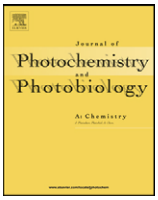
Journal of Photochemistry and Photobiology A: Chemistry 209 (2010) 181–185

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



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

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ARTICLE INFO

*Article history:*
Received 14 September 2009
Received in revised form 29 October 2009
Accepted 18 November 2009
Available online 24 November 2009

*Keywords:*
Hydrogen bonding
Excited-state
Fluorescence quenching
TD-DFT
Internal conversion

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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doi:10.1016/j.jphotochem.2009.11.012

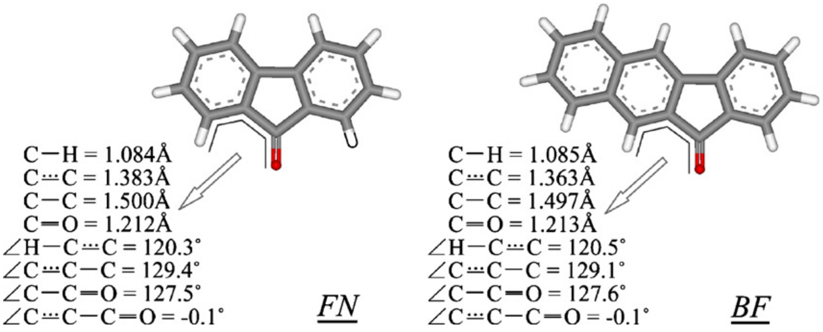

**Fig. 1.** The optimized geometrical structures of BF and FN in ground state, and the bond lengths (Å), bond angles (degree) and dihedral angels (degree) of the primary part of BF and FN molecule.

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.

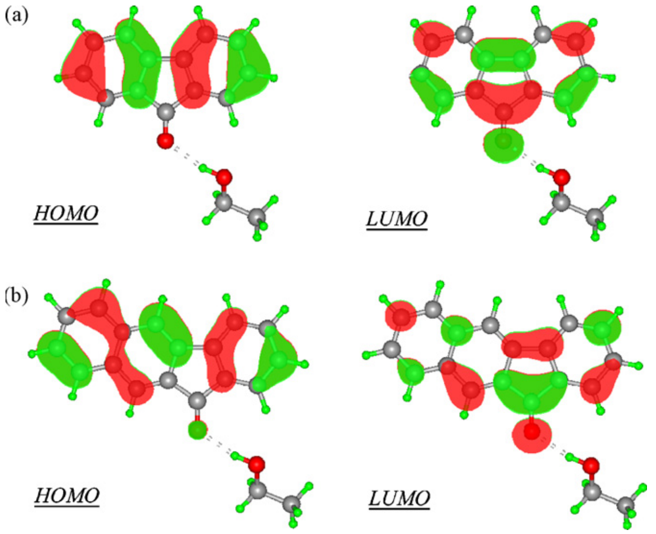

**Fig. 2.** Optimized geometric structures of the hydrogen-bonded BF–EtOH and FN–EtOH complexes and the frontier molecular orbitals (MOs) of the hydrogen-bonded FN–EtOH (a) and BF–EtOH (b) complexes.

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 |