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Phosphorescence of Benzophenone in Sol–Gel Silica

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The phosphorescence spectra of benzophenone (BP) were studied in tetramethoxysilane (TMOS) sol–gel systems at 77 K. The phosphorescence spectra ascribed to solvent-free benzophenone (f-BP), aggregated benzophenone (a-BP), and a benzophenone–water complex (w-BP) were observed in these systems. The results showed that the spectra varied with the BP concentration and sol–gel conditions, such as the water/TMOS ratios, catalyst, and the various sol–gel reaction stages. The w-BP phosphorescence lifetimes showed a single-exponential decay of 8 ms in sol systems and a double-exponential decay of 8—12 ms and 31 ms in xerogel systems. The longer lifetime component corresponds to a w-BP complex hydrogen bonded with silanol groups. These changes are discussed in terms of the sol–gel structure and surface adsorption effects.

Previous studies have shown that the phosphorescence spectra of benzophenone (BP) are strongly affected by the nature of solvents and additives.[1—4] The phosphorescent state of BP at 77 K was considered to obtain the $\pi\pi^*$ character in very polar hydrogen-bonding solvents, and to attain a protonated $\pi\pi^*$ state in strongly acidic solvents. This is based on the increased lifetime and loss of the vibrational structure of the BP phosphorescence with respect to its $n\pi^*$ character, as observed in non-polar and weak hydrogen-bonding solvents.[1)]

The phosphorescence spectra of BP in aqueous solutions showed blue shifts with increasing additive concentration of CH_3COONa or H_2SO_4. The observed spectral changes were attributed to the formation of BP–water complexes (w-BP) at 77 K.[2)]

Dual phosphorescence was observed in spectra of BP in ethanol (EtOH) and water mixtures at 77 K.[3)] In addition to emissions with a lifetime of 5.6 ms at 413, 442, and 478 nm in neat EtOH, new emission bands with a lifetime of 8.0 ms appeared at 400, 428, and 455 nm with increasing H_2O content. These dual phosphorescence emissions were assigned to solvent-free BP (f-BP) and w-BP, respectively. In mixtures containing 2,2,2-trifluoroethanol (TFE) and water, dual phosphorescence was also observed. In this case, w-BP showed peaks at 397, 421, and 452 nm with a lifetime of 15.9 ms.[4)] The phosphorescent states of w-BP in EtOH–H_2O and TFE–H_2O were assigned to the $n\pi^*$ character and mixed $n\pi^*$–$\pi\pi^*$character, respectively. In pure TFE, aggregated BP (a-BP) appeared at high concentrations (ca. 1×10^{-3} mol dm^{-3}), as indicated by red-shifted spectral peaks at 421, 452, and 490 nm.[4)]

The photophysics and photochemistry of adsorbed molecules on solid surfaces have been of a great interest. The electronic states of adsorbed BP were distorted by the interaction of the non-bonding carbonyl electrons with the proton-donor or electron-acceptor centers of metal oxides.[5)] The phosphorescence spectra of BP adsorbed on the cation-exchanged ZSM-5 zeolite showed the presence of a protonated BP (BPH^+) and w-BP, the concentrations of which varied depending on the desorption temperature and cations exchanged.[6)] The photochemistry of BP adsorbed on microcrystalline cellulose also varied depending on the swelling agents used in the experiment.[7)]

Sol–gel matrices containing organic molecules are attractive systems for studying photophysical and photochemical processes as well as preparing photonic materials with new applications.[8)] The phosphorescent states of BP show the characteristic spectra, such as f-BP, a-BP, w-BP, and BPH^+, as shown above. Therefore, observing the phosphorescence in sol–gel systems is expected to provide valuable information on the sol–gel process and trapping of organic molecules in silica. Based on the present study we report the phosphorescence spectra and lifetime of BP in sol–gel silica prepared under various conditions, and discuss the phosphorescent species trapped within the silica in relation to the applied preparatory conditions.

Experimental

Chemicals. Benzophenone (BP, Wako) and tetramethoxysilane (TMOS, Tokyo Kasei) were used without additional purification. Ethanol (EtOH, Katayama) was of a spectroscopic grade. Water was deionized and distilled.

Sample Preparation. TMOS (10.0 mL), EtOH (10.0 mL) containing 1×10^{-3}—5×10^{-2} mol dm^{-3} BP, and water (2.5—10.0 mL) were mixed at room temperature. The concentrations of BP in sol–gel systems were denoted as those in EtOH. The molar ratio of TMOS : water : EtOH for 5.0 mL of water was 1 : 4.1 : 2.6. A small amount of HCl (200 μL of 1 mol dm^{-3}) or NH_4OH (20 μL of **1** mol dm^{-3}) was added to some solutions as a catalyst. Only the results of the neutral and acidic systems are presented in this paper, because very similar results were obtained for both neutral and basic systems. After stirring for 1 h, the mixtures were kept in polystyrene beakers sealed with parafilm with several pinholes and

left to gel at room temperature. Adsorbed gels used for comparative studies were prepared by soaking nondoped SiO_2 xerogels (0.4 g) in EtOH (20 mL) containing 1×10^{-3} mol dm^{-3} BP for approximately 1 d and drying in air.

Measurements. Steady-state phosphorescence and phosphorescence excitation spectra were taken with a JASCO FP-770 spectrophotometer at 77 K. Unless otherwise stated, the excitation wavelength was 334 nm. Phosphorescence decay profiles were obtained with a N_2 laser (Usho AN-200) and a photomultiplier (Hamamatsu Photonics R955).

Results and Discussion

Phosphorescence Spectra. The phosphorescence spectra of BP were measured in various EtOH–water mixtures at 77 K. Figure 1(a) shows the phosphorescence spectrum of 5×10^{-2} mol dm^{-3} BP in EtOH. The spectrum shows peaks at 416, 446, 481, and 520 nm due to a carbonyl vibrational progression of 1600 cm^{-1}. The phosphorescence lifetime was 5.7 ms. These results are very similar to previous ones assigned to solvent-free BP, f-BP.[3] Similar results were obtained when a lower concentration of 5×10^{-3} mol dm^{-3} of BP in EtOH was studied.

A weak band appeared at 400 nm in a solution of EtOH/water = 6/4 (v/v), as shown in Fig. 1(b). The observed lifetime was 8.1 ms. This band was assigned to the phosphorescence of the BP and water hydrogen bonded complex, w-BP.[3] The vibronic bands of w-BP at 428 and 455 nm were not resolved in this spectrum.

Further changes were observed in a solution of EtOH/water = 4/6 (v/v), as shown in Fig. 1(c). New bands appeared at 429, 460, 497, and 538 nm in addition to the dual phosphorescence. These bands can also be explained by the carbonyl vibrational progression at 1600 cm^{-1}. The lifetime of the bands was 3.2 ms. These bands are due to aggregated benzophenone, a-BP,[4] which forms at high water concentrations in EtOH, because of its low solubility in water (7.5×10^{-4} mol dm^{-3}).[9]

Figure 2 shows the phosphorescence spectra of BP measured at the initial stage of the neutral sol–gel process for TMOS–EtOH (containing benzophenone at 5×10^{-2} mol dm^{-3}) with water/TMOS = 5 mL/10 mL. Just after mixing, the spectrum showed f-BP bands at 416, 446, 479, and 520 nm and a weak w-BP band at around 400 nm, as shown in Fig. 2(a). After 2 d, the relative intensities at 402 and 429 nm increased, indicating an increase in w-BP (see Fig. 2(b)). After 8 d (not shown here), distinct bands were observed at 458, 494, and 533 nm due to a-BP as well as the those due to w-BP, while peaks due to f-BP disappeared. These changes suggest that a-BP is formed mainly from f-BP during the initial stage of the sol–gel process. The spectrum measured after 3 weeks is outlined in Fig. 2(c), and significantly shows a strong carbonyl vibrational progression of 1600 cm^{-1} due to a-BP at 426, 457, 494, and 534 nm, and a weak peak at approximately 400 nm due to w-BP. These results show that w-BP decreases and a-BP increases relative to each other. This suggests that a-BP is also formed from w-BP during the gel-drying process. These changes are visually shown in Fig. 3. The relative intensity of the phosphorescence 0–0 band of each species is used as a rough measure of each concentration.

Phosphorescence spectra were taken for the xerogels prepared from various BP concentrations in water/TMOS = 5 mL/10 mL and dried for 4 months. Figure 4(a) shows peaks of w-BP at 402, 427, and 450 nm at 5×10^{-3} mol dm^{-3}. The phosphorescence spectrum in Fig. 4(b) indicates the presence of a-BP as well as w-BP at 5×10^{-2} mol dm^{-3}. The phosphorescence spectra for various BP concentrations indicate that BP molecules exist mainly as w-BP at lower concentrations ($\leq5\times10^{-3}$ mol dm^{-3}), and gradually form a-BP as

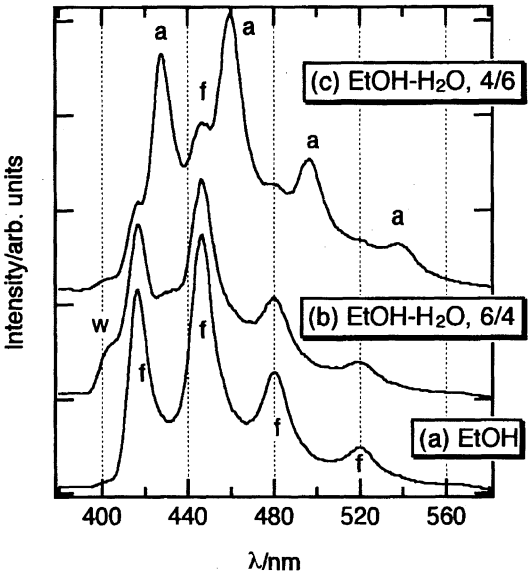


Fig. 1. Phosphorescence spectra of benzophenone at 77 K in EtOH (5×10^{-2} mol dm^{-3}) (a), EtOH (5×10^{-2} mol dm^{-3})–H_2O (6/4, v/v) (b), and (4/6, v/v) (c). λ_{ex} = 334 nm.

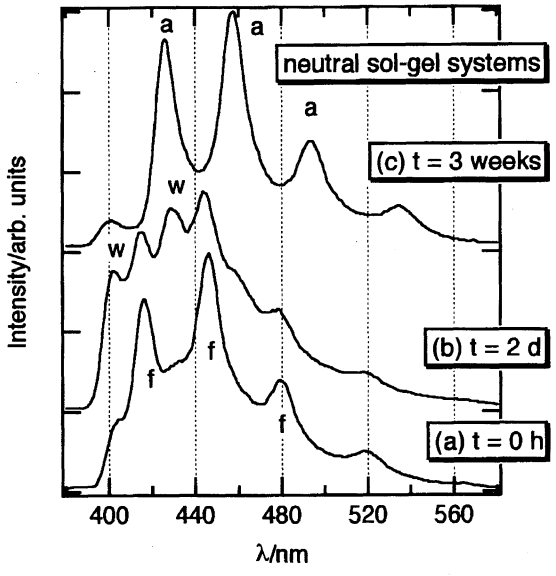


Fig. 2. Phosphorescence spectra of benzophenone (5×10^{-2} mol dm^{-3}) at 77 K for three stages of the neutral sol–gel process excited at 334 nm: (a) just after mixing; (b) after 2 d; (c) after 3 weeks. λ_{ex} = 334 nm.

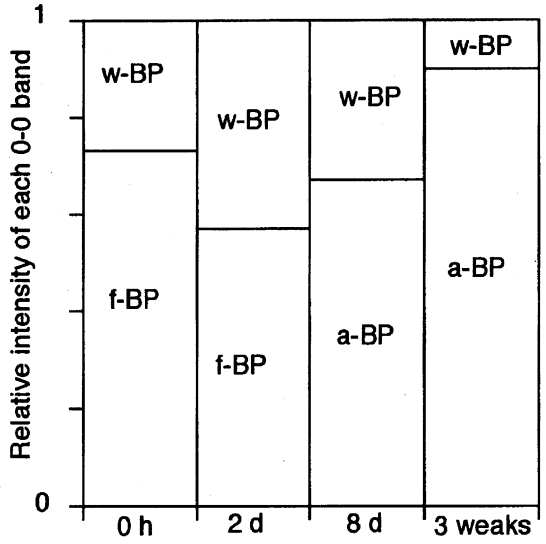


Fig. 3. Relative intensity of the phosphorescence 0–0 band for f-BP (416 nm), w-BP (400 nm), and a-BP (ca. 425 nm) during the initial stages of the neutral sol–gel process. λ_{ex} = 334 nm.

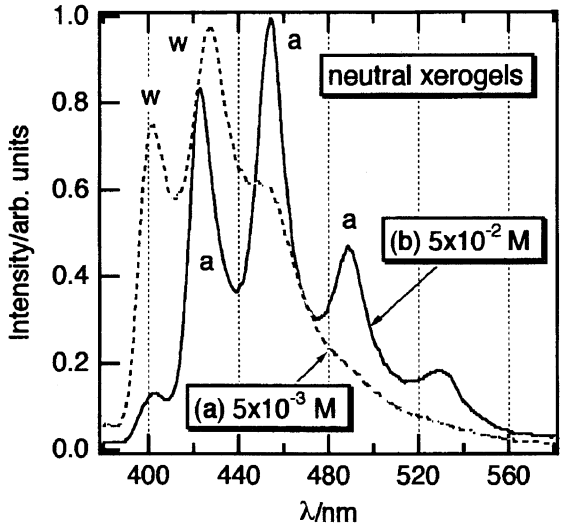


Fig. 4. Phosphorescence spectra of benzophenone at 77 K for neutral xerogels aged for 4 months with different benzophenone concentrations: (a) 5×10^{-3} mol dm^{-3}; (b) 5×10^{-2} mol dm^{-3}. λ_{ex} = 334 nm.

the concentration of BP increases. At concentrations above 10^{-2} mol dm^{-3}, a-BP is the dominant species.

The phosphorescence spectra of BP, measured after 5 months for neutral xerogels derived from TMOS–EtOH (containing BP at 5×10^{-2} mol dm^{-3}) with water/TMOS = 2.5 mL/10 mL, 5 mL/10 mL, and 10 mL/10 mL, are outlined in Fig. 5. Figure 5(a) shows the spectrum of a-BP for xerogels with water/TMOS = 2.5 mL/10 mL. The main peaks were observed at 420, 450, 485, and 523 nm. However, the w-BP peak at 400 nm was not observed in this spectrum. For xerogels with water/TMOS = 5 mL/10 mL, the phosphorescence spectrum showed further blue-shifted peaks at 421, 451, 485, and 526 nm due to a-BP after 5 months, as outlined in Fig. 5(b), while the relative intensity of w-BP at 400 nm

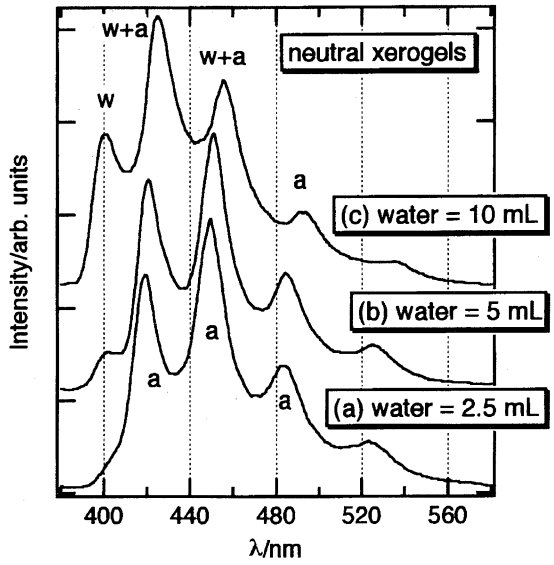


Fig. 5. Phosphorescence spectra of benzophenone (5×10^{-2} mol dm^{-3}) at 77 K for neutral xerogels aged for 5 months with various water/TMOS ratios: (a) 2.5 mL/10 mL; (b) 5 mL/10 mL; (c) 10 mL/10 mL. λ_{ex} = 334 nm.

was similar to those observed after 3 weeks (see Fig. 2(c)) and 4 months (see Fig. 4(b)). These results indicate that most of the BP molecules exist mainly as a-BP and a small amount of w-BP in xerogels prepared under these conditions. For xerogels with water/TMOS = 10 mL/10 mL, as shown in Fig. 5(c), the relative intensities of w-BP increased. The results in Fig. 5 indicate that w-BP increases along with an increase of the water/TMOS ratios in xerogels.

The phosphorescence 0–0 band of a-BP shows a blue shift as the sol–gel reactions go on (see Fig. 6). The blue shift in the spectrum of a-BP toward that of f-BP suggests that the aggregated structure is broken into smaller aggregations of a′-BP during the ageing process of the xerogels. This can

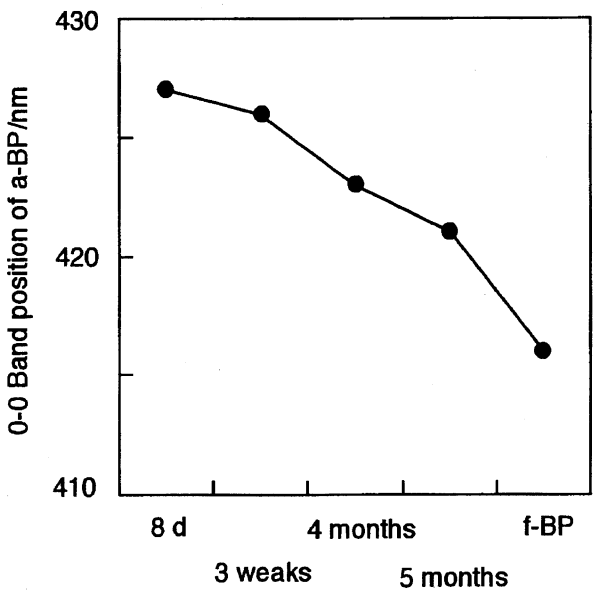


Fig. 6. Wavelength of the phosphorescence 0–0 band of a-BP against the reaction time in neutral sol–gels systems.

probably be ascribed to shrinkage of the silica cage, making the aggregations unstable, as can be seen in the excimer fluorescence of pyrene.[10,11]

Figure 7 shows the phosphorescence spectra of the acidic xerogels after 4 months, prepared with different BP concentrations at water/TMOS = 5 mL/10 mL. Figure 7(a) shows the poorly resolved spectrum obtained for xerogels at 5×10^{-2} mol dm^{-3} when excited at 334 nm. The spectrum of f-BP became clearly resolved as the excitation wavelength was increased to 368 nm (Fig. 7(b)). Figure 7(a) can therefore be assigned to overlapped spectra of w-BP and f-BP. When the BP concentrations are less than 1×10^{-2} mol dm^{-3}, w-BP is the dominant species, as shown in Fig. 7(c). It should be noted here that BP exists as a-BP and w-BP at 5×10^{-2} mol dm^{-3} and as w-BP at concentrations less than 5×10^{-3} mol dm^{-3} in neutral xerogels. Figure 8 summarizes the relative intensity of the phosphorescence 0–0 band of each species in the acidic and neutral xerogels after 4 months. It can be clearly seen that the acidic xerogels are capable of more efficient isolation of BP molecules than the neutral xerogels, which will be discussed later.

Phosphorescence Lifetimes. Table 1 summarizes the phosphorescence lifetimes of BP in various systems at 77 K. The lifetimes of 5.7 ms in EtOH due to f-BP, 8.1 ms in EtOH–water (6/4) due to w-BP, and 3.2 ms in EtOH–water (4/6) due to a-BP agree with results reported previously.[3,4] The phosphorescence lifetimes in neutral sols at 400 nm due to w-BP and 445 nm to f-BP are 8.0 and 7.1 ms, respectively. The lifetime at 445 nm is close to that of w-BP, and slightly longer than that for f-BP. This is possibly ascribed to w-BP and f-BP overlapping, as can be seen in Fig. 2(a).

After 4 months, the lifetime of w-BP showed two decay components. The lifetime for neutral xerogels at 400 nm exhibits a double-exponential decay of 31 and 8 ms. The

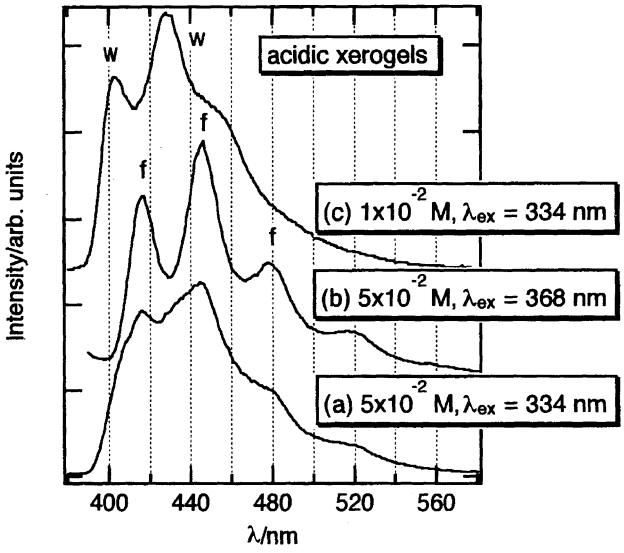


Fig. 7. Phosphorescence spectra of benzophenone at 77 K for acidic xerogels aged for 4 months: (a) 5×10^{-2} mol dm^{-3}, λ_{ex} = 334 nm; (b) 5×10^{-2} mol dm^{-3}, λ_{ex} = 368 nm; (c) 1×10^{-2} mol dm^{-3}, λ_{ex} = 334 nm.

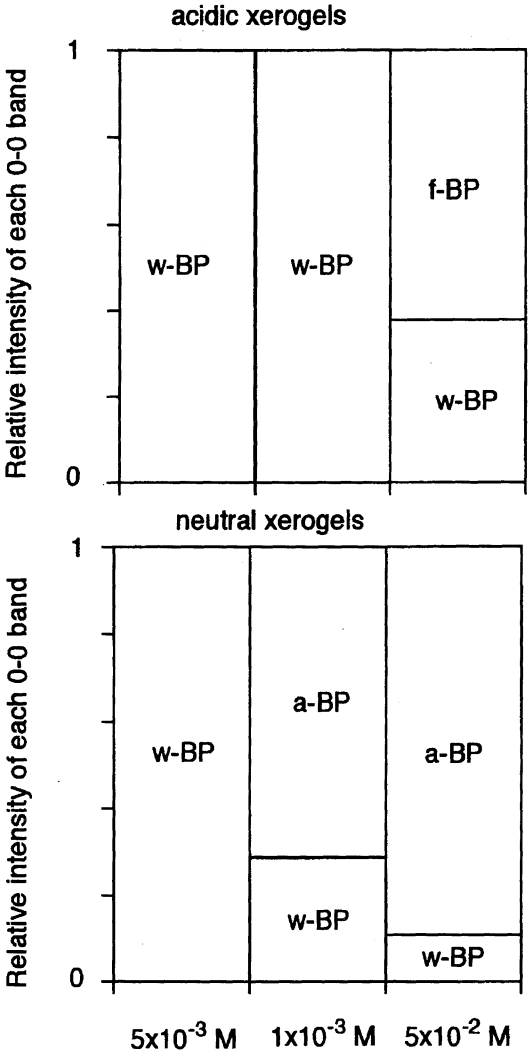


Fig. 8. Relative intensity of the phosphorescence 0–0 band for f-BP (416 nm), w-BP (400 nm), and a-BP (423 nm) in the acidic and neutral xerogels after 4 months. λ_{ex} = 334 nm.

short-lifetime component is analogous to those of w-BP in EtOH–water and in sols. This indicates that conventional w-BP formed at the sol stage is still trapped in xerogels. The long lifetime is approximately the same as w-BP adsorbed on sol–gel silica gels (ca. 50 ms) described below, and suggests the formation of an adsorbed complex of BP–H_2O–SiOH via hydrogen bonding in xerogels. Similar results were obtained for acidic xerogels.

The phosphorescence spectra of BP adsorbed on SiO_2 xerogels were measured for xerogels soaked for 1 d and dried for 1 h or dried for 7 d. Both of the spectra showed peaks at approximately 402 and 427 nm, indicating the presence of w-BP. The lifetime was fitted by a single-exponential curve (τ = 9 ms) for xerogels dried for 1 h and by a double-exponential curve for xerogels dried for 7 d (τ = 8 and 51 ms with relative intensities at t = 0 ms of 47% and 53%, respectively). The short lifetime of 8—9 ms agrees well with that of w-BP in EtOH–water. The long component of 51 ms corresponds approximately with that of adsorbed BP

Table 1. Phosphorescence Lifetimes (τ) for Benzophenone at Various Monitoring Wavelengths in Various Matrices at 77 K (Excitation at 337 nm)
Percentage Indicates a Relative Phosphorescence Intensity of Each Lifetime Component at t = 0 ms for a Double-Exponential Decay.

System	τ/ms, Percentage of each component at t = 0 ms for a double-exponential decay (λ/nm or BP species)			
EtOH[a]	5.7 (416)	5.6 (446)		
EtOH–water (6/4, v/v)[a]	8.1 (400)			
EtOH–water (4/6, v/v)[a]	3.2 (429)	3.1 (460)		
Neutral sols just prepared[b,c]	8.0 (400)	7.9 (416)	7.9 (429)	7.1 (445)
Neutral gels aged for 4 months[a,c]	31, 43% (400)	8, 57% (400)	6.3 (426)	6.3 (450)
Acidic gels aged for 4 months[a,d]	31, 55% (400)	12, 45% (400)	9 (416)	10 (445)
Sol–gel silica gel-EtOH[e]	9 (400)			
Sol–gel silica gel-EtOH[f]	51, 47% (400)	8, 53% (400)		
TFE–water[g]	15.9 (w-BP)	3.6 (f, a-BP)		
EtOH–water[h]	8.0 (w-BP)	5.6 (f-BP)		
Silica gel-methylcyclohexane[i]	81 (393)		110—210 (434)	
Na^+-ZSM-5[j]	21(w-BP)	280 (BPH^+)		

a) [BP] = 5×10^{-2} mol dm^{-3} in EtOH. b) [BP] = 1×10^{-2} mol dm^{-3} in EtOH. c) Preparation conditions of sols and gels: TMOS 10 mL, EtOH 10 mL, and water 5 mL. d) Preparation conditions of sols and gels: TMOS 10 mL, EtOH 10 mL, water 5 mL, and 1 mol dm^{-3} HCl 200 μL. e) Adsorbed on SiO_2 xerogels in EtOH followed by air drying for 1 h. f) Adsorbed on SiO_2 xerogels in EtOH followed by air drying for 7 d. g) Taken from Ref. 4. h) Taken from Ref. 3. i) Taken from Ref. 1. j) Taken from Ref. 6.

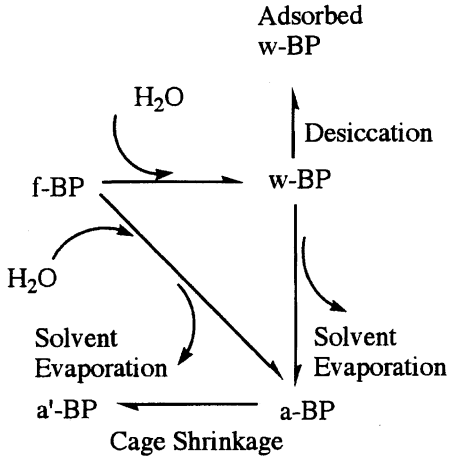
on SiO_2 (81 ms at 393 nm).[1] These findings suggest that the conventional structure of w-BP is initially deposited on the silica–gel surface, and gradually converts into a hydrogen-bonded w-BP complex with silanol groups, resulting in an adsorbed complex of BP–H_2O–SiOH.

The phosphorescence lifetime of w-BP is influenced by the solvents used; the phosphorescence lifetimes of w-BP in TFE–H_2O and EtOH–H_2O are 15.9 and 8.0 ms, respectively.[3,4] These differences can be explained by the stronger hydrogen-bonding ability of TFE over EtOH, which can readily mix the $\pi\pi^*$ character with the $n\pi^*$ character.[1,3,4] A similar phenomenon also occurs on metal oxides; the $n\pi^*$ transitions of adsorbed on metal oxides are systematically raised and the $\pi\pi^*$ transitions lowered with increasing surface acidity, adding the $\pi\pi^*$ character to the $n\pi*$ phosphorescent state.[5]

Considering all of these results, we conclude that w-BP in sols is initially located in the liquid medium composed mainly of EtOH–water. As the sol–gel process proceeds, w-BP is adsorbed on the silica-gel surface via hydrogen-bonding with silanol groups. The phosphorescence lifetime increases due to the increased $\pi\pi^*$ character due to the hydrogen bond. However, the w-BP adsorbed the on silica-gel surface is different from BPH^+, since this protonated species exhibits considerably longer lifetimes: i.e. 1.03 s in 98% H_2SO_4; 0.66 s in 85% H_3PO_4; 0.41 s on H^+-ZSM-5; 0.28 s on Na^+-ZSM-5.[1,6] The surface acidity of xerogels is not considered strong enough to form BPH^+.

Trapping Mechanism. In neutral sol–gel systems, the following results were obtained: Figure 3 shows that a-BP is initially formed from f-BP, and then from w-BP in neutral sol–gel systems. The relative intensity of w-BP increases with increasing H_2O/TMOS ratios (see Fig. 5). Blue shifts due to a-BP are observed as the sol–gel reaction proceeds, as summarized in Fig. 6. As the BP concentration decreases, the relative intensity becomes weaker for a-BP and stronger for w-BP. Below concentrations of 5×10^{-3} mol dm^{-3}, w-BP is the main phosphorescent species present (see Fig. 8). The lifetime for neutral xerogels at 400 nm exhibits a longer decay component of 31 ms due to w-BP adsorbed on sol–gel silica gels.

These results are summarized in Scheme 1. In general, f-BP and w-BP are considered to exist in equilibrium in sol–gel systems, as in EtOH–water mixtures.[3,4] At high concentrations ($\geq1\times10^{-2}$ mol dm^{-3}), f-BP and w-BP transform into a-BP, because of its poor solubility in water, since the EtOH solvent and methanol (MeOH) produced from TMOS evaporate. Some molecules of w-BP remain trapped in the silica and become surface adsorbed via hydrogen-bonding with SiOH, as indicated by an increase in the lifetime. Ag-



Scheme 1. Trapping processes of BP in neutral sol–gel systems at [BP]$\geq10^{-2}$ mol dm^{-3}.

gregations (a-BP) are broken into smaller aggregations (a′-BP) during the ageing process of the xerogels, possibly due to shrinkage of the silica, as shown in the blue shift of a-BP toward f-BP. On the other hand, at low concentrations ($\leq 5\times10^{-3}$ mol dm^{-3}), the majority of f-BP is converted into w-BP and trapped in silica without forming aggregations. Adsorbed w-BP on silica gel is also formed from w-BP.

As for the trapping process in acidic systems, it is notable that some of w-BP is converted into f-BP as desiccation of the gels proceeds, and that no peaks due to a-BP are observed in xerogels (see Fig. 8). This indicates that acidic xerogels are capable of more efficient isolation of BP molecules than neutral xerogels. The efficient isolation of BP molecules in acidic xerogels is considered to be due to their branched compact structure.[10] Under acid catalyzed conditions, primarily linear or randomly branched polymers are formed, which entangle and form additional branches, resulting in gelation.[12] Under basic and neutral conditions, particle-like species are formed.[12] These colloidal particles coalesce to gel. Therefore, acidic xerogels result in the formation of a more branched compact structure compared with basic and neutral xerogels.

Conclusions

The results obtained during the present investigation can be summarized as follows:

(a) Under neutral sol–gel conditions, the majority of f-BP and a considerable amount of w-BP transform into a-BP at high concentrations ($\geq 1\times10^{-2}$ mol dm^{-3}) as EtOH and MeOH evaporate. As the silica structure collapses by desiccation and shrinkage, a-BP molecules are broken into smaller aggregations by repulsive forces. At low concentrations ($\leq 5\times10^{-3}$ mol dm^{-3}), the majority of f-BP are converted to w-BP and no aggregations are formed.

(b) For acidic xerogels prepared at 5×10^{-2} mol dm^{-3}, w-BP and f-BP formed from w-BP are the phosphorescent species. Below 1×10^{-2} mol dm^{-3}, w-BP is the main phosphorescent species, as in the neutral xerogels.

(c) From (a) and (b) we conclude that acidic xerogels are capable of more efficient isolation of benzophenone molecules than neutral xerogels. The efficient isolation of the benzophenone molecules in acidic xerogels is attributed to their branched compact structure.

(d) From the phosphorescence lifetimes of w-BP, we conclude that some of the w-BP trapped in xerogels becomes an adsorbed complex on the silica-gel surface via hydrogen-bonding with silanol groups as the sol–gel reaction proceeds.

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