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Optical Properties and Dimer Formation in Copper Phthalocyanine-Doped Sol-Gel Matrices

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Abstract. Dimer formation in sol-gel matrices was studied using optical absorption spectroscopy of copper phthalocyanine tetrasulfonate dopants in silicate and aluminosilicate sol-gel matrices. Changes in the optical absorption spectra of dimers and monomers were correlated with various stages of the sol-gel process. Dimerization is strongly influenced by the chemistry of the pore liquid. The primary factors that control dimerization are the quantity of solvent remaining in the pores, pore solvent alcohol/water ratio, and presence of protons which can be either from the catalyst or from silanol groups on the silicate pore surfaces. Synthesis conditions which cause dye protonation invariably lead to dimerization during the latter stages of drying when the pore liquid becomes water-rich and there is a high dye concentration. These studies also identify chemical conditions which are able to avoid dye protonation and subsequently reduce dimer formation.

Keywords: copper phthalocyanine, dimer, monomer, optical absorption

1. Introduction

Metallophthalocyanines (MPcs) have received considerable scientific study because of their novel electrical and optical properties and their chemical and thermal stability. They are of interest for a number of applications including photovoltaics, electrical conductors, chemical sensors, chromophores in color reprographic systems and for their potential as photochemical tumorcides. In recent years certain MPcs received considerable attention because of large nonlinear susceptibilities and their exceptional promise as optical limiters [1–4]. The latter are based on a nonlinear absorption mechanism involving excited state absorption.

An important direction for MPcs and other chromophores is that they be adapted into solid state materials because of the inherent advantages in the design and development of solid-state optical components. One very attractive approach for fabricating phthalocyanine based solid-state optical devices is to use sol-gel methods. This technique has been widely applied to a variety of organic and organometallic molecules using inorganic host materials such as SiO_2, Al_2O_3, aluminosilicates, TiO_2 and ZrO_2 [5]. Researchers have shown that many organic dopants retain their optical properties in the matrix and thus have produced solid-state materials which exhibit such properties as laser action, photochromism and nonlinear optical properties [6]. Prior sol-gel research on phthalocyanines has included the incorporation of metal-free phthalocyanine into alumina films [7], the study of porphyrin and phthalocyanine heterodimers in siloxane/zirconia hosts [8], and optical limiting of metallophthalocyanines in sol-gel hosts [9, 10].

The issue of dimer formation of the organic dopants in sol-gel matrices has received relatively little attention despite the fact that dimer formation is a vital

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consideration in determining the optical properties of dye-doped sol-gel materials. The dye's aggregation state can affect the linear absorption spectrum, cause quenching of dye fluorescence and change the yield of photochemical processes. If dye doped solid-state optical devices are ever to become practical, the issue of dimer formation and its effect on a material's optical properties must be resolved.

The present paper considers the synthesis and properties of copper phthalocyanine tetrasulfonate (CuPcts)-doped sol-gel materials. In addition to being an interesting material system for optical limiter applications, CuPcts offers an excellent opportunity to characterize dimer formation because its monomer and dimer bands are well identified using optical spectroscopy. In this paper changes in the optical absorption spectra of dimers and monomers are correlated with various stages of the sol-gel process. The results indicate the important relation between dye protonation and dimerization and identify chemical conditions which are able to produce materials with reduced dimer formation.

2. Background

2.1. Dimerization of Phthalocyanines

Phthalocyanine is a 16 member ring with 18 π electrons and this unique structure leads to extraordinary thermal and chemical stability. For example, copper phthalocyanine is known to be stable at 900°C in vacuum [11]. Although CuPc is insoluble in many common solvents including alcohol and water, it may be solublized by adding four sulfonate groups SO_3^- to the Pc ring. This compound, copper phthalocyanine tetrasulfonate tetrasodium salt (CuPcts), was used in the experiments described in this paper. The structure of CuPcts is given in Fig 1. In other metallophthalocyanines, the central copper is replaced accordingly.

Two absorption bands dominate the absorption spectrum of monomeric phthalocyanine. These bands are the intense "Q" band which peaks near 660 nm and the less intense "B" band (also called the Soret band) which peaks at about 350 nm. In addition, a weak satellite band is observed near 600 nm. This weak band has been attributed to higher vibrational levels of the relevant electronic state [11]. Absorption bands in the 500–800 nm range are shown in Figs. 2 and 3 for CuPcts in solutions of varying pH and methanol content.

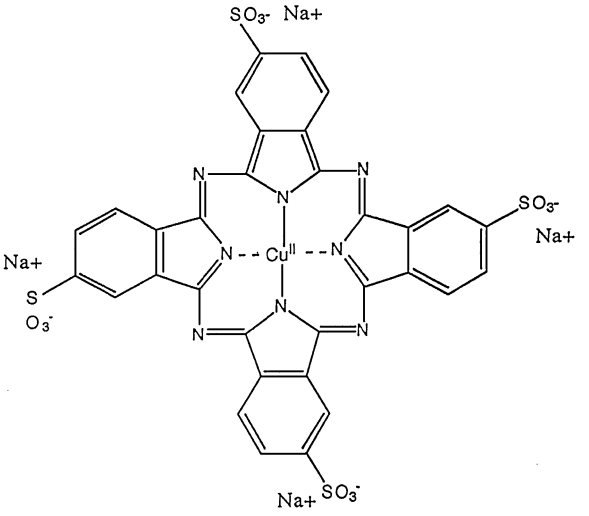


Figure 1. The structure of 4, 4′, 4″, 4‴ copper phthalocyanine tetrasulfonic acid tetrasodium salt (CuPcts).

Phthalocyanines are known to dimerize and even further agglomerate with a concomitant change in their optical properties [12–16]. In general, the absorption spectrum for MPcs in solution are strongly dependent upon concentration. As the MPc concentration increases, the absorption of the monomer band decreases relative to an emerging band at about 600 nm. This absorption was attributed to the Q band of dimeric species [12]. Other researchers report that higher levels of aggregation are possible in phthalocyanines and that higher aggregates are accompanied by further blue shifts in the Q band [13]. The fundamental theory explaining the blue shift involves cofacial association of π-electron systems as described by an exciton model [14].

The total dye concentration and the dimerization constant affect the concentration of different species as shown in the following analysis. If one assumes that only monomers and dimers are present in solution, the total concentration of CuPcts, $[C_t]$, can be described by Eq. (1).

$$[C_t] = [M] + 2[D] \tag{1}$$

where $[M]$ and $[D]$ are the molar concentrations (mole/liter) of the monomer and dimer, respectively. Furthermore, the equilibrium between the monomer and dimer concentration is governed by the law of mass

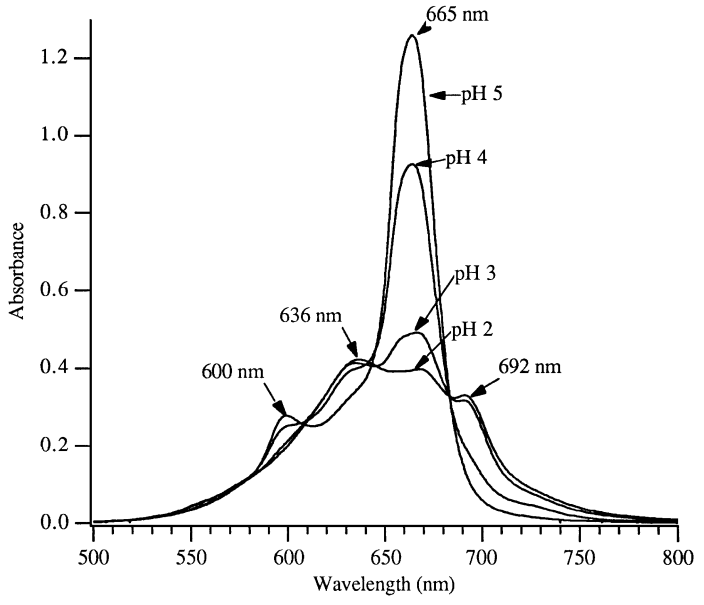


Figure 2. Q-band absorption for 10 μM CuPcts in acidic solutions of varying pH.

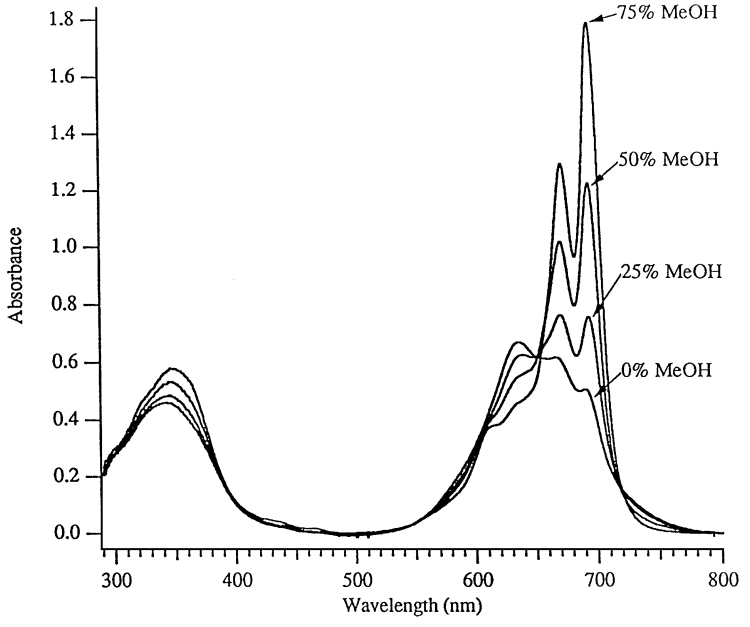


Figure 3. Absorption spectra for 10 μM CuPcts in 0.01 N HCl solution with varying ratios of water and methanol. The Soret band (B-band) peak is at ≈350 nm.

action.

$$2[M] \overset{K_d}{\longleftrightarrow} [D] \tag{2}$$

$$K_d = \frac{[D]}{[M]^2} \tag{3}$$

Where K_d is the dimerization constant (liters/mole.)

These equations can be combined to describe the dimer to monomer ratio,

$$\frac{[D]}{[M]} = \frac{\sqrt{1 + 8K_d[C_t]} - 1}{4} \tag{4}$$

This equation shows that the concentration of dimers

increases relative to the concentration of monomers as the dimerization constant, K_d, and total concentration, $[C_t]$ increase.

2.2. *Optical Spectroscopy of Copper Phthalocyanine Reference Solutions*

Figure 2 shows the absorption spectra of CuPcts in aqueous solutions acidified with HCl to pH 5, 4, 3, and 2. Three isobestic points appear at 609, 642 and 684 nm. The emergence of the absorption at 636 nm indicates that decreased pH encourages dimer formation. Dimer formation is consistent with the argument that the dye is being protonated. In previous studies, acid reactions led to protonation at the pyridine-like nitrogen atoms of the azomethine bridges on the edge of the Pc ring [17]. Since it is the negatively charged sulfonate groups that allow the dye to dissolve in water, it is reasonable to assume that by protonating the dye and thus decreasing the net negative charge on each molecule, the dyes will experience less electrostatic repulsion and thus greater aggregation.

One method for allowing the protonated dye to remain monomeric is to dissolve the CuPcts in acidic methanol/water solutions (Fig. 3). From this experiment one can see that monoprotonation of dye causes the neutral Q band peak at 663 nm to split into two peaks at 672 nm and 695 nm. Monoprotonation of the CuPcts molecule changes the molecule's symmetry which has the effect of splitting the Q band absorption. In this case K_d decreases and the equilibrium is shifted towards the existence of protonated CuPcts monomers in acidic methanol-rich CuPcts solutions. Upon increasing the water content, the protonated species become increasingly dimeric.

3. Synthesis of Copper Phthalocyanine-Doped Sol-Gel Materials

Copper phthalocyanine tetrasulfonic acid tetrasodium salt (CuPcts) was obtained commercially (Kodak) and used without further purification. Sol-gel monoliths were prepared using tetramethoxysilane (TMOS) from Aldrich or sec-butoxy aluminoxy triethoxy silane (ASE) from Hüls America. Copper Pcts was incorporated into a silica host made by the sonogel method as described below. This particular composition was chosen for its extremely high optical quality. Bulk samples made this way exhibited very little scatter. Acid catalysis and low solvent content are the keys to small pore sizes that account for the minimal optical scatter from this highly porous monolith.

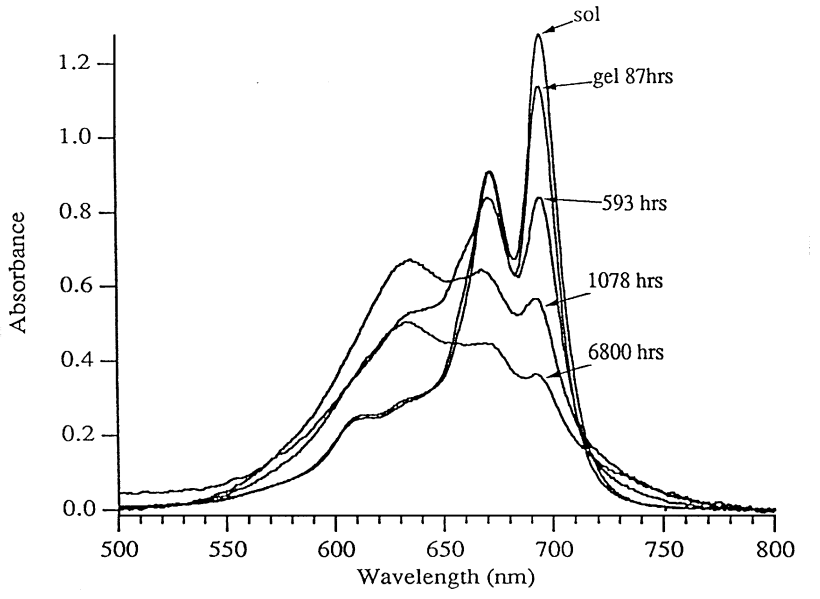
Most of the silicate samples in this study were CuPcts-doped silica prepared using the sonogel method [18]. The initial step was to prepare a silica sol by combining 15.25 g of TMOS and 6.95 g of distilled water in a 50 ml polypropylene beaker. 25 ml of 0.04 N HCl was then added as an acid catalyst to yield a $4:1:10^{-4}$ mole ratio of H_2O : TMOS : HCl. This diphasic solution was sonicated in a room temperature bath for 30 minutes. The ultrasonic energy serves to mix the reactants and to accelerate the hydrolysis and condensation reactions of the silicate species. Raman studies show that after 30 minutes no monomeric silane species remain. To this sol, enough aqueous CuPcts (3×10^{-3}M) was added to yield a 10 μM dye concentration in the sol. The sols were cast into polystyrene cuvettes and then sealed with parafilm. After gelation, but before significant syneresis occurred, the film was perforated with small holes to initiate drying. After drying, monolithic pieces of one-eighth the original volume were obtained. The standard 4 : 1 (water : TMOS) acid catalyzed xerogels were homogeneous and had very small pores. As a result, the bulk samples showed very little optical scatter, even under laser illumination.

Aluminosilicate samples were prepared using the method of Pouxviel et al. [19]. A mixture of 5 ml of water and 10 ml of 2-propanol were added dropwise to a stirred solution of 10 ml sec-butoxyaluminoxy triethoxysilane (ASE) and 10 ml of 2-propanol. A small amount of the dye was dissolved in water to produce a 10 μM dye concentration in the sol. The doped sol was stirred at room temperature before being cast into polystyrene cuvettes and sealed with parafilm. Gelation occurred within one day. The use of a silica-alumina double alkoxide allows one to form transparent, monolithic gels without the addition of an acid or a base catalyst. Furthermore, the amphoteric nature of the Al─OH species tends to buffer the precursor sol to a value near pH 7.

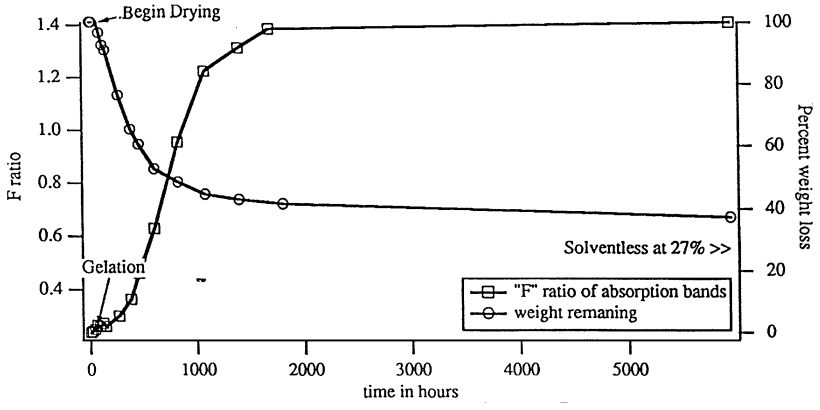
4. Results

4.1. *Sol-Gel-Xerogel Transition in Silica Matrices*

Absorption spectroscopy was used to monitor dimer formation of CuPcts during the sol-gel-xerogel transition (Fig. 4). The first spectra were taken within two hours of synthesis. Gelation occurred quickly and the



(a)



(b)

Figure 4. CuPcts doped in acid catalyzed silica sol-gel matrix. Dopant concentration in the initial sol was 10 μM. (a) Q-band absorption as the material progresses during the sol-gel-xerogel transition and (b) ratio of dimer to monomer absorption peaks (F ratio) and sample weight loss as a function of time.

second spectra were taken after gelation but still within 14 hours of synthesis. Little change occurred during gelation. This is consistent with the widely held view that gelation is a macroscopic effect and has little influence on the local chemical environment which is controlled by the properties of the solvent phase.

The absorption spectra in Fig. 4 show splitting of the Q band which indicates the existence of protonated monomers. Note the similarity between the spectra of the sol and those of the methanol rich aqueous solutions shown in Fig. 3. Simple interpolation would imply that CuPcts in 2 hour old sol behaves like CuPcts in a 2 : 1 solution of MeOH : H_2O. This behavior is consistent with the solution chemistry of the hydrolysis reaction in that the sol was acid catalyzed, leading to rapid hydrolysis and a methanolic solution. Water is one of the reactants of the hydrolysis reaction, so water is being consumed at the same time that methanol is being released. Since these samples were prepared using 4 moles of water per mole TMOS, the water could be consumed by complete hydrolysis. The result is that the ratio of methanol to water increases during the initial stage of

the reaction. Thus, the dimerization constant, which is solvent dependent, decreases and monomers prevail.

As the sol-gel process proceeds, methanol evaporates and water, a product of the condensation reaction, is formed. This decreases the methanol/water ratio which increases the dimerization equilibrium constant for monoprotonated species (vide supra). This is evident in Fig. 4 by the decrease in the absorbance of the split monomer bands at 670 and 695 nm and an increase in the absorption band at 636 nm which is presumably due to a protonated dimer species. With continued drying, the gel structure becomes further crosslinked and the remaining methanol and water continue to evaporate. The effective concentration of the dye in the pore solvent increases. The dimer band seems to grow slowly during the first 87 hours and then more quickly. By 1078 hours, the dimer peak is nearly the same magnitude as that of the higher energy monomer band. In the spectrum taken after 6800 hours, the monomer absorption peaks are faint and only a small amount of the monomer remains.

The ratio of the dimer peak magnitude (636 nm) to the corresponding monomer peak magnitude (695 nm) was used to characterize the relative concentration changes of the monomeric and dimeric species during the sol-gel-xerogel transition. This ratio, which is defined as "*F*", is plotted along with the weight of the sample as a function of time. As the dimer band grows and the monomer band shrinks, the ratio increases from 0.24 to 1.4, where it appears to reach a constant value.

In summary, dimerization during drying is driven by the change in the methanol/water ratio in the pores, from methanol rich to water rich. This change increases the equilibrium dimerization constant which favors dimer formation. Another factor is the reduction in volume of the pore solvent. During drying, the gel structure shrinks to about 1/6 of its original volume and the volume of pore solvent decreases as solvent evaporates. The net result is that the concentration of the dye in the remaining solvent increases dramatically. This further shifts equilibrium towards dimer formation and perhaps towards greater aggregation.

4.2. Sol-Gel-Xerogel Transition in Buffered Silica Matrices

Since the pores of the silica gels in the previous section were too acidic to preserve the unprotonated form of the guest dye, an alternative route was pursued to further increase the pH of the gel. In principle, a buffer solution could be added to the sol and then remain in the pore liquid to buffer the fluid to some desired value. In this way the dye should remain unprotonated and thus highly monomeric.

A two step process was used to create a series of buffered gels. Synthesis begins with the standard HCl acid catalysis and sonication of a TMOS sol. Acid catalysis in the first step ensures complete hydrolysis. After 30 minutes, an equal volume of 0.05 molar pH buffer solution is added to the sol. The buffer solutions were prepared according to the CRC Handbook of Chemistry and Physics. The components consisted of HCl-KCl for pH 2, HCl-potassium hydrogen phthalate for pH 3 and pH 4. A pH 7 buffer was obtained from potassium dihydrogen phosphate and NaOH. Figure 5 shows the results of using various buffers. The buffer dominates the pore environment such that protonation is hardly evident when buffers of above pH 4 are added to the sol. With the increased pore pH, strong absorption bands from unprotonated monomers are observed. Some evidence of dimerization is still evident in the xerogel stage (spectrum not shown), which is a result of the increased salt content from the buffer. As solvent is lost, both the dye and the buffer salt concentration in the pore solvent increase and promote dimerization.

5. Discussion

5.1. Dimer Formation During the Sol-Gel-Xerogel Transition

Figure 4 shows the evolution of the spectral changes associated with the sol-gel-xerogel process for CuPcts doped in a TMOS derived silica matrix. By observing the "*F*" ratio (the ratio between the dimer peak at 636 nm and the monomer peak at 695 nm) as a function of weight loss during the drying stage, it is possible to gain considerable insight as to the nature of dimer formation in sol-gel derived materials.

Figure 4(a) indicates that in the sol state the dye consists mostly of protonated monomers. The mole ratio of water to TMOS was initially 4 : 1, which is just enough for complete hydrolysis without condensation. The hydrolysis product is methanol so it follows that after hydrolysis the sol must consist of methanol, silicic acid, the catalyst and some small quantity of free water. As condensation begins, water is released into the sol and the sample continues to polymerize until a porous silica network is formed. The figure shows that dimerization occurs during aging, before the sol has been

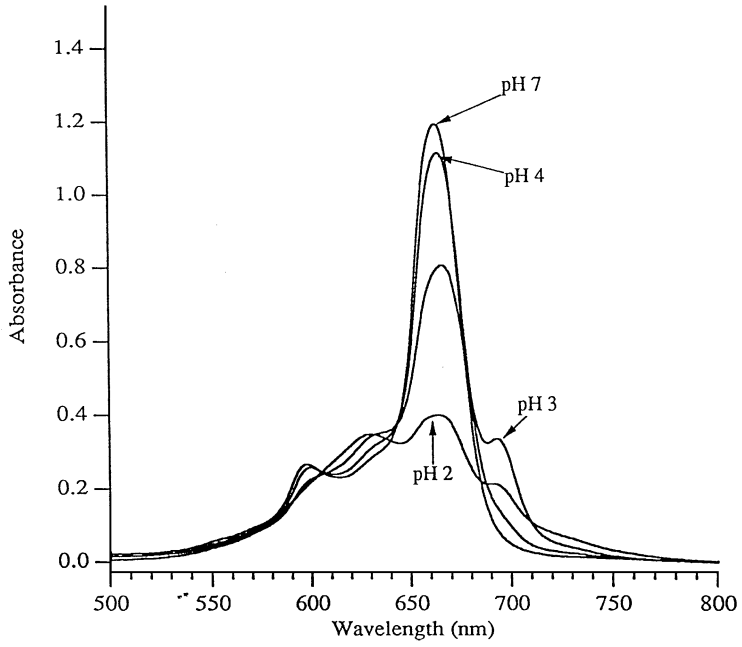


Figure 5. Q-band absorption for CuPcts-doped silica sol-gels which had various pH buffers added to the sol. These spectra were taken after gelation but before drying.

unsealed. These changes must be a result of further condensation in which water is produced. If condensation proceeded to completion, without evaporation, the sol would have a 1 : 2 mole ratio of water to methanol in its pores.

Drying begins when the pore solvent is allowed to escape by perforating the parafilm cover. Since methanol has a higher vapor pressure than water, it evaporates preferentially, decreasing the relative amount of methanol in the pores. These are conditions that encourage dimerization of the protonated species (see Fig. 3). By examining the change in weight one can understand the role that evaporation plays in forming dimers. In Fig. 4(b) it is evident that the sample loses a substantial fraction of weight before a significant change in F occurs. The F ratio begins to increase only after the sample lost 35% of its original weight (or $\approx$50% of its solvent). At this point, the rate of weight loss begins to slow and the F ratio increases dramatically.

This behavior can be explained by a combination of two factors; a change in the solvent composition and the quantity of the solvent. In the early stages of the reaction, the pore liquid evolves from almost exclusively methanol to a more water rich environment. This has the effect of increasing K_d which promotes dimers as expected from Eq. (4). Experimentally, a slight increase in F is observed before drying begins (see Fig. 4(b)).

The quantity of solvent is an important contribution in view of its effect on dye concentration. The decrease in the amount of solvent, as indicated by the significant weight loss, causes the effective concentration of CuPcts in the pore solvent to increase accordingly. The increase in dimer content as a result of increased dye concentration is also predicted by Eq. (4).

It is interesting to note that a series of CuPcts-doped silica samples prepared without acid catalyst exhibited similar spectra to those of Fig. 4. That is, even without the presence of acid, the characteristic monomer bands from dye protonation (at 670 and 695 nm) were observed. In this case the source of protons is the silicate matrix itself. Since the isoelectric point of silica is approximately 2, one would expect the surface of the silica particles to be negatively charged when the pH is above the isoelectric point (i.e., without acid added). The silanol groups apparently dissociate to form Si—O^- surface species and the CuPcts accepts protons from the silanols. Dimer formation then proceeds in much the same fashion as shown in Fig. 4.

From these results, it is evident that dimerization is primarily due to the chemical environment inside a

pore. The primary factors that control dimerization are the quantity of solvent remaining in the pores, pore solvent alcohol/water ratio, and presence of protons which can originate from either the catalyst or from silanol groups on the silicate particle surfaces. To control dimer formation, several methods are possible. The approach taken in this study and described below was to select another matrix whose different chemical environment successfully suppressed dimer formation.

5.2. Copper Phthalocyanine-Doped Aluminosilicate Gels

One means of circumventing the acidic nature of the silica gel surface is to incorporate another metal oxide that has a higher point of zero charge (PZC). Alumina has an PZC of about 9 so its surface is charged positively in solutions of pH < 9.

Aluminosilicate (ASE) monoliths were fabricated by the hydrolysis and condensation of sec butoxyaluminoxy triethoxysilane (vide supra). The spectra of the dye molecule in an ASE host shows no signs of protonation at any stage of gelation. Although the ASE gels still have silanol groups which can release their proton, this composition also has aluminol groups that can bind the proton.

Figure 6 shows the changes in the Q band absorption of CuPcts in the aluminosilicate during gelation and drying. Notice that there is no evidence of protonation in the sol stage and that there is little growth of the dimer band at 630 nm relative to the silica gels. What dimerization is observed is very likely to be due to the increase of the dye concentration as a result of shrinkage and solvent evaporation.

A likely consequence of alumina's high PZC is that the surface of alumina particles should be positively charged. In fact, the Al─OH species have an amphoteric nature which buffers the solution to maintain values close to 7.1 [19]. These aluminol groups must be protonated if they are to compensate for the acidic nature of silanol in the solution. One could predict that in ASE, the negatively charged dye molecule associates with alumina-rich regions because of their positive surface charge, as opposed to silica-rich regions, which have a negative surface charge. This is also suggested by the work of Pouxviel et al. where pyranine (8-hydroxy trisulfonated pyrene) molecules adsorbed on the alumina-rich regions of the particles [19].

The F ratio is plotted along with the weight loss of a doped ASE sample in Fig. 6(b). The dimerization is greatly reduced in this system as compared to the silicates. The magnitude of the dimer absorption peak is very small, even after significant weight loss. After 50% weight loss, the F factor is only 0.57.

6. Conclusions

The doping of copper phthalocyanine in sol-gel derived materials provides a model system in which to investigate the process of dimer formation in sol-gel matrices. The well established monomer and dimer absorption bands for CuPcts reference solutions were used to interpret the absorption spectra of the doped sol-gel materials during the various stages of the sol-gel process and to provide insight about the mechanisms which lead to dimer formation. These studies also identify the chemical conditions which are able circumvent dimer formation in the sol-gel matrix.

A fundamental consideration observed with silica matrices is that the hydrolyzed sol was found to be acidic enough to protonate the dye. The reference solution studies indicate that in an aqueous environment, the protonated species will dimerize; in a methanolic environment, the dye will remain monomeric. Thus, once the dye is protonated by the silica sol, dimerization invariably occurs during the latter stages of drying when the pore liquid becomes increasing water-rich. The high dye concentration in the pore liquid also favors dimer formation. During aging and the early stages of drying, the dye can remain monomeric because of the higher methanol content of the pore liquid. In this way the aggregation state of the CuPc dye molecule evolves continuously during the sol-gel-xerogel process because of the varying methanol/water compositions and the dye concentration. This evolution is reflected by the changing ratio of dimer to monomer absorption peaks.

The flexibility of the sol-gel process enables one to tailor chemical conditions so that dimer formation is suppressed. For example, in silicate samples that had their pores neutralized by the addition of a buffer, CuPcts was found to be unprotonated and dimer formation was reduced significantly in aged gels. A more important result was obtained by using a sol-gel derived aluminosilicate matrix whose synthesis conditions did not lead to dye protonation. In addition, the rate of dimer evolution in this matrix was very slow because of electrostatic attraction between the negatively charged dyes and the positively charged alumina-rich regions of the matrix. Such attraction also prevents the dye from

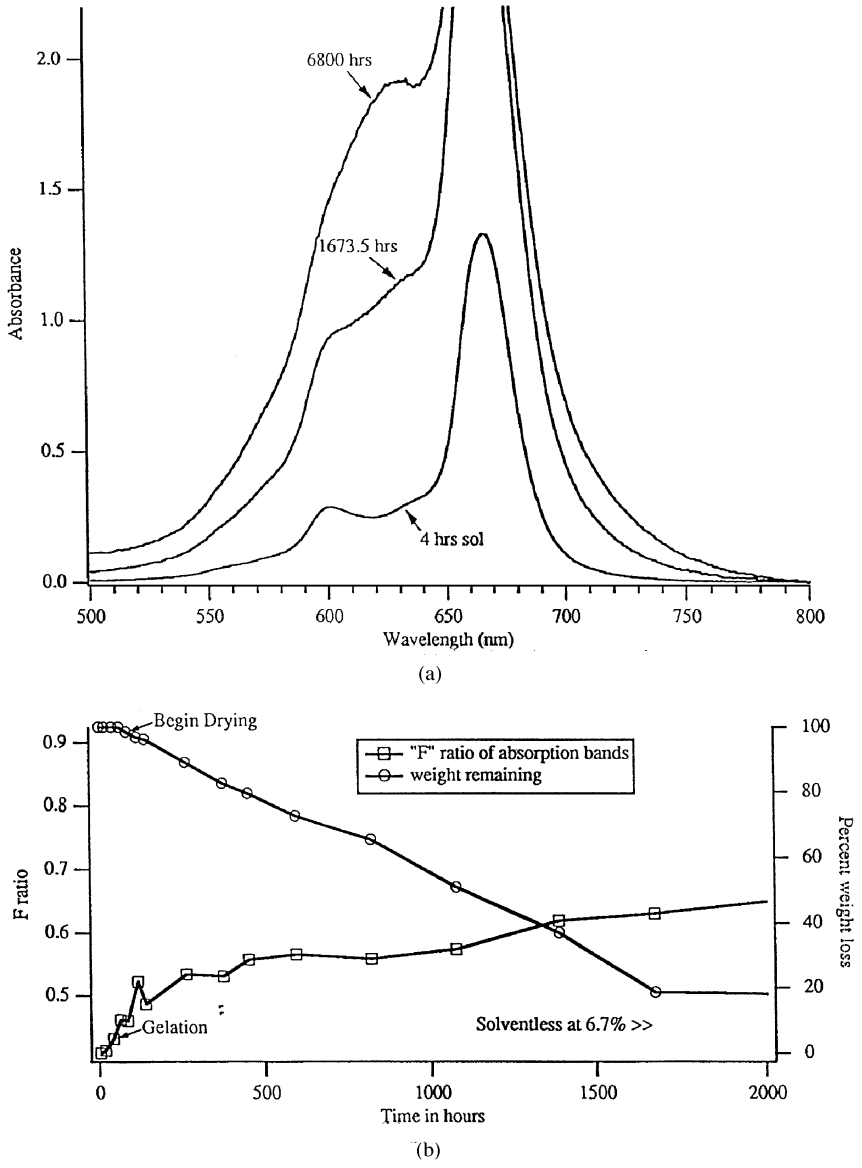


Figure 6. CuPcts doped in an aluminosilicate sol-gel matrix. Dopant concentration in the initial sol was 10 μM. (a) Q-band absorption for the material as a sol, a partially dried gel and a xerogel and (b) ratio of dimer to monomer absorption (F ratio) and sample weight loss as a function of time.

migrating to adjacent pores and forming aggregates. By comparison, the dyes easily migrate within silica matrices where the surfaces are negatively charged and electrostatic repulsion between the dye and the matrix occurs.

This study demonstrates that modifying the sol-gel processing conditions of organic dye-doped metal oxides can result in changes in the protonation and aggregation state of the organic dye. The understanding gained regarding the dimerization of this class of molecules in metal oxide hosts should lead to improved control of material properties that are of central importance for the development of optical devices.

Acknowledgments

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