Commun. Comput. Chem. Vol.5, No.1, pp.1-9
doi: 10.4208/cicc.2017.v5.n1.1 April 2017

COMMUNICATION

A possible attributions of excited-state process for PIP and PIP-c system in methanol solvent

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Received 10 March 2017; Accepted (in revised version) 10 April 2017

Abstract: In this work, based on the DFT/TDDFT methods, we theoretically studied isomerides (2-phenylimidazo[4,5-b]pyridine (PIP) and 2-(phenyl)imidazo[4,5-c]pyridine (PIP-c)) about their excited state behavior in methanol solvents. Via comparing potential energy barriers, we deem that the single emission for these two systems should be attributed to the normal fluorescence mentioned in previous experiments if ESIPT could not occur. While if the potential barriers are suitable for ESIPT, the non-radiative path should be great mechanism in the excited state. Intersection and intersystem crossing could successfully explain the single fluorescence phenomenon for PIP and PIP-c system.

AMS subject classifications: **65D18, 78M50, 74E40**

Keywords: Hydrogen bond, ESIPT, potential energy barrier, MOs.

Excited state intra- or inter- molecular proton transfer (ESIPT) reaction is the initial event of numerous photo-physical and photochemical processes exiting in nature, and it crucial in chemistry [1-5]. In addition, because of the transient property of its ground state, molecules containing ESIPT has been used in several applications. The basic photophysical principle of ESIPT refers to a hydrogen transfer from proton donor to proton acceptor, which leads to a corresponding balance between enol and keto tautomers, stimulating a dual emission and large Stocks Shifts [6-8]. Based on excitation, electrons are facilitated to the single excited state of enol structure form enol*. In turn, the ultrafast ESIPT happens forming keto* configuration. In general, due to their structures, the keto* emits a low energy than enol* tautomer. Thus two fluorescence bands are observed and a broader range of the steady-state emission can be

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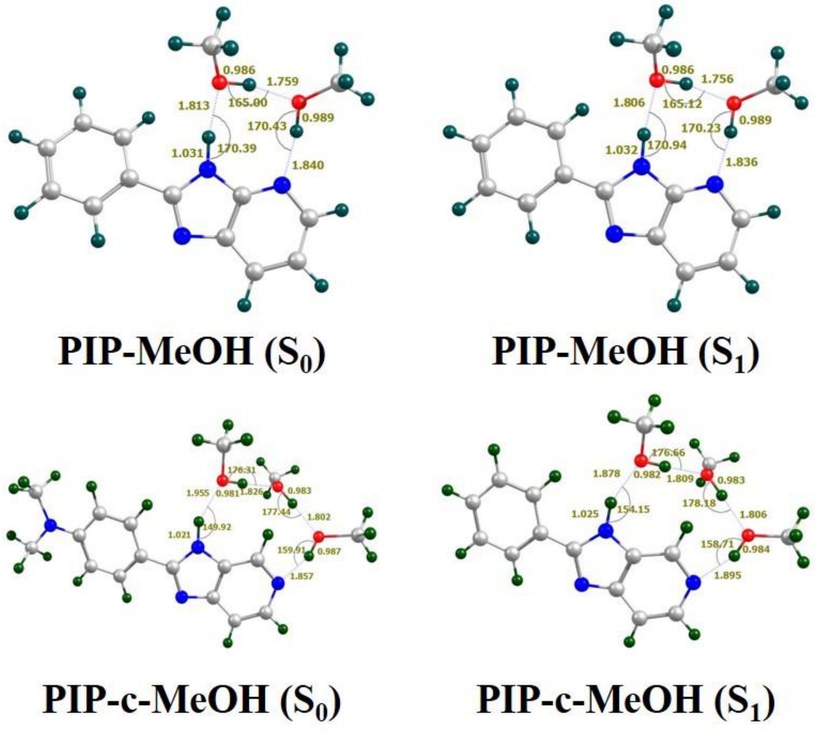
*Corresponding author. *E-mail address*: songpeng@lnu.edu.cn (S. Peng) covered, making these ESPT molecules suitable for optical chemosensors, white emitting OLEDs, material chemistry and UV filters, among other applications [9-15]. Microenvironment is a key factor for maintaining normal cell metabolism, which abnormal changes might lead to cytopathy [16-18]. As a kind of biologically active system, 2-phenylimidazo[4,5-b]pyridine (**PIP**) and 2-(phenyl)imidazo[4,5-c]pyridine (**PIP-c**) have been tested to be the inhibitor for Aurora-A, Aurora-B and Aurora-C kinases [19-21], which have been also certified to be good probes for microenvironment [18]. Krishnamoorthy and co-workers investigated these two system experimentally and found that only single emission in polar protic methanol solvent, which is different from 2-(4′-N,N-Dimethylaminophenyl)imidazo[4, 5-b]pyridine and 2-(4′-N,N-dimethylaminophenyl)imidazo[4,5-c]pyridine containing two emissions [19, 20]. Recently, Zhao *et al*. have proved that the rotation reaction do not exist in the S_1 state [22], that is to say, **PIP** and **PIP-c** should have familiar properties with 2-(4′-N,N-Dimethylaminophenyl)imidazo[4, 5-b]pyridine and 2-(4′-N,N-dimethylaminophenyl)imidazo[4,5-c]pyridine. Thus why **PIP** and **PIP-c** only own single fluorescence is our focus in this present work.



PIP-MeOH (S_0) **PIP-MeOH (S_1)**

PIP-c-MeOH (S_0) **PIP-c-MeOH (S_1)**

Figure 1: The forms for **PIP** and **PIP-c** systems in methanol (MeOH) solvents. Herein, two MeOH molecules connecting with **PIP** (**PIP-MeOH**) and three MeOH molecules connecting with **PIP-c** (**PIP-c-MeOH**) should be the most stable configurations, respectively.