



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Photophysical properties of ESIPT inspired fluorescent 2-(2-hydroxyphenyl)-6-methylimidazo[4,5-f]isoindole-5,7(1H,6H)-dione and its derivative: Experimental and DFT based approach



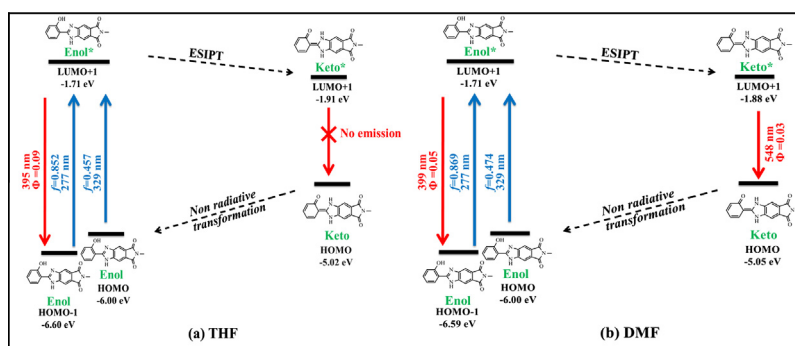
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HIGHLIGHTS

- Synthesis of phthalimide based ESIPT molecules.
- Spectroscopic investigations of a series of new benzimidazole.
- Existence of ESIPT has been experimentally and is computationally supported.
- Good thermal stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 January 2014
 Received in revised form 3 July 2014
 Accepted 12 July 2014
 Available online 22 July 2014

Keywords:

o-Hydroxyphenyl benzimidazole
 ESIPT
 Fluorescence
 Solvatochromism
 Thermal stability
 TD-DFT

ABSTRACT

The excited-state intramolecular proton transfer chromophores 2-(2-hydroxyphenyl)-6-methylimidazo[4,5-*f*]isoindole-5,7(1*H*,6*H*)-dione and 2-(4-(diethylamino)-2-hydroxyphenyl)-6-methylimidazo[4,5-*f*]isoindole-5,7(1*H*,6*H*)-dione are synthesized from 4,5-diamino-*N*-methylphthalimide. The photophysical behavior of the synthesized chromophores was studied using UV–visible and fluorescence spectroscopy in the polar and non-polar solvents. The synthesized *o*-hydroxyphenyl benzimidazole derivatives are fluorescent and very sensitive to the solvent polarity. These dyes are thermally stable up to 317 °C. Density Functional Theory computations have been used to understand the structural, molecular, electronic and photophysical properties of the chromophores. The experimental absorption and emission wavelengths are in good agreement with the computed vertical excitation and theoretical emission obtained by Density Functional Theory and Time Dependent Density Functional Theory.

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Introduction

Excited state intramolecular proton transfer (ESIPT) is of prime importance in molecular probes [1], luminescent materials [2,3], metal ion sensors [4–6], organic light emitting devices (OLEDs)

[7–10] and molecular logic gates [11]. The most significant photophysical property of the ESIPT chromophores is the large Stokes shift, compared to the normal fluorophores such as fluorescein, boron-dipyrromethene (BODIPY) or rhodamine [12,13]. The large Stokes shift is a distinct characteristic for fluorophores because the self-absorption, or the inner filter effect, can be avoided and the fluorescence can be improved with this kind of fluorophores. It is difficult to increase the Stokes shift of the conventional fluorophores by chemical modification [14].

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Upon photoexcitation to the first excited state, the acidity of the acidic center and the basicity of the basic center increase simultaneously because of the redistribution of the charge density of the chromophore realized in the first singlet excited state. This leads to the migration of the acidic proton of the acidic center to the basic nitrogen unit via the already existing hydrogen bond coordinate to give the phototautomer. The ESIPT process is a very fast process occurring within subpicosecond time scale, and on excitation the molecule passes to the potential well and then relaxes vibrationally [15,16]. Generally the ESIPT chromophores show dual emission, one being to the normal emission from the local excitation and the second which is largely Stokes shifted (up to $10,000\text{ cm}^{-1}$), due to the tautomer formed by proton transfer [14].

Therefore, taking into consideration the wide applications and importance of ESIPT inspired molecules and in continuation of our research work on ESIPT materials [17–19] herein, we report the synthesis, photophysical properties and the computational study of novel *o*-hydroxyphenyl benzimidazole (HPBI) derivatives, wherein the phthalimide–imidazole fused heterocycle. It may possess good electron-accepting ability. So the substitution by amine leads to push–pull dipolar compounds. Prominent red-shifted absorption of **6a** is due to the ICT present in this compound. Phthalimide and naphthalimide-based dyes are interesting due to their excellent electron accepting properties [20].

Experimental section

Materials and equipments

All the commercial reagents and the solvents were purchased from S. D. Fine Chemicals Pvt. Ltd. Mumbai and were used without purification. The reaction was monitored by TLC using 0.25 mm silica gel 60 F₂₅₄ precoated plates, which were visualized with UV light. Melting points were measured on standard melting point apparatus from Sunder industrial product Mumbai, and are uncorrected. FT-IR spectra were recorded on Jasco 4100 using ATR accessory. ¹H NMR spectra were recorded on VARIAN 400/500-MHz

instrument (USA) using TMS as an internal standard. Mass spectra were recorded on Finnigan mass spectrometer. The visible absorption spectra of the compounds were recorded on a Perkin Elmer Lambda 25 spectrometer; fluorescence emission spectra and fluorescence quantum yields were recorded by using quinine sulfate (0.54 in 0.1 M H₂SO₄) as reference [21] on Varian Cary Eclipse fluorescence spectrophotometer. Simultaneous DSC–TGA measurements were performed on SDT Q 600 v8.2 Build 100 model of TA instruments Waters (India) Pvt. Ltd.

Computational methods

The compounds **6a–6b** and their tautomers involved are illustrated in Fig. 1. The ground state (S₀) geometry of the tautomers of compounds **6a** and **6b** in their C_s symmetry was optimized using the tight criteria in the vacuum phase using Density Functional Theory (DFT) [22]. The functional used was B3LYP. The B3LYP method combines Becke's three parameter exchange functional (B3) [23] with the nonlocal correlation functional by Lee, Yang, and Parr (LYP) [24]. The basis set used for all atoms was 6-31G(d), the latter has been justified in the literature [25–27] for the current investigation. The vibrational frequencies at the optimized structures were computed using the same method to verify that the optimized structures correspond to local minima on the energy surface [28]. The vertical excitation energy and oscillator strengths at the ground state equilibrium geometries were calculated using TD-DFT with the same hybrid functional and basis set [29–31]. The low-lying first singlet excited state (S₁) of the dyes was relaxed using TD-DFT to obtain its minimum energy geometry. The difference between the energies of the optimized geometries at the first singlet excited state and the ground state was used in computing the emissions [32,33]. Frequency computations were also carried out on the optimized geometry of the low-lying vibrationally relaxed first excited state of the conformers. All the computations in solvents of different polarities were carried out using the Polarizable Continuum Model (PCM) [34]. All the electronic structure computations were carried out using the Gaussian 09 program [35].

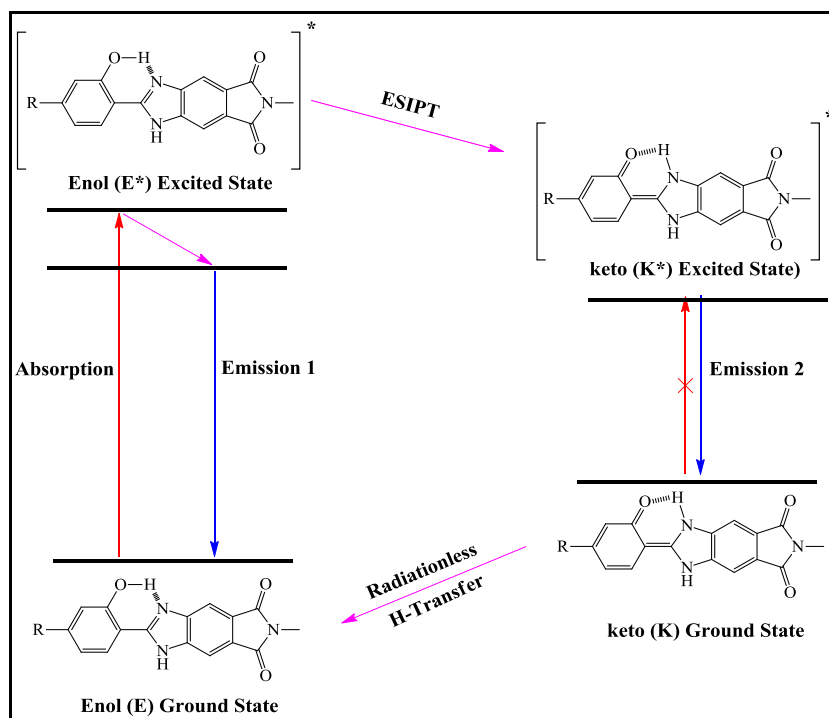


Fig. 1. Excited state intramolecular proton transfer (ESIPT) pathway.

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