

## Excited-state Intramolecular Proton Transfer of 1,5- and 1,8-Dihydroxyanthraquinones Chemically Adsorbed onto SiO<sub>2</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> Matrices

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In order to investigate the excited-state intramolecular proton transfer (ESIPT) process of dihydroxyanthraquinones (DHAQ: 1,5-DHAQ and 1,8-DHAQ) in organic-inorganic hybrid matrices, transparent SiO<sub>2</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> matrices chemically bonded with DHAQ were prepared using a sol-gel technique. The absorption maxima of 1,5- and 1,8-DHAQ in SiO<sub>2</sub> matrices are observed at around 420 nm, whereas those of DHAQ in both SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> matrices are markedly shifted to longer wavelength compared with those in SiO<sub>2</sub> matrix. This indicates that DHAQ forms a chemical bond with an Al atom of Al<sub>2</sub>O<sub>3</sub>. The DHAQ in SiO<sub>2</sub> matrix shows a markedly Stokes-shifted emission which is originated from the ESIPT in DHAQ. Based on the emission lifetimes of DHAQ, the ESIPT of DHAQ was found to be strongly affected by the chemical interaction with Al atom in the Al<sub>2</sub>O<sub>3</sub>-related matrices.

**Key Words :** Excited-state intramolecular proton transfer, Organic-inorganic hybrid matrix, Dihydroxyanthraquinone

### Introduction

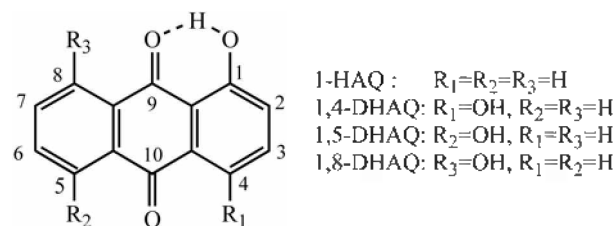
Hybrid materials have attracting a great deal of attention because they can easily combine the superior properties of the organic and inorganic compounds.<sup>1</sup> A sol-gel method has become an excellent way of obtaining transparent and mechanically stable inorganic materials such as films, bulk glasses, powders and fibres. This method also enables the preparation of organic-inorganic composite materials,<sup>2,3</sup> where metal alkoxide solutions containing functional organic molecules are used as the starting materials. The most widely used are alkoxy-silanes such as tetraethoxysilane (TEOS). Consequently, the research for the polymerization of metal alkoxide has led to the preparation of materials of optical interest such as solid laser dye blocks and films,<sup>4</sup> photochromic glasses, hole-burning materials,<sup>5</sup> light guides, and nonlinear optical materials.<sup>6</sup> Usually, most studies on organic-inorganic hybrid compounds have been performed to reveal the preparation and the properties of organic molecules in inorganic matrix.

Based on the interaction among the different compounds or phases in hybrid systems, these hybrid materials can be divided into two classes. Firstly, the hybrid materials prepared mostly by physical doping of the organic compound have demonstrated that the dopants are present as individual organic molecules in the inorganic matrix. There are weak interactions such as hydrogen bonding, van der Waals force or weak static effect. In this case, the dopant in hybrid materials retains its property in the matrix as in the solution.<sup>7,8</sup> In other words, the functionalities of dopant are also retained even in solid state, allowing the physically doped materials to be used in various applicable devices. Secondly, the organic-inorganic hybrid materials have been known to

be efficiently prepared by chemical bonding between organic guests and inorganic hosts. The covalent bonds can be helpful to the forming of the single phase. This preparation method has been regarded as one direction for the new design and improvements of properties in the hybrid materials.<sup>9,10</sup>

Dihydroxyanthraquinones (DHAQ, see Scheme 1) have been attracted a great attention as a useful dopant in the Si-Al binary oxide systems, which would improve optical properties. Actually, the optical properties of 1,4-dihydroxyanthraquinone (1,4-DHAQ) in inorganic gel systems are affected by the morphology change of matrix.<sup>9</sup> On the other hand, DHAQ have served as model systems for the chromophore of biological and pharmaceutical interest<sup>11</sup> and as the dispersed dye for coloring synthetic polymer materials.<sup>12</sup> The steady-state emission spectra of DHAQ show a characteristic dual emission.<sup>13,14</sup> DHAQ has a weak normal fluorescence together with a markedly Stokes-shifted emission which is attributed to a tautomer species formed upon the excited state intramolecular proton transfer (ESIPT).<sup>15-17</sup>

The ESIPT of the DHAQ is usually affected by a certain chemical environmental change. However, no studies have been done on the photophysical properties of DHAQ in inorganic matrices related to the ESIPT process as well as



Scheme 1

chemical bonding with matrices in spite of the possibility of covalently binding of DHAQ with the inorganic systems. In this regard, we studied about the photophysical properties of 1,4-DHAQ and 1-hydroxyanthraquinone (1-HAQ) in alumina related matrices.<sup>18</sup> The ESIPT process of 1,4-DHAQ and 1-HAQ is inhibited by the chemical interaction with Al in the alumina-related matrices such as SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. On the other hand, the photophysical behaviours of 1,5- and 1,8-DHAQ differed from significantly from 1-HAQ and 1,4-DHAQ. For example, the fluorescence quantum yields and fluorescence lifetime of 1,5- and 1,8-DHAQ are much smaller and shorter than those of 1,4-DHAQ, in spite of these molecules having the same kind of intramolecular hydrogen bonding. A difference in substitution in simple anthraquinone may generate different characteristics in the excited state, which are attributed from molecular symmetry.

In this study, we investigated the photophysical properties of 1,5- or 1,8-DHAQ doped SiO<sub>2</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> matrices, because it is expected that the chemical interaction with inorganic matrices and the structural symmetry of 1,5- and 1,8-DHAQ are different from those of 1,4-DHAQ and 1-HAQ. The photophysical properties of each system were investigated in terms of ESIPT process by using the absorption and fluorescence spectra, and fluorescence lifetimes.

### Experimental Section

Organic dopants, 1,5-DHAQ and 1,8-DHAQ, were purchased from the Aldrich Chemical Co. and further purified by several times of recrystallization in ethanol. TEOS and Al(OBu-s)<sub>3</sub> were purchased from the Aldrich Chemical Co. and used without further purification.

DHAQ-doped SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> systems were prepared by hydrolysis of TEOS and Al(OBu-s)<sub>3</sub>, respectively, and by mixing with ethanol solutions of DHAQ, H<sub>2</sub>O and HCl. The final mixed solution was kept at 30 °C for about a week to form a transparent gel matrix sample. DHAQ/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> matrix system was synthesized by two-step hydrolysis process of TEOS and Al(OBu-s)<sub>3</sub>, since the rate of hydrolysis for both alkoxides are different. Mixtures of TEOS, H<sub>2</sub>O and HCl in ethanol were used as the prehydrolysis solutions. After holding the prehydrolysis solution at 40 °C for 24 h, Al(OBu-s)<sub>3</sub> dissolved in ethanol stock solution of DHAQ and HCl was added to the prehydrolysis solution. Compositions of the starting materials of Al/Si binary oxides are listed in Table 1.

**Table 1.** Compositions of the starting materials of the Al/Si binary oxides (molar ratio)

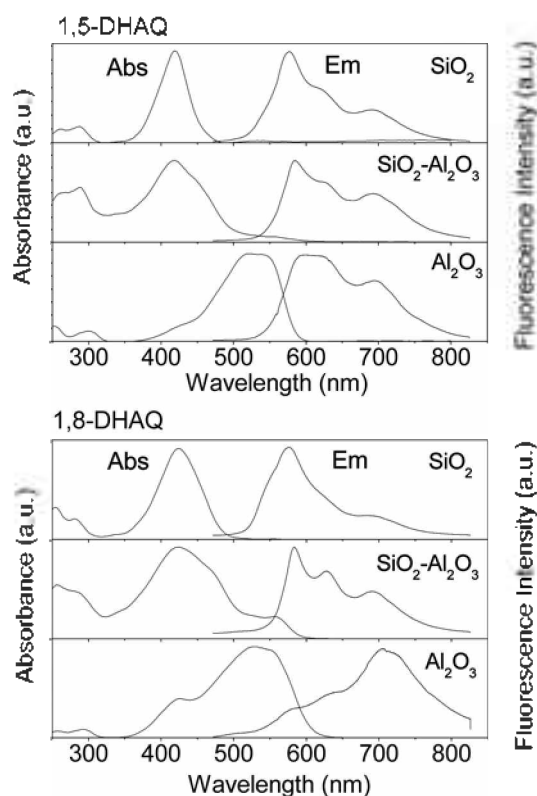
samples	TEOS	Ethanol	H <sub>2</sub> O	HCl	Al(OBu-s) <sub>3</sub>	DHAQ
<b>A</b>	1	8	2	10 <sup>-4</sup>	0	10 <sup>-5</sup>
<b>B</b>	1	8	2	10 <sup>-4</sup>	2 × 10 <sup>-3</sup>	10 <sup>-5</sup>
<b>C</b>	1	8	2	10 <sup>-4</sup>	4 × 10 <sup>-3</sup>	10 <sup>-5</sup>
<b>D</b>	1	8	2	10 <sup>-4</sup>	6 × 10 <sup>-3</sup>	10 <sup>-5</sup>
<b>E</b>	0	8	2	10 <sup>-4</sup>	1	10 <sup>-5</sup>

Diffuse reflectance absorption spectra were recorded by using a Shimadzu UV-3101PC spectrophotometer equipped with an integrating sphere. Absorption spectra of ground state are evaluated by the Kubelka-Munk function. The measurement of fluorescence spectra were performed with a CCD detector (Princeton Instruments, Inc.; SpectraMax RTEA/CCD-128-H), a monochromator (Acton Research Corporation; SpectraPro-300i) and a He/Cd laser (Omni-chrome; Series 74) to excite the samples.

Temporal profiles of the fluorescence decays were measured by using time-correlated single photon counting method (TCSPC). The excitation source is a self mode-locked femtosecond Ti:sapphire laser (Coherent) pumped by an Nd:YVO<sub>4</sub> laser. Laser output can span the excitation wavelength in the range of 350–490 nm by second-harmonic generation. All the standard electronics for the TCSPC were from the Edinburgh Instruments. The instrumental response function was measured by detecting the scattered laser pulse with quartz crystal. The resultant FWHM is 60 ps. This method allows a time resolution of about 30 ps after deconvolution.

### Results and Discussion

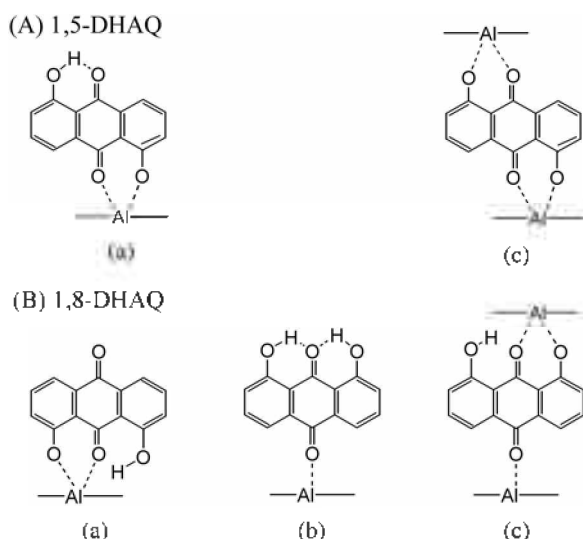
**Absorption spectra.** The diffuse reflectance absorption spectra of 1,5- and 1,8-DHAQ in various inorganic matrices are shown in Figure 1. The spectroscopic properties are summarized in Table 2. The absorption spectra of 1,5-



**Figure 1.** Absorption and fluorescence spectra of 1,5-DHAQ (upper) and 1,8-DHAQ (bottom) in SiO<sub>2</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (sample C in Table 1) and Al<sub>2</sub>O<sub>3</sub> matrices, respectively.

**Table 2.** Absorption and fluorescence maxima (nm) of each system

	in nonpolar		SiO <sub>2</sub> (A)		Al <sub>2</sub> O <sub>3</sub> (E)		SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (C)	
	abs	flu	abs	flu	abs	flu	Abs	flu
1,5-DHAQ	414 <sup>a</sup>	nd	418	577	528	596	418	585
1,8-DHAQ	433	522	424	576	528	704	424	584

<sup>a</sup>from ref 22.**Figure 2.** Structures of DHAQ in various inorganic matrices.

DHAQ/SiO<sub>2</sub> and 1,8-DHAQ/SiO<sub>2</sub> systems look similar to those in toluene solution, showing the absorption maxima around 420 nm.<sup>19</sup> This implies that the photophysical properties of organic molecule are retained without special interaction in the SiO<sub>2</sub> matrix. However, the absorption maxima of DHAQ/Al<sub>2</sub>O<sub>3</sub> systems were markedly red-shifted by ~100 nm from those of SiO<sub>2</sub> matrix, indicating an influence by Al atom on the Al<sub>2</sub>O<sub>3</sub> matrices. Bräuchle *et al.*<sup>20,21</sup> and Cho *et al.*<sup>18</sup> have proposed the chemical bonding model for the 1,4-DHAQ/Al<sub>2</sub>O<sub>3</sub> and 1-HAQ/Al<sub>2</sub>O<sub>3</sub> systems, *i.e.* one proton of 1,4-DHAQ or 1-HAQ forming an intramolecular hydrogen bond was replaced by an Al atom. Actually, the DHAQ were not observed from crushed DHAQ-doped Al<sub>2</sub>O<sub>3</sub> kept in nonpolar solution such as CHCl<sub>3</sub> or toluene. This indicates that 1,5- and 1,8-DHAQ in these systems formed a chemical bond with one or two Al atoms in the surface of the Al<sub>2</sub>O<sub>3</sub> matrices as shown in Figure 2.

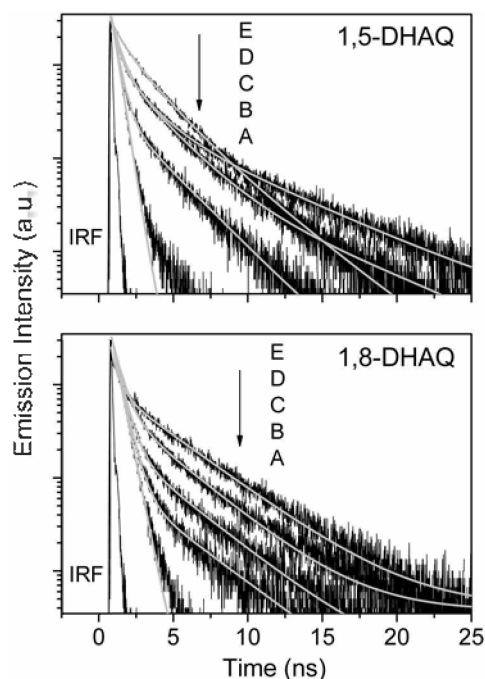
1,5- and 1,8-DHAQ have the symmetric elements of an inversion center and a reflection plane, respectively, and both DHAQ have two binding sites. Therefore, the binding patterns between C9=O or C10=O with Al atom are not distinguishable as depicted in Figure 2. In the case of 1,8-DHAQ, the electronic structure can be changed according to whether C9=O or C10=O bonded with Al atom. Now, it is hard to determine the binding sites from the absorption spectra.

The chemical ligation keeps the closed configuration of DHAQs so that the delocalized electron distribution is more available to be energetically stabilized to exhibit the red-shift of the absorption band. Further, the shift of absorption band

on substituted anthraquinones was dependent on the electron donation power of the substituent. The magnitude of energy-shift of DHAQ adsorbed and/or bonded on oxides is affected by microscopic optical basicity, which represents the electron donating ability of oxy-groups in the molecules. It is believed that the electron donating character of matrix is also responsible for the red-shifts in the absorption spectra. Actually, the absorption bands of 1,5-DHAQ and 1,8-DHAQ in Al<sub>2</sub>O<sub>3</sub> matrices are red-shifted to around 530 nm.

The absorption band of 1,5- and 1,8-DHAQ/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems exhibit broadening and red-shifting band compared with their DHAQ/SiO<sub>2</sub> system. The absorption band at around 420 nm decreases and a new absorption appears around 530 nm with an increase in concentration of Al<sub>2</sub>O<sub>3</sub>. Thus, the spectra at each [Al]/[DHAQ] ratio were expressed by the mixture of each spectrum for DHAQ/SiO<sub>2</sub> and DHAQ/Al<sub>2</sub>O<sub>3</sub> systems. This result also indicates that DHAQ in SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> system form the chemical bonding with Al atom. Otherwise, there is no evidence on chemical bonding with Si atom in SiO<sub>2</sub> matrix, and it seems that 1,5- and 1,8-DHAQ doped in SiO<sub>2</sub> matrix.

**Fluorescence and fluorescence lifetimes.** *1,5-DHAQ:* The fluorescence spectra of 1,5-DHAQ doped in a SiO<sub>2</sub> matrix are consist of a broad and intense emission band around 577 nm, exhibiting a large Stokes shift (*ca.* 6500 cm<sup>-1</sup>) as shown in Figure 1. This spectral feature is similar to those in toluene solution.<sup>19</sup> The Stokes-shifted emission band (~577 nm) of SiO<sub>2</sub> matrix is attributed to the emission from an excited  *keto*-tautomer formed *via* ESIPT process.<sup>14,19</sup>

**Figure 3.** Fluorescence decay profiles of 1,5- (upper) and 1,8-DHAQ (lower) monitored at 600 nm in various inorganic matrices. Molar ratios; (Sample A) DHAQ/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 10<sup>-5</sup>/1/0, (Sample B) DHAQ/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 10<sup>-5</sup>/1/2 × 10<sup>-3</sup>, (Sample C) DHAQ/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 10<sup>-5</sup>/1/4 × 10<sup>-3</sup>, (Sample D) DHAQ/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 10<sup>-5</sup>/1/6 × 10<sup>-3</sup>, and (Sample E) DHAQ/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 10<sup>-5</sup>/0/1.

The very weak emission at short wavelength of *ca.* 500 nm is identified as a normal fluorescence from the excited *enol*-tautomers. Above spectral features imply that the photo-physical properties of molecules are retained in SiO<sub>2</sub> matrix without any special interaction. The emission spectra of 1,5-DHAQ are also markedly changed in Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> matrices.

The emission decay profiles of DHAQ are strongly dependent on the compositions of matrix as shown in Figure 3. The decay time constants are summarized in Table 3. In the case of 1,5-DHAQ/SiO<sub>2</sub> matrix (sample *A* in Table 1), the emission decay profiles observed at 600 nm are well fitted into a single exponential function as shown Figure 3 (upper). The residuals were less than 1.3 for each system. The probe wavelengths were changed to confirm the electronic state from structural band. One measured at 520 nm is mainly responsible for emission decay profiles of *enol*-tautomer. The decay profile of *enol*-tautomer in the early decay time looks like the instrumental response function of the current TCSPC system (data do not shown). This indicates that the fluorescence lifetime of *enol*-tautomer is shorter than 30 ps, which is consistent with the low fluorescence quantum yield of *enol*-tautomer. Meanwhile, the emission decay profiles measured at both 600 and 700 nm exhibit the identical decay-time constants of 0.43 ns, which were mainly originated from same electronic state, namely *keto*-tautomer emission. The energy gaps between the fine structures of *keto*-tautomer emission are *ca.* 1530 cm<sup>-1</sup>, which is attributed to aromatic ring-stretching motion. It is also noteworthy that an emissive *keto*-tautomer in SiO<sub>2</sub> matrix is formed by ESIPt process. From these results, we suggest that 1,5-DHAQ is simply doped in SiO<sub>2</sub> matrix.

On the other hand, in 1,5-DHAQ/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system (sample *B* in Table 1), the fluorescence decay profile was fitted by the biexponential function of 0.43 and 1.6 ns. In 1,5-DHAQ/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems of different compositions (*C* and *D* matrices in Table 1), the longer decay component of 1.6 ns increases as shown in Figure 3. The decay time of 0.43 ns is similar with one in SiO<sub>2</sub> matrix whereas the long decay time is similar to that observed in Al<sub>2</sub>O<sub>3</sub>. The short decay component is attributed to doped 1,5-DHAQ species in SiO<sub>2</sub>-rich region of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> matrix because the portion of free doped 1,5-DHAQ decreases with increasing the ratio of Al. The longer decay time constant of 1.6 ns is attributed to 1,5-DHAQ interact with Al atom of Al<sub>2</sub>O<sub>3</sub> in Al<sub>2</sub>O<sub>3</sub>-rich region as shown in Figure 2A(a). Furthermore, the longer decay time constant of *ca.* 3.3 ns can also be observed in 1,5-DHAQ/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (sample *C* and *D*) as well as 1,5-DHAQ/Al<sub>2</sub>O<sub>3</sub> system (sample *E*). It could be assigned that the longer decay time constant is attributed to two moieties of 1,5-DHAQ bonded with Al atom of Al<sub>2</sub>O<sub>3</sub> as shown in Figure 2A(c).

In 1,5-DHAQ/Al<sub>2</sub>O<sub>3</sub> system, the decay profile shows three components of 0.51, 1.6 and 3.3 ns. Based on the results of 1,5-DHAQ/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems, the former one of 0.51 ns can be easily assigned as doped species. The 1.6 and 3.3 ns decay components could be originated from 1,5-DHAQ

**Table 3.** Fluorescence lifetimes (ns) and its amplitudes of each system monitored at 600 nm

samples	1,5-DHAQ	1,8-DHAQ
<b>A</b>	0.43 (100)	0.54 (100)
<b>B</b>	0.43 (97), 1.6 (3)	0.56 (99), 3.7 (1)
<b>C</b>	0.48 (88), 1.6 (7), 3.3 (5)	0.57 (98), 3.4 (2)
<b>D</b>	0.48 (81), 1.4 (13), 3.4 (6)	0.59 (94), 3.3 (6)
<b>E</b>	0.51 (50), 1.6 (33), 3.3 (17)	0.53 (82), 3.7 (18)

bonded with one and two Al atoms, respectively, in Al<sub>2</sub>O<sub>3</sub> matrices.

**1,8-DHAQ:** The fluorescence spectra of 1,8-DHAQ doped in SiO<sub>2</sub> matrix consists with a broad and intense emission band at 571 nm, exhibiting a large Stokes shift (*ca.* 6300 cm<sup>-1</sup>) as shown in Figure 1. This fluorescence spectral feature looks similar to that in solution. However, the emission band of 1,8-DHAQ in Al<sub>2</sub>O<sub>3</sub> matrix is red-shifted compared with SiO<sub>2</sub> matrix, and a new emission band around 700 nm is enhanced. The energy gap between the fine structures of these emission bands is *ca.* 1600 cm<sup>-1</sup>. Furthermore, the emission lifetimes are identical values when monitored at 600 and 700 nm as the maxima position of fine structures. Thus, these emission bands are assigned to vibrational structure at same excited electronic state, indicating the vibrational structures is attributed to the anthraquinone ring stretching modes. The enhancement of emission around 700 nm indicates that the distribution of DHAQ in matrix could be orientated to inhibit the relaxation through the ring stretching vibration. It is inferred that the vibrational energy loss is reduced dominantly if the number of Al-ligation site of the chromophore is increased in the binary matrix.

The fluorescence decay trends of 1,8-DHAQ system is shown in Figure 3. The fluorescence lifetime in 1,8-DHAQ/SiO<sub>2</sub> is 0.54 ns. The fluorescence decay profile of 1,8-DHAQ/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is shown two component of time constants of *ca.* 0.57 and 3.5 ns. The shorter lifetime components are comparable to that in SiO<sub>2</sub> matrix, indicating 1,8-DHAQ is doped in SiO<sub>2</sub> matrix. Base on this result, the 1,8-DHAQ in SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> matrix is also possible to be the ESIPt process. Otherwise, the longer components can be assigned that one carbonyl group of 1,8-DHAQ interacts with Al atom in SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> matrices. However, the amplitude of longer component is very small (few %) even in Al<sub>2</sub>O<sub>3</sub> as well as various SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> matrices. This result implies that the interaction of 1,8-DHAQ with Al atom is not strong.

In Al<sub>2</sub>O<sub>3</sub> matrix, observed fluorescence decay profile is also fitted two components of 0.53 and 3.7 ns. Although the longer component in Al<sub>2</sub>O<sub>3</sub> matrix could be assigned as one carbonyl group of 1,8-DHAQ interacted with one Al atom, the amplitude is quite small even. Form these results, the binding geometry of 1,8-DHAQ with Al atom likes as the structure (a) in Figure 2B which is more appropriate rather than structure (b) or (c). 1,8-DHAQ in structure (a) acts as a chelating bidentate ligand forming with the metal. A six-membered ring is expected to be stabilized by a considerable delocalization of the  $\pi$ -electron density.<sup>23</sup>

### Conclusion

DHAQ-doped organic-inorganic  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  matrices of high optical quality have been successfully prepared by the sol-gel method. The obtained materials have been investigated by the absorption and the emission spectroscopic techniques. The observed results indicate that DHAQ displays a red-shift of the absorption maximum while DHAQ were chemisorbed to Al atom on matrices. The time-resolved emission spectra have been recorded. The photophysical properties including ESIPT process of DHAQ are strongly affected to the interaction with Al atom of matrices. Based on the chelates of DHAQ, many photoluminescent materials can be prepared for the use of materials of optical interest.

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