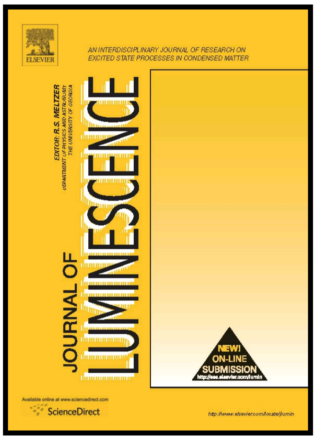

www.elsevier.com/locate/jlumin

Stimuli-responsive luminescent coumarin thiazole hybrid dye: Mechanism of excited-state intramolecular double proton transfer

Yu Zhao, Yunfan Yang, Yanzhen Ma, Yongqing Li

PII: S0022-2313(18)30115-7
DOI: https://doi.org/10.1016/j.jlumin.2018.04.064
Reference: LUMIN15579

To appear in: *Journal of Luminescence*

Received date: 22 January 2018
Revised date: 20 April 2018
Accepted date: 28 April 2018

Cite this article as: Yu Zhao, Yunfan Yang, Yanzhen Ma and Yongqing Li, Stimuli-responsive luminescent coumarin thiazole hybrid dye: Mechanism of excited-state intramolecular double proton transfer, *Journal of Luminescence,* https://doi.org/10.1016/j.jlumin.2018.04.064

Stimuli-responsive luminescent coumarin thiazole hybrid dye: Mechanism of excited-state intramolecular double proton transfer

Yu Zhao, Yunfan Yang, Yanzhen Ma, Yongqing Li*

Department of Physics, Liaoning University, Shenyang 110036, P. R. China.

*Corresponding author. yqli@lnu.edu.cn (Yongqing Li).

ABSTRACT

Recently, a novel coumarin thiazole hybrid dye with azomethine linkage is synthesized. It is revealed that the symmetrical structures 3,3'-(5,5'-((1E,1'E)-hydrazine-1,2-diylidenebis(methanylylidene))bis(2-morpholinothiazole-5,4-diyl))bis(4-hydroxy-2H-chromen-2-one) (abbreviated as CS) takes shape two intramolecular hydrogen bonds and that excited-state intramolecular proton transfer (ESIPT) takes place with thiazole nitrogen atoms [Dyes Pigments. **142**, 2017, 121]. However the corresponding reaction mechanisms are lacking. This study uses density functional and time-dependent density functional theory to calculate hydrogen-bond lengths, hydrogen-bond angles, infrared vibrational spectra and Mulliken charges of relevant groups, which confirm the excited-state hydrogen-bond strengthening mechanism. Enhanced hydrogen-bond strength facilitates the ESIPT process of the CS molecule. The absorption and fluorescence emission spectra of CS in dimethyl formamide (DMF) are calculated, which are consistent with the observed results in experiment. To further illustrate mechanism of excited-state double proton transfer (ESDPT) reactions, the potential energy surfaces of CS are constructed and analyzed, which demonstrate ESDPT more likely occur stepwise rather than concertedly. The frontier molecular orbitals of CS system are also calculated and display the nature of the charge redistribution, which demonstrate that CS system exhibits light fastness because ESIPT process inhibits intramolecular charge transfer.

Keywords

Hydrogen bond; Excited-state intramolecular double proton transfer; Light fastness; Intramolecular charge transfer