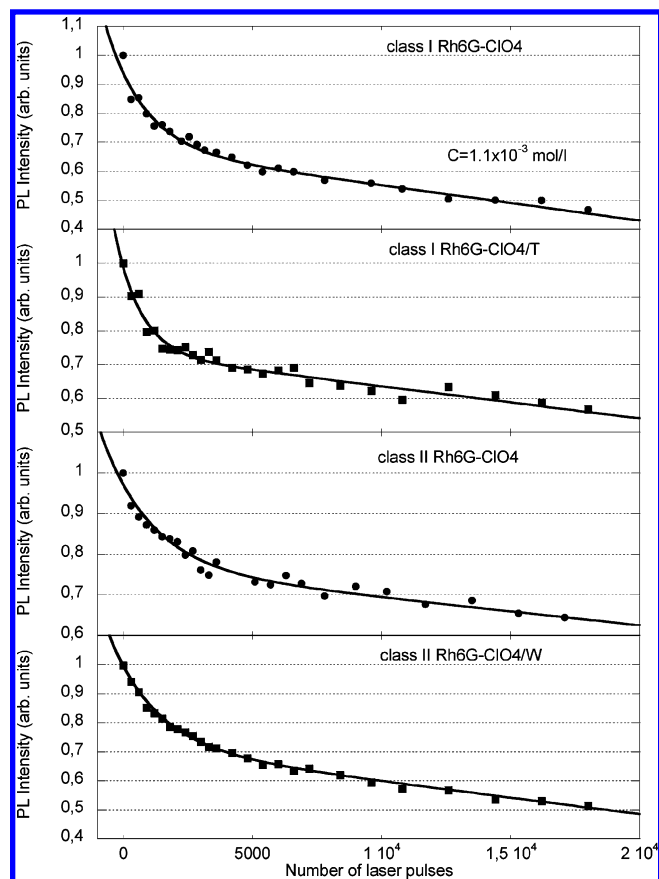
As previously described, class II samples were expected to reduce the leaching phenomenon typically observed in class I samples. Indeed, the performed washing procedure evidenced small leaching effects in the most concentrated class II samples. The effect of the washing procedure on the PL feature of the class II samples is shown in Figure 5. Two main differences



**Figure 5.** Normalized PL spectra of class II samples before and after washing procedure.

can be individuated: a small systematic red shift of the emission peak (of about 1–2 nm) and the presence of a pronounced bump on the long-wavelength side in the samples with the largest concentration of Rh6G.

The washing procedure can be regarded as an aging process that modifies the morphology, i.e., the porosity, of the samples.<sup>2,3</sup> In addition, the procedure also modifies the relative content of solvent trapped in the porous matrix: as-prepared samples contain both H<sub>2</sub>O and EtOH; washed samples contain only water.<sup>38</sup> Indeed, during the aging four different processes can occur: polycondensation, syneresis, coarsening, and phase transformation. Depending on different parameters, such as time, temperature, and pH, different effects can be observed: an increase of the network connectivity (polycondensation), a spontaneous shrinkage of the matrix (syneresis), and a variation in the mean pore diameter with a change of the specific surface because of dissolution and reprecipitation (coarsening). The modification of the PL spectra can be interpreted in terms of the presence of aggregates, such as dimers, whose formation is enhanced by the washing procedure, or in terms of reformation of the molecule, i.e., the presence of molecules in different environments because of the modification of the chemical surroundings induced by the performed treatment.<sup>39,40</sup> Indeed, a bimodal distribution of the pore diameter can be observed in SiO<sub>2</sub> xerogel samples, and the washing procedure increases the diameter of the micropores (diameter < 2 nm) while decreasing the diameter of the mesopores (2 < diameter < 50 nm).<sup>38</sup> A modification in the pore diameter distribution allows the dye molecules to sense different surroundings allowing the formation of H bonds with –OH groups of SiO<sub>2</sub> or entrapped H<sub>2</sub>O (reconformation) or aggregation with other



**Figure 6.** Photostability of class I and class II samples (Rh6G concentration  $1.1 \times 10^{-3}$  mol/L).

dye molecules (dimers). If the systematic red shift of the emission band can be satisfactorily explained by the formation of dye aggregates, which is expected to increase as the dye concentration increases, the spectral modification at the long-wavelength side reported for the samples with the largest dye concentration, the ones where the leaching test removed a small amount of molecules from the samples, calls for the presence of different environments surrounding the dye molecules.<sup>23,33,39,40</sup> Indeed, recent single molecule spectroscopy (SMS) studies have shown that the heterogeneity of hybrid sol–gel samples plays a key role in the emission properties of the dye molecules.<sup>40</sup>

It is well-known that one of the main disadvantages of solid-state dye samples with respect to solution is the fast degradation of the samples as the number of exciting laser pulses increases. By studying the photostability of dye-doped sol–gel host, the presence of dye molecules entrapped in two different environments was reported, calling for nonencapsulated and isolated molecules.<sup>32,38</sup> In the framework of a bimodal distribution of the pore diameters, we can individuate isolated dye molecules as molecules within the micropores, and nonencapsulated dye molecules as molecules located within the mesopores. A different mobility of the dye molecules in different physical and chemical environments was recently reported in comparable systems and a different reactivity can be expected.<sup>41</sup> Thus, the investigation of the photostability properties of the samples allows us to further discuss the presence of different environments for the molecules and to assess the quality of the prepared samples for optical device applications.

In Figure 6 the decrease of the PL signal as a function of the number of pulses for the different kinds of samples (dye concentration  $1.1 \times 10^{-3}$  mol/L) is reported (excitation power of 10 kW/mm<sup>2</sup> pulse). Indeed, above an excitation power



threshold of about 100 W/mm<sup>2</sup> pulse, all the samples displayed a composite decay with a fast exponential component and a slow linear one. Among the investigated concentrations, samples with concentration in the 10<sup>-3</sup> mol/L range displayed the highest photostability. The data were successfully fitted with a theoretical curve given by the sum of the two cited components. It can be observed that among the samples investigated the nonwashed class II samples show the highest hardness to the impinging radiation. For all the samples, the fluorescence signal could not be recovered and the observed photodegradation was permanent: a burned region could be observed after the total exposure.

Photobleaching is the photoinduced permanent modification of a fluorescent molecule into a nonfluorescent one. The main mechanisms involved in the photodegradation process are the oxidation of the molecule and the multiphoton ionization.<sup>42</sup> The relative contribution of the two mechanisms largely depends on the guest–host interactions, that is, the different physical and chemical environments sensed by the fluorescent dye molecule, and on external parameters such as the temperature and the excitation power.<sup>39–42</sup> The photobleaching process is mediated by triplet and higher excited states. Recently, the presence of dark states, where the fluorescent species can rest silently, were also reported to mediate the photoionization increasing the extent of multiphoton processes.<sup>43,44</sup>

The double nature of the reported photobleaching effect can be interpreted in the proposed framework of dye molecules surrounded by different environments, that is, tumbling molecules at the surface of larger pores and molecules caged by the silica network. As reported in comparable hybrid systems, because of the different mobilities of the two subpopulations and the differing availability of molecular oxygen in micro- and mesopores,<sup>41</sup> tumbling molecules may easily react with molecular oxygen or other impurities leading to a photochemical destruction of the molecule: the fast exponential decay is ascribed to this species.<sup>32,44</sup> On the contrary, isolated molecules are characterized by a longer photostability, represented by the linear decay of the fluorescence signal in the reported spectra: we hypothesize that their photodegradation is mainly related to multiphoton ionization through the presence of dark states.

The different photostabilities of class I and class II samples are expected to be related to the differing bonding of the two species to the silica glass. Indeed, covalent bonding allows the dye molecule to better dissipate the energy excess to the silica host; on the other hand, class I samples are expected to display a larger mobility of dye molecules because of the weaker bonding to the silica surface and to experience a larger distribution of photodegradation pathways. It is interesting to note that the 65 °C drying procedure increases the performance of the class I samples. The thermal treatment can be viewed as a “soft” thermal aging where the polycondensation process proceeded further allowing a better isolation of the dye molecules and a more efficient elimination of the traces of EtOH and H<sub>2</sub>O. On the contrary, the washing procedure decreases the photostability of the class II samples because the aging procedure causes an increase of the micropore diameter and a larger amount of tumbling molecules is expected.

A final comment pertains to the quality of the prepared samples as solid-state devices in the optical field. It is well-known that xantene dyes display a large photodegradation because of their poor photochemical stability.<sup>37</sup> The encapsulation of dye molecules in sol–gel silicates is expected to enhance the dye photostability,<sup>37,41</sup> but the performances of xantene-doped sol–gel samples are still not comparable to those of liquid solution. However, due to its spectral properties, and in particular

the high quantum yield, Rhodamine 6G is a system model to study the host–guest interactions and to explore new routes to improve its performances as a solid-state device.<sup>42</sup> The reported data allow us to conclude that by covalently bonding the dye molecule to the silica host (class II samples) an enhancement of the photostability properties of the hybrid samples is obtained as compared to the properties of samples where the fluorescent species is electrostatically bonded (class I), allowing a significant improvement with respect to previously studied comparable hybrid systems.<sup>29</sup>

#### IV. Conclusions

We have reported the analysis of the photoluminescence properties of different Rhodamine 6G–silica samples. The investigated samples were class I and class II hybrids. The prepared solid-state samples displayed photoluminescence properties comparable to that of the dye molecule in solution. The analysis of the physical and chemical properties of the samples indicated the presence of two species of dye molecules, tumbling and isolated molecules. The different surroundings sensed by the dye affects its photostability, with nonencapsulated molecules showing faster photodegradation than isolated ones. The class II samples showed the best photohardness properties with respect to high power laser irradiation and can be regarded as good candidates for solid-state dye laser applications.

#### References and Notes

- (1) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956.
- (2) Brinker, C. J.; Schere, G. W. *Sol Gel Science: The Physics and Chemistry of Sol–Gel Processing*; Academic Press: San Diego, 1990.
- (3) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.
- (4) Reisfeld, R. *Opt. Mater.* **2001**, *16*, 1.
- (5) Oh, H. T.; Kam, H.-S.; Kwon, T. Y.; Moon, B. K.; Yun, S. I. *Mater. Lett.* **1992**, *13*, 139.
- (6) Rao, A. P.; Rao, A. V. *Sci. Technol. Adv. Mater.* **2003**, *4*, 121.
- (7) Sanchez, C.; Lebeau, B.; Chaput, F.; Boilot, J.-P. *Adv. Mater.* **2003**, *15*, 1969.
- (8) Proposito, P.; Casalboni, M. *Handbook of Organic-Inorganic Hybrid Materials and Nanocomposites*; American Scientific Publisher: Stevenson Ranch, CA, 2003.
- (9) Reisfeld, R.; Yariv, E.; Minti, H. *Opt. Mater.* **1997**, *18*, 31.
- (10) Dubois, A.; Canva, M.; Burn, A.; Chaput, F.; Boilot, J. P. *Appl. Opt.* **1996**, *35*, 3193.
- (11) Yariv, E.; Schultheiss, S.; Saraidarov, T.; Reisfeld, R. *Opt. Mater.* **2001**, *16*, 29.
- (12) Kobbe, E. T.; Dunn, B.; Fuqua, P. D.; Nishida, F. *Appl. Opt.* **1990**, *29*, 2729.
- (13) De Matteis, F.; Proposito, P.; Sarcinelli, F.; Casalboni, M.; Pizzoferrato, R.; Russo, M. V.; Vannucci, A.; Varasi, M. *J. Non-Cryst. Solids* **1999**, *245*, 15.
- (14) Anedda, A.; Carbonaro, C. M.; Clemente, F.; Corpino, R.; Grandi, S.; Mustarelli, P.; Magistris, A. *J. Non-Cryst. Solids* **2005**, *351*, 1850.
- (15) Drexhage, K. H. *Laser Focus* **1973**, *9*, 35.
- (16) Lo, D.; Lam, S. K.; Ye, C.; Lam, K. S. *Opt. Commun.* **1998**, *156*, 316.
- (17) Sakka, S. *Sol-Gel Science and Technology, Processing, Characterisation and Applications*; Kluwer Academic Publishers: Boston, Dordrecht, 2005.
- (18) Seddon, A. B.; Illston, T. J.; Cannell, A. C.; Bagnall, C. *Chemtronics* **1991**, *5*, 117.
- (19) Makishima, A.; Tani, T. *J. Am. Ceram. Soc.* **1986**, *69*, C-72.
- (20) Narang, U.; Bright, F. V.; Prasad, P. N. *Appl. Spectrosc.* **1993**, *47*, 229.
- (21) Innocenzi, P.; Kozuka, H.; Yoko, T. *J. Non-Cryst. Solids* **1996**, *201*, 26.
- (22) Malashkevich, G. E.; Poddeneznyi, E. N.; Zelnichenko, I. M.; Prokopenko, V. B.; Demyanenko, D. V. *Phys. Solid State* **1998**, *40*, 427.
- (23) Hungerford, G.; Suhling, K.; Ferreira, J. A. *J. Photochem. Photobiol., A: Chem.* **1999**, *129*, 71.
- (24) Zhu, X.-L.; Lam, S.-K.; Lo, D. *Appl. Opt.* **2000**, *39*, 3104.
- (25) Rao, A. P.; Rao, A. V. *Mater. Lett.* **2003**, *57*, 3741.
- (26) Harrison, C. C.; McGivern, J. K.; Li, X. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 855.

- (27) Gall, G. J.; Li, X.; King, T. A. *J. Sol-Gel Sci. Technol.* **1994**, 2, 775.
- (28) Deshpande, A. V.; Namdas, E. B. *Chem. Phys. Lett.* **1996**, 263, 449.
- (29) Weiss, A. M.; Yariv, E.; Reisfeld, R. *Opt. Mater.* **2003**, 24, 31.
- (30) Costela, A.; Garcia-Moreno, I.; Figuera, J. M.; Amat-Guerri, F.; Sastre, R. *Appl. Phys. Lett.* **1996**, 68, 593.
- (31) Abedin, K. M.; Alvarez, M.; Costela, A.; Garcia-Moreno, I.; Garcia, O.; Sastra, R.; Counts, D. W.; Webb, C. E. *Opt. Commun.* **2003**, 218, 359.
- (32) Suratwala, T.; Gardlund, Z.; Davidson, K.; Uhlmann, D. R. *Chem. Mater.* **1998**, 10, 199.
- (33) Del Monte, F.; Levy, D. *J. Phys. Chem. B* **1998**, 102, 8036.
- (34) Xu, C.; Xue, Q.; Zhong, Y.; Cui, Y.; Ba, L.; Zhao, B.; Gu, N. *Nanotechnology* **2002**, 12, 47.
- (35) Reisfeld, R.; Zusman, R.; Cohen, Y.; Eyal, M. *Chem. Phys. Lett.* **1988**, 147, 142.
- (36) Anedda, A.; Carbonaro, C. M.; Clemente, F.; Corpino, R.; Ricci, P. C. *J. Non-Cryst. Solids* **2005**, 351, 1850.
- (37) Shaefer, F. P. *Dye Lasers*; Topics in Applied Physics 1; Springer: Berlin, 1973.
- (38) Grandi, S.; Mustarelli, P.; Tomasi,.; Sorarù, G.; Spanò, G. *J. Non-Cryst. Solids* **2004**, 343, 71.
- (39) Julien, C.; Debarre, A.; Nutarelli, D.; Richard, A.; Tchenio, P. *J. Phys. Chem. B* **2005**, 109, 23145.
- (40) Julien, C.; Debarre, A.; Nutarelli, D.; Richard, A.; Tchenio, P. *J. Phys. Chem. B* **2006**, 110, 3902.
- (41) Viteri, R. C.; Gilliland, J. W.; Yip, W. T. *J. Am. Chem. Soc.* **2003**, 125, 1980.
- (42) Zondervan, R.; Kulzer, F.; Kol'chenko, M.; Orrit, M. *J. Phys. Chem. A* **2004**, 108, 1657.
- (43) Hoongenboom, J. P.; van Dijk, E. M. H. P.; Hernando, J.; van Hulst, N. F.; Garcia-Parajo, M. F. *Phys. Rev. Lett.* **2005**, 95, 97401.
- (44) McKiernan, J. M.; Yamanaka, S. A.; Dunn, B.; Zink, J. I. *J. Phys. Chem.* **1990**, 94, 5652.