Silylated Coumarin Dyes in Sol−Gel Hosts. 1. Structure and Environmental Factors on Fluorescent Properties

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Several silylated coumarin dyes with different linkages and degrees of functionality have been synthesized and incorporated in both SiO_2 xerogels and various solvent hosts. The absorption and fluorescence spectra were examined to explore selected structural and environmental effects on the optical properties of these dyes. Silylated dyes (also referred to as grafted or functionalized dyes) are dye molecules that have been chemically altered to provide alkoxysilane functionality allowing the active molecule to be covalently bonded to the host. Silylation of dye molecules had little effect on the absorption and fluorescence spectra in neutral solvent environments. The optical spectra of silylated dyes compared to those of their conventional counterpart were less influenced by the local chemical environment (e.g., pH) and thus allow for greater control and stability of the fluorescent properties of the dyes in different host environments. Spectroscopy during the drying/gelling of a derCoum xerogel film containing a silylated coumarin dye illustrate changes in the chemical forms of the dye molecules associated with changes in the local chemical environment of the dye.

1. Introduction

The development of a tunable solid-state laser in the visible has been the subject of extensive research during the past decade. Organic laser dyes within various hosts represent attractive materials for use in such applications because of their large fluorescent bandwidth in the visible. The type of host (liquid or solid) will largely determine the characteristics of the laser performance. Liquid dye lasers require pumping of a dye solution through a resonator to maintain photostability, and hence suffer from inherent problems with physical pumping and the use of solvent systems (such as solvent and dye poisoning).[1] Incorporating the laser dyes within a solid host would eliminate many of these problems. Furthermore, a solid-state medium would provide ease of use and replacement, along with expanded applications as slab waveguide lasers, tunable fiber-optic lasers, and solid-state dye laser rods. The lack of photostability of the gain medium has been the major factor limiting the commercial use of solid-state dye lasers.

Laser dye molecules have been doped into both polymers[1−14] and sol−gel hosts.[15−33] Inorganic hosts are attractive because they have relatively high laser damage thresholds. Caging lasing dyes within a sol−gel host has shown improved (but still inadequate) photostability and has permitted the use of high dye concentrations without undesirable dye aggregation.[34] Dye/

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host interactions can in principle enhance control of the fluorescence spectra, improve photostability, and even improve the quantum efficiency of fluorescence.

In a previous paper, we reported the incorporation of a silylated coumarin dye within xerogel hosts.[26] Silylated dyes are organic dye molecules that have been chemically altered to provide alkoxysilane functionality. This allows the dye molecule itself to participate in the hydrolysis and condensation reactions along with the other alkoxide precursors. The result is a covalently bonded active molecule within the xerogel structure. The use of a silylated laser dye resulted in (1) improved solubility of the silylated dye with respect to its unsilylated counterpart, allowing for higher concentrations of active molecules within the sol−gel matrix, (2) higher fluorescence efficiency, attributed to the greater rigidity and isolation of the silylated dye within its host, and (3) improved chemical stability, associated with the inability to leach the dye from the host.[26]

With these attractive features, further investigation of silylated laser dyes seemed justified. In addition, the area of dye-doped glasses is still in its infancy, and improved scientific understanding is needed to process such materials controllably. In the present paper, the synthesis of a number of silylated coumarin dyes with various linkages and degrees of functionality is described. The absorption and fluorescence properties of these dyes are compared and related to their structural characteristics. The dyes are incorporated in various solvents and in a xerogel host, and their optical properties are related to the local environment of the fluorescent species. In a subsequent paper, we will report the photostability characteristics of silylated laser dyes within various sol−gel derived hosts and their relation to processing conditions.[35]

2. Experimental Section

Silylated Dye Synthesis. *7-(3-Triethoxysilylpropyl)-O-(4-methylcoumarin)urethane (derCoum).* Dry, recrystallized 7-hydroxy-4-methylcoumarin (Coum, Aldrich, 0.114 mol, 20.0 g) was dissolved in anhydrous tetrahydrofuran (THF, 175 mL) to yield a clear, colorless solution. Isocyanatopropyltriethoxysilane (United Chemical Technologies, 0.133 mol, 32.5 g) was added along with several drops of dibutyltin dilaurate (Aldrich). The solution was refluxed for 4 days before cooling to room temperature and flash evaporating the solvent. Unreacted isocyanatopropyltriethoxysilane was removed by heating under high vacuum. The synthesis was monitored using Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer 1725x) by the disappearance of the isocyanate peak (2290 cm^{-1}) and the increase in the urethane peak (1765 cm^{-1}).

7-(3-(Triethoxysilyl)propoxy)-4-methylcoumarin (derPCoum). Recrystallized Coum (0.12 mol, 20.8 g) was dissolved in methanol (MeOH, 200 mL) containing potassium hydroxide (7.3 g) and potassium bromide (0.7 g). Dissolution was accomplished by gentle heating, and allyl bromide (0.132 mol, 16 g) was added. The clear, yellow solution was refluxed for 5 h, cooled to room temperature, mixed with water, and extracted with diethyl ether to yield 7-allyloxy-4-methylcoumarin. After crystallization from methanol and drying, the allyloxycoumarin was dissolved in anhydrous toluene (200 mL). The clear solution was treated with triethoxysilane (United Chemical Technologies, 0.167 mol, 27.4 g) and chloroplatinic acid (5.2×10^{-5} mol). The reaction was followed by the loss of the −SiH peak at 1209 cm^{-1} using FTIR. After 4 days at 70 °C, the yellow solution was flash evaporated to yield derPCoum.

5,7-Bis(N-triethoxysilylpropyl)-O-(4-methylcoumarin)urethane (2derCoum). Anhydrous 5,7-dihydroxy-4-methylcoumarin (Pfaltz & Bauer, 0.052 mol, 10.0 g) was dissolved in anhydrous THF (100 mL) to yield a clear, orange solution. Isocyanatopropyltriethoxysilane (0.120 mol, 29.7 g) was added along with 10 drops of dibutyltin dilaurate. The cloudy, yellow solution was refluxed for 24 h before cooling to room temperature and flash evaporating the solvent. FTIR was used to confirm completion of the reaction in the same manner as with derCoum. Unreacted isocyanatopropyltriethoxysilane was removed with heating under high vacuum.

5,7-Bis(3-(triethoxysilyl)propoxy)-4-methylcoumarin (2derPCoum). 5,7-Dihydroxy-4-methylcoumarin (0.108 mol, 19.2 g) was dissolved in anhydrous acetone (400 mL). Anhydrous potassium carbonate (40 g) and allyl bromide (0.220 mol, 26.6 g) were added. The mixture was refluxed for 18 h before cooling to room temperature. Acetone was removed by flash evaporation and the resulting solid was stirred for 3 h in dilute aqueous hydrochloric acid. The neutral dispersion was extracted with diethyl ether. After drying over anhydrous magnesium sulfate, the ether was removed and the product, 5,7-diallyloxy-4-methylcoumarin, was recrystallized from absolute ethanol. After drying, the tan solid was dissolved in anhydrous toluene (150 mL). The clear solution was treated with triethoxysilane (0.160 mol, 26.3 g) and chloroplatinic acid (0.000 052 mol). The reaction was followed by the loss of the −SiH peak at 1209 cm^{-1} using FTIR. After 5 h at 110 °C the solution was flash evaporated to yield 5,7-bis(triethoxysilylpropyloxy)-4-methylcoumarin.

The structures of Coum and the four synthesized dyes are shown in Figure 1. Proton NMR was performed on the synthesized dyes to confirm successful synthesis (Table 1). Differential scanning calorimetry (DSC, Perkin-Elmer DSC-7) was used to evaluate the crystallinity and melting points of the dyes. Coum and derCoum had definite melting points, while no such peak was observed for derPCoum, 2derCoum, and 2derPCoum in the temperature range of 25−350 °C.

Sample Preparation. *Acid / Base Solutions.* Various acid/base stock solutions were made by dissolving concentrated HCl at 10^{-1}, 10^{-3}, and 10^{-5} M and by dissolving concentrated NaOH at 10^{-1}, 10^{-3}, and 10^{-5} M in anhydrous MeOH. All the Coumarin dyes were separately incorporated in these acid/base solutions at concentrations of 10^{-5} M.

Xerogel Films. All the coumarin dyes were separately dissolved in anhydrous THF at 11 wt %. Deionized H_2O (acidified to 0.15 M HCl) was added at H_2O:dye mole ratios of 1.5:1 for derCoum, 3:1 for 2derCoum, 1.5:1 for derPCoum, and 3:1 for 2derPCoum. These H_2O:dye mole ratios correspond to half of the stoichiometric ratio, where the stoichiometric ratio represents one H_2O molecule for every alkoxide group on the Si precursor. No H_2O was added for the Coum:THF mixture. The solutions were refluxed for various lengths of time. Separately, tetramethoxysilane (TMOS), THF, and deionized

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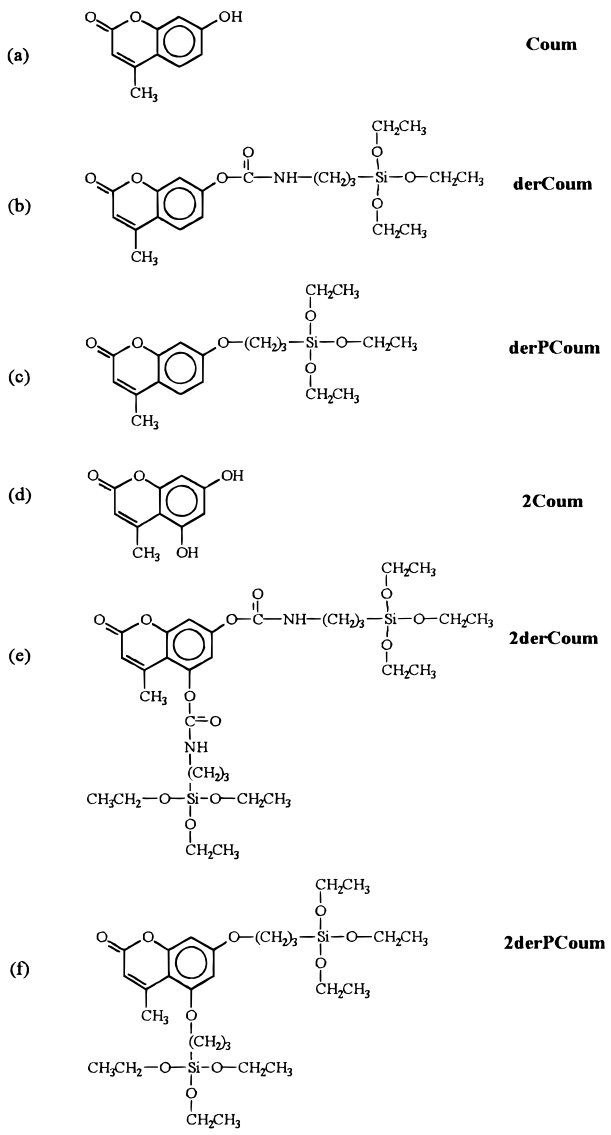

Figure 1. Structure of coumarin dyes: (a) Coum, (b) derCoum, (c) derPCoum, (d) 2Coum, (e) 2derCoum, and (f) 2derPCoum.

H_2O (acidified to 0.15 M HCl) were mixed in a glass vial at a TMOS:H_2O:THF molar ratio of 1:4:5. The solution was mixed for a few minutes allowing the TMOS to hydrolyze. The dye/H_2O/THF solutions were mixed with the TMOS/H_2O/THF solutions in proper amounts, resulting in a dye:Si mole ratio of 0.05:1 ($r = 0.05$). After aging for 24 h, the xerogel solutions were passed through 0.2 μm filters and spin coated on precleaned microscope slides (Gold Seal) at 2000 rpm for 20 s. The films were dried at 125 °C for 48 h in vacuum. All films were about 0.5 μm in thickness, as measured with a Dektak II profilometer, and were optically transparent in the visible spectrum. Fluorescence in the blue was observed upon ultraviolet (UV) light excitation.

Spectroscopic Measurements. Absorption spectra were measured using a Perkin-Elmer Lambda 3B UV/vis spectrophotometer. A blank microscope slide was used as a reference for the film spectra. Fluorescence spectra were measured by a ISI SPEX FluoroMax2 fluorescence spectrometer. Solutions were measured in transmission, while films and bulk samples were measured in reflection.

3. Results and Discussion

Effects of Dye Structure. The absorption spectra of all the coumarin dyes in methanol used in the present study were found to be similar, with an absorption maximum around 320 nm (Figure 2). The fluorescence spectra showed a distinct difference in spectral properties; 2Coum and the bifunctionalized dyes (2derCoum, 2derPCoum) were red shifted with respect to Coum and the monofunctionalized dyes (derCoum, derPCoum; see Figure 2). This red shift of 2derCoum and 2derPCoum is attributed to the inherent optical properties of their parent dye molecule, 2Coum. Comparing Coum to derCoum and derPCoum, the spectra are almost identical, with a fluorescence maximum around 385 nm. Consequently, silylation of the dyes did not inherently alter the fluorescent properties of the aromatic portion of the silylated dye. Therefore, it is possible to synthesize new dyes from a parent dye without destroying the absorption and fluorescent properties of the parent dye.

Since the bifunctionalized dyes were not synthesized directly from Coum, but from 2Coum, direct comparison should only be made of the silylated molecules with their parent molecule. Therefore, Coum and the monofunctionalized dyes will often be discussed separately from 2Coum and the bifunctionalized dyes. 2Coum and 2derCoum also had very similar fluorescence spectra, with a fluorescence maximum around 435 nm. However, 2derPCoum showed anomalous behavior in its fluorescence spectra by exhibiting a 9 nm blue shift with respect to its parent dye, 2Coum.

Effects of Acid/Base Environments. To understand the effects of dye/matrix interactions on the fluorescent properties, one needs to explore how a dye behaves in different molecular environments. For a solute in a solvent (liquid or solid), the environmental effects on fluorescence can be divided into two major categories: (1) interaction of a permanent or induced dipole moment of the dye molecule with the permanent or induced dipole moment of the solvent and (2) chemical effects (e.g., hydrogen bonding, pH, electron transfer, complex formation, intermolecular electronic energy transfer).[36,37]

Many have described the four dipole interactions (permanent−permanent, permanent−induced, induced−induced, and induced−permanent), which are the same as category (1) discussed above, by a single polarity parameter that depends on the dipole moment (μ) and the polarizability (α) of both the solvent and solute.[36,38,39] Polarity parameters, such as E_T^N and the Kosower Z value, have been established to compare quantitatively the polarity of different solvents.[38,39] Specifically, the Kosower Z value is an empirical scale based on the transition energies of 1-ethyl-4-carbomethoxypyridinium iodide in various solvents which is utilized as a standard of solvent polarity.[39] Linear shifts in the optical spectra for many dyes have been observed as a function of these polarity parameters.

Organic molecules that have acidic or basic substituents are often prone to chemical effects through hydrogen donating or accepting which alter the optical

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Table 1. Properties of Coumarin Dyes Studied

dye	name	mol wt	melting point (°C)	^{1}H NMR peaks (in $CDCl_3$, δ)
Coum	7-hydroxy-4-methylcoumarin	176.17	192	2.4 (2H), 6.1 (1H), 6.9 (2H), 7.5 (1H)
derCoum	7-(*N*-triethoxysilyl)-*O*-(4- methylcoumarin)urethane	423.54	95	0.6 (2H), 1.2 (9H), 2.4 (3H), 3.1 (2H), 3.9 (6H), 4.1 (2H), 6.1 (1H), 6.9 (3H)
2derCoum	5,7-bis(*N*-triethoxysilyl propyl)-*O*-(4-methylcoumarin)urethane	686.90	*a*	0.6 (4H), 1.2 (18H), 2.4 (3H), 3.1 (4H), 3.9 (12H), 4.1 (4H), 6.0 (1H), 6.8 (3H)
derPCoum	7-(3-(triethoxysilyl)propoxy)-4-methylcoumarin	380.52	*a*	0.8 (2H), 1.2 (9H), 2.0 (2H), 2.6 (3H), 3.9−4.0 (8H), 6.0 (1H), 6.5 (2H)
2derPCoum	5,7-bis(3-(triethoxysilyl)propoxy)-4-methylcoumarin	600.85	*a*	0.8 (4H), 1.2 (18H), 2.0 (4H), 2.6 (3H), 3.8−4.0 (16H), 6.0 (1H), 6.5 (2H)

[a] No melting found via DSC.

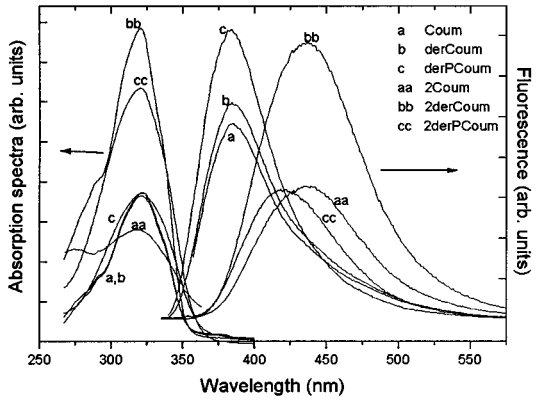

Figure 2. Absorption and fluorescence spectra of coumarin dyes in MeOH at 10^{-5} M.

properties. The variation of spectral shifts with hydrogen bonding is not well understood. Typically, distinct changes in the fluorescence spectra occur, but these can be only poorly predicted.[36,40]

A multiparameter approach for describing spectral shifts due to a number of environmental effects has been reported by Kamlet and Taft.[41,42] The wavenumber (ν) of the absorption or fluorescence maximum can be described as

$$\nu = \nu_0 + S\pi^* + a\alpha + b\beta \ldots$$

where ν_0 is the wavenumber of the absorption or fluorescence maximum in a reference solvent, π^* is a measure of polarity/polarizability effects of the solvent, α is the hydrogen-donor capability (i.e., acidity) of the solvent, β is the hydrogen-acceptor capability (i.e., basicity) of the solvent, and S, a, and b are measures of the change in absorption or fluorescence maxima with changes in solvent polarity/polarizability, acidity, and basicity, respectively.[37,41,42] π^*, α, and β values are tabulated for particular solvents, where the values were determined empirically via solvatochromic comparisons.[43,44] Only three major terms in the equation above have pertinence to the present study.

Coum is a laser dye whose optical properties have been well studied. The dye is known to adopt a number of chemical forms (associated with the hydrogen-donating and hydrogen-accepting capability of the dye) depending on its molecular environment (e.g., pH), each of which have different optical spectra. Three of the ground state forms—neutral, anionic, and cationic—absorb at 320, 365, and 340 nm, respectively, and fluoresce at 400, 455, and 420 nm, respectively. The zwitterionic exciplex, which exists only in the excited state, fluoresces at 475−480 nm.[15,25,35,45,46] The structure of the chemical forms of Coum and their optical properties have been well established (Table 2). Consequently, Coum can be tuned to the desired fluorescence by adjusting its molecular environment.

The silylation of coumarin dyes should affect the hydrogen-donating and -accepting capabilities of the dyes and hence their fluorescent properties in different pH environments. To explore this, the fluorescence spectra of Coumarin dyes in MeOH in various acidic (10^{-1}, 10^{-3}, and 10^{-5} M HCl) and basic (10^{-1}, 10^{-3}, and 10^{-5} M NaOH) environments were examined (Figure 3a−f).

Coum has a complex fluorescence behavior upon change in pH (Figure 3a). The neutral form of the dye is present under neutral and acidic conditions, as indicated by the fluorescence at 385 nm. Under highly acidic conditions at 10^{-1} M, the zwitterionic form of Coum is clearly present with fluorescence at 480 nm. Under basic conditions of 10^{-3} and 10^{-1} M NaOH, fluorescence from the neutral form (385 nm) disappears, and fluorescence from the anionic form (450 nm) appears. The fluorescence behavior of Coum in the present study matches the previously reported pH behavior of Coum shown in Table 2.[45]

DerCoum has an acid/base behavior similar to that of Coum. The major difference is that derCoum is more resilient to the formation of the anionic species from the neutral species upon making the environment more basic (Figure 3b). At 10^{-3} M NaOH, both the neutral and anionic species are present for derCoum, while only the anionic species is present for Coum. The fluorescence behavior of derPCoum showed even more resilience to the formation of the anionic and zwitterionic forms (Figure 3c). Under highly basic conditions (10^{-1} M NaOH), more of the neutral form is present than the anionic form. Also, a very small amount of the zwitterionic form was present in derPCoum compared to Coum and derCoum at 10^{-1} M HCl. To summarize, the silylated coumarin dyes are more resilient to hydrogen donating or accepting and therefore are less affected by their molecular environment than their unfunctionalized counterpart.

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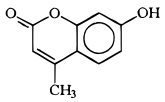
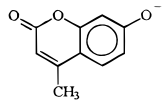
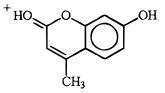
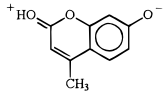
Table 2. Chemical Forms and Spectral Properties of Coum

name	structure	absorption max	fluorescence max	conditions
Neutral		322 nm	385 nm	Found in neutral and slightly acidic environme
Anionic		365 nm	455 nm	Found in basic environments
Cationic		350 nm	415 nm- 430 nm	Found in strongly acidic environments
Zwitterionic (exciplex)		----	480 nm	Found in acidic environments in the presence water

A quite different acid/base fluorescence behavior was observed for the bifunctionalized dyes and its parent dye, 2Coum (Figure 3d−f). The fluorescence behavior of 2Coum has not been as well characterized as Coum in the literature; therefore different chemical forms of these could not be identified. The acid/base behavior is summarized in Table 3, which shows the fluorescence maximum of 2Coum and its derivatives as a function of the acid or base environment. The results in the table clearly indicate that the dye consistently red shifts on going from acidic environment to basic environments. The shift in the spectra is more gradual than with Coum and the monofunctionalized dyes. It is believed that different chemical forms of 2Coum and its bifunctionalized dyes exist because they possess acid and base substituents on the structure just as Coum does. The different chemical forms may have fluorescence spectra that overlap; so the observed spectra shifts of 2Coum and the bifunctionalized dye may be due to the convolution of different spectra of different chemical forms.

The silylated dyes exhibited slightly less red shift than their parent molecule upon change in the pH (Table 3). 2Coum showed a 30 nm shift in spectra from a strongly acidic environment (10^{-1} M HCl) to a strongly basic environment (10^{-1} M NaOH), while 2derCoum had a 27 nm shift and 2derPCoum had a 25 nm shift. These data also support the conclusion for Coum-based dyes that the silylated dyes are more resilient to change in their optical properties under different molecular environments compared to the parent molecule.

The silylated Coumarin dyes with propyl linkages (derPCoum, 2derPCoum) were less affected by their environment than the corresponding urethane linked dyes (derCoum, 2derCoum; see Figure 3 and Table 3). This can be explained by the fact that the urethane linkage can experience greater electron transfer than the propyl linkage. Inspection of the structures of derCoum (Figure 1b) and derPCoum (Figure 1c) shows that derCoum can lose a proton on the nitrogen atom in the presence of a base, whereas derPCoum does not have any labile protons. Loss of the proton allows stronger resonance effects, with the result of a more ionic structure. Therefore, it is relatively easy to form the different chemical forms of the dye with a urethane linkage compared to the propyl linked dyes; and the nature and degree of functionalization of the dye molecules can be used to control the amount of dye/matrix interactions and thereby to control optical spectra.

The propyl-linked dyes should not be able to form the anionic or zwitterionic species based on the fact that the propyl linkage should not allow electron transfer; but the anionic and zwitterionic forms were observed with derPCoum, a propyl-linked dye. Since the propyl-linked dyes could not be recrystallized upon synthesis to completely isolate the product, it is believed that the presence of some unreacted Coum still exists in the final product of derPCoum. The presence of some Coum in derPCoum may be causing the slight presence of the anionic peak (455 nm) in basic environments and the zwitterionic peaks (480 nm) in acidic environments.

Solvent vs Xerogel. The fluorescence maxima of all the dyes in solvent (MeOH) and xerogel hosts are summarized in Table 4. There is a dramatic change in the fluorescence spectra upon changing from solvent to solid hosts. In methanol, the neutral and anionic species are present; while in the xerogel host, it appears that only the cationic form is present. The cationic form is found only in highly acidic environments, as concentrated sulfuric acid.[15] The fluorescence maxima for the cationic form of the coumarin dyes were determined by measuring the spectra in concentrated sulfuric acid with the results described in Table 4. Although the silanol surface is not as acidic as concentrated sulfuric acid, the presence of the cationic form of the dye in xerogel does reveal the acidic nature of the silica surface and the ability of the surface to share or donate a proton to the dye.

It is reasonable that the cationic form can exist with all the silylated dyes. The cationic form exists when the carbonyl group on the 2 position of the aromatic system accepts a proton. On the basis of the structure

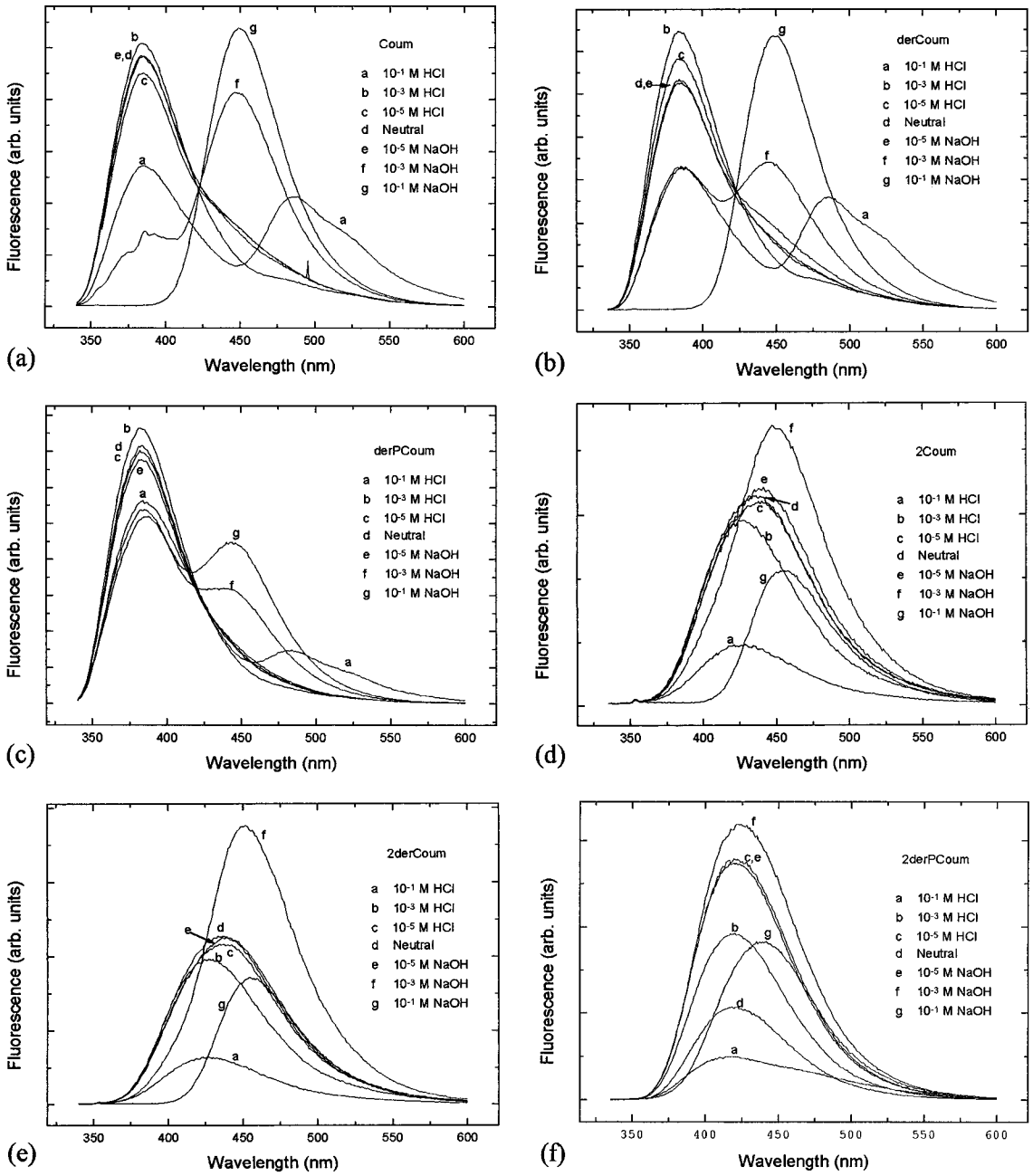


Figure 3. Fluorescence spectra of coumarin dyes: (a) Coum, (b) derCoum, (c) derPCoum, (d) 2Coum, (e) 2derCoum, and (f) 2derPCoum in different chemical environments.

Table 3. Fluorescence Maxima (nm) of 2Coum, 2dCoum, and 2dPCoum in MeOH at Different Acidic and Basic Environments

dye	10^{-1} M HCl	10^{-3} M HCl	10^{-5} M HCl	neutral	10^{-5} M NaOH	10^{-3} M NaOH	10^{-1} M NaOH	red shift[a]
2Coum	425	427	438	436	441	448	455	30
2derCoum	427	427	437	436	439	451	454	27
2derPCoum	416	419	421	418	419	422	441	25

[a] Red shift represents the change in fluorescence maxima from 10^{-1} M HCl to 10^{-1} M NaOH.

of the silylated dyes, the carbonyl group is not chemically blocked, so a proton could effectively attach to the carbonyl group just as in Coum.

Since little is understood about the dye/solvent interactions of 2Coum and the bifunctionalized dyes; it is more difficult to discuss the effects of a solid host on the fluorescence spectra. Hence the results for 2Coum and the bifunctionalized dyes are presented only, but not discussed.

Table 4. Fluorescence Maxima (nm) of Dyes in Solvent Host and Xerogel Host

dye	MeOH (neutral)	SiO_2 xerogel host	concn H_2SO_4
Coum	384, 448	432	410−425
derCoum	384, 450	438	410−425
derPCoum	384, 449	430	414
2Coum	446		465
2derCoum	447	462	468
2derPCoum	424	437	480

The cationic form of the dye appears to be present in the xerogel host, although the fluorescence maximum appears to be red shifted compared to the maximum of the cationic form in H_2SO_4. The discussion below will suggests possible reasons for this.

The presently observed red shift can be explained by examining the effects of solvent polarity on the dye molecule. Organic molecules with the (n,π*) transition as their lowest energy transition display a blue shift with increase in polarity of the host. In polar solvents, there is greater dipole−dipole interaction with the ground state than with the excited (n,π*) state, lowering the energy of the ground state. The transition energy increases, and a blue shift occurs. On the other hand, a red shift is generally observed with increase in solvent polarity for molecules having the (π,π*) transition as their lowest energy transition. The (π,π*) excited state is more polar and more polarizable than the ground state, resulting in greater lowering of the excited state and reducing the transition energy.[47] Coum's lowest energy transition is the (π,π*) transition, and therefore it experiences a red shift upon increase in solvent polarity.[40] In fact, fluorescence is observed only in polar solvents (e.g., water, alcohol) and not in nonpolar solvents (e.g., dioxane, toluene, heptane). The observed red shift with the coumarin dyes in xerogel hosts is consistent with the highly polar nature of the silica surface, which represents the silica cage surrounding the dye molecule. The polar silica surface, which reflects the highly polar silanol groups present at the surface, has been extensively investigated.[34,38,39,48−53] The Kosower *Z* value (defined above) has been assigned as $Z = 88$ for the silica surface, which is between that of water ($Z = 94.6$) and MeOH ($Z = 83.6$).[39,52] Numerous examples of a red shift associated with laser dyes in sol−gel hosts have been reported.[31,34,49,50,54]

To summarize, we suggest that a red-shifted cationic form of the coumarin dyes exists in the xerogel host. The presence of the cationic species reflects the acidic nature of the silica surface. The red shift is justified by the polar nature of the silica surface. Previous studies of coumarin in xerogel hosts suggest that the cationic form is present in xerogel hosts when prepared under acidic conditions.[25,46] It is likely that the coumarin dyes are adsorbed on the silica surface, such that it accepts or shares a proton from the silanol surface to form the cationic species. The nature of the silica surface can be altered by varying the synthesis conditions (e.g., pH, water content, precursor composition), which could be used to control which chemical form of the dye exists in the host. The hypothesis that both hydrogen-bonding effects and polarity effects are contributing to changes in the optical spectra is well supported by the drying/gelling study discussed below.

Homogeneity of Chemical Forms. It is possible for more than one chemical form of Coum to exist at a particular pH. By optically pumping the samples at different wavelengths of 320, 337, 365 nm, we were able to probe distinct species in the host because different forms of the dye have different absorption spectra. The heterogeneity of the types of dyes present in the host can then be determined by observing changes in the fluorescence spectra due to variations in the pump wavelength. The results of such probing for all the dyes in methanol host clearly suggest the presence of numerous forms of the dye (Figure 4). The results for the dyes in the xerogel host were quite different. Regardless of the pump wavelength, the fluorescence maximum did not change. Only a change in the intensity of the fluorescence was observed, which was caused by the difference in absorptivity of the dye at different wavelengths. This suggests that only one form of the dye exists in the solid xerogel host, namely, the cationic form.

Drying/Gelling Effects. Before the drying behavior is discussed, a reference fluorescence spectrum of the coating solution (i.e., synthesized solution just before spin coating) itself is deserving of discussion (Figure 5). The spectrum of the derCoum coating solution reveals the presence of neutral (385 nm) and the exciplex form (480 nm) of the dye. The neutral form is known to be present in mildly acidic conditions which coincides with the pH of the coating solution (pH $\approx$ 2.2), while the exciplex form exists under acidic conditions in the presence of H_2O (see Table 2 and Figure 6). The coating solution must then contain some unreacted H_2O. On the basis of the ratio of the intensities, there is more neutral form than the exciplex form in the coating solution.

The nature of the silica cage was examined in more detail by carrying out spectroscopy during drying and gelling of one of the sol−gel solutions. A microscope slide was dip coated with a derCoum sol−gel solution in MeOH solvent, and the fluorescence spectra were measured as a function of time (Figure 7).

Immediately after dip coating, the fluorescence was light blue in appearance, with a fluorescence maxima at 385 and 480 nm, indicating the presence of the neutral form and the exciplex form of the dye. This spectrum is very similar to that of the coating solution, except there is more exciplex present. More H_2O must be present due to condensation reactions upon initial drying. Further drying causes the exciplex form (480 nm) of the dye to decrease due to the consumption of water through further hydrolysis or evaporation. Also, the neutral peak at 385 nm is red shifted to 390 nm, caused by an increase in the polarity of the environment. The polarity of the silica surface is higher than that of MeOH, as discussed above.[39,52] Further drying leads to an increase in the neutral peak and a decrease in the exciplex peak. The fluorescence spectra then stabilizes after 30 min, after which no noticeable change in the spectra is observed reflecting little loss of solvent from or shrinkage of the film.

Hydrolysis and condensation reactions occur during drying, causing gelation and resulting in the formation

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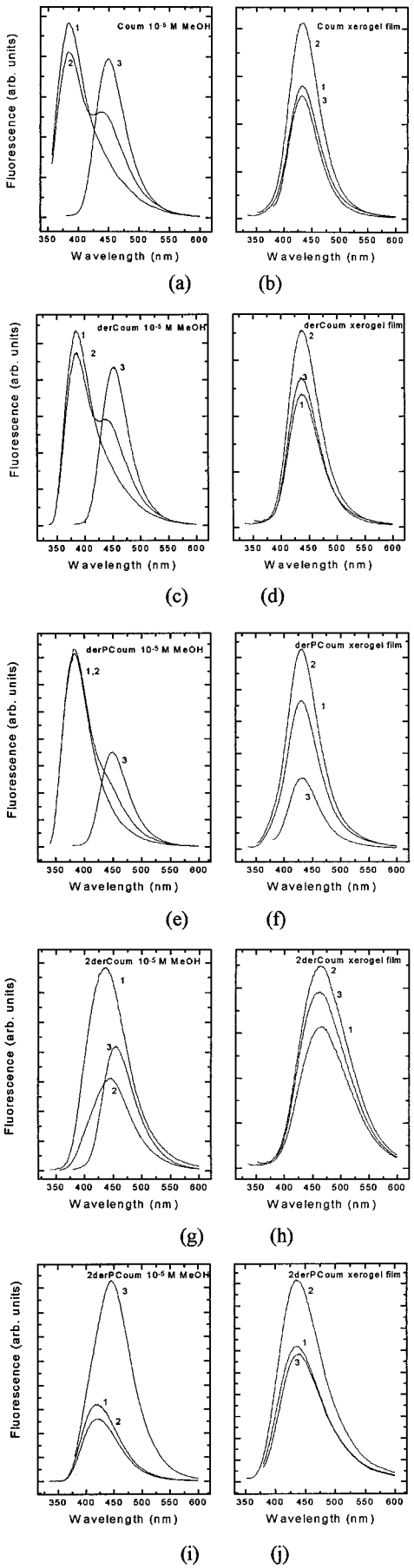

Figure 4. Fluorescence spectra of coumarin dyes in MeOH and xerogel host (synthesized by route 1) when pumped at (1) 320, (2) 337, and (3) 365 nm.

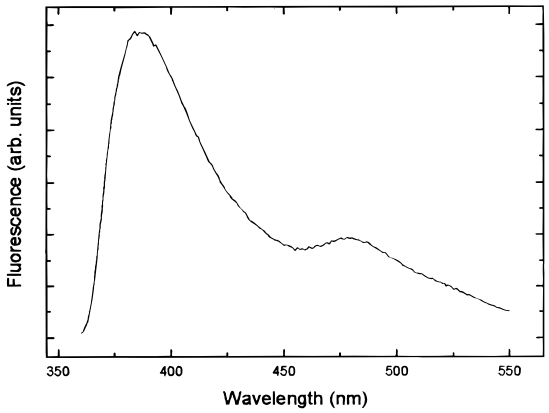

Figure 5. Fluorescence spectra of a derCoum xerogel solution (synthesized by route 1) pumped at 337 nm.

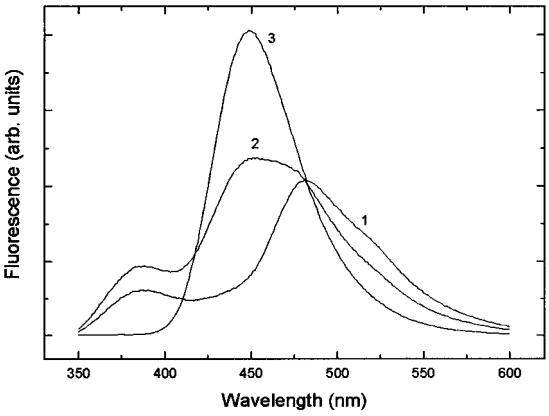

Figure 6. Fluorescence spectra of derCoum in MeOH/water mixture (9:1): (1) 0.10 M HCl, (2) neutral, and (3) 0.10 M NaOH.

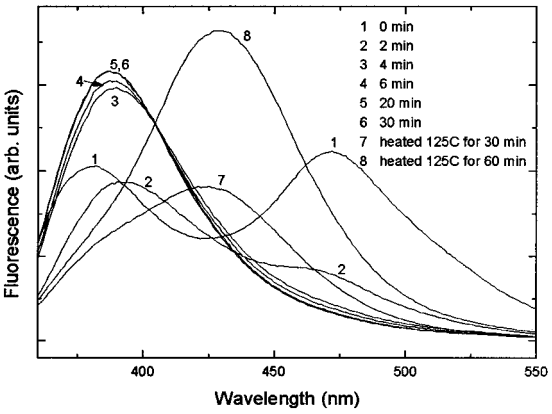

Figure 7. Fluorescence spectra of a dip coated derCoum xerogel solution (synthesized by route 1) at different drying times and heating times when pumped at 337 nm.

of a porous network. Within the porous network of this air-dried film is where the dye and remaining solvent (MeOH and H_2O) are located. The presence of solvent in the air-dried film is confirmed by observing a large −OH band at 3400 cm^{-1} in the film's IR spectra (Figure 8). The presence of the neutral species in the air-dried film suggests that most of the dye molecules are in a MeOH environment. This reflects the much greater solubility of the Coumarin dyes in MeOH than in H_2O: the solubility of Coum in MeOH is 10 mg/mL, while in H_2O it is only 0.1 mg/mL.[55] Also, some of the dye must be interacting with the silica surface due to the red shift

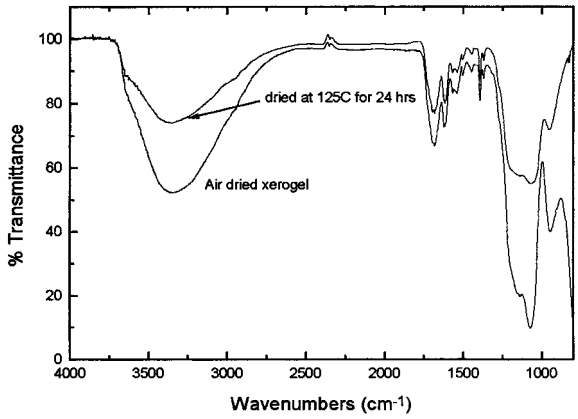

Figure 8. FTIR transmittance spectra of a derCoum xerogels (synthesized by route 1) air-dried and after heating at 125 °C.

in the spectra.

Heating the dip-coated film caused dramatic changes in the fluorescence spectra (Figure 7, curves 7 and 8). The neutral peak (385 nm) decreases, and the cationic (425−430 nm) peak increases. If this change in the spectra were caused by a change in the polarity and not chemical effects, we would expect to see a gradual red shift in the spectra. This is clearly not the case; as heating takes place, the neutral peak decreases and the cationic peak increases, confirming that a chemical effect is occurring. Heating of the film lead to the removal of MeOH and H_2O from the pores as well as shrinkage of the pores. This causes the environment of the dye to change from a mostly MeOH environment to a silica environment. The formation of the cationic species is likely caused by the adsorption of the dye on silanol surface which allows the carbonyl group on the dye to accept or share a proton with the silanol surface. FTIR spectra of the same solution (derCoum coating solution synthesized by route 1) dip-coated on a $CaFl_2$ disk reveal a dramatic decrease of the broad −OH band (3400 cm^{-1}) due to loss of MeOH and/or H_2O in the film after annealing at 125 °C (Figure 8), which supports the above suggestion.

4. Conclusions

Silylated laser dyes are attractive species for incorporation within solid hosts for use as tunable solid-state lasers. The structural and environmental effects on the spectral properties of several synthesized silylated coumarin dyes on the spectral properties have been examined. Complex fluorescence behavior was observed with all the coumarin dyes due to the formation of different chemical forms of the dye upon changes in the molecular environment. Silylation of the dyes did not destroy the fluorescence but in fact provided little change in the fluorescence characteristics under neutral conditions. The pH behavior indicated that both the monofunctionalized and bifunctionalized dyes were more resilient to change in chemical forms of the dyes when compared to their unfunctionalized parent dye. Placing the dyes within a solid host reduced the heterogeneity of chemical forms that exist within the matrix. Drying/gelling studies revealed dramatic changes in the molecular environment of the dye which correspond to changes in chemical forms of the dye and polar interactions between the dye and the host. The neutral form of the dye was present in the wet gel and in the unheated xerogel. Upon heating, the dye changed to the cationic form, indicating greater interaction between the dye and the acidic silica environment.

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