Solvent Effects on Spectral Property and Dipole Moment of the Lowest Excited State of Coumarin 343 Dye

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Steady-state absorption and fluorescence spectra, and time-resolved fluorescence spectra of coumarin 343 (C343) were measured in different solvents. The effect of the solvent on the spectral properties and dipole moment of the lowest excited state of C343 were investigated. It was found that the absorption and fluorescence spectra red-shifted slightly and strongly with increasing solvent polarity, respectively, because the charge distribution of the excited state leaded to the increasing difference between the absorption and fluorescence spectra with increasing solvent polarity. The dipole moment of the lowest excited state of C343 was determined from solvatochromic measurements and the quantum chemical calculation, and the results obtained from these two methods were fully consistent. Investigations of the time-resolved fluorescence of C343 in different solvents indicated that the fluorescence lifetimes increased nearly linearly with increasing solvent polarity from 3.09 ns in toluene to 4.45 ns in water. This can be ascribed to the intermolecular hydrogen bonding interactions between C343 and hydrogen donating solvents.

Key words: Time-resolved fluorescence, Dipole moment, Solvent polarity function, Quantum chemical calculation, Intermolecular hydrogen bonding interaction

I. INTRODUCTION

The effects of molecular structure and configuration, intermolecular hydrogen bonds, and solvent environment on emissive organic compounds play many significant roles in the photophysical processes and photochemical reactions. In dye sensitized solar cells (DSSC) system the dye molecules are distributed in analogous solvent environment that consists of TiO\textsubscript{2} nanoparticles and water/methanol [1, 2]. In this system, many important properties, including the structure of the excited-state dye molecule, changes in reorganization energy and electronic coupling strength, different initial vibrational wave packets and intermolecular hydrogen bonding dynamics in the electronically excited state, can significantly influence the ultrafast electron transfer from the excited electronic state of the dye molecule to a semiconducting surface [3, 4]. Interfacial electron transfer in coumarin 343 (C343) sensitized TiO\textsubscript{2} nanoparticles with femtosecond stimulated Raman carried out by Frontiera \textit{et al.} indicated that the electron transfer pathway was mediated substantially by the vibrational modes, such as C=C, C−C, and C−N stretching modes, in the excited dye state [5]. It has been demonstrated that the protic solvents like water can form the intermolecular hydrogen bonds (C=O···H−O) with the coumarin chromophore [6−21]. Therefore, the excited state intermolecular hydrogen bonding dynamics which formed between hydrogen donor and acceptor molecules have been widely investigated through the experimental and theoretical methods [6−21]. These investigations indicate that the excited state intermolecular hydrogen bonding dynamics play a significant role in the fundamental photophysical processes and photochemical reactions, such as internal conversion, intersystem crossing, excited-state proton or hydrogen transfer, fluorescence quenching or enhancement and intramolecular charge transfer, and so on [4]. To best understand the effects of the molecular structure and configuration, intermolecular hydrogen bonding dynamics and solvent environment on electronic spectra, C343 is selected in this work because of its well characterized physical and chemical properties [22].

C343 is a crucial laser dye [23] and sensitizer with a charge transfer type excited single state, and is used in very extensive range of applications such as local friction in solution [24] and DSSC [4, 25, 26]. C343 has significant radiative rate, fairly rigid molecular struct-
tire, and significant solvatochromism [27]. It has been found that the fluorescence spectra of C343 are sensitive to solvent polarity [28]. The significant increase in the dipole moment going from the ground to the excited state leads to the strong solvatochromism for C343, and the red-shift in fluorescence is correlated linearly to the solvent polarity [27, 29]. It has been demonstrated by Han and co-workers that the intermolecular hydrogen bonding interactions have significant influence on the fluorescent states of the coumarin chromophore in hydrogen bonding solvents, and the strengthened hydrogen bonding leads to red-shift of hydrogen-bonding related vibrational spectra and photoinduced electron transfer [4, 6–8]. Therefore, they successfully proposed a new fluorescence modulation mechanism related to hydrogen bonding to explain different fluorescence lifetime of chromophore in hydrogen-bonding and nohydrogen-bonding solvents.

In the present work, we measured the steady-state absorption and fluorescence spectra of C343 in different solvents, and the time-correlated single photon counting technique was used to investigate the fluorescence lifetimes. The results of quantum chemical calculations provide insight into the ground and excited state charge distributions and bond orders of C343 which lead to its solvatochromism. The lowest excited state dipole moment has been determined experimentally based on fluorescence shifts in different solvents, and the calculated dipole moment is in good agreement with the experimental result. It is confirmed that the fluorescence lifetime of C343 in hydrogen-bonding solvents is much longer than that in nohydrogen-bonding solvents due to the excited-state hydrogen-bonding dynamics.

II. EXPERIMENTAL AND CALCULATIONS

A. Materials

C343 was purchased from Sigma-Aldrich Chemical Co. and was used without further purification. The molecular structure is shown in Fig.1. The solvents used in this study were of spectroscopic quality. The solvent parameters are listed in Table I [30]. The solutions for steady-state absorption, fluorescence, and time-resolved fluorescence spectra were diluted to the concentration of 0.1 µmol/L.

B. Apparatus and methods

A brief description of the experimental methods is given here, the details have been described previously [31]. The absorption spectra at room temperature were measured with the UV-visible spectrophotometer. The fluorescence spectrum was recorded with the spectroscopy meter (Chromex 500IS/SM, BRUKER) and CCD (DU440, Andor) on excitation at 400 nm by a femtosecond laser. Fluorescence lifetimes were carried out using the time-correlated single photon counting (TCSPC) system with excitation wavelength of 375 nm. The instrument response function (IRF) of the system was about 60 ps.

C. Calculations

All the quantum chemical calculations were carried out with Gaussian 03, Revision E.01 suite of programs [32]. The ground state investigations of C343 were calculated by density functional theory (DFT) B3LYP method and 6-311G(d,p) basis set. The excited states properties were calculated by B3LYP/6-311G(d,p) with single configuration interaction (CIS).

The dipole moment of the excited state can be measured experimentally on the basis of the solvent polarity dependence of the fluorescence emission maxima \( \tilde{\nu}_F \) which can be expressed as [33, 34]:

\[
\tilde{\nu}_F = -\frac{\mu_e(\mu_e - \mu_n)}{2\pi\varepsilon_0\hbar c^2} f(\varepsilon, n) + \text{const}
\]  

(1)

TABLE I Polarity, static dielectric constants, and refractive index of the solvents.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>( \varepsilon^* )</th>
<th>( \varepsilon )</th>
<th>( n_D )</th>
<th>( f(\varepsilon) )</th>
<th>( f(n) )</th>
<th>( f(\varepsilon) - f(n) )</th>
<th>( f(\varepsilon) - 0.5f(n) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.49</td>
<td>2.38</td>
<td>1.494</td>
<td>0.315</td>
<td>0.291</td>
<td>0.014</td>
<td>0.127</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.45</td>
<td>5.99</td>
<td>1.370</td>
<td>0.624</td>
<td>0.226</td>
<td>0.200</td>
<td>0.292</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>0.55</td>
<td>7.58</td>
<td>1.405</td>
<td>0.687</td>
<td>0.245</td>
<td>0.210</td>
<td>0.309</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.62</td>
<td>20.56</td>
<td>1.356</td>
<td>0.867</td>
<td>0.218</td>
<td>0.285</td>
<td>0.375</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.6</td>
<td>32.66</td>
<td>1.327</td>
<td>0.913</td>
<td>0.202</td>
<td>0.300</td>
<td>0.393</td>
</tr>
<tr>
<td>Water</td>
<td>1.09</td>
<td>78.50</td>
<td>1.333</td>
<td>0.963</td>
<td>0.206</td>
<td>0.320</td>
<td>0.405</td>
</tr>
</tbody>
</table>

FIG. 1 Optimized molecular structure of C343.
The Lowest Excited State of Coumarin 343 Dye

III. RESULTS AND DISCUSSION

The absorption and fluorescence spectra of C343 measured in various solvents are shown in Fig.2, and the dependences of their corresponding maxima and FWHM (full width at half maximum) on the solvent polarity are shown in Fig.3. It is seen from Fig.3(a) that fluorescence emission maximum \( \tilde{\nu}_F \) of C343 undergoes a large red-shift of 1055 cm\(^{-1}\) from toluene (21455 cm\(^{-1}\)) to water (20400 cm\(^{-1}\)). However, in case of the absorption spectra there is much smaller red-shift of 365 cm\(^{-1}\), from 23041 cm\(^{-1}\) in toluene to 22676 cm\(^{-1}\) in water. Hence, according to theoretical and experimental investigations of Han and co-workers [4, 6–8], the intermolecular hydrogen bond between C343 and water can be indicated by the absorption and fluorescence spectral red-shift of C343 in water by comparison with that in toluene [7]. The increased Stokes shift in polar solvents suggests that the fluorescence of C343 should be very sensitive to the intermolecular hydrogen bonding interactions. On the other hand, the frequency-polarity relationships based on charge distribution in the ground and excited states indicate that positions of the absorption and emission spectral maxima do not depend on the refractive index of the solvent. However, they are linearly correlated to dielectric constant, and the ability of solvation in the excited state is stronger than that in the ground state [35]. These properties suggest that the electrostatic interactions of the excited state and ground state with the solvent environment can substantially shift the spectral profiles [36, 37].

It is seen from Fig.3(b) that the FWHM of the absorption and emission spectra exhibit immediate correlations with the solvent polarity. The FWHM of absorption and fluorescence spectra increases with increasing solvent polarity. On the other hand, the slope of the fitted line of the fluorescence spectra is smaller than that of the absorption spectra. According to the ef-

\[ f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2} \frac{n^2 - 1}{2n^2 + 1} \]  

where \( \rho \) is the Onsager radius of C343 solute, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon \) is the dielectric constant, \( c \) is the velocity of light in vacuum, \( h \) is the Planck constant, and \( n \) is the refractive index of solvent. \( \mu_g \) and \( \mu_e \) are the dipole moments of the ground and the lowest excited states, respectively.
The line drawn on Fig. 4 is the best least squares fits: 

\[ f(\varepsilon, \eta) \]

between the emission maxima and solvent polarity.

Additional changing of the ground state potential energy surface by interactions between the polar solvents and polar carbonyl group can result in further spectral broadening [36]. Because the charge distribution of the excited state slightly depends on the ability of solvation, changes in the fluorescence FWHM with polarity reflect changes in Frank-Gordon transition factor. At the same time, intermolecular hydrogen bonding interactions between C343 and hydrogen donating solvents (methanol and water) can also lead to the varieties of the fluorescence FWHM with polarity [6].

Dipole moment of the ground state used in the Eq.(1) is \( \mu_g = 9.86 \) D for C343 [38]. The \( \tilde{\nu}_F \) of C343 in different solvents are plotted in Fig.4 as a function of the solvent polarity parameter \( f(\varepsilon, \eta) \). There is a linear correlation between the emission maxima and solvent polarity. The line drawn on Fig.4 is the best least squares fits: 

\[ \tilde{\nu}_F = 21.938 - 3.419f(\varepsilon, \eta) \times 10^3 \text{ cm}^{-1} \]

Given the slope of this plot, a value of the Onsager radius \( \rho = 4.76 \) Å [39], and \( \mu_g \) and \( \mu_e \) of the excited state for C343 can be calculated by employing Eq.(1) and the value \( \mu_e \) is 12.73 D.

In order to give further evidence for the excited state dipole moment of C343, a comparison was made between the experimental result and the quantum chemical calculation. Figure 5 shows the frontier molecular orbitals of the isolated C343. The calculated electronic excitation energy and main orbital transition contribution, and corresponding oscillator strengths of the low-lying electronically excited states are listed in Table II. From the calculated results, it is evident that the \( S_1 \) state has the largest oscillator strengths. Thus, C343 can be directly excited to the \( S_1 \) state upon photoexcitation. It is noted that the \( S_1 \) state corresponds to the orbital transition from the HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital). On the other hand, the bond length of optimized structures for ground state and excited state of C343 are listed in Table II. The calculated excited state dipole moment \( \mu_e = 14.37 \) D (−14.36, 0.15, −0.26) is in good agreement with experimental result. The calculated ground state dipole moment is \( \mu_g = 11.69 \) D (−11.69, 0.10, 0.26). The calculation indicates that C343 has a significant projection of its dipole moment along the long axis of the conjugated \( \pi \)-electron system, and charge distribution of the excited state is very different from that of the ground state. These behaviors are attributed to the intramolecular charge separation from the closed-ring amine system to the aromatic ring and carbonyl of C343, especially the significant variations of the bond orders in N−C7, C3=C4, C7=C8, C4−C10, C10−C5, C9=C10, C2=O2, and so on (Table II). These characters explain larger dipole moment of the excited state for C343 in solution upon photoexcitation. It is important to note that difference between the experimental and calculated excited-state dipole moments for C343 results from the Eq.(1) on the basis of the continuum dielectric model that treats the solute as a nonpolarizable point dipole centered in a spherical cavity of radius \( \rho \). This model only considers the dipole-dipole interactions, and neglects the specific solute-solvent interactions in high polar solvents, such as site-specific intermolecular hydrogen bonding interaction between hydrogen donor and acceptor molecules [4, 6−8, 18].

To further investigate the influence of environment on spectral properties and dipole moment of C343, the time-resolved fluorescence decay dynamics of C343 in various solvents have been measured at the excitation

![FIG. 4 The fluorescence emission maxima \( \tilde{\nu}_F \) of C343 in a series of solvents at room temperature versus solvent polarity function \( f(\varepsilon, \eta) \).](image)

![FIG. 5 Frontier molecular orbitals of the isolated C343.](image)

**TABLE II Calculated electronic excitation energy and corresponding oscillator strength \( f \), and main orbital transition contribution of the low-lying electronically excited state for the isolated C343.**

<table>
<thead>
<tr>
<th>State</th>
<th>( E/\text{nm} )</th>
<th>( f )</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_0 \rightarrow S_1 )</td>
<td>293</td>
<td>0.936</td>
<td>HOMO→LUMO</td>
</tr>
<tr>
<td>( S_0 \rightarrow S_2 )</td>
<td>233</td>
<td>0.003</td>
<td>HOMO→LUMO+1</td>
</tr>
</tbody>
</table>
TABLE III Comparison of the bond length between the optimized structures for ground state and excited state of the isolated C343 and the difference $|\Delta|$.  

| Bond type | Bond length/Å | $|\Delta|$/Å |
|-----------|--------------|------------|
| O1−C2    | 1.382        | 1.360      | 0.022 |
| C2−C3    | 1.449        | 1.441      | 0.008 |
| C3=C4    | 1.367        | 1.403      | 0.036 |
| C4−C10   | 1.415        | 1.393      | 0.022 |
| C10−C5   | 1.408        | 1.424      | 0.016 |
| C5=C6    | 1.375        | 1.358      | 0.017 |
| C6−C7    | 1.434        | 1.438      | 0.004 |
| C7=C8    | 1.419        | 1.432      | 0.013 |
| C8−C9    | 1.388        | 1.360      | 0.028 |
| C9−C10   | 1.408        | 1.433      | 0.025 |
| N−C7     | 1.378        | 1.359      | 0.019 |
| N−C11    | 1.462        | 1.454      | 0.008 |
| N−C12    | 1.462        | 1.454      | 0.008 |
| C2=O2    | 1.218        | 1.195      | 0.023 |
| C3−C13   | 1.502        | 1.481      | 0.021 |
| C13=O3   | 1.207        | 1.189      | 0.018 |
| C13−O4   | 1.338        | 1.320      | 0.018 |
| C6−C14   | 1.514        | 1.510      | 0.004 |
| C14−C15  | 1.527        | 1.521      | 0.006 |
| C15−C12  | 1.523        | 1.518      | 0.006 |
| C11−C16  | 1.523        | 1.517      | 0.006 |
| C16−C17  | 1.527        | 1.521      | 0.006 |
| C17−C8   | 1.512        | 1.512      | 0.000 |

TABLE IV Fluorescence lifetimes of C343 in different solvents.  

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\lambda$/nm</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$\tau_1$/ns</th>
<th>$\tau_2$/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>465</td>
<td>1.00</td>
<td></td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td>ETAC</td>
<td>475</td>
<td>1.00</td>
<td></td>
<td>3.45</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>481</td>
<td>0.95</td>
<td>0.05</td>
<td>3.57</td>
<td>57</td>
</tr>
<tr>
<td>Acetone</td>
<td>485</td>
<td>1.00</td>
<td></td>
<td>3.92</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>484</td>
<td>0.95</td>
<td></td>
<td>4.06</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>492</td>
<td>0.79</td>
<td>0.21</td>
<td>4.45</td>
<td>69</td>
</tr>
</tbody>
</table>

wavelength of 375 nm. Figure 6 shows three representative decay kinetic curves of the time-resolved fluorescence spectra of C343 in toluene, tetrahydrofuran (THF), and water. The fluorescence lifetimes in all the selected solvents are collected in Table IV. From these results, one can concludes that the fluorescence emission spectra of C343 exhibit single exponential decay kinetics in low polarity solvents, such as toluene, ETAC, and acetone. However, C343 in THF displays double-exponential decay kinetics with short-lived component lifetime of $\tau_2=57$ ps and pre-exponential factors of $A_2=0.05$; the decay kinetics can be treated as single-exponential function due to very small pre-exponential factors. In high polarity hydrogen donating solvents (such as water), double exponential terms were required to fit the decay kinetics. It is seen from Fig.7 that the experimental fluorescence lifetimes $\tau_1$ of the lowest excited state significantly depend on solvent polarity, and the fluorescence lifetimes increase nearly linearly with increasing solvent polarity from 3.09 ns in toluene to 4.45 ns in water. It is noticed that the fluorescence lifetimes for C343 in hydrogen-bonding solvents are much longer than those in non-hydrogen-bonding solvents. This can be ascribed to the intermolecular hydrogen
bonding interactions between C343 and hydrogen donating solvents (methanol and water) [4, 6–8, 18]. The fluorescence lifetime of C343 in water is much longer than that in methanol because the hydrogen donor ability of water is stronger than that of the methanol.

To investigate the intermolecular hydrogen bond between C343 and hydrogen-bonding solvents (water and methanol), we have theoretically studied the isolated C343 and hydrogen-bonded C343-(CH$_3$OH)$_2$ and C343-(H$_2$O)$_2$ complexes. Figure 8 presents the intermolecular hydrogen bonds of geometric structures of hydrogen-bonded C343-(CH$_3$OH)$_2$ and C343-(H$_2$O)$_2$ complexes in the ground state. At the same time, the calculated hydrogen bonding lengths and hydrogen bonding groups in different electronic states are listed in Table V. It is evidently shown that the hydrogen bonds C=O···H–O can be formed between C343 and solvents in hydrogen-donating environments for the two conformations [4, 10, 16]. The lengths of the hydrogen bonds between H and O atom are 1.939 and 2.063 Å, 2.066 and 2.089 Å for the hydrogen-bonded C343-(CH$_3$OH)$_2$ and C343-(H$_2$O)$_2$ complexes, respectively. Moreover, the hydrogen bonding energy of C=O···H–O in the C343-(H$_2$O)$_2$ complex is calculated to be 67.0 kJ/mol, which is larger than that in the C343-(CH$_3$OH)$_2$ complex (63.1 kJ/mol). This suggests that the fluorescence lifetime of C343-(H$_2$O)$_2$ complex is much longer than that of the C343-(CH$_3$OH)$_2$ complex, which is in agreement with the results in our experiments. In addition, the lengths of both the C=O and H–O bonds are increased because of the intermolecular hydrogen bonding interactions between C343 and donating solvents. For example, the bond length of $L_{C343=O3}$ is increased by 0.961 Å from 1.207 Å for the C343-(CH$_3$OH)$_2$ complex, and the $L_{H1=O5}$ is also increased to 0.968 Å from 0.961 Å in the same complex. Therefore, it is indicated that the C=O and H–O will be lengthened in stronger hydrogen-bonding solvents, which is in accordance with the conclusion of Han group [4–16]. As we know, molecular orbitals analysis is useful to understand the nature of the excited states [4, 10]. Figure 9 depicts the frontier molecular orbitals of the hydrogen-bonded C343-(CH$_3$OH)$_2$ complexes and C343-(H$_2$O)$_2$ complexes. It is evident that both the electron densities of LUMO and HOMO-1 orbitals are mainly localized over the C343 molecule for the C343-(CH$_3$OH)$_2$ complex. In addition, density of HOMO is almost completely localized in the methanol molecule. However, the electron densities of the molecular orbitals of the C343-(H$_2$O)$_2$ complex are completely opposite to those of the C343-(CH$_3$OH)$_2$ complex. From theoretical calculations (CIS) of all optimized conformations of C343-(CH$_3$OH)$_2$ complex, we can find that the state with the largest oscillator strength ($f=0.980$) of the complex corresponds to the orbital transition from HOMO to LUMO. This state may be assigned to charge-transfer (CT) state because of charge-transfer reaction between C343 and methanol [10]. The S$_2$ state corresponding to orbital transition (oscillator strength $f=0.003$) from HOMO-1 to LUMO should be the locally excited (LE) state due to the ππ*(character in the Fig.9(a) [10]. Upon photoexcitation to the S$_3$ state of the C343-(CH$_3$OH)$_2$ complex, charge redistribution occurs in C343 molecule. The transition from the LE state (S$_2$) to the CT state (S$_1$) may take place within 200 fs time scale [10, 18, 40]. Thus, it is reasonable to conclude that the fluorescence decay kinetics of the C343-(CH$_3$OH)$_2$ complex exhibits single-exponential function. On the other hand, the energy level of the CT state (S$_2$, HOMO–1→LUMO) is higher than that of the LE state (S$_1$, HOMO→LUMO) for the C343-(H$_2$O)$_2$ complex. Upon photoexcitation of the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
 & $L_{H(1,2)\cdots O(3,6)}$ & $L_{C343=O3}$ & $L_{C2=O2}$ & $L_{C13=O3}$ \tabularnewline
\hline
\hline
C343 & 0.961 & 1.207 & 1.218 & 1.214 \tabularnewline
\hline
Complexes & 1.207 & 1.189 & 1.211 & 1.939 \tabularnewline
\hline
$S_0$ & 0.944 & 2.035 & 2.066 & 2.064 \tabularnewline
\hline
$S_1$ & 0.968 & 2.035 & 2.066 & 2.153 \tabularnewline
\hline
\end{tabular}
\caption{Calculated hydrogen bonding lengths and hydrogen bonding groups in different electronic states.}
\end{table}
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IV. CONCLUSION

The effect of the solvent environment on spectral properties and dipole moment of the lowest excited state of C343 was investigated in this work. The absorption spectra red-shifted slightly with increasing solvent polarity. The fluorescence spectra red shifted linearly with the increasing of the solvent polarity function. This was ascribed to the slight solubility dependence of charge distribution of the excited state. Based on Eq. (1), the dipole moment of the lowest excited state has been estimated to be 12.73 D, which was larger than the ground state dipole moment. The quantum chemical calculation of the excited state for C343 showed that the charge antisymmetric distribution and bond order changes of the excited state relative to the ground state, and intramolecular charge separation were responsible for the larger excited state dipole. Time-resolved fluorescence spectra revealed that the fluorescence lifetimes of C343 increased nearly linearly with increasing solvent polarity. The fluorescence lifetime in hydrogen-bonding solvents was much longer than that in nonhydrogen-bonding solvents due to the intermolecular hydrogen bonding interactions between C343 and hydrogen donating solvents (methanol and water).

V. ACKNOWLEDGMENTS

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