Theoretical study on excited state intramolecular proton transfer (ESIPT) of bipyridine derivatives

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Abstract: Excited state intramolecular proton transfer (ESIPT) of bipyridine derivatives has been studied because of its applications in biosensor and optoelectronic devices. In this study, ESIPT of four compounds having bipyridine as a core with single and double hydroxy (OH) or amine (NH₂) substitutions namely [2,2’-bipyridyl]-3-ol (BP(OH)), [2,2’-bipyridyl]-3-amine (BP(NH₂)), [2,2’-bipyridyl]-3,3’-diol (BP(OH)₂), and [2,2’-bipyridyl]-3,3’-diamine (BP(NH₂)₂) in ground state (S₀) and excited state (S₁) was investigated by B3LYP and TD-B3LYP with TZVP basis set, respectively. The results of static calculations show that hydrogen bonds are strengthened in the S₁ confirmed by the shortened intramolecular hydrogen bonds and the red-shifts of the O-H and N-H vibrational modes. The absorption and emission spectra agree well with experiment and the stroke shifts of bipyridine with single substitution (BP(OH), BP(NH₂)) are larger than those of bipyridine with double substitution (BP(OH)₂, BP(NH₂)₂). The PT barriers of OH substitution from potential energy curves (PECs) is lower barrier than NH₂ substitution, thus the ESIPT occurs easily because OH group as proton donor is more acidic than NH₂ group. For dynamics simulations, the results confirm that ESIPT time of OH substitution is faster than NH₂ substitution. Moreover, double PT of BP(OH)₂ and BP(NH₂)₂ occurs through stepwise mechanism not concerted.

Keywords: Theoretical; Density functional theory; Excited state intramolecular proton transfer; Bipyridine derivatives