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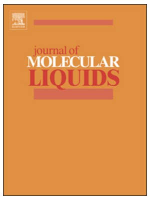

Zwitterions of the excited 4-([2,2′-bipyridine]-4-yl) phenol photoacid molecules: Formation and fluorescence

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ABSTRACT

Based on the density functional theory and time-dependent density functional theory, we have investigated the zwitterionic structure of the excited 4-([2,2′-bipyridine]-4-yl) phenol (bpy-phenol) photoacid molecules. The zwitterion can be formed stepwisely via a proton-coupled electron transfer (PCET) reaction in a H-bonded bpy-phenol…F^- complex and an intermolecular excited state proton transfer (ESPT) reaction between HF molecules and excited deprotonated anions of bpy-phenol. Supported by the results of Hirshfeld population analysis and electrostatic potential, a basic site was generated in the bpy residue due to the PCET process. With a proper F^- ions concentration, the ESPT reaction can be occurred with little barrier between the HF molecules and the bpy-phenol anions, leading to the generation of zwitterions. Moreover, the zwitterion fluoresces at 550 nm, which is longer than that of bpy-phenol anions at 490 nm. Our finding not only discovers the zwitterionic process of photoacid molecules, but also pioneers a frontier field of activity study after PCET reactions.

1. Introduction

Proton-coupled electron transfer (PCET) reactions exist widely in activities of biology and chemistry, such as photosynthesis, respiration and solar fuel cells [1–4]. According to previous studies, the mechanism of PCET could be as that protons and electrons transfer concertedly or stepwisely [5]. PCET reactions are sensitive to electronic structures of molecules and usually have close relations with H-bonds [6–8]. In general, the overall strength of H-bonds will be enhanced or weakened after optical excitation, resulting in photophysical and photochemical changes, such as intramolecular charge transfer (ICT), photo-induced electron transfer (PET), fluorescence resonance energy transfer (FRET), excited state proton transfer (ESTP), etc. [9–15] H-bonds often provide pre-set pathways for intermolecular ESPT, a common phenomenon in photoacid-base H-bonding complexes [11,13,16]. Photoacids own greater ability to provide protons after absorbing photons. However, some photoacids not only have acidic sites to be deprotonated but also have basic sites to be protonated [17–18]. Within such kind of photoacids, besides intermolecular ESPT, ICT can also occur. As such, PCET in a photoacid-base complex is featured by an intermolecular ESPT following an ICT within hundreds of femtoseconds, which makes the complex stay in a state of charge separation [19]. The nature of this charge separation is the spirit of photosynthesis. However, few studies focus on the events after the PCET charge separation process, although they are important in the biological and material fields.

Charge-separation configurations after PCET, known as zwitterions, are ubiquitous in chemical and biological processes [20–22]. Some amino acids and neurotransmitters have no net charge at physiological conditions, but they exist as zwitterions with the carboxyl deprotonated and one of the nitrogen atoms protonated [23]. Due to favorable noncovalent interactions, the zwitterionic structures are also crucial for self-assembly and design of conductive materials [24]. The prototypes of these zwitterions share one common feature that the acidic site and the basic site are located in the same molecule but at opposite positions. However, the zwitterionic forms of photoacids with both acidic sites and basic sites have received relatively little attention. It is therefore interesting and necessary to extend the studies on the capabilities and characteristics of the photoacids in their zwitterionic forms, except the common features such as proton pumps and fluorescent indicators.

Recently, a new synthetic photoacid, 4-([2,2′-bipyridine]-4-yl) phenol, has been reported by Sandeep Verma et al. [18] This photoacid is a typical phenol derivative with both acidic and basic sites, and can also be viewed as an analogue of tyrosine. For simplicity, we termed it as

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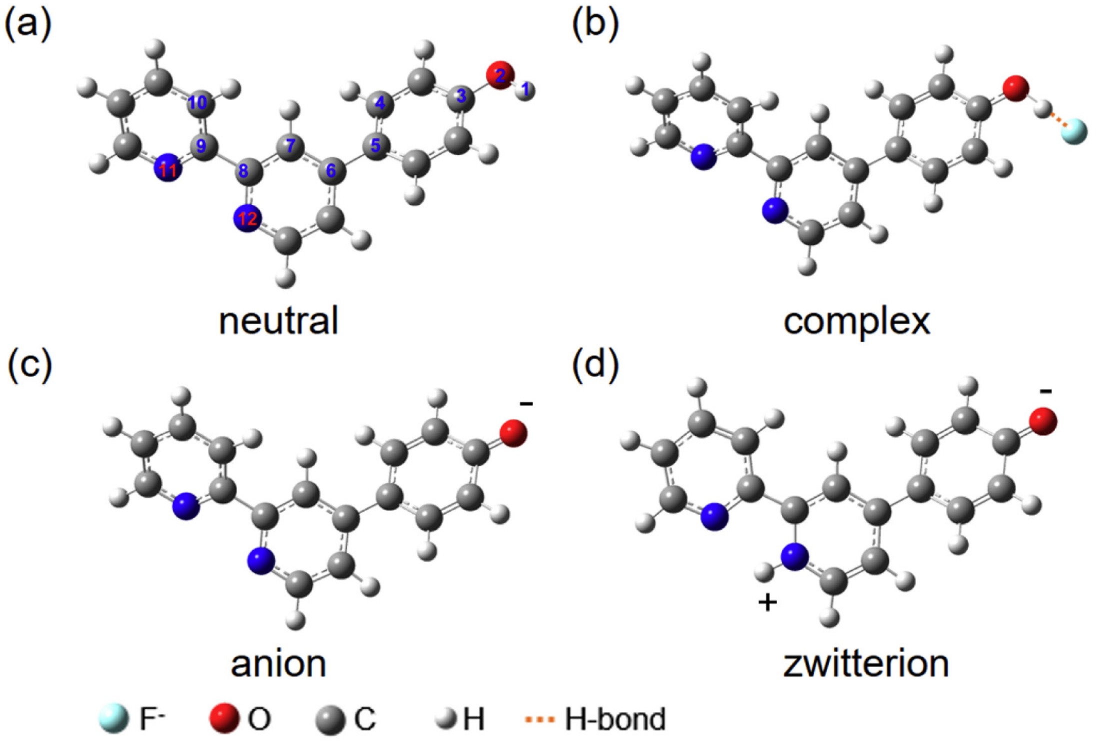

Fig. 1. Schematic illustration of bpy-phenol in the form of (a) neutral, (b) complex, (c) anion and (d) zwitterion.

bpy-phenol below. It can be used as anion probes, especially for F^- anions. In the above-mentioned work, photoexcitation of the bpy-phenol molecule led to a PCET reaction including an ICT from phenol to the bpy residue and a proton transfer from the phenol to the F^- ion. The timescales of ESPT was 150 femtoseconds, indicating a strong H-bonding effect between the phenol hydroxyl and the base F^- ion [25]. However, the fluorescent phenomena in this experiment were unique. The three emission bands peaking at 400, 490 and 550 nm were assigned to the neutral, deprotonated anionic and H-bonding complex form of bpy-phenol, respectively. According to the H-bonding effects on spectra, it is uncommon for the H-bonding complex to emit a lower energy photon than the anionic one [8,14,26–27]. Such a rare experimental result means that there is lying something undetected for the bpy-phenol molecule after the PCET reaction, which deserves further investigation.

In this work, density functional theory (DFT), time-dependent DFT [28] (TDDFT) and wave function analysis [29] (WFA) methods have been used to explore the unclear fluorescent mechanism of the newly synthesized bpy-phenol molecule. Results from Hirshfeld population analysis [30] (HPA), the calculated electrostatic potential [31] (ESP), potential energy surfaces (PESs) and absorption and emission spectra, all evidenced and supported that a bpy-phenol zwitterion has been generated after the PCET reaction, which, instead of the H-bonding complex, is responsible for the emission band centering around 550 nm.

2. Computational details

All theoretical calculations were performed by dispersion-corrected [32] DFT and TDDFT methods and carried out in Gaussian 16 program suite [33]. The HPA and ESP results were obtained via Multiwfn suite [34]. All the molecular geometries in the ground S_0 state and the excited S_1 state were fully optimized without any constraints at the level of M06-2X [35] /6-311 + G** [36] and TD-M06-2X/6-311 + G**, respectively. Vibrational frequency calculations have been used to analyze the optimized structures to conform that these structures corresponded to the local minima with no imaginary frequency. The excited-state PESs along two proton transfer coordinates were obtained at TD-M06-2X/TZVP [37] level. The absorption and emission spectra were calculated by TD-PBE0 [38] method with TZVP basis set. In all the calculations, the acetonitrile solvent was selected and performed with the continuum solvation model based on solute electron density (SMD) method [39].

Table 1
Primary bond length (Å), dihedral angle (°) and relative energy (kcal/mol) of the neutral and zwitterion of bpy-phenol in the S_0 and S_1 states. δ: dihedral angle. E: the amount of energy relative to the S_0 state of the neutral form, only including the neutral and zwitterion of bpy-phenol due to the same numbers of atoms. Atom labels are marked in Fig. 1.

Electronic state	Neutral		Complex		Anion		Zwitterion	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
H-bond	–	–	1.252	1.016	–	–	–	–
H_1-O_2	0.966	0.971	1.097	1.365	–	–	–	–
O_2-C_3	1.358	1.332	1.321	1.274	1.266	1.245	1.252	1.243
C_5-C_6	1.482	1.403	1.478	1.421	1.468	1.439	1.454	1.436
C_8-C_9	1.494	1.492	1.494	1.486	1.495	1.467	1.485	1.452
δ(C_4-C_5-C_6-C_7)	−33.1	−0.5	−30.9	−0.5	−26.1	−13.8	−28.7	−14.4
δ(C_7-C_8-C_9-C_{10})	−34.1	−33.4	−35.2	−26.4	−35.1	−14.7	9.6	0.0
E	0.0	93.7	–	–	–	–	8.8	69.5