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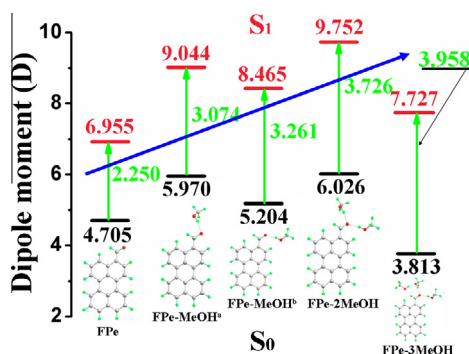
Study on the modulation of spectral properties of the formylperylene-methanol clusters by excited-state hydrogen bonding strengthening

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HIGHLIGHTS

- From FPe to FPe–3MeOH, hydrogen bonds are strengthened and increases dipole moment.
- In S_1 , hydrogen bonds are further strengthened and leads to larger dipole moments.
- Hydrogen-bond strengthening plays important role in the charge transfer process.
- Hydrogen-bond strengthening lead to red-shifts of electronic and vibrational spectra.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, the charge transfer (CT) process within the formylperylene (FPe)–methanol (MeOH) systems facilitated by intermolecular hydrogen bonding interactions is theoretically studied in both the ground state S_0 and the first singlet excited state S_1 . The geometric structures, electronic spectra and the infrared spectra of the FPe monomer as well as the various hydrogen-bonded FPe–MeOH complexes in both states were calculated with the density functional theory (DFT) method and time-dependent density functional theory (TD-DFT) methods, respectively. It is demonstrated that the total effect of the intermolecular hydrogen bonding between FPe and the MeOH molecules becomes strengthened in the ground state as the number of the MeOH molecules hydrogen-bonded to the FPe molecule increases from zero to three, which induces large increases in the dipole moment as well as systemic redshifts of the absorption spectra of FPe. Furthermore, upon photoexcitation of the FPe molecule, the intermolecular hydrogen bonds formed in the various hydrogen-bonded FPe–MeOH complexes are further strengthened which leads to even larger dipole moments as well as obvious redshifts of the fluorescence spectra. The calculated electronic spectra of the various hydrogen-bonded FPe–MeOH complexes are in agreement with the steady-state absorption and fluorescence spectra of FPe observed in the binary mixed solvents with different MeOH concentration. The intermolecular hydrogen bonding strengthening in both the ground and excited states are further confirmed by the infrared spectra shifts. Moreover, the vitally important role played by the intermolecular hydrogen bonding interaction and its strengthening upon electronic excitation in the CT process is discussed.

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Introduction

The study of solute–solvent interactions has long been one of the focal points of solution chemistry [1–4]. Solvation dynamics after excitation of the chromophore to a new electronic state has

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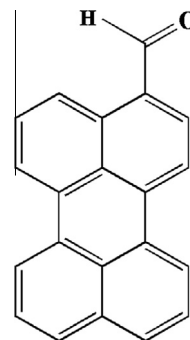
been the subject of many experimental studies where time-resolved fluorescence Stokes-shift measurements and excited-state transient absorption [1] were the important tools as well as absorption line-shape analysis [2], resonance Raman scattering [3] and coherent techniques [4]. Solute–solvent interactions are mainly due to the dielectric properties of the solvent. Another common type of solute–solvent interaction results from hydrogen bonding. In this case, hydrogen bonds are formed between specific solute and solvent atoms [5]. Based on the intramolecular hydrogen bonding interactions, an intramolecular proton transfer mechanism in the excited state was first proposed by Weller to account for the unusually large Stokes shift in the fluorescence properties of the methyl salicylate parent molecule [6]. To quantitatively describe the site-specific solute–solvent hydrogen bonding interaction and its influence on the photophysical properties of the chromophore molecules, Kamlet and Taft have developed the solvatochromic model (Kamlet–Taft model) that quantifies the specific interactions due to hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) contributions of the solvents, and separate them from nonspecific ones [7]. The Kamlet–Taft solvatochromic scale has been used widely to correlate the energies associated with the Stokes shifts in different kinds of solvents. Mataga and co-workers have contributed to the recognition of the role of hydrogen bonds in photochemistry and photobiology [8]. Moreover, Hynes have investigated the hydrogen bonds in the hydration shells of ions, photo-biological reactions and interactions between drugs and DNA [9].

Both types of solvation interactions act to reduce the free energy of the solute. In the event of rapid excitation of the chromophore to a new electronic state, the solvent rearranges itself around the solute molecule, so as to minimize the free energy of the solute in its newly formed electronic state. The dynamic aspects of polar solvation have been studied extensively over the past 30 years and have resulted in a detailed description of polar solvation [1–4]. In contrast, relatively few studies on the dynamic aspects of solvation by specific hydrogen-bonding interactions have been carried out [5–9]. Zhao and Han have theoretically demonstrated that intermolecular hydrogen bonds formed between carbonyl chromophores and polar protic solvents can be significantly strengthened in electronically excited states of carbonyl chromophores. Furthermore, it has also been observed that some radiationless deactivation processes of photoexcited carbonyl chromophores can be strongly facilitated by excited-state intermolecular hydrogen bond strengthening [10]. Moreover, TDDFT studies on the fluorescent sensing mechanism of anions such as cyanide and fluoride based on intermolecular and/or intramolecular hydrogen bonding interactions have been carried out by Li and coworkers [11].

Hydrogen bonding in the ground state has been extensively studied by many different experimental and theoretical methods. However, little is known about electronic excited-state hydrogen bonding, due to the extremely short timescales involved. The excited-state hydrogen bonding dynamics are dominantly determined by the vibrational motions of the hydrogen donor and acceptor groups, which typically occur on ultrafast time scales of hundreds of femtoseconds [10–12]. To directly monitor the ultrafast dynamical behavior of hydrogen bonds in the excited state, various femtosecond time-resolved spectroscopic techniques have been used, such as femtosecond vibrational spectroscopy, femtosecond transient absorption, and femtosecond time-resolved fluorescence spectroscopy [10–12]. However, apart from the time-resolution limit of the present femtosecond laser pulse used in these spectroscopic techniques, the excited-state hydrogen bonding dynamics is coupled with the electronic excitation; thus, they are difficult to separate. Therefore, the combination of femtosecond time-resolved spectroscopy and accurate excited-state quan-

tum chemistry calculations is necessary to overcome this issue with laser experiments.

The above-mentioned studies have been performed on a limited number of hydrogen-bonded complexes. In view of the great variety, high abundance and crucial importance of the hydrogen-bonding interaction to solution chemistry and biochemistry, it is clear that more additional experimental and theoretical works are needed to comprehend the dynamic aspects of the hydrogen-bonding interactions. It has been demonstrated that the molecular photochemistry in solution can be tuned by hydrogen bonding interactions in electronically excited states. However, knowledge about how this happens is rather limited. Recently, in order to examine the crucial role of hydrogen bonding in the CT process, Mohammed and coworkers have intentionally chosen formylperylene (FPe, see Scheme 1) as the probe molecule and studied it in a series of binary mixtures of solvents [13]. The FPe molecule has only one carbonyl group which is the active site responsible for both the site-specific intermolecular hydrogen bond formation and the intramolecular charge accepting. The binary mixtures are composed of solvents with different hydrogen bonding affinities but similar polarities, protic solvent methanol (MeOH) and aprotic solvent acetonitrile (ACN) [13]. In the absorption spectra of FPe in MeOH/ACN binary mixtures, a systematic change in the red tail with the increase of MeOH concentration is observed and has been attributed to the formation of a hydrogen-bonded complex by FPe and MeOH in the ground state, which has been confirmed by the steady-state IR measurements [13]. Furthermore, the emission spectra are substantially red-shifted relative to the absorption spectra and more redshifts of the emission spectra are observed as the MeOH concentration increases from 0% to 100%, which indicates the important role of the site-specific intermolecular hydrogen bonding in the stabilization of the CT state of the hydrogen-bonded complexes. In addition, to investigate the ultrafast excited-state hydrogen bonding dynamics coupled to the charge transfer process of FPe, the picosecond-resolved fluorescence Stokes shifts have been recorded by Mohammed and coworkers in the series of binary mixtures of MeOH and ACN in their experiments, from which the time-dependent spectral evolution of the fluorescence spectra can be directly perceived. It is noted that, as the MeOH concentration increases from 5%, via 10% and 20% to 100%, the amounts of the fluorescence spectral shifts get more and more larger within the observation time 150 ps (see Fig. 3 in Ref. [13a]). The increase of the spectral shifts indicates that the excited-state FPe molecules have undergone more and more stabilization impacts imposed by the excited-state hydrogen bonding strengthening upon photoexcitation with the increase of the MeOH concentration. However, how exactly the intermolecular hydrogen bonding changes and its concrete role in the stabilization of the CT state of the hydrogen-bonded complex upon photoexcitation have not been discussed in detail.



Scheme 1. The schematic chemical structure of formylperylene (FPe).

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