

REGULAR ARTICLE

Cooperative Excited-state Hydrogen Bond Strengthening and Weakening and Concerted Excited-State Proton Transfer and Twisted Intramolecular Charge Transfer of Thiazolidinedione Derivatives in Solution

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Abstract: The time-dependent density functional theory (TDDFT) method has been performed to investigate the photochemical properties of the hydrogen-bonded complexes of thiazolidinedione derivatives with dimethylformamide (DMF), water and methanol solvents. A cooperative mechanism of the excited-state intermolecular hydrogen bond strengthening and weakening upon photoexcitation has been proposed for the TZD-A-2DMF trimer. Moreover, we have also first demonstrated that the excited-state proton transfer (ESPT) and twisted intramolecular charge transfer (TICT) are coupled together in TZD-A-DMF dimer and significantly facilitated by the excited-state intermolecular hydrogen bonding. When TZD-C is dissolved in protic solvents, e.g. water and methanol, the hydrogen bond is further assessed for its specific role in understanding the photochemistry properties of TZD-C.

AMS subject classifications: 65D18, 74E40, 78M50

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1 Introduction

Intermolecular hydrogen bonding interaction has been stated to be the important and indispensable site-specific interaction in the investigation of the photochemical and photophysics processes [1-5]. The intermolecular hydrogen bond strengthening mechanism between Coumarin 102 chromophore and solvent upon photoexcitation has been demonstrated for the first time by Han and coworkers [6], which is in contrast to the mechanism of excited-state intermolecular hydrogen bond cleavage proposed by Nibbering and coworkers [7]. Then, as reconsidered and verified by many other groups [8-10], Nibbering and coworkers also accepted the excited-state intermolecular hydrogen bond strengthening mechanism in 2012, and with the help of the mechanism, they have clarified the photoinduced electron-transfer dynamics of 9-fluorenone in amine solvents [11]. Interestingly, an investigation of thiocarbonyl chromophores in solutions indicates an electronic excited-state intermolecular hydrogen bond weakening phenomenon [12]. What's more, it has been demonstrated that both the excited-state hydrogen bond strengthening and weakening play very significant roles in the processes of internal conversion (IC) [13], electronic spectral shifts (ESS) [12], photoinduced electron transfer (PET) [14], intramolecular charge transfer (ICT) [15,16], and metal-to-ligand charge transfer (MLCT) [17,18], and so on. It is important to mention that an effective rule, illustrating and inferring excited-state hydrogen bonding strengthening or weakening via an electronic spectral red-shift or blue-shift, have been presented recently [12,19], and the effective rule has been taken into account to explain the experiment by other groups [20-26]. A great deal of the studies have been focused on the hydrogen bonding dynamics, however, it is still desirable to carry out further works dealing with the effect of the excited-state hydrogen bonding dynamics on the photochemistry, photophysics and photobiology.

The new-synthesized thiazolidinedione derivatives (TZDs) have been proved to be sensitive to trace the quantities of diverse hydrogen bonding interactions [27]. As a result of the presences of electron rich carbonyl groups around -NH group in the thiazolidinedione moiety, the -OH group in the aryl moiety, and the keto groups on both sides of the thiazolidinedione moiety, the TZDs are host-guest of hydrogen bond series. Most importantly, the TZD-A of electronic donor (D) and acceptor (A) linked by a single bond, without the bulk steric effect, may induce a twisted configuration form. Thus, it is expected that the configuration twist may take place in the excited states, and then confirmed by our