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Fluorescence quenching phenomena facilitated by excited-state hydrogen bond strengthening for fluorenone derivatives in alcohols

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ABSTRACT

Spectroscopic studies on benzo[*b*]fluorenone (BF) solvatochromism in several aprotic and alcoholic solvents have been performed to investigate the fluorescence quenching by hydrogen bonding and proposed a weaker ability to form intermolecular hydrogen bond of BF than fluorenone (FN). In this work, the time-dependent density functional theory (TD-DFT) method was used to study the excited-state hydrogen bonding of both FN and BF in ethanol (EtOH) solvent. As a result, it is demonstrated by our theoretical calculations that the hydrogen bond of BF–EtOH complex is almost identical with that of FN–EtOH. Moreover, the fluorescence quantum yields of FN and BF in the alcoholic solvent is efficiently dependent on the energy gap between the lowest excited singlet state (fluorescent state) and ground state, which can be used to explain the fluorescence quenching by the excited-state hydrogen bond strengthening.

1. Introduction

The phenomenon of hydrogen bonding has been recognized for its importance in physics, chemistry, and biology [1–8]. Fluorenone and its derivates have become very popular molecular models to study the excited-state hydrogen bonding behaviors, because of the rather unique spectroscopic and photophysical properties that have made them the subject of many investigations [9–20]. In aprotic solvents, the deactivation of the photoexcited fluorenone is governed dominatively by the dependence of intersystem crossing (ISC) process to the triplet state on the solvent polarity [6–8]. However, in protic solvents, the triplet state yield falls and the internal conversion (IC) from the fluorescent state to ground state becomes the most important dissipative process [9–12]. Therefore, intermolecular hydrogen bonds formed between fluorenone and protic solvents play a very important role on the fluorescence quenching phenomena [9–20].

In our previous works, the relationship between the excited-state hydrogen bonding dynamics and the IC process has been qualitatively demonstrated [21–24]. We theoretically found that the intermolecular hydrogen bond $C{=}O\cdots H{-}O$ between fluorenone (FN) and alcoholic molecules can significantly be strengthened in the electronic excited-state upon photoexcitation of the hydrogen-bonded complex [21–24]. Moreover, the hydrogen bond strengthening in electronic excited-states can increase the Stokes' shift [25–28], namely, decrease the energy gap between the electronic excited and ground states. Hence, the IC process would be facilitated by the excited-state strengthened hydrogen bond. As a result, the fluorescence of FN in ethanol solvent is substantially quenched by the intermolecular hydrogen bonds compared with that in acetonitrile, an aprotic solvent of comparable polarity.

Recently, Williams and co-workers have reported the spectroscopic studies on BF solvatochromism in several aprotic and alcoholic solvents to represent exploration of photophysical differences related to the replacement of one of the phenyl groups in FN by a naphthyl group [16]. Interestingly, they found that there are significant differences in the relative effect of ethanol on the spectral properties of BF compared with FN [16–18]. For FN in ethanol, the reported relative fluorescence intensity is only one-twentieth that observed in acetonitrile of the comparable polarity [17,18]. However, the relative fluorescence intensity of BF in ethanol is nearly two-thirds that observed in acetonitrile [16]. Therefore, it is suggested that the ethanol can more efficiently quench the relative fluorescence of FN in comparison with that of BF. They believed this difference relates to the intermolecular hydrogen bonding, since the relative fluorescence intensity of BF in stronger hydrogen donor 2,2,2-trifluoroethanol (TFE) is dramatically quenched, qualitatively resembling that of FN in alcoholic solvents [16].

In this work, we are motivated to calculated FN and BF molecule and their hydrogen bonding complexes, to investigate how hydrogen bonding quenches the fluorescence as well as the relationship between the fluorescence intensity and the energy gap (between the lowest excited singlet state and ground state). Our calculation has been demonstrated to be reliable by the good agreement with

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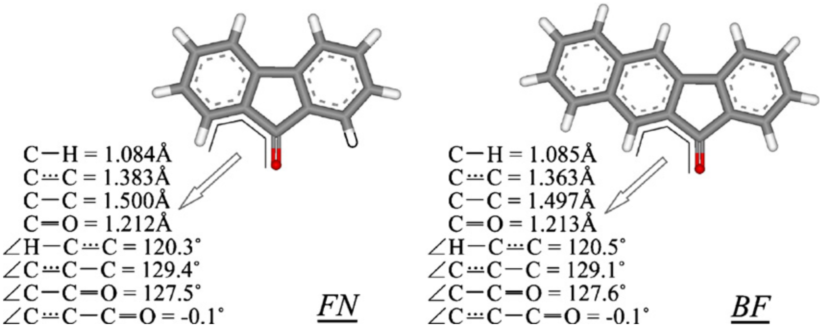

Fig. 1. The optimized geometrical structures of BF and FN in ground state, and the bond lengths (Å), bond angles (degree) and dihedral angels (degree) of the primary part of BF and FN molecule.

the steady state spectra in experiments [15,16]. The theoretical calculations show that, in both ground state and lowest excited singlet state, the hydrogen bond of BF–EtOH is almost identical with that of FN–EtOH complex. Moreover, the fluorescence quantum yield is efficiently dependent on the energy gap between the lowest excited singlet state (fluorescent state) and ground state, since IC is the dominant process to dissipate to ground state. Therefore, for FN and its derivatives in the alcohol solvents, the determined factor of fluorescence intensity is the energy gap between the fluorescent state and ground state, which can be used to explain hydrogen bond strengthening in excited-state can facilitate IC process. By introducing a benzene ring to FN molecule, the remarkable blue shift is shown in emission spectra of BF, which indicates larger energy gap than FN. This restrains IC process from fluorescent state to ground state and thus increases the fluorescent quantum yields.

2. Theoretical methods

All the electronic structure calculations were carried out using the Turbomole program suite [29–33]. The geometry optimizations of the isolated monomers and the hydrogen-bonded solute–solvent complexes considered here for the ground state were performed, using density functional theory (DFT) with Becke's three-parameter hybrid exchange function with Lee–Yang–Parr gradient-corrected correlation functional (B3-LYP functional) [30]. The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as basis sets throughout [31]. The excited-state electronic structures were calculated using time-dependent density functional theory (TD-DFT) with B3-LYP hybrid functional and the TZVP basis set. Fine quadrature grids 4 were also employed [32]. Both the convergence thresholds for the ground state and excited-state geometric optimization were reset to be 10^{-8}.

3. Results and discussion

To investigate the intermolecular hydrogen bond between BF and alcoholic solvents, the ground state conformations of hydrogen-bonded BF–alcohol complexes are fully optimized, which are shown in Fig. 1. By comparing the geometries, the whole structure of BF is almost unchanged than that of FN, except for the introduced phenyl group.

At the same time, the corresponding hydrogen-bonded complexes formed by FN and alcohols are also optimized for comparison. Fig. 2 presents the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the optimized hydrogen-bonded BF–EtOH and FN–EtOH complexes. From TD-DFT results, the S_1 state of the hydrogen-bonded complex corresponds to the orbital transition from HOMO to LUMO. The π character for the HOMO as well as the π* character for LUMO can be clearly seen from Fig. 2. It is almost the same between the BF–EtOH and FN–EtOH complexes. The results of Mulliken population analysis are shown in Table 1. It is distinct that there is more electron density distribution located around the oxygen atom in C=O group of BF/FN–EtOH hydrogen-bonded complexes after an excitation. The increased electron density suggests that the intermolecular hydrogen bond should be strengthened in the excited-state after photoexcitation.

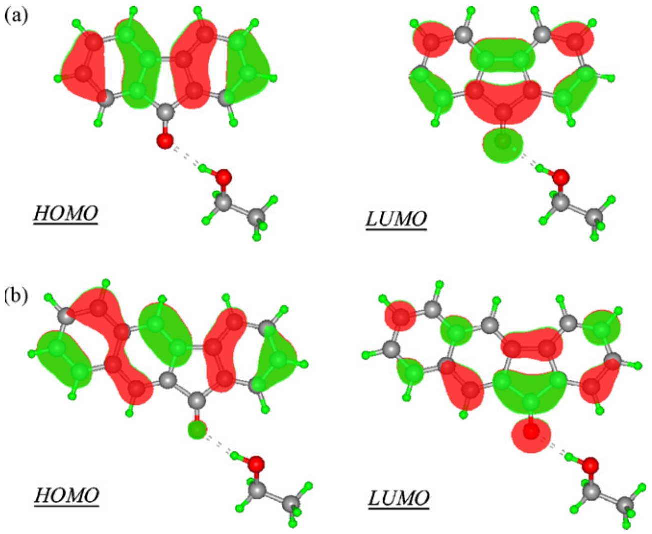

Fig. 2. Optimized geometric structures of the hydrogen-bonded BF–EtOH and FN–EtOH complexes and the frontier molecular orbitals (MOs) of the hydrogen-bonded FN–EtOH (a) and BF–EtOH (b) complexes.

The calculated and corresponding experimental absorption and fluorescence spectral results for the hydrogen-bonded BF–EtOH and FN–EtOH complexes are listed in Table 1, as well as the isolated BF and FN molecules. And the calculated absorption spectra from 200 nm to 600 nm are shown in Fig. 3. It can be clearly noted that the very strong absorption peaks for isolated BF/FN and their hydrogen-bonded complexes are at around 250–300 nm. Moreover, the relatively weak S_1 absorption bands at around 400 nm. One can see that all the calculated absorption spectral features are in good agreement with the spectral results recorded in experiments [15,16].

Table 1
The Mulliken population analysis of C=O group of isolated BF/FN and BF/FN–EtOH complexes in ground and the lowest singlet excited-state.

	BF	FN	BF–EtOH	FN–EtOH
C=O				
S_0	−0.281	−0.249	−0.320	−0.282
S_1	−0.448	−0.431	−0.435	−0.414

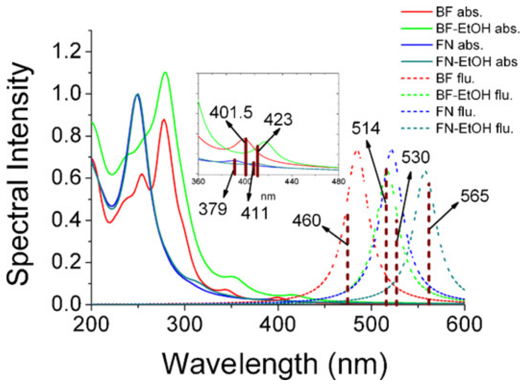

Fig. 3. Calculated absorption and fluorescence spectra of isolated BF/FN and the hydrogen-bonded BF/FN–EtOH complexes. Inset shows details of the absorption bands for the S1 state; Violet lines denote the corresponding peaks in experiments [16].

Table 2
Electronic excitation energies (nm) of the hydrogen-bonded BF/FN complexes as well as the isolated BF/FN.

	Absorption		Fluorescence	
	Calculated	Experimental[b]	Calculated	Experimental[b]
FN[a]	392	379	521	514
FN–EtOH	410	411	557	565
BF	400	401.5	484	460
BF–EtOH	417	423	517	530
BF–TFE	427	427	532(557[c])	570

[a] Ref. [22].
[b] Ref. [16].
[c] Calculated with COSMO method ($\varepsilon = 8.55$).

The calculated fluorescence spectra are also presented in Fig. 3. Moreover, the fluorescence maxima are also listed in Table 2 and compared with the corresponding experimental values. One can note that our calculated fluorescence results are accordant with experimental results [15,16]. The formation of intermolecular hydrogen bond induces the fluorescence spectra shift to red for both the FN and BF systems. However, it is noted that the fluorescence spectra of isolated BF is significantly blue-shifted by comparison with that of isolated FN. So the introduced phenyl group plays an important role on the fluorescence spectral changes for these systems. The energy gap between the fluorescent state and ground state for BF is larger than that of FN. For the hydrogen-bonded BF–EtOH complex, the fluorescence wavelength is also shorter than that of the hydrogen-bonded FN–EtOH complex. The calculated fluorescence wavelength of the hydrogen-bonded BF–TFE complex is red-shifted by comparison with that of BF–EtOH, but is much shorter than the experimental value. When the solvation effects of TFE on the BF are considered, the calculated fluorescence continues to shift to red and can be comparable to the experimental result [16].

The calculated hydrogen bond binding energies and hydrogen bond lengths of these complexes in ground state and the lowest excited singlet state are listed in Table 2. The lengths of the hydrogen bond C═O···H–O between oxygen and hydrogen atoms in BF–EtOH and FN–EtOH complexes are calculated to be 1.916 Å and 1.936 Å, and the calculated hydrogen bond binding energy is 27.72 kJ/mol and 27.07 kJ/mol in ground state, respectively. In addition, the strength of hydrogen bond of BF–EtOH is almost identical with that of FN–EtOH in ground state. As we expected, the intermolecular hydrogen bond binding energy between BF and TFE is markedly increased to 37.99 kJ/mol.

In the S_1 state, one can note that all the intermolecular hydrogen bonds of the hydrogen-bonded FN–EtOH, BF–EtOH, and BF–TFE complexes are significantly strengthened in comparison with those in ground state. At the same time, all the hydrogen bond lengths are shortened in the S_1 state. Moreover, the differences of the hydrogen bonding strength between the S_1 and S_0 states are also shown in Table 3. The order of differences of hydrogen bond strength is BF–EtOH ≈ FN–EtOH < BF–TFE. This suggests that the fluorescence quenching of fluorenone derivatives is indirectly related to the change of hydrogen bond binding energy, since the ethanol can more strongly quench the relative fluorescence of FN in comparison with that of BF.

From the information of the lowest excited singlet state in Table 3, we can evidently conclude that the intermolecular hydrogen bonds C═O···H–O of both BF–EtOH and FN–EtOH complexes are significantly strengthened since the binding energy increases after excitation to the excited-state. Therefore, the relatively weak intermolecular hydrogen bond C═O···H–O between BF/FN and ethanol in ground state becomes a strong hydrogen bond upon electronic excitation to the S_1 state. All the calculated results are similar to the case of our previous works, in which the hydrogen bond strengthening has also been demonstrated upon photoexcitation to the electronic excited-state [21–24].

Based on our calculations, the strength of hydrogen bond of BF–EtOH is almost identical with that of FN–EtOH, which is opposite to the proposal of Williams and co-workers [16]. They have suggested the hydrogen bond between BF and ethanol should be weaker than that of FN, because of the less relative fluorescence intensity compared with that in cyclohexane and acetonitrile [16]. To resolve the conflict with experimental proposal in hydrogen bond, we should discuss the mechanism of fluorescence quenching in detail.

In general, fluorenone is very weakly fluorescent in solution [9]. In protic solvents, the triplet state yield falls and the internal conversion (IC) from the fluorescent state to ground state becomes the most important dissipative process [9–12]. In this quenching process, the hydrogen bond acts as an efficient accepting mode for radiationless deactivation processes. It has been demonstrated that deactivation of excited-state via IC can be strongly enhanced by the intermolecular hydrogen bonding interactions [22].

Biczók and co-workers have demonstrated that, as the polarity of the solvent increase, fluorescence is weak, short-lived, and sharply red-shifted, the triplet yield falls, and IC becomes by far the most important dissipative process when FN and its derivatives are dissolved in alcoholic solvents [9–12]. IC rate constant is two orders larger than spontaneous emission (SE) rate constant, and one order

Table 3
Calculated hydrogen bond binding energies E_b (kJ/mol) and corresponding lengths (Å) of hydrogen bonds and dipole moments (Debye) in different electronic states.

	FN[a]	FN–EtOH			BF	BF–EtOH			BF–TFE		
	μ	$L_{O\cdots H}$	E_b	μ	μ	$L_{O\cdots H}$	E_b	μ	$L_{O\cdots H}$	E_b	μ
S_0	3.522	1.936	27.07	4.066	3.657	1.916	27.72	4.487	1.814	37.99	7.558
S_1	5.979	1.797	41.61	6.841	6.829	1.791	42.00	8.134	1.686	58.99	11.361
Δ	2.457	0.138	14.54	2.775	3.172	0.124	14.28	3.647	0.128	21.00	3.803

[a] Ref. [22].

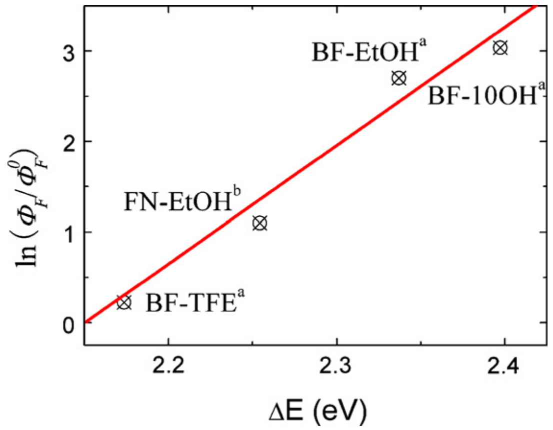

Fig. 4. Logarithm of the relative fluorescence intensity plotted as a function of the energy gap between the lowest excited singlet state and ground state ([a] using the experimental data from Ref. [16]; [b] using the experimental data from Refs. [11,12]).

larger than that of ISC [11,12]. Thus, we can neglect ISC and SE, so we get

$$\frac{\Phi_F}{\Phi_{IC}} = \frac{\Phi_F}{1-\Phi_F} = \frac{k_F}{k_{IC}} \tag{1}$$

$$\Phi_F = \frac{k_F}{k_F + k_{IC}} \approx \frac{1}{k_{IC}} \tag{2}$$

where Φ_F, Φ_{IC}, k_F and k_{IC} are the quantum yields and the rate constants of SE and IC separately. We can write the IC rate constant in quantitative form in terms of the energy gap law [34,35], like

$$k_{IC} \propto \exp\left(\frac{-\gamma \Delta E}{\hbar\omega_M}\right) \tag{3}$$

where $\hbar\omega_M$ is the energy of the characteristic accepting mode, and γ is considered a constant because it is a weakly varying function of ΔE. And this formula has been proved by the good linear correlation between logarithm of the IC rate constant and the energy gap between the first excited-state and ground state of several derivatives [9]. Using Eqs. (2) and (3), we obtain

$$\frac{\Phi_F}{\Phi_F^0} \propto \Phi_F \approx \frac{1}{k_{IC}} \propto \exp\left(\frac{\gamma \Delta E}{\hbar\omega_M}\right) = \exp(A\Delta E) \tag{4}$$

$$\ln\left(\frac{\Phi_F}{\Phi_F^0}\right) \propto A\Delta E \tag{5}$$

where Φ_F, Φ_F^0 is the fluorescent quantum yield of BF/FN in alcohol solvent and cyclohexane separately, and A is a constant. Notice that, Eq. (5) is available only for BF/FN in protic solvents. Additionally, when FN is dissolved in nonpolar solvent (cyclohexane), S_1 decays almost entirely by ISC to the lowest triplet state ($\Phi_{ISC} = 1$) [11,12]. Therefore, using the experimental data of the relative fluorescence intensity of BF in alcohols [15], the linear relationship of Eq. (5) is shown in Fig. 4. As shown, the good linear relationship confirms that our model for fluorescence quenching can simulate the real dynamic process very well, and the fluorescence intensity is dependent on the energy gap of the fluorescent state and ground state. This is in accordance with the experimental conclusion that the IC becomes the most important (even dominant) dissipative process in alcoholic solvents given by Biczók and co-workers [9–12]. For BF/FN in cyclohexane, the fluorescence quantum yields are governed dominatively by the dependence of intersystem crossing (ISC) process to the triplet state [11,12]. Introducing a phenyl group into FN could make the molecule more conjugate and extends the π bond, which should be hardly to influence the rate of ISC. Herein, we can suppose that the fluorescent quantum yields of BF and FN are almost the same in cyclohexane, which could be demonstrated to be reasonable by the good accordance of (the relative fluorescence intensity of) FN in ethanol with the linear relationship for BF in alcohols shown in Fig. 4.

Therefore, we transform the puzzle of fluorescence intensity into the easy-handled fluorescence wavelength, because of their linear relationship between them. We can note the bathochromic effect in Table 2 by comparing the spectra of the isolated BF/FN and BF/FN–EtOH hydrogen bond complexes. Hydrogen bond strengthening in the excited-state could lower the energy of the fluorescent state, which means a smaller energy gap and redshift of the spectra. Moreover, in Table 2, one can tell that, the hydrogen bond has enhanced the difference of the dipole moments in lowest singlet excited-state and ground state, which will interact with polarity to shift the spectra efficiently. Therefore, the fluorescence of BF/FN could efficiently quenched by the excited-state hydrogen bond strengthening.

As we have already discussed above, the fluorescence intensities of FN and its derivatives in alcohol solvents are determined by the energy gap between the fluorescent state and ground state. By comparing the influencing of structure changing, hydrogen bond is just the minor factor, and not the determinate one. The greater fluorescence intensity for BF in ethanol than that of FN is caused by the notable blue shift in the emission spectrum of isolated BF than that of FN (shown in Fig. 2), which means a larger energy gap between the lowest excited singlet state and ground state for BF molecule and restrains IC process from fluorescent state to ground state and increases the fluorescent quantum yields.

4. Conclusion

The excited-state hydrogen bonding of BF/FN in hydrogen donating ethanol solvents was investigated using the time-dependent density functional theory (TD-DFT) method. The geometric structures and energetics of hydrogen-bonded BF/FN–alcohol complexes as well as the isolated BF/FN in ground state and the lowest excited singlet state were discussed. All the calculated spectral features are in good agreement with the spectral results recorded in experiments. It has been demonstrated that the ground state and the lowest excited singlet state of the hydrogen-bonded BF/FN–alcohol complexes presented here can well delineate the ground and electronic excited-states of BF/FN in alcoholic solvents. To investigate the detailed aspects of excited-state hydrogen bonding dynamics, hydrogen bond binding energies and lengths as well as the hydrogen-bonded groups both in ground state and the electronic excited-state are also calculated using the TD-DFT method. By comparing the hydrogen bond binding energies in different electronic states, it is demonstrated that the intermolecular hydrogen bond $C{-}H\cdots H{-}O$ between benzo[*b*]fluorenone and ethanol is significantly strengthened in the electronic excited-states upon photoexcitation. Moreover, with our calculated results, a good linear relationship between the logarithm of the relative fluorescence intensity and the energy gap is confirmed. This suggests that the fluorescence intensity can be determined by the energy gap between the fluorescent state and ground state. The remarkable blue shift is shown in emission spectra of BF indicates larger energy gap than that of FN. It restrains the IC process from fluorescent state to ground state and increases the fluorescent quantum yields, which is caused by the additive benzene ring in BF molecule. At the same time, the hydrogen bond strengthening in excited-state could also quench the fluorescence by decreasing the energy gap.

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