



# Intramolecular hydrogen bonding promoted excited state double proton transfer mechanism based on a typical molecule: Porphycene

Yumei Dai<sup>a</sup>, Mengru Zhang<sup>a</sup>, Meixia Zhang<sup>b</sup>, Liting Sun<sup>c</sup>, Jia Meng<sup>a</sup>, Peng Song<sup>b,d,e,\*</sup>

<sup>a</sup> Normal College, Shenyang University, Shenyang 110044, China

<sup>b</sup> College of Physics, Liaoning University, Shenyang 110036, China

<sup>c</sup> Mechanical Engineering College, Shenyang University, Shenyang 110044, China

<sup>d</sup> Liaoning Key Laboratory of Semiconductor Light Emitting and Photocatalytic Materials, Liaoning University, Shenyang 110036, China

<sup>e</sup> State Key Laboratory of Molecular Reaction Dynamics, Dalian, China

## ARTICLE INFO

### Article history:

Received 7 October 2017

Received in revised form 13 April 2018

Accepted 22 April 2018

Available online 24 April 2018

### Keywords:

Excited state intramolecular proton transfer

Electronic Spectrum

Frontier molecular orbital

Potential energy surface

## ABSTRACT

The double excited state intramolecular proton transfer (ESIPT) mechanisms of porphycene, were theoretically studied. The primary bond lengths, IR vibrational spectra and hydrogen-bond energy indicate that the intramolecular hydrogen bonds were strengthened in the first excited state, which facilitate the ESIPT processes. To elucidate the proposed mechanism, the potential-energy surfaces of the ground state and first excited state were constructed as functions of N–H bond lengths and its relative torsional angle rotation. The intramolecular proton transfer of porphycene is more likely to occur through lengthwise pathway and proceed in the concerted coordinated transfer manner.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

In recent years, photoinduced proton transfer has been recognized for its importance in physics, chemistry and biology [1–10]. The study of excited state intramolecular proton transfer (ESIPT) processes has been one of the most active areas of research since Weller et al. observed the phenomenon experimentally [11]. ESIPT signifies the transfer process of a hydroxyl (or amino) proton to an oxygen or nitrogen acceptor atom within a hydrogen bond already formed in the electronic ground state. Shifts in electron density after electronic excitation lead to a significant enhancement of the acidity of the proton-donating group and the basicity of the acceptor group, which facilitates intramolecular proton transfer [12–18]. The ESIPT process exists in nature, and is an elementary proton transfer type [19–21]. To date, it has been reported often in experimental and theoretical processes [22–29].

For cases involving more than one proton, which is one of the fundamental chemical reaction, the transfer mechanism is complicated and multidimensional. Few systems have been reported that exhibit multiple proton/hydrogen transfer. Tetraproton transfer has been detected in calix[4]arenes and in the 7-hydroxyquinoline·(NH<sub>3</sub>)<sub>3</sub> complex [30]. Double-proton transfer has been investigated extensively, such as in benzoic acid dimers [31]. It has been difficult to establish the proton-

donor mechanism because of the instantaneous condition of a multiple proton transfer process. Multiple proton transfer is classified by concerted and stepwise mechanisms, as reported by Schowen [32]. In the last few decades, an investigation of porphyrin **1** has manifested that porphyrin is a useful double-proton transfer model where tautomerization involves two inner-cavity hydrogen atoms. Braun et al. demonstrated that the porphyrin double-proton transfer mechanism is stepwise, and converts *trans* tautomer into its chemically equivalent *cis* form [33–35].

In 1986, Vogel et al. synthesized porphycene **2** (the first constitutional isomer of porphyrin), which stimulated an increasing interest in the study of its mechanism and application [36]. Porphycene still remains the essential structural element as porphyrin with four pyrrole rings, four methine units, and an N4 coordination site [37,38]. After photoexcitation, the intramolecular acid–base balance will be readjusted, the N–H group becomes more acidic with increasing proton-donating capacity and the nitrogen becomes more basic with increasing proton-accepting capacity. The question arises as to whether porphycene transfer is a sequence of single-proton translocations as the parent porphyrin or a synchronous process. It should also be established what kind of synchronous proton transfer will occur mostly. Hence, in 1997, infrared (IR), Raman, ultraviolet, site-selective fluorescence and fluorescence excitation spectra were measured by Malsch and Hohlneicher to derive force fields for the most probable tautomeric forms [39]. Thereafter, Kozłowski et al. concluded that *trans*–*trans* inner hydrogen migration in porphycene occurs via a two-step mechanism that involves a *cis*

\* Corresponding author at: College of Physics, Liaoning University, Shenyang 110036, China.

E-mail address: [songpeng@lnu.edu.cn](mailto:songpeng@lnu.edu.cn). (P. Song).

intermediate, which is similar to the related migration in porphyrin, by a scaled quantum-mechanical analysis of the Becke three-parameter Lee–Yang–Parr (B3-LYP)/6-31G\* force constants and a comparison of experimental information [40]. Gil and Waluk found that tautomerization proceeds as thermally activated synchronous double hydrogen tunneling experimentally and theoretically [41]. In 2014, Yoshikawa et al. found that double-proton transfer occurs predominantly through a concerted pathway via a second-order saddle-point structure and that a contribution of the stepwise mechanism increases with a temperature increase in the semiempirical PM6 method [42]. Porphycene proton transfer has been investigated extensively experimentally and theoretically. Because we can gain only indirect information from the spectroscopic technology mentioned above, the multiple proton transfer mechanism cannot be deciphered in detail.

To obtain a detailed ESIPT mechanism of porphycene that contains two protons, in this work, investigations based on density-functional theory (DFT) and time-dependent DFT (TDDFT) calculations were performed to reveal the plausible proton transfer mechanisms. The ground state ( $S_0$ ) or first excited state ( $S_1$ ) were optimized, and vertical excitation energies, steady-state absorption and fluorescence spectra, IR vibrational spectra, hydrogen-bond energies, frontier molecular orbitals and potential-energy surfaces (PESs) of  $S_0$  and  $S_1$  states were calculated. The calculated results were analyzed and provide the possibility and supplement on the ESIPT mechanism of porphycene molecule.

## 2. Computational Details

$S_0$  and  $S_1$  state geometric optimizations of porphycene were performed using DFT and TDDFT, respectively [43–47]. Becke's three-parameter hybrid exchange function with the B3LYP gradient-corrected correlation functional were used throughout. While optimizing the geometric structure, the diffuse functions for full characterization of the hydrogen-bond interactions were considered based on the 6-31 + G(d,p) basis set and no constraints were applied to the atoms, bonds, angles or dihedral angles in the  $S_0$  or  $S_1$  states during the geometric optimization [48,49]. All local minima were confirmed by the absence of an imaginary mode in the vibrational analysis calculations. The  $S_0$  and  $S_1$  PESs of porphycene were scanned by constrained optimizations and frequency analyses to obtain thermodynamic corrections in the corresponding electronic state, that is, the geometrical structures in the ground state and first excited state were optimized, keeping the N–H distance fixed at a series of values, at the TDDFT/B3LYP/6-31 + G(d,p) level.

Fine quadrature size 4 grids were used. Harmonic vibrational frequencies in the ground state and excited state were determined by diagonalization of the Hessian. The excited state Hessian was obtained by numerical differentiation of analytical gradients using central

differences and default displacements of 0.02 Bohr. IR intensities were determined from the gradients of the dipole moment. All electronic calculations were carried out by using the Gaussian 09 program suite [50].

## 3. Results and Discussion

### 3.1. Geometric Structures

The molecular structure of porphycene is shown in Fig. 1a. Its geometry in the ground state was optimized based on the B3LYP functional, 6-31 + G(d,p) basis set, without constraint of bonds lengths, angles and dihedral angles. Vibrational frequencies were calculated to analyze the optimized structures to confirm that the structures were in the local minima. The vertical excitation energy and the  $S_1$  structure of porphycene was performed based on the ground optimized structure using the TDDFT method. As proposed, the photo-induced proton transfer could take place through two pathways that are crosswise and lengthwise, respectively. For clarity, we labeled serial numbers on the atoms connected to the hydrogen bonds, as can be seen in Fig. 1b.

The primary bond lengths (Å) of porphycene in the  $S_0$  and  $S_1$  states are listed in Table 1. The calculated bond lengths of N4–H5, N9–H5, N16–H5, N23–H24, N16–H24 and N9–H24 of the porphycene in  $S_0$  state are 1.026, 2.468, 2.160, 1.026, 2.467 and 2.160 Å, respectively. Upon photo excitation to its  $S_1$  state, these bond lengths change to 1.026, 2.439, 2.191, 1.020, 2.427 and 2.201 Å, respectively. Hydrogen bonds N9···H5 and N16···H24 are found to be shortened, and hydrogen bonds N16···H5 and N9···H24 are elongated, which indicates that the intramolecular hydrogen bonds N9···H5 and N16···H24 are strengthened and that the hydrogen bonds N16···H5 and N9···H24 are weakened in the  $S_1$  state. The excited state intramolecular hydrogen bond can be expected to play an important role in the ESIPT process.

The phenomenon of hydrogen bond strengthening can also be explained by monitoring the vibrational spectral shifts. The calculated vibrational spectra of porphycene in the  $S_0$  and  $S_1$  states are shown in Fig. 2a. It should be noted that, only the characteristic vibrational modes of the functional groups involved in the formation of intramolecular hydrogen bonds are significantly responsible for the intramolecular proton transfer process [48]. Though the porphyrin-like molecules are notoriously sensitive to puckering distortions, the backbone distortion could be expected to play less role in characterizing the intramolecular proton transfer process, taking place in N–H···N functional groups in porphycene studied here. So two vibrational frequency regions should be focused on, that are 1350–1650  $\text{cm}^{-1}$  and 3300–3500  $\text{cm}^{-1}$ , respectively, which are simulated to be related to N–H···N vibrational modes. Vibrational frequency analysis demonstrated the formation of the intramolecular hydrogen bonds N–H···N. In detail, the stretching vibrational frequencies of N4–H5 and N23–H24 are located at 3382  $\text{cm}^{-1}$  in the  $S_0$

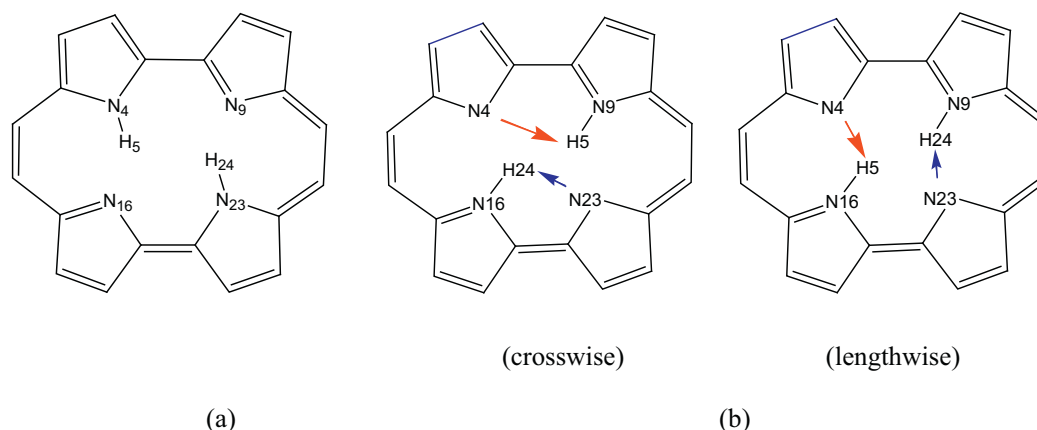


Fig. 1. (a) Molecular structures of porphycene and (b) two concerted possible double ESIPT processes of porphycene.

Download English Version:

<https://daneshyari.com/en/article/7668868>

Download Persian Version:

<https://daneshyari.com/article/7668868>

[Daneshyari.com](https://daneshyari.com)