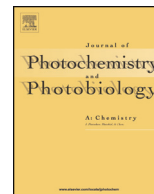




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Invited feature article

Excited state behavior of benzoxazole derivatives in a confined environment afforded by a water soluble octaacid capsule



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ABSTRACT

This feature article presents a brief description of the excited state intramolecular proton transfer mechanism (ESIPT), describes the solvent dependence of the ESIPT phenomenon and present the potential applications that can be envisaged for these fluorophores. Photophysics of three dye molecules exhibiting ESIPT were examined free in solution and within a water soluble supramolecular host, octaacid (OA) by steady-state and time resolved fluorescence emission techniques. Inclusion of the above dyes within OA was confirmed by ¹H NMR spectra. The free and octaacid complexed dyes had electronic absorption in the UV region. Within the OA container the fluorophores showed fluorescence emission similar to that in benzene, dichloromethane and acetonitrile. Moreover, the observed large Stokes' shift in the emission of the dyes when confined within OA capsule was unlike that in aqueous medium. The results suggest that a confined medium is a powerful tool to tailor the fluorescence emission of ESIPT compounds in aqueous media.

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1. Introduction

1.1. A brief background on ESIPT process

Excited state intramolecular proton transfer (ESIPT) is a photochemical process that produces a tautomer with a different electronic structure from the initial ground state conformer [1]. This process has been extensively investigated in the past decade due to their importance in chemistry, biology and biochemistry [2–9]. The driving force for ESIPT is the redistribution of the electron density in the excited state, where the donor group (phenol or aniline scaffold) is significantly more acidic and the acceptor group (imino/azonitrogen- or carbonyl-oxygen-containing ring skeleton) [1] more basic, thereby enhancing proton transfer at a faster rate relative to the ground state [10,11]. The ESIPT process can generally be found in flavonols, chromones and benzoxazoles structures and this phototautomerism can be understood on the basis of a four-level model ($N \rightarrow N^* \rightarrow T^* \rightarrow T \rightarrow N$, Fig. 1).

Despite the fact that the four-level diagram can be applied to most compounds, there are significant differences between species involved in the photophysical cycle, also known as Forster cycle. Usually, these compounds present absorption in the UV region due to structural isomers possessing an intramolecular hydrogen bond (IHB). Upon excitation these generate new excited tautomers by an ultrafast intramolecular proton transfer [12–16]. The excited tautomer is more stable than the excited state of the original conformer [17–19]. For benzoxazoles, in apolar or aprotic media an enol-*cis* conformer is the most stable conformer in the ground state with a strong IHB between the phenolic or anilinic hydrogen and the azolic nitrogen. In the excited keto tautomer, the nitrogen and the carbonyl group are also bonded by an intramolecular hydrogen bond [20]. The tautomer decays emitting fluorescence to a keto tautomer (T^*) and the initial enol form is regenerated without any photochemical change. Despite proposals involving zwitterionic species or intermediates in the ESIPT mechanism for benzoxazoles [21–25], nowadays, neutral species are believed to take place in the excited state. On the other hand, flavonols and chromones differ from benzoxazoles since the locally excited species presents an intramolecular charge transfer character (ICT) [26–29]. Moreover, certain flavonols containing organic groups such as dialkylamino, suggest that a twisted intermolecular charge transfer processes (TICT) takes place in the excited state [13,30],

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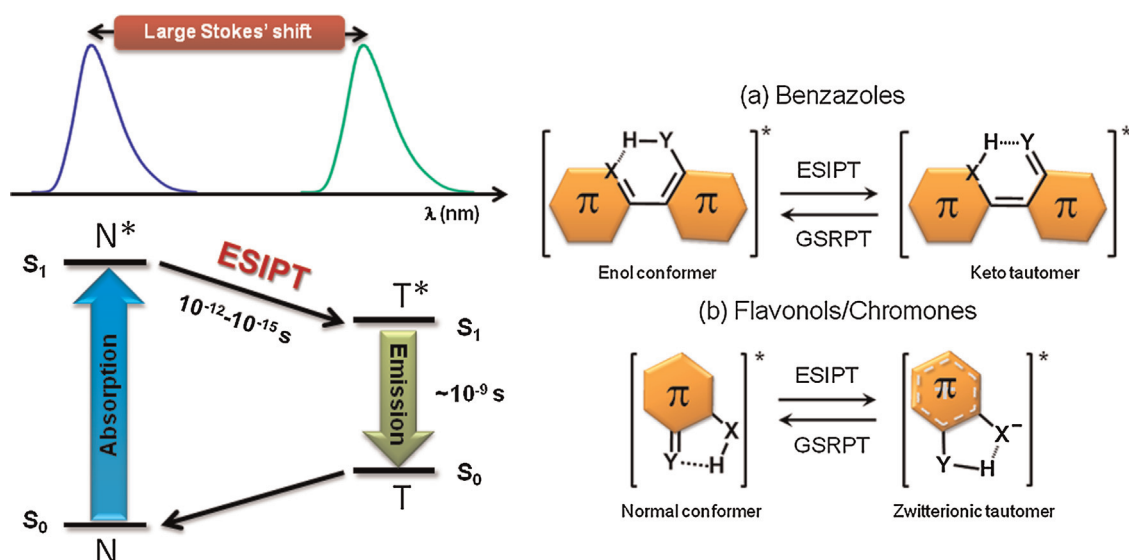


Fig. 1. Four-level model for the ESIPT process. In the right side is presented the generic structure of (a) 2-(2'-hydroxyphenyl) benzazoles and (b) flavonols/chromones, where the asterisk indicates the excited-state. After deactivation of the excited state by fluorescence emission these compounds present ground state retro proton transfer (GSRPT).

allowing a more significant loss of energy from the excited state, leading to a more redshifted emission than expected in the absence of these groups.

The first remarkable photophysical property of the ESIPT fluorophores is the large Stokes' shift (Fig. 1), compared to the normal fluorophores [3]. The excited tautomer produced from the excited enol-*cis* conformer in benzazoles or from the excited normal specie in flavonols/chromones presents a totally different electronic structure from the initial excited form, which gives rise to a fluorescence with an anomalously large Stokes shift [1]. The proton transfer emission from the excited tautomer generally occurs with a Stokes' shift of 8000 – 10000 cm^{-1} [31]. As discussed by Zhao et al. [3], a large Stokes' shift can be a powerful tool in the optical sensors field, since reduces drastically the inner filter effect, improving the fluorescence analysis. Additionally, it is difficult to increase the Stokes' shift of classical fluorophores by simple chemical modification.

1.2. Compounds exhibiting ESIPT

According to Kasha there are a few requirements to observe intramolecular transfer in ESIPT fluorophores [6]. The main one is the existence of an IHB between the H atom of the donor group and the acceptor within a distance less than 2 \AA [32]. Additionally, this compound must possess both photoacid and photobasic character, where either the acidic or basic moieties of the same molecule become stronger acid or base, respectively in the excited state. According to the literature the ESIPT mechanism can occur mostly from four types of intramolecular hydrogen bonds (Figs. 2 and 3) [28], although a few cases are known where a nitrogen atom can function as the donor and a carbon atom as the acceptor [33–35]. In this way, several organic structures have been proposed including a broad class of heterocycles. The most common and simple structures, include up to two fused aromatic rings comprising aromatic hydroxy compounds (1–4, 6, 7–9, 10, 12–13), hydroxypyridines (5) and naphthol derivatives (11, 14–16, 17–19) (Fig. 2).

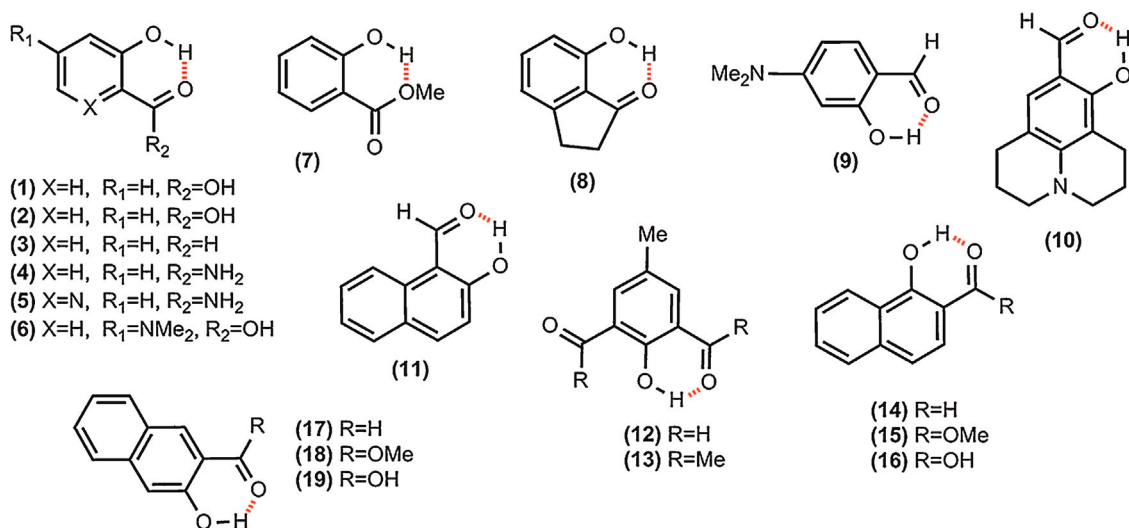


Fig. 2. Simple structures of ESIPT compounds, where the IHB is presented as a red dash line.

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