PÔSTER - RESUMO - MATERIAIS E BIOMATERIAIS

ESIPT OR ICT? HOW THE MODULATION OF EXCITED-STATE DETERMINES THE APPLICATIONS OF HYDROXYPHENYLBENZOTHIAZOLE DYES

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Excited-State Intramolecular Proton Transfer (ESIPT) dyes have attracted considerable attention owing to their unique four-level fluorescence cycle, which arises from tautomerization in the excited state(1,2). This process imparts distinctive photophysical features, including large Stokes shifts, high photostability, and pronounced sensitivity to the surrounding environment(3). In particular, the balance between the enol (E*) and keto (K*) excited-state tautomers is strongly influenced by solvation, enabling dual fluorescence emission that can be tuned by changes in the microenvironment(4,5). These properties make ESIPT dyes highly versatile for applications ranging from bioimaging to optoelectronics(4,6,7). However, in polar environments or under specific substitution patterns, ESIPT efficiency can be undermined by competing excited-state processes, namely intramolecular charge transfer (ICT)(8–10). In this work, we aim to contribute to the understanding of this complex relationship through the design and synthesis of a library of 2-(2-hydroxyphenyl)benzothiazole (HBT) derivatives, where ESIPT and ICT contributions are intentionally modulated. This way, derivatives of HBT containing either a carbamate or a carbonate substituent were prepared through

a one-pot, base-selective acylation strategy. The optical behavior of these compounds was systematically studied using UV-vis and fluorescence spectroscopy in solvents of varying polarity and viscosity. Quantum yield and time-resolved fluorescence data were collected to analyze the excited-state dynamics. Our findings reveal that carbonate-substituted 5-HBTE compounds exhibit a classical ICT character with Stokes shifts in the range of ~ 4000 cm-1 (~ 55 nm) while the positional isomer 4-HBTE showed progressive Stokes shifts with increasing polarity. Moreover, for 4-HBTE surprisingly large Stokes shifts (> 12000 cm-1 or 180 nm) and solvent-sensitive fluorescence were observed. While the ESIPT active analogs 4- and 5-HBTA showed negative solvatochromism and high quantum yield in the solid state, 4- and 5-HBTE derivatives showed positive solvatochromism and elevated quantum yields in solution. Understanding the balance between ESIPT and ICT in dyes provides a promising pathway for extending their applicability to highly polar environments, thereby advancing their potential in polarity probes and material design.

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Palavras-chave: excited-state intramolecular proton transfer; intramolecular charge transfer; solvatochromism; excited-state dynamics.