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Molecular Probing for the Microenvironment of Photonics Materials Prepared by the Sol–Gel Process

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The absorption and fluorescence spectra of the solvatochromic dye 9-diethylamino-5*H*-benzo[*a*]phenoxazin-5-one (Nile Red) were studied in modified SiO_2 gels prepared from tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), triethoxysilane (HTES), and triethoxymethylsilane (MTES). Nile Red showed a remarkable spectral shift during the sol–gel process, the direction and extent of which depended on the gel properties. E_T^N, empirical parameters of the solvent polarity, were determined based on the spectral shifts. As the precursors for the xerogels changed, E_T^N of the xerogels decreased in the order TEOS≈TMOS > MTES > HTES. E_T^N of the xerogels were 0.88—0.99 for TMOS and TEOS; this result showed the polarity of the xerogels form TMOS and TEOS to be almost the same as that of water (1.000). On the contrary, the polarity of the xerogels from HTES and MTES were as hydrophobic as haloalkane (0.1—0.3).

In recent years, sol–gel-derived matrices doped with organic dyes have received increased interest in connection with preparing photonic materials with new applications, viz., photochemical hole burning,[1—4] lasing,[5—8] photochromism,[9] nonlinear optics,[10] optical switches,[11] and the likes.[12—14] Although these materials are promising, it is necessary to understand the interaction between dyes and matrices to design desirable photonic materials and to achieve good optical performance. The optical properties of dyes, such as the absorption and emission wavelengths, lifetime and yields of emission, are often dependent on the particular solvent used. It is thus important to characterize the "solvent properties" of sol–gel matrices.

One of the most convenient and useful methods to study the optical properties of sol–gel systems is fluorescence probes. For example, sol–gel matrices have been examined by using solvent-sensitive pyrene fluorescence as a probe.[15—20] It has been shown that the "solvent polarity" of sol–gel matrices can be explained by using the dielectric constants (ε) as a polarity parameter: ε of tetraethoxysilane (TEOS)-derived xerogel≈67; ε of triethoxymethylsilane (MTES)-derived xerogel≈18; and ε of triethoxysilane (HTES)-derived xerogel≈13.[18,19]

Actual solute/solvent interactions, however, cannot always be described quantitatively by simple physical parameters, such as the dielectric constants and dipole moments. Therefore, many empirical parameters of solvent polarity have been proposed, such as the Z scale, π^* scale, and E_T (30) scale.[21] E_T (30) defined as Eq. 1 is one of the frequently used scales. The solvent polarity is evaluated from the spectral shift of pyridinium phenolate betaine dye in a solvent,

$$E_T\,(30)/\mathrm{kcal\,mol^{-1}} = 28591/\lambda_{\max}(\mathrm{nm}), \tag{1}$$

where $\lambda_{\max}$ is the wavelength of the longest absorption band of the betaine dye in the solvent. Furthermore, the so-called normalized E_T^N have been introduced as dimensionless figures,

$$E_T^N = \frac{E_T\,(30)\text{ of solvent} - E_T\,(30)\text{ of TMS}}{E_T\,(30)\text{ of water} - E_T\,(30)\text{ of TMS}}, \tag{2}$$

The E_T^N values range from 0.000 for tetramethylsilane (TMS), the least-polar solvent, to 1.000 for water, the most-polar solvent.[21] We consider E_T^N to be a more suitable parameter than E_T (30), itself, for the intuitive and semiquantitative measure of complex systems like sol–gel matrices.[22—24] 9-Diethylamino-5*H*-benzo[*a*]phenoxazin-5-one (Nile Red) (Fig. 1) is an excellent probe because it is extremely solvatochromic and highly fluorescent.[25—27] In this study we used the absorption and fluorescence of Nile Red to investigate the molecular-level structures of sol–gel systems of tetramethoxysilane (TMOS), TEOS, MTES, and HTES. The "solvent properties" of these xerogel cages are discussed based on E_T^N estimated from the spectra of Nile Red.

Experimental

Chemicals. Nile Red (Aldrich) was used as-received. $Si(OCH_3)_4$ (TMOS), $Si(OC_2H_5)_4$ (TEOS), $HSi(OC_2H_5)_3$ (HTES), and $CH_3Si(OC_2H_5)_3$ (MTES) purchased from Tokyo Kasei were used without additional purification. All of solvents used were of spectroscopic grade. Water was deionized and distilled.

Sample Preparation. The compositions of the sol–gel solutions are shown in Table 1. In a 150-mL polystyrene beaker,

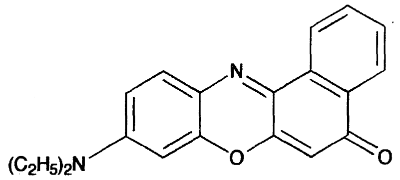

Fig. 1. Molecular structure of Nile Red.

Table 1. Estimates of Solvent Polarity Parameter E_T^N Values for Sols and Xerogels from Absorption and Fluorescence λ_{max} of Nile Red in Sols and Xerogels

No.	Alkoxysilane	Catalyst	$\lambda_{max}^{abs.}$/nm	E_T^N	$\lambda_{max}^{flu.}$/nm	E_T^N	ε
Sol (just prepared)							
1[a]	TMOS	HCl	566	0.77	634	0.78	
2[b]	TMOS	—	552	0.68	630	0.72	
3[c]	TMOS	NaOH	553	0.70	630	0.72	
4[d]	TEOS	HCl	563	0.78	634	0.79	36[i], 42[j]
5[e]	HTES	HCl	555	0.71	630	0.72	36[k]
6[f]	MTES	HCl	557	0.72	630	0.72	
Xerogel (after 2 months)							
1[a]	TMOS	HCl	595, (638)[g]	0.97	657	0.96	
2[b]	TMOS	—	592	0.96	657	0.96	
3[c]	TMOS	NaOH	588	0.93	647	0.91	
4[d]	TEOS	HCl	594, (637)[g]	0.97	665	0.99	67[i], 84[j]
5[e]	HTES	HCl	—[h]	—	578	0.13	13[k]
6[f]	MTES	HCl	540	0.40	604	0.27	18[k]
Xerogel (after 1 year)							
1[a]	TMOS	HCl	596, (634)[g]	0.99	652	0.94	
2[b]	TMOS	—	593	0.96	648	0.92	
3[c]	TMOS	NaOH	585	0.92	643	0.88	
4[d]	TEOS	HCl	594, (637)[g]	0.97	652	0.94	
5[e]	HTES	HCl	—[h]	—	583	0.15	
6[f]	MTES	HCl	—[h]	—	599	0.24	

Alkoxysilane : Water : Ethanol : Catalyst (molar ratio): a) $1:4.1:2.5:3\times10^{-3}$; b) $1:4.1:2.5:0$; c) $1:4.1:2.5:3\times10^{-2}$; d) $1:6.1:3.8:4.5\times10^{-3}$; e) $1:6.6:1.4:3.7\times10^{-3}$; f) $1:5.5:5.3:5.5\times10^{-5}$; g) Absorption peak due to the protonated form of Nile Red. See Ref. 25. h) We could not obtain suitable xerogels for absorption measurement due to cracks in xerogels. i) Estimated from the intensity ratio of the vibronic bands of pyrene fluorescence. Taken from Ref. 18. j) Estimated from the fluorescence shift of 3-pyrenecarbaldehyde. Taken from Ref. 18. k) Estimated from the intensity ratio of the vibronic bands of pyrene fluorescence. Taken from Ref. 19.

10.0 mL of alkoxysilane, ethanol containing Nile Red (2×10^{-5} mol dm^{-3}) and water were mixed at room temperature. In order to fix the Nile Red concentration, we had measured the fluorescence spectra for TMOS sols and xerogels containing Nile Red from 10^{-4} to 10^{-7} mol dm^{-3} in ethanol and confirmed that the fluorescence spectra are almost the same for these concentrations. Therefore, we believe that Nile Red aggregation is less probable under the conditions employed in this experiment. The volumes of ethanol and water were set according to the compositions. HCl or NaOH was added as a catalyst. Having been stirred for 1 h, the mixtures were kept in polystyrene beakers sealed with parafilm with several pinholes, and left to gel at room temperature. For the spectral measurements and gravimetry over time, two sets of acidic samples were prepared for each TMOS and HTES. Slight aliquots were taken from the beakers for the spectral measurements.

Measurements. The absorption and fluorescence spectra were taken with JASCO Ubest-50 and FP-770 spectrophotometers at room temperature. IR spectra were taken using a spectrophotometer (Shimadzu FTIR-4100). Thermal gravimetric analyses (TGA) were performed using a Shimadzu DTS-40 TG at 1 °C min^{-1}.

Results and Discussion

The absorption spectra of Nile Red showed λ_{max} at 552 nm for starting solutions of TMOS without a catalyst, and shifted to 592 nm in the xerogels after 2 months, as shown in Figs. 2a and 2b. For MTES, the peak shifted from 557 to 540 nm from the starting solutions to the xerogels (Fig. 2c). The fluorescence λ_{max} of Nile Red also shifted from 630 to 657 nm and 630 to 604 nm during the sol–gel reactions of TMOS and MTES, as shown in Figs. 3a, 3b, and 3c. The fluorescence λ_{max} also showed peak shifts with time for HTES systems: 630 nm in a starting sol–gel solution and 578 nm in the xerogel.

The absorption and fluorescence spectra of Nile Red measured in various solvents showed remarkable peak shifts, as previously reported.[25—27] The inverted λ_{max} values of absorption and fluorescence ($1/\lambda_{max}$) of Nile Red are plotted against E_T^N of various solvents in Fig. 4. Although not ideal enough, it shows an available correlation between $1/\lambda_{max}$ of Nile Red and the E_T^N values of the solvents.

The E_T^N values for the sol–gel systems were estimated from the relationships given in Fig. 4. Table 1 indicates that the E_T^N values based on the absorption and emission closely agreed with each other. E_T^N of the sol–gel solutions were around 0.75, whatever the alkoxysilane. It shows that Nile Red is located

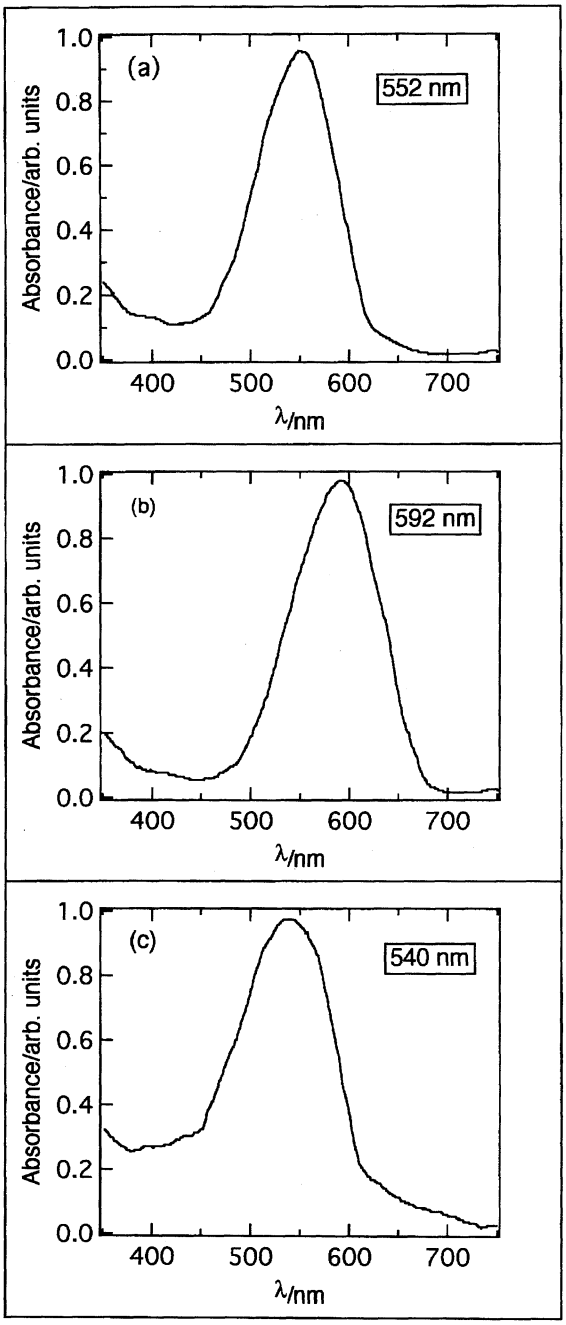

Fig. 2. Absorption spectra of Nile Red in sols (a) and xerogels (b) from TMOS and xerogels (c) from MTES.

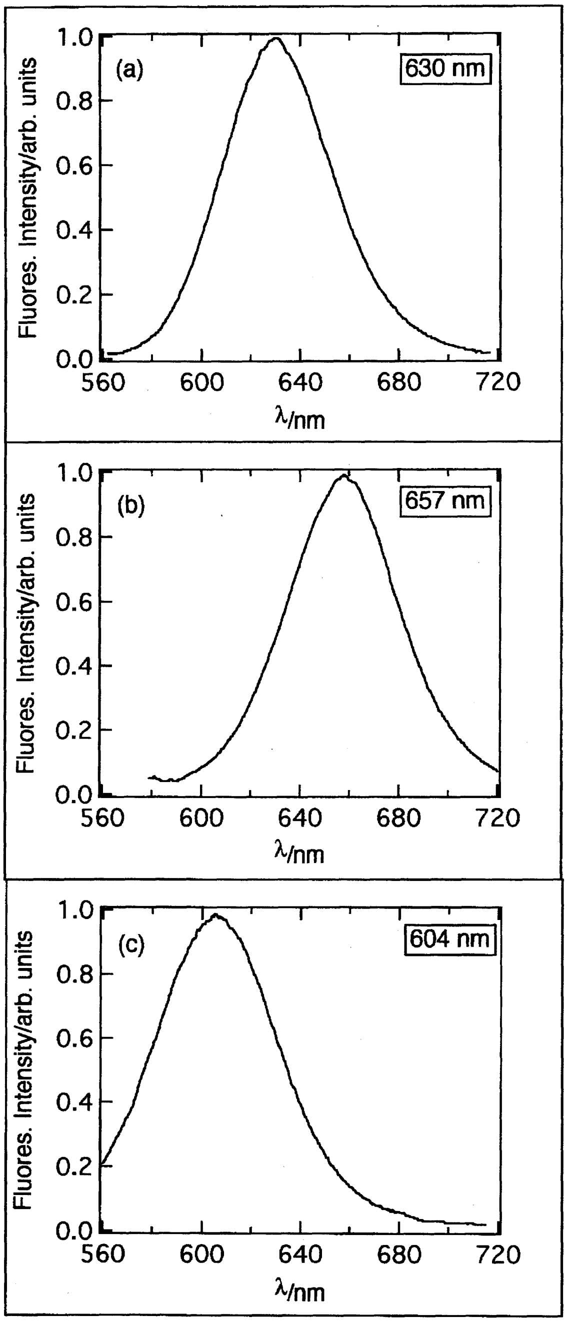

Fig. 3. Fluorescence spectra of Nile Red in sols (a) and xerogels (b) from TMOS and xerogels (c) from MTES.

in a very similar microenvironment in the starting sol–gel solutions irrespective of the precursors. The $E_{\mathrm{T}}^{\mathrm{N}}$ values were close to that of the binary ethanol–aqueous solvent ($E_{\mathrm{T}}^{\mathrm{N}}=0.765$ for the mole fraction of ethanol=0.223) and somewhat exceeded that of ethanol (0.654). The environmental polarity of sols would appear to be mainly determined by the solvent and water.[18,19)]

The microenvironment, however, changes according to the precursors during the sol–gel reactions. $E_{\mathrm{T}}^{\mathrm{N}}$ of TMOS and TEOS xerogels after 2 months were 0.91—0.99, these xerogels being highly polar. On the contrary, HTES and MTES xerogels showed smaller $E_{\mathrm{T}}^{\mathrm{N}}$ such as 0.13 and ca. 0.3, suggesting these xerogels to be hydrophobic. Especially HTES-derived xerogels are as hydrophobic as styrene (0.127) or methylnaphthalene (0.142).[21)] $E_{\mathrm{T}}^{\mathrm{N}}$ of xerogels decreases in the same manner as ε as previously noted by pyrene[18,19)]: TEOS$\approx$TMOS$>$MTES$>$HTES (Table 1). This suggests the validity of estimated $E_{\mathrm{T}}^{\mathrm{N}}$. The hydrophobicity of HTES and MTES xerogels is induced by the hydrophobic Si–H or Si–CH_3 groups.[19)] It was also reported that xerogels prepared from triethoxyethylsilane have apolar surfaces because of Si–CH_2CH_3 groups.[8)] Although the polarity may decrease by increasing the chain length of the alkyl substituent,[20)] it is still uncertain why HTES xerogels are somewhat more

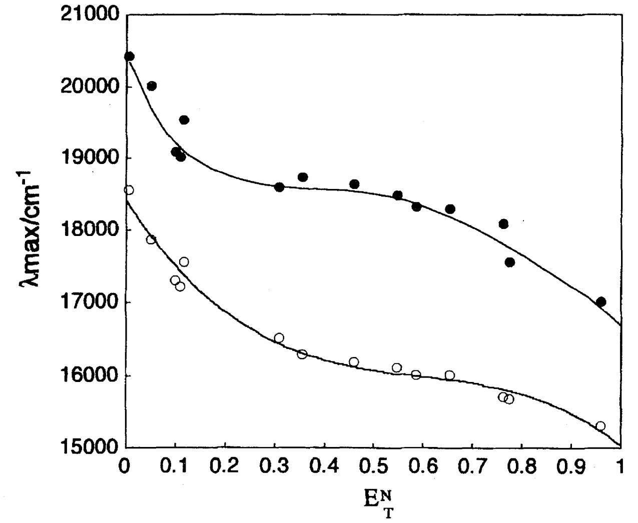

Fig. 4. Correlations of $1/\lambda_{\max}$ of absorption (●) and fluorescence (○) for Nile Red with E_T^N in various solvents: cyclohexane, tetrachloromethane, toluene, benzene, diethyl ether, dichloromethane, acetone, acetonitrile, 2-propanol, 1-butanol, ethanol, methanol, formamide, water/ethanol 9 : 1 (v/v) (left to right in the figure).

hydrophobic than MTES xerogels with respect to the ε and E_T^N polarity scales.

In order to investigate the spectral changes during the sol–gel process, the fluorescence spectra of Nile Red and the relative weight of the sol–gel systems for TMOS and HTES were measured in a time sequence during the sol–gel-xerogel stages. The samples were kept at room temperature in polystyrene beakers sealed with parafilm with several pinholes. Figure 5 shows the changes in the fluorescence $\lambda_{\max}$ as well as the relative weight for TMOS (a) and HTES (b). We can see that the remarkable red shift of the fluorescence for TMOS and blue shift for HTES occur simultaneously along with a decrease in the weight of the sol–gel systems, and that the fluorescence shows a small shift, since the weight has a barely noticeable decline. It is accepted that the initial weight loss of sol–gel systems is induced by a volatile component, such as methanol or ethanol.[28] These results indicate that the evaporation of the ethanol solvent and ethanol produced from TEOS and HTES or methanol form TMOS by hydrolysis leaves Nile Red in the gel matrices, in which Nile Red shows the characteristic fluorescence for the starting alkoxysilane.

The E_T^N values of the xerogels changed little after 1 year (Table 1), indicating that the xerogels almost attained equilibrium after 2 months, and became stable for 1 year. Xerogels from TMOS, MTES and HTES aged for 1 year were examined by IR spectroscopy and TGA. There was a peak at around 1639 cm^{-1} due to the adsorbed water molecules on silanol groups for the TMOS xerogels, but no definite peak of adsorbed water or silanol for the MTES and HTES xerogels, as previously found.[19] Upon heating over the range 25—200 °C, the xerogels experienced a weight loss, which was most likely associated with the desorption of water. The weight losses were 15.4, 1.7, and 1.6% for TMOS, MTES, and HTES. These results suggest that the polar nature of the xerogels is correlated with the adsorbed water. The terminal groups play an important role for anchoring water molecules which determine the environmental polarity of xerogels; Si–OH (TEOS, TMOS); Si–CH_3 (MTES); Si–H (HTES).

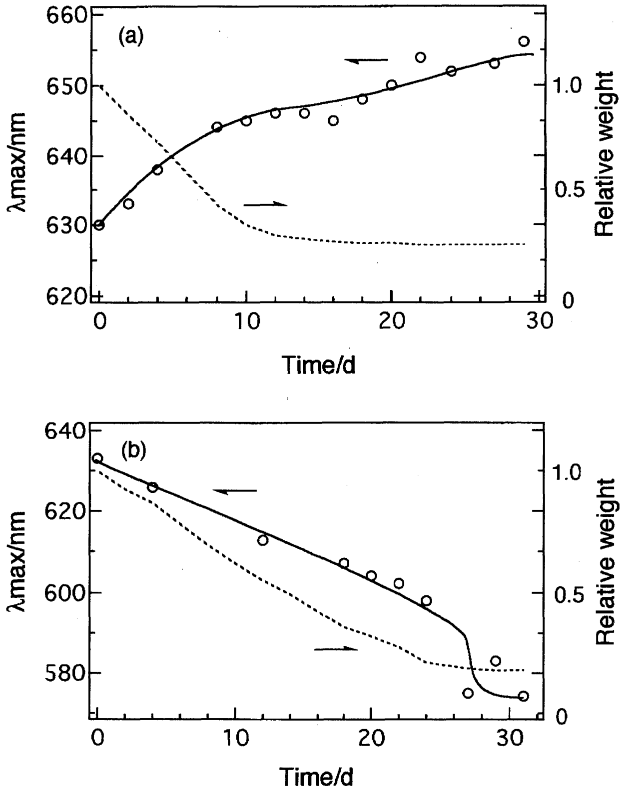

Fig. 5. Changes in fluorescence $\lambda_{\max}$ of Nile Red (—) and relative weight of the sol–gel systems (····) over time for TMOS (a) and HTES (b).

The fluorescence spectra were measured for the 1-year-aged xerogels from TMOS and HTES after heating at 350 °C under 1 Pa in order to clarify the effect of adsorbed water. The fluorescence peak shifted from 652 to 629 nm and 583 to 568 nm for TMOS and HTES, respectively, after heating for over 4 h. E_T^N changed from 0.94 to 0.70 for the TMOS-derived xerogels and 0.15 to 0.08 for the HTES-derived xerogels. These results indicate that dehydration manifests the quasi-intrinsic properties of the xerogels composed of Si–O–Si networks and Si–OH groups from TMOS or Si–O–Si networks and Si–H groups from HTES.

As for the gel structures, the formation of hydrophobic domains, like micelles comprising Si–H or Si–CH_3 groups, is anticipated. Nile Reds may be selectively dissolved in such hydrophobic domains, which induce fluorescence shifts. However, the polarity of xerogels obtained from I_3/I_1 of the pyrene fluorescence changed almost linearly, not critically, in mixed sol–gel systems of HTES/TEOS or MTES/TEOS.[19] Therefore, we believe that the hydrophobic domain model is improbable.

In conclusion, the absorption and fluorescence spectra of Nile Red are shown to be good probes for examining the microenvironmental properties of xerogels from the viewpoint of a molecular scale. The E_T^N of xerogels derived from TMOS, TEOS, HTES, and MTES decrease in the order TEOS≈TMOS > MTES > HTES. A semiquantitative evaluation as a "solvent" will be useful for developing the photonics materials presented here. This probing method can also be applied for studying the surface and interface properties of other material systems, such as porous silicon, Langmuir–Blodgett films and so on.

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