

## Photophysical properties of Reactive ESIPT Processes

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**Abstract**

This work describes the photophysical properties of new salicylidene derivatives which undergoes excited state intramolecular proton transfer (ESIPT) and the role of solvent polarity and specific interactions with the dyes. These observations were obtained by steady-state and time-resolved electronic absorption and fluorescence techniques. Salicylidene derivatives were synthesized by Schiff's condensation using an acid catalyst and they were characterized successfully by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, FT-IR, HRTOF-MS and single-crystal X-ray diffraction and their photophysical properties were studied by the addition of a bromide moiety of the aromatic amine ring.

**Key words:**

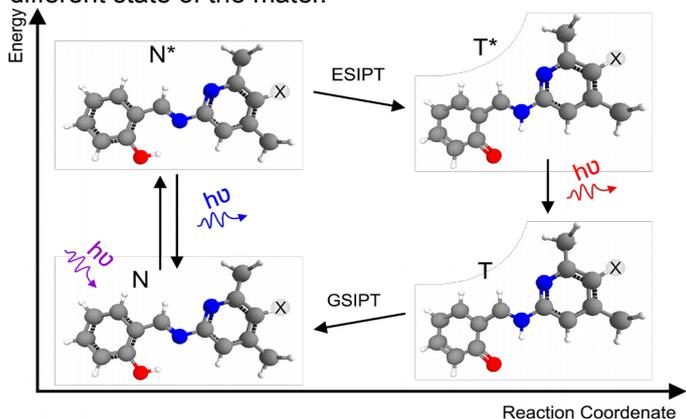
ESIPT, electronic spectroscopy, photophysics.

**Introduction**

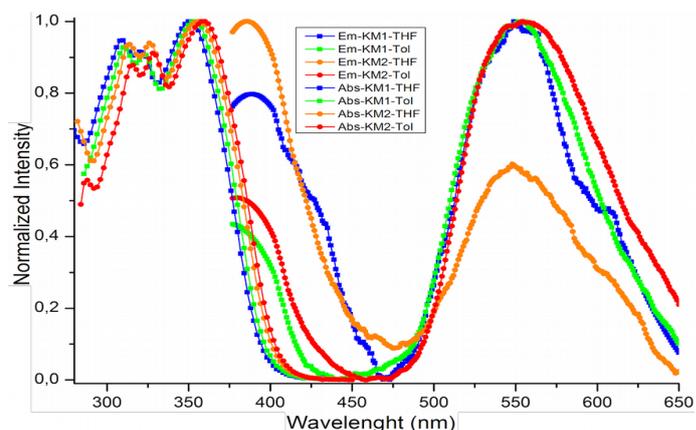
ESIPT is a phenomenon that occurs in the excited-state with an ultrafast time-scale, where the formed species (normal\* -  $\text{N}^*$  and tautomer\* -  $\text{T}^*$ ) must be in balance or not, exhibiting a radiative decay along the visible spectrum, causing it generates white-light for lightning applications. <sup>1,2</sup> Thus, these molecules should be present an acid hydrogen that is sensitive by the media polarity and refractive index. Therefore, in this study we obtain two new salicylidene derivatives (Figure 1) and their ESIPT processes were available as function of the solvent polarity by steady-state and time-resolved electronic spectroscopies techniques, obtaining different ratios of the  $\text{N}^*$  and  $\text{T}^*$  emission bands as function of media polarity, bromide substitution and excitation wavelengths.

**Results and Discussion**

Salicylidene were synthesized and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, FT-IR, HRTOF-MS and single-crystal X-ray diffraction. Ideally diluted solutions of salicylidene molecules were made ( $C=2 \times 10^{-5} \text{ mol.L}^{-1}$ ) for photophysical and photochemical measurements via electronic absorption, photoluminescence and photoluminescence excitation spectra (Figure 2), as well as, time-resolved fluorescence measurements. Also, photophysical measurements were done at solid-state by the same techniques. Thus, we successfully evaluated the reactive ESIPT processes of the 2 new salicylidene molecules as function of the solvent, the bromide substitution and in different state of the mater.



**Figure 1.** Schematic representation of the ESIPT processes for the two new salicylidene molecules. Where "X" is H (KM1) or Br (KM2).



**Figure 2.** Normalized electronic absorption and emission spectra of the KM1 and KM2 in THF and Toluene solutions ( $C=2 \times 10^{-5} \text{ mol.L}^{-1}$ ;  $\lambda_{\text{exc}} = 350 \text{ nm}$ ).

The optical properties of the new salicylidenes revealing a high reactive ESIPT process, presenting two emission bands centered at  $\lambda_{\text{PL}} \approx 390$  and  $550 \text{ nm}$  with a Stokes shift around  $\text{SS} = 2,500$  and  $10,000 \text{ cm}^{-1}$  for the  $\text{N}^*$  and  $\text{T}^*$  species, respectively. Which corroborates directly to the occurrence of ESIPT reaction and white-light generation principle. Also, the ratio intensity and the energy of the  $\text{N}^*$  and  $\text{T}^*$  emission bands were sensitive to the media polarity and principally by the substitution of the H by the Br atom on the salicylidene framework.

**Conclusions**

New salicylidene molecules were successfully synthesized and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, FT-IR, HRTOF-MS and single-crystal X-ray diffraction and their photophysical properties were studied by the addition of a bromide moiety of the aromatic amine ring and the variation of the media polarity. Thus, obtaining two new molecular systems able to white-light generations which will be used as active layer for white organic light-emitting diodes (WOLEDs) in the next step of this work.

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