

The Influences of Structural Evolution of Silica Gel Glass on the Photophysical Properties of Benzoic Acid

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Benzoic acid was dispersed into silica gel glass at molecular level by sol-gel process. The luminescence properties of benzoic acid in gel glass heat-treated at various temperatures were studied. The changes in gel glass structure and the surrounding environment of benzoic acid resulted in different electronic transitions, and thus the different luminescence spectra. The fluorescence bands centered at 320 nm and 355 nm, respectively induced by the $S_{1\pi\pi^*} \rightarrow S_0$ transition of benzoic acid and $S_{1n\pi^*} \rightarrow S_0$ transition of benzoate anions, respectively, were observed when the doped gel glass was heat-treated at the temperatures below 200°C and at the temperature range 300 ~ 400°C, respectively. On heating at 500°C, benzoate anions were steadily immobilized in the cages of the Si-O network with the SiO₄ tetrahedra formation and the RTP of benzoate anions is observed. It is proposed that the luminescence spectra of benzoic acid can be used as a structural evolution probe of gel glass.

KEY WORDS: Benzoic acid; room temperature phosphorescence; photophysical properties.

INTRODUCTION

There has been much research on combining the advantages of organic and inorganic materials at molecular or nanometer level to obtain inorganic-organic hybrid optical solids [1-4]. Considering that organics typically decompose at relatively low temperatures and inorganic crystals and glass of superior optical quality are generally formed at high temperatures, the low-temperature sol-gel process has been successfully demonstrated to combine optically active organics with the appropriate inorganic host matrices. The success of synthesizing sol-gel-derived gel glass doped with photoactive organics has led to some new application opportunities in non-linear optics, solid-state tunable laser, photochromic devices, electroluminescent diodes, and photochemical hole burning, etc. [5-8].

Sol-gel glass transition is a complicated process involving some physicochemical changes, and a variety of techniques have been applied to study the structural and componential changes of the sol and gel during gelation and heat treatment, as reviewed by James [9]. Recently, some organic dyes, which are sensitive to the trapped surroundings and show remarkable changes in molecular structures and consequently in photoluminescence properties, during the sol to gel to gel glass conversions, have been used as environment-sensitive probes for the microstructural evolutions in these conversions [10-15].

In this work, benzoic acid molecules were dispersed in silica gel glass and some novel photophysical phenomena of benzoic acid during gelation and heat treatment, such as room temperature phosphorescence, are reported.

EXPERIMENTAL PROCEDURE

Sample Preparation

The samples were prepared by the acidic (HCl) hydrolysis of tetraethoxysilane (TEOS) in ethanol as

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reported previously [16]. Analytical grade benzoic acid, TEOS, ethanol and hydrochloric acid were used in this work. The starting solution contained 1 mole TEOS, 4 moles ethanol, and 4 moles deionized water. Benzoic acid dissolved in ethanol was introduced into the starting solution. The mixed solution was adjusted to $\text{pH} \approx 2$ by the addition of HCl, stirred vigorously for 1 hr at room temperature, and then placed in sealed plastic containers. The precursor solution converted to wet gel after several days' gelation at 40°C , and it was continuously dried at room temperature to obtain silica xerogel doped with benzoic acid. The derived benzoic acid-doped silica xerogel was heat-treated as follows: heated to required temperature at a rate of 20°C hr^{-1} and kept at this temperature for 24 h in air, followed by cooling in the furnace. Transparent monolithic doped gel glasses for measurement were obtained.

Measurement

The fluorescence spectra and infrared spectra were measured with a Hitachi 850 spectrofluorometer and a Perkin-Elmer 983 infrared spectrophotometer with KBr as the matrix material, respectively. The phosphorescence spectra and phosphorescence decay curve were measured with a Hitachi MPF-4 spectrofluorometer assembled with phosphorescence measurement accessories.

RESULTS AND DISCUSSIONS

Fluorescence of Benzoic Acid Embedded in Silica Gel Glass

Using 70% H_2SO_4 as a solvent, the band fluorescence emission of benzoic acid centered at around 385 nm was observed [17]. Benzoic acid, however, is non-fluorescent in a neutral solution. The changes in molecular structure of benzoic acid in different solutions result in above phenomena [18]. In neutral solutions, benzoic acid molecules will ionize. The electronic transitions and the lowest excited states of free benzoate anion are $n \rightarrow \pi^*$ and $n\pi^*$, respectively. For the organic fluorophore molecule, the value of the singlet-triplet splitting $\Delta(S_n - T_n)$, the energy difference between the singlet S_n level and the corresponding triplet level T_n , is usually greater for excited states resulting from $\pi \rightarrow \pi^*$ transitions than for $n \rightarrow \pi^*$ transitions [19], as shown in Fig. 1. Therefore the intersystem crossing from S_n level to T_n level for benzoate anion is very easy. Because of the long lifetime of the triplet state, intermolecular collisional quenching processes, and intramolecular vibrational-rotational

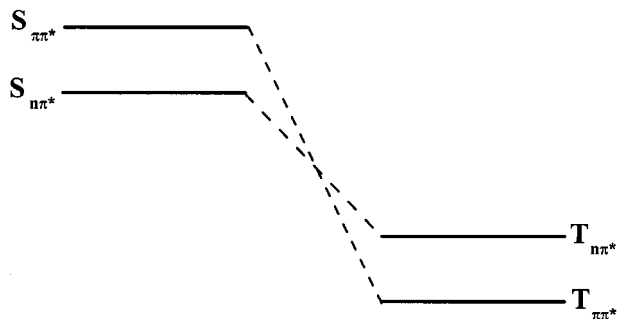


Fig. 1. Singlet-triplet splitting $\Delta(S_n - T_n)$ of organic fluorophore molecule.

relaxation, non-radiative relaxation is the dominant deactivation process of the triplet state, and any fluorescence and phosphorescence of benzoic acid in neutral solutions cannot be observed. In acidic solution, benzoic acid exists as protonation and the lowest excited states are $\pi\pi^*$. The large energy difference $\Delta(S_n - T_n)$ decreases the probability of intersystem crossing, and the fluorescence induced by the transition from the lowest singlet state to ground state $S_{1\pi\pi^*} \rightarrow S_0$, is observed.

Entrapped in silica gel glass, we also observed the fluorescence emission of benzoic acid centered at 320 nm excited with 290-nm UV light, as shown in Fig. 2. The fluorescence decay curve was measured with an Applied Photophysics SP-70 nanosecond spectrofluorometer based on time-correlated, single-photo counting technique, and the fluorescence lifetime is 4.8 ns. The doped gel glass was prepared by the acidic (HCl) hydrolysis of TEOS in ethanol, and benzoic acid molecules were isolated in the tiny pores of the derived monolith

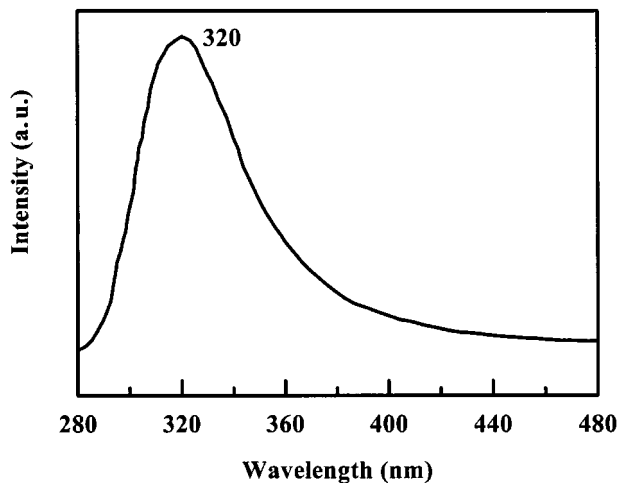


Fig. 2. Emission spectrum of benzoic acid doped in silica gel glass measured at room temperature, excited at 290 nm.

with the residual water, ethanol, and HCl. The surroundings of benzoic acid molecules are acidic, so benzoic acid in gel glass exhibits fluorescence emission. The broad-band emission of benzoic acid in gel glass shifts toward the blue part, from 385 nm to 320 nm, with respect to that of benzoic acid in 70% H_2SO_4 , which may be induced by the solvent effects [17]. The orientation polarizability of the surrounding environment of benzoic acid molecules trapped in the small pores of silica gel glass is lower than that in 70% H_2SO_4 solution. The Stokes' losses result in a blue-shifted emission spectrum with respect to the emission spectrum of benzoic acid in 70% H_2SO_4 .

As mentioned above, the silica gel glass is formed by a cluster-cluster aggregation process and thus is an amorphous porous solid, and benzoic acid molecules exist in the pores with the residual water, ethanol, and HCl. The pore shape of silica gel glass is similar to an ink bottle, with an average radius of about 17 Å [12]. The essential feature of the bottle-like pores is that the large cavities are accessible only through smaller channels or



Fig. 3. Infrared spectra of benzoic acid-doped gel glass heat-treated at 200°C (a) and 500°C (b) for 24 hr and un-doped silica gel glass without heat treatment (c).

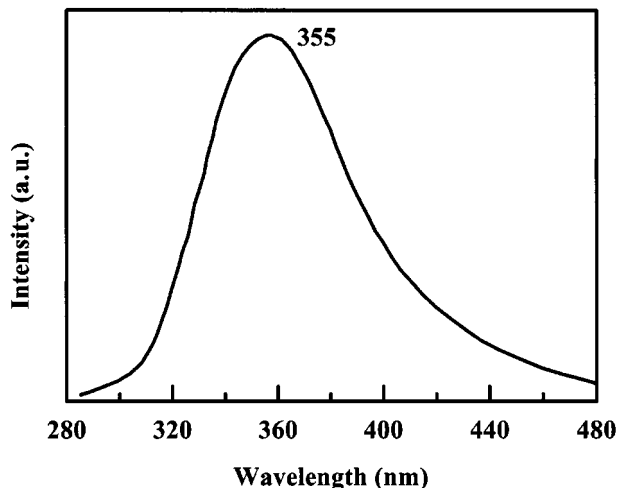


Fig. 4. Emission spectrum of benzoate anions doped in silica gel glass heat-treated at the range 300 ~ 400°C for 24 hr measured at room temperature, excited at 290 nm.

orifices. It is difficult for benzoic acid molecules trapped in these pores to be removed from the pores, even at the temperatures greater than the boiling point ($\sim 249^\circ\text{C}$). Figure 3 shows the infrared spectra of benzoic acid-doped gel glass heat-treated at various temperatures and un-doped silica gel glass. The appearance of the 1692 cm^{-1} and 710 cm^{-1} bands owing to carboxylic group stretching vibration $\nu(\text{C}=\text{O})$ and monosubstituted benzene out-of-plane bending vibration $\gamma(\text{C}-\text{H})$, respectively, suggests that benzoic acid molecules exist in the gel glass. Owing to the shield of silica network, the thermal stability of benzoic acid molecules entrapped in silica gel glass increases to over 500°C .

The fluorescence spectrum of benzoic acid in gel glass heat-treated at the temperatures below 200°C shows no changes, with the broad band centered at 320 nm. On heating at an elevated temperature (up to 400°C), the fluorescence spectrum of benzoic acid exhibits remarkable changes. The broad band centered at 355 nm is substituted for the broad band at 320 nm, as shown in Fig. 4. It is suggested that the changes in the surroundings of benzoic acid result in the shift of the fluorescence emission band of benzoic acid. After heating at the temperatures above 100°C , the residual water, ethanol, and HCl in the pores vaporize gradually and are almost removed on heating at 250°C [20]. With the removal of the residual water, ethanol, and HCl, benzoic acid is isolated into the tiny pores of the silica gel glass. Because the surroundings of benzoic acid become neutral, benzoic acid exists as anion in the pores. The lowest excited states of free benzoate anion are $n\pi^*$, which is lower than the energy level $\pi\pi^*$, as shown in Fig. 1. In contrast to the

cases of benzoic acid dissolved in neutral solutions, when benzoate anion is trapped in the tiny pores, the non-radiative relaxation probabilities of intermolecular collisional quenching processes and intramolecular vibrational-rotational relaxation decrease. Therefore the fluorescence band centered at 320 nm arising from the $\pi \rightarrow \pi^*$ transitions of benzoic acid molecules disappears, and the fluorescence emission located at 355 nm induced by the $n \rightarrow \pi^*$ transitions is observed.

On heat-treated at the temperatures over 400°C, the luminescence spectrum of benzoate anion in silica gel glass changes further, and the room temperature phosphorescence (RTP) of benzoate anion is observed.

Room Temperature Phosphorescence of Benzoic Acid in Silica Gel Glass

The phosphorescence of organics is induced by the transition from excited triplet state to ground state, $T_1 \rightarrow S_0$. Because of the long lifetime of the triplet state in liquid solutions at room temperature, a number of quenching processes, such as intermolecular collisional quenching processes, intramolecular vibrational-rotational relaxation, and oxygen quenching processes, lead to rapid non-radiative deactivation of the triplet state. In general, the phosphorescence can be observed when the triplet molecule is entrapped in a rigid medium to restrict radiationless deactivation. Winefordner and Tin [21] investigated the phosphorescence of organic compounds in rigid ethanol solutions and observed the phosphorescence of benzoic acid at 77 K.

When heat-treated at the temperatures over 400°C for 24 hr, the luminescence band at 355 nm also disappears. When excited at 290 nm, the sample exhibits a new luminescence spectrum located at the wavelength range 350 ~ 550 nm measured at room temperature, as shown in Fig. 5. The excitation and emission spectra are

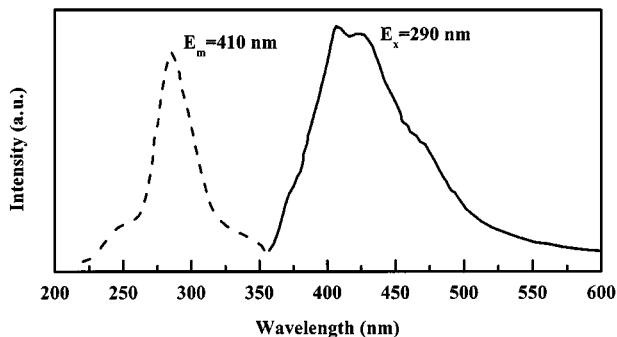


Fig. 5. RTP excitation (dotted line) and emission (solid line) spectra of benzoate anions doped in silica gel glass heat-treated at 500°C for 24 hr.

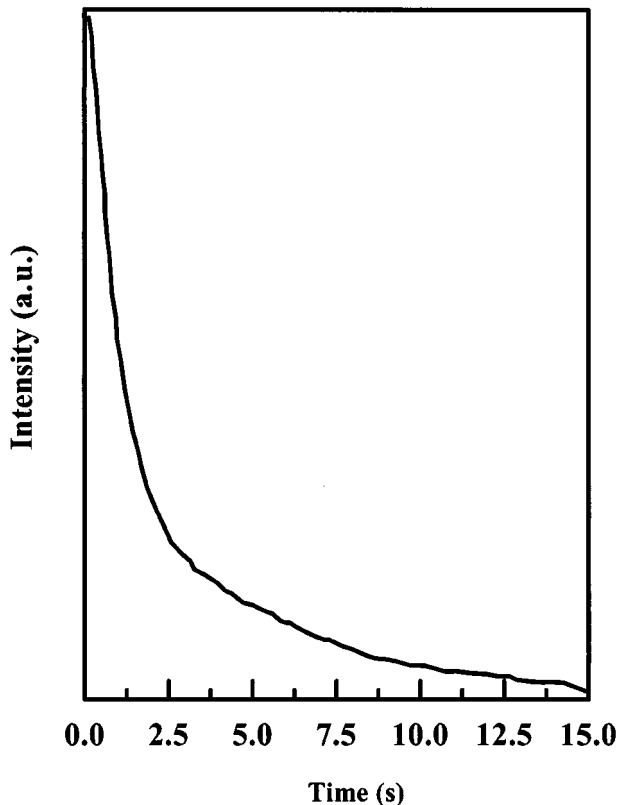


Fig. 6. RTP decay curve of benzoate anions in silica gel glass heat-treated at 500°C for 24 hr monitored at 410 nm.

similar to the phosphorescence excitation and emission spectra observed for benzoic acid in ethanol solution at 77 K [21]. The luminescence decay monitored at 410 nm is obtained, as shown in Fig. 6, and the calculated lifetime is 1.5 s. So it is reasonable to suggest the luminescence in the wavelength range 350 ~ 550 nm is the RTP of benzoic acid.

As mentioned above, benzoic acid exists as anion in the pores of silica gel glass heat-treated at temperatures over 300°C. The electronic transitions of benzoate anions are $n \rightarrow \pi^*$. The value of the singlet-triplet splitting $\Delta(S_n - T_n)$ for $n \rightarrow \pi^*$ transitions is lower than that for $\pi \rightarrow \pi^*$ transitions, which increases the transition probabilities of the intersystem crossing from S_n level to T_n level for benzoate anions. When benzoate anion is not immobilized in a sufficiently rigid medium, non-radiative relaxation is the dominant deactivation process of the triplet state, and the phosphorescence of benzoate anions cannot be observed at room temperature. After heating at elevated temperatures, with the removal of the residual water, ethanol, and HCl, the Si-O network is formed gradually. The SiO_4 tetrahedra are almost formed on heating at 500°C for 24 hr [20]. The sample shows rapid linear

shrinkage resulting mainly from the collapse of tiny pores and the structural relaxation. Benzoate anions are steadily absorbed in the cages of the Si–O network, and the radiationless deactivation processes of the triplet state are restricted. The RTP of benzoate anions is observed. Of course, the rigid immobilization of the cages of the Si–O network for benzoate anions is less than the low-temperature rigid matrices, so the lifetime of the phosphorescence of benzoate anions in silica gel glass is lower than that in ethanol solution at 77K, 2.3 s [21].

According to the molecular structure and the corresponding energy level and electronic transitions of benzoic acid entrapped in silica gel glass heat-treated at various temperatures, we suggest the schematic energy level diagrams for benzoic acid at various temperature range, as shown in Fig. 7.

CONCLUSIONS

When silica gel glass doped with benzoic acid is heat-treated at various temperatures, the changes in molecular structure and the surrounding environment of benzoic acid result in different electronic transitions. The fluorescence band at 320 nm is induced by the $S_{1\pi\pi^*} \rightarrow S_0$ transition of benzoic acid in gel glass on heat-treating at the temperatures below 200°C, and the fluorescence lifetime is 4.8 ns. When heating at the temperature range 300 ~ 400°C, the 320 nm fluorescence band disappears

and a new fluorescence band at 355 nm is observed, which is attributed to the $S_{1n\pi\pi^*} \rightarrow S_0$ transition of benzoate anions entrapped in silica gel glass and indicates the removal of the residual water, ethanol, and HCl from the gel glass. With the SiO_4 tetrahedra near formation on heating at 500°C, benzoate anions are steadily immobilized in the cages of the Si–O network and the RTP of benzoate anions is observed. The luminescence spectra of benzoic acid doped in silica gel glass, which changes with the heat-treatment temperatures, can be used as a structural evolution probe of gel glass.

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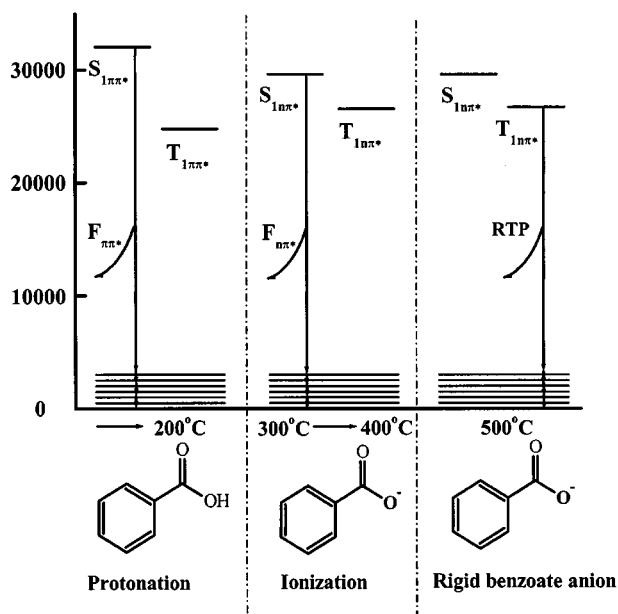


Fig. 7. Schematic energy level diagrams for benzoic acid doped in silica gel glass heat-treated at various temperatures.

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