



# A two-channel mechanism for the asymmetric excited-state intramolecular double proton transfer in a hydroxyflavone derivative

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## ABSTRACT

The excited-state proton transfer (ESPT) mechanism of 3,7-dihydroxy-2-phenyl-6-acetyl-4H-chromen-4-one (DPACO) fluorophore was studied by the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) with CAM-B3LYP functional and 6–31 + G(d,p) basis set. The computation levels are reliable as evidenced by the accordance between theory and experiment. In the ground state of DPACO, two intramolecular hydrogen bonds were formed. After photo-excitation, the electron density redistributions provide the driving force for hydrogen-bonding strengthening and ESPT. The constructed potential energy surfaces (PESs) along proton transfer (PT) coordinates indicate that two PT channels exist in the excited state. Among various PT tautomers, T4\* is theoretically assigned as the main fluorescence emitter, while the low fluorescence quantum yield possibly correlate with the accelerated internal conversion pathway in the PT tautomer T6\*.

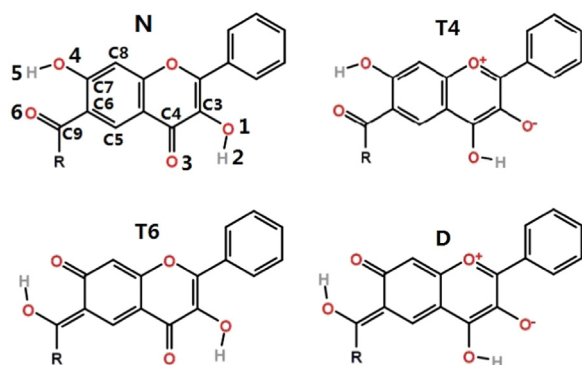
## 1. Introduction

Excited state proton transfer (ESPT) reaction, one of the most elementary processes in chemistry and biology [1–10], has attracted tremendous attention since the first experimental observation of the phenomenon by Weller [11,12]. ESPT has been widely observed and applied in a variety of areas including organic light emitting devices [13–15], photoswitches [16], laser dyes [17], fluorescent sensors [18], drug delivery [19], etc. Systems undergoing ESPT usually comprise proton donor and acceptor groups in close proximity through intra- or intermolecular hydrogen bonds. Common proton donor can be hydroxyl or amino group while common proton acceptor can be carbonyl oxygen or pyridinyl nitrogen atom. Being a unique site-specific interaction, hydrogen bonding plays important role in excited-state dynamical processes of molecules [20]. Electronic excited-state hydrogen bonding should have effects on many photophysical or photochemical processes such as fluorescence quenching [21], photoinduced electron transfer [22] and ESPT [23,24], etc. Recently, Han and coworkers have provided new insight into the influence of hydrogen bonding on photodynamical processes in the electronic excited state [21,22,25–27]. On this account, many processes involving excited-state hydrogen bonding should be revisited.

Hydroxyflavone derivatives have important biological applications

[28,29] and also serve as model molecules for ESPT researches [30–35]. Recently, Serdiuk and Roshal have synthesized a series of new hydroxyflavone derivatives, including 3,7-dihydroxy-2-phenyl-6-(3-phenylpropanoyl)–4H-chromen-4-one (abbreviated as DPPCO), with the aim to investigate the excited-state intramolecular double proton transfer (ESIDPT) [30]. In this work, we truncated DPPCO to DPACO by substituting the phenylpropanoyl group with acetyl group for calculation cost consideration. Structures of all possible DPACO tautomers are shown in Fig. 1, where ‘N’ represents the normal form, ‘T4’ or ‘T6’ represents the tautomerization occurs approximate to carbon C4 or C6, and ‘D’ represents tautomerization occurs on both sites. Unless specifically stated, ‘N\*’, ‘T4\*’, ‘T6\*’ and ‘D\*’ represent corresponding stable structures in the excited state of S1. DPPCO (or DPACO for the truncated one) has two intramolecular hydrogen bonding sites and emits fluorescence with large Stokes shift ( $\Delta\nu = 10940 \text{ cm}^{-1}$ ), but the low fluorescence quantum yield suggests existence of an efficient dark deactivation pathway. Time-resolved fluorescence spectroscopy of DPPCO showed that there are two decay components with lifetimes of  $\sim 25 \text{ ps}$  and  $5.89 \text{ ns}$ . It was experimentally proposed that the short decay component corresponds to T6\* and the long decay component corresponds to D\*. As pointed out by the original authors, the two proton transfer (PT) sites are asymmetric, and they excluded the possibility of emission from T4\* base on their analysis of the steady-state and time-

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**Fig. 1.** Structures of DPACO ( $R = \text{CH}_3$ ) and DPPCO ( $R = (\text{CH}_2)_2\text{Ph}$ ) in N, T4, T6, and D forms. Also atomic numberings are labeled in N form structure.

resolved spectroscopy [30]. But is the PT process in O1-H2-O3 site really suppressed by that in O4-H5-O6 site? What is the relationship between the processes in the two PT sites? In order to get more insight into these ESPT processes, we carried out theoretical research on PT mechanism of DPACO fluorophore. All possible tautomers of DPACO in electronic ground and excited states have been optimized. Frontier molecular orbitals, Mulliken and NPA charge distribution, electronic vertical excited energies (EVEEs) were calculated. The 2-dimensional potential energy surfaces scanned along two PT coordinates as well as transition state optimization results indicate a two-channel ESPT mechanism, somewhat different from the experimental suggestion.

## 2. Theoretical method

All calculations were performed using Gaussian 16 program suite [36]. Density functional theory (DFT) [37] and time-dependent DFT (TD-DFT) [38] were used for ground-state and excited-state geometric optimizations as well as energy calculations. The TD-DFT method has been shown to be a very powerful tool to describe hydrogen bonding and PT reactions in the excited state [22,25,26,39–42]. Becke three-parameter hybrid exchange functional with Lee-Yang-Parr gradient-corrected correlation functional in Handy and coworker's long-range-corrected version, the CAM-B3LYP [43] functional was used with the 6–31 + G(d,p) basis set. All the optimized local minima and transition state geometries were confirmed by the vibrational frequency analysis. Methylcyclohexane was chosen as the solvent throughout our calculations. Linear response polarizable continuum model (LR-PCM) was used for EVEE calculations. Potential energy surfaces were relaxedly scanned along two generalized internal coordinates, PT1 and PT2, which are defined as  $\text{PT1} = R(\text{O1}, \text{H2}) - R(\text{H2}, \text{O3})$  and  $\text{PT2} = R(\text{O4}, \text{H5}) - R(\text{H5}, \text{O6})$ . Potential energy curves were also relaxedly scanned along dihedral angle C5-C6-C9-O6. Atomic numberings are depicted in Fig. 1. The integral accuracy was  $10^{-12}$  and DFT grid was ultrafine, as being the default settings in Gaussian 16.

Since relaxed scan of PES is very time-consuming, we have replaced the phenylpropanoyl group in DPPCO with the acetyl group in DPACO throughout our calculation. To confirm the rationality of such truncation, the EVEEs of DPPCO and DPACO have been listed and compared in supporting information (Table S1), which showed little difference as being within about 0.01 eV. Further, tautomers of DPACO have the same energy sequence with those of DPPCO (Table S2), which also proved the reliability of this treatment.

## 3. Results and discussion

### 3.1. Geometric structures

Key geometric parameters related to intramolecular hydrogen bonding were given in Table 1. All the optimized geometries were

**Table 1**

Key geometric parameters of optimized DPACO tautomers in S0 and S1. Units of internuclear distance 'R' and bond angle 'Alpha' are in (Å) and ( $^\circ$ ), respectively.

	N	N*	T4*	T6*	D*
R(O1,H2)	0.979	1.002	2.024	0.9927	1.967
R(H2,O3)	1.999	1.821	0.980	1.869	0.984
R(O1,O3)	2.613	2.523	2.615	2.543	2.584
Alpha(O1,H2,O3)	118.6	124.2	116.7	122.4	118.4
R(O4,H5)	0.993	1.011	1.007	1.574	1.451
R(H5,O6)	1.651	1.561	1.578	1.011	1.044
R(O4,O6)	2.546	2.491	2.501	2.506	2.434
Alpha(O4,H5,O6)	147.8	150.4	149.8	150.8	154.1

testified to be local minima by the absence of imaginary mode in vibrational frequency analysis. Note that T4, T6 and D tautomers have no corresponding optimized geometries in S0 while T4\*, T6\* and D\* do have in the S1 state. Since O1, H2, O3 belong to a five-member ring while O4, H5, O6 belong to a six-member ring, the hydrogen bonding distance in (O1,H2,O3) is longer than that in (O4,H5,O6), as being 1.999 to 1.651 (Å) in N, 1.821 to 1.561 (Å) in N\*, 2.024 to 1.578 (Å) in T4\*, 1.869 to 1.574 (Å) in T6\*, 1.967 to 1.451 (Å) in D\*, respectively. Therefore, the closer proximity in six-member ring can make ESPT reaction in O4-H5-O6 site more feasible. N form was testified to be the most stable tautomer in the ground state. After photo-excited to N\*, bond lengths of O1-H2 and O4-H5 elongate from 0.979 and 0.993 to 1.002 and 1.011 (Å), respectively. Bond lengths of O3...H2 and O6...H5 shorten from 1.999 and 1.651 to 1.821 and 1.561 (Å), respectively. The distances between (O1,O3) and (O4,O6) also shorten from 2.613 and 2.546 to 2.523 and 2.491 (Å), respectively. Meanwhile the bond angles of O1-H2...O3 and O4-H5...O6 increase from 118.6 and 147.8 to 124.2 and 150.4 ( $^\circ$ ), respectively. All these changes, as well as the vibrational frequency shifts shown in Fig. S1, indicate that the intramolecular hydrogen bonding of O1-H2...O3 and O4-H5...O6 are strengthened in N\* compared to those in N. The alteration in equilibrium geometry can facilitate ESPT reaction. This strengthening is caused by photoinduced charge redistribution, which is also the driving force for ESPT. More details about charge distribution will be discussed in Section 3.2.

### 3.2. Electronic spectra and charge distribution analysis

The EVEEs in optimized geometries were calculated and given in Table 2. For comparison, the experimental results are also shown. Calculated results show that two major absorption peaks, centered in 328 nm and 264 nm, originate from N-S0 to N-S1 and N-S0 to N-S5 electronic state transitions. This agrees well with experimental absorption peaks in 352 nm and 284 nm. N-S1 exhibits typical  $\pi-\pi^*$  character, which is composed mainly (88.8%) of highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) electronic excitation. As shown in Fig. 2, HOMO and LUMO exhibit significant charge redistribution character in O1, O3, O4 and O6 atoms. The Mulliken and NPA charge distributions in four ESPT-related oxygen atoms are given in Table 3. It can be seen that after photo-excitation, O1 loses more electron density than O4, meanwhile O3 acquires more electron density than O6, which indicates O1-H2-O3 site has more potential to undergo ESPT reaction.

Emission data were obtained by calculating the EVEEs of DPACO tautomers optimized in S1 with LR-PCM method and were shown in Table 2. The calculated emission peaks originated from the four tautomers are quite different. The emission peaks shift to red in sequence of N\*(384 nm), T6\*(461 nm), T4\*(554 nm) and D\*(677 nm). Emission peak from T4\* agrees best with the major fluorescence peak (562 nm) detected experimentally in Ref. [30]. As for emissions from other tautomers, no noticeable peak can be observed in the experimental steady-state emission spectra.

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