World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:13, No:11, 2019

# Intriguing Modulations in the Excited State Intramolecular Proton Transfer Process of Chrysazine Governed by Host-Guest Interactions with Macrocyclic Molecules

**Authors :** Poojan Gharat, Haridas Pal, Sharmistha Dutta Choudhury

**Abstract :** Tuning photophysical properties of guest dyes through host-guest interactions involving macrocyclic hosts are the attractive research areas since past few decades, as these changes can directly be implemented in chemical sensing, molecular recognition, fluorescence imaging and dye laser applications. Excited state intramolecular proton transfer (ESIPT) is an intramolecular prototautomerization process display by some specific dyes. The process is quite amenable to tunability by the presence of different macrocyclic hosts. The present study explores the interesting effect of p-sulfonatocalix[n]arene (SCXn) and cyclodextrin (CD) hosts on the excited-state prototautomeric equilibrium of Chrysazine (CZ), a model antitumour drug. CZ exists exclusively in its normal form (N) in the ground state. However, in the excited state, the excited N* form undergoes ESIPT along with its pre-existing intramolecular hydrogen bonds, giving the excited state prototautomer (T*). Accordingly, CZ shows a single absorption band due to N form, but two emission bands due to N* and T* forms. Facile prototautomerization of CZ is considerably inhibited when the dye gets bound to SCXn hosts. However, in spite of lower binding affinity, the inhibition is more profound with SCX6 host as compared to SCX4 host. For CD-CZ system, while prototautomerization process is hindered by the presence of β-CD, it remains unaffected in the presence of γCD. Reduction in the prototautomerization process of CZ by SCXn and βCD hosts is unusual, because T* form is less dipolar in nature than the N*, hence binding of CZ within relatively hydrophobic hosts cavities should have enhanced the prototautomerization process. At the same time, considering the similar chemical nature of two CD hosts, their effect on prototautomerization process of CZ would have also been similar. The atypical effects on the prototautomerization process of CZ by the studied hosts are suggested to arise due to the partial inclusion or external binding of CZ with the hosts. As a result, there is a strong possibility of intermolecular H-bonding interaction between CZ dye and the functional groups present at the portals of SCXn and βCD hosts. Formation of these intermolecular H-bonds effectively causes the pre-existing intramolecular H-bonding network within CZ molecule to become weak, and this consequently reduces the prototautomerization process for the dye. Our results suggest that rather than the binding affinity between the dye and host, it is the orientation of CZ in the case of SCXn-CZ complexes and the binding stoichiometry in the case of CD-CZ complexes that play the predominant role in influencing the prototautomeric equilibrium of the dye CZ. In the case of SCXn-CZ complexes, the results obtained through experimental findings are well supported by quantum chemical calculations. Similarly for CD-CZ systems, binding stoichiometries obtained through geometry optimization studies on the complexes between CZ and CD hosts correlate nicely with the experimental results. Formation of βCD-CZ complexes with 1:1 stoichiometry while formation of γCD-CZ complexes with 1:1, 1:2 and 2:2 stoichiometries are revealed from geometry optimization studies and these results are in good accordance with the observed effects by the βCD and γCD hosts on the ESIPT process of CZ dye.

**Keywords :** intermolecular proton transfer, macrocyclic hosts, quantum chemical studies, photophysical studies
**Conference Title :** ICPCPB 2019 : International Conference on PhotoChemistry and PhotoBiology
**Conference Location :** Dubai, United Arab Emirates
**Conference Dates :** November 07-08, 2019