Heteroatom substitution effect on electronic structures, photophysical properties, and excited-state intramolecular proton transfer processes of 3-hydroxyflavone and its analogues: A TD-DFT study

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ABSTRACT

The effects of the electron-donating capacity altered by heteroatom substituents on the electronic structures, photophysical properties, and excited-state intramolecular proton transfer (ESIPT) processes of 3HX analogues (3HF, 3HQ, 3HTF, and 3HSO where X=O, NH, S, and SO₂, respectively) have been investigated by both static calculations and dynamic simulations using density functional theory (DFT) and time-dependent DFT (TD-DFT) methods at B3LYP/TZVP level for ground state (S₀) and excited-state (S₁), respectively. The static results indicate that the intramolecular hydrogen bonds of all molecules are strengthened in the S₁, confirmed by the red-shift of IR vibrational spectra and the topology analysis. Heteroatom substitutions cause the red-shift on enol absorption and keto emission spectra of 3HX with relatively larger Stoke shift corresponding to their HOMO–LUMO gaps compared with that of 3HF. Frontier molecular orbitals (MOs) show that upon the photoexcitation, the charge redistribution between the proton donor and proton acceptor groups have induced the ESIPT process. Moreover, the potential energy curves (PECs) of proton transfer (PT) processes of all molecules reveal that the PT processes of all molecules are most likely to proceed in the S₁ state because of low barriers and exothermic reaction. The chance of ESIPT for all molecules is in this order: 3HSO > 3HTF > 3HF > 3HQ. The results of dynamic simulations confirm that the ESIPT processes of all molecules easily occur with the ultrafast time scale (48, 55, 60, 70 fs for 3HSO, 3HTF, 3HF, and 3HQ, respectively). Furthermore, the PT time is anti-correlated with the electronegativity of heteroatoms in 3HX, supported by Mulliken analysis. The ESIPT process of 3HSO is the fastest among 3HX in accordance with its highest intramolecular hydrogen bond strength, lowest PT barrier, and highest exothermic reaction. Nevertheless, after the ESIPT is complete, the twisted structure of 3HSO has initiated the conical intersection, leading to no keto emission observed in the experiment.

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1. Introduction

Organic bifunctional molecules with an intramolecular hydrogen bonding, connected by proton donors such as –OH or –NH₂ groups and proton acceptors, for example, –C=O or –N= groups, can undergo an excited-state intramolecular proton transfer (ESIPT) process [1,2]. The ESIPT process is a keto-enol tautomerization, which is driven by the charge redistribution between the proton donor and the proton acceptor groups upon electronic excitation, described by the four-level photocycle of the ESIPT process (Scheme 1). Typically, the ESIPT process starts from photoexcitation of enol (E) form in the ground state to the excited state, the redistribution of electronic charge takes place, resulting in greater acidity of the proton donor

and the basicity of the proton acceptor of excited enol (E*) form [3–5]. As a result, a rapid proton transfer (PT) process occurs via the intramolecular hydrogen bonding from the proton donor to the proton acceptor which leads to the formation of excited keto (K*) form. After that, the K* form returns to the electronic ground state and releases a fluorescence. Since its keto (K) form is not thermodynamically stable, a back-proton transfer (BPT) usually occurs to its initial position (E form) [6]. This four-level photocycle brings the totally different electronic structures between the enol and keto forms, leading to unique photophysical properties as the dual emission and large Stokes shift (~200 nm) without self-absorption [6] which are useful characters for a lot of applications such as in fundamental photophysical dynamics studies, optoelectronic devices and laser application [2], light-emitting diodes [7] and especially in fluorescent probes [8,9].

Generally, the fluorescent probes in biological systems require highly sensitive to environmental and specific binding to analyst in

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Scheme 1. Diagram of the general ESIP, a proton donor (–OH)

and proton acceptor (C=O)

are circled with blue and red, respectively.

Fig. 1. Molecular structures of 3HX analogues, where X=O, NH, S, and SO₂ namely 3HF, 3HQ, 3HTF, and 3HSO.

cells [10,11]. The desirable characters for probing specific targets using chromophores in cells and tissue samples include absorption of visible light, emission at long wavelengths (preferably in red or near-infrared) with high fluorescence intensity [10–14]. Successful fluorescent probes have been reported such as the derivatives of fluorescein [15], rhodamine [16], coumarin [17,18], boron-dipyrromethene (BODIPY) [19], and cyanine [20]. Among the reported fluorescent probes, a flavonol family with ESIPT chromophore has emerged as a new potential class because of its unique photophysical properties and abundance in nature [21–24]. 3-Hydroxyflavone (3HF), one of the flavonol family as shown in Fig. 1 (when X=O), has been not only used as fluorescent probes but also as a model molecule to study the ESIPT process due to its unique large Stokes shift (190 nm) [25] and dual emissions [26–29]. However, a wider application of 3HF as a fluorescent probe has been limited due to its enol absorption and keto emission not being in the longer wavelength, the proper ratio of dual emission (N^*/I^*) and low intensity of fluorescence.

3HF derivatives with improved photophysical properties have been both experimentally and theoretically reported by many researchers [30–37]. Various 3HF derivatives can be obtained by substitutions of the electron donating groups (at the position 4', 2, 6, and 7 of 3HF). The introduction of electron donor at the position 4' of 3HF and replacing phenyl group with furanyl, thiophenyl, and benzofuranyl at position 2 not only shifts the enol absorption and keto emission spectra to longer wavelengths, but also strongly modulates the ESIPT behavior, resulting in increase of the ratio of the dual emission (N^*/I^*), as well as increase in intensity of fluorescence. By introduction of fused furan heterocycle (2-aryl-3-hydroxyfyrano[3,2-g]chromone) at position 6 and 7 of 3HF [38,39], the highly polarizable π -electron has improved photophysical properties in term of red-shifting of enol absorption and keto emission, leading to larger Stokes shift, and higher fluorescent intensity of 3HF derivatives with 3HF. For other 3HF derivatives, the substitutions of pyrazole and pyrrole at position 2 of 3HF, however, shift the enol absorption and keto emission to shorter wavelengths and decrease the fluorescent intensity, compared with 3HF [40–42].

As mentioned above, the substituent effects on the electronic structures and photophysical properties as well as the ESIPT behavior of 3HF derivatives have been intensively investigated by many researchers. So far, there are just a few reports on the heteroatom substitution effect on the electronic and photophysical properties as well as the occurrence of the ESIPT process. The nitrogen heteroatom substituted 3HF, namely 3-hydroxyquinolone (3HQ), was synthesized by Feng et al. [43] and their experimental results indicated that the higher electronegativity of the nitrogen atom in 3HQ reduced the Stokes shift, compared with that of 3HF. For other analogues of 3HF, the sulfur heteroatom substituted 3HF, 3-hydroxythioflavone (3HTF) was synthesized and its photophysical properties were characterized by Meng et al. [44] and the lower electronegativity of the sulfur heteroatom in 3HTF was somehow found to increase the Stokes shift, compared with those of 3HF and 3HQ. Moreover, the photophysical properties and the chance of the ESIPT process for 3HTF was inves-

Table 1

Calculated maximum wavelengths of enol absorption ($\lambda_{\max}$), oscillator strength (f), and the deviation between the calculated and experimental wavelength ($\Delta\lambda$) of 3HF, 3HTF, and 3HSO in cyclohexane and 3HQ in toluene computed using various TD-DFT methods with TZVP basis set.

TD-DFT	$\lambda_{\max}$ (nm)	f	MOs (%) Contribution)	$\Delta\lambda$ (nm)
3HF				
Experiment	340 [25]			
TD-B3LYP	343	0.513	HOMO → LUMO (98%)	3
TD-PBE0	333	0.488	HOMO → LUMO (98%)	−7
TD-M06-2X	304	0.549	HOMO → LUMO (97%)	−36
TD-CAM-B3LYP	309	0.543	HOMO → LUMO (96%)	−31
TD-LC-BLYP	278	0.598	HOMO → LUMO (90%)	−62
TD-LC-BLYP ($\mu=0.200$)	294	0.650	HOMO → LUMO (91%)	−46
TD-LC- ω PBE ($\mu=0.141$)	304	0.612	HOMO → LUMO (93%)	−36
3HQ				
Experiment	371 [43]			
TD-B3LYP	362	0.228	HOMO → LUMO (97%)	−9
TD-PBE0	361	0.232	HOMO → LUMO (97%)	−10
TD-M06-2X	356	0.221	HOMO → LUMO (97%)	−15
TD-CAM-B3LYP	356	0.221	HOMO → LUMO (97%)	−15
TD-LC-BLYP	349	0.218	HOMO → LUMO (97%)	−22
TD-LC-BLYP ($\mu=0.200$)	365	0.249	HOMO → LUMO (98%)	−6
TD-LC- ω PBE ($\mu=0.141$)	366	0.235	HOMO → LUMO (97%)	−5
3HTF				
Experiment	380 [44]			
TD-B3LYP	371	0.264	HOMO → LUMO (97%)	−9
TD-PBE0	370	0.270	HOMO → LUMO (97%)	−10
TD-M06-2X	364	0.257	HOMO → LUMO (97%)	−16
TD-CAM-B3LYP	364	0.253	HOMO → LUMO (97%)	−16
TD-LC-BLYP	357	0.245	HOMO → LUMO (97%)	−23
TD-LC-BLYP ($\mu=0.200$)	375	0.287	HOMO → LUMO (97%)	−5
TD-LC- ω PBE ($\mu=0.141$)	376	0.272	HOMO → LUMO (97%)	−4
3HSO				
Experiment	370 [44]			
TD-B3LYP	377	0.189	HOMO → LUMO (98%)	12
TD-PBE0	364	0.208	HOMO → LUMO (97%)	11
TD-M06-2X	329	0.175	HOMO → LUMO (67%)	−41
TD-CAM-B3LYP	332	0.172	HOMO → LUMO (84%)	−38
TD-LC-BLYP	290	0.224	HOMO → LUMO (59%)	−90
TD-LC-BLYP ($\mu=0.200$)	398	0.219	HOMO → LUMO (90%)	28
TD-LC- ω PBE ($\mu=0.141$)	429	0.159	HOMO → LUMO (93%)	59

tigated by DFT and TD-DFT methods by Sun et al. [45] and their results indicate that the substitution of sulfur heteroatom cause the red-shift of enol absorption and keto emission of 3HTF to longer wavelengths with larger Stokes shift, compared with those of 3HF and

Fig. 2. Optimized enol form in the S_0 state of 3HF, 3HTF, and 3HSO in cyclohexane and 3HQ in toluene computed at B3LYP/TZVP level. Intramolecular hydrogen bond distances are shown as dashed lines.

Table 2

Covalent bonds (O1–H1), intramolecular hydrogen bonds (O2...H1), the distances between heavy atoms (O1...O2) and selected dihedral angles ($^\circ$) of enol form of 3HF, 3HTF, and 3HSO in cyclohexane and 3HQ in toluene computed at TD-B3LYP/TZVP level.

	3HF		3HQ		3HTF		3HSO	
	S_0 state	S_1 state	S_0 state	S_1 state	S_0 state	S_1 state	S_0 state	S_1 state
Distance (Å)								
O1–H1	0.978	0.999	0.980	0.995	0.981	1.008	0.978	1.024
O2...H1	2.012	1.847	1.994	1.888	1.909	1.730	1.934	1.648
O1...O2	2.625	2.541	2.620	2.561	2.554	2.473	2.556	2.433
Bond angle ($^\circ$)								
O1H1O2	118	123	119	122	121	127	119	129
Dihedral angle ($^\circ$)								
O1C1C2X1	0.7	1.1	1.5	2.8	0.1	10.6	2.9	13.5
O1C1C5O2	0.3	0.5	0.6	1.6	0.7	8.2	0.5	8.3
C2C3C4C5	15.8	0.06	40.2	26.8	44.6	23.6	53.6	30.1

The X represents the heavy atoms of the investigated molecules (O3, N1, and S1 as shown in Fig. 2).

Fig. 3. The simulated IR spectra of enol form of all molecules both in S_0 state (black line) and S_1 state (red line). The vibrational bands of the O1–H1 stretching modes both in S_0 and S_1 states are labelled as black and red, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Selected bond critical point parameters (in a.u.) related to the hydrogen bonds of enol forms for all molecules.

Molecule	$\rho(r)$	H(r)	G(r)	$\nabla^2\rho(r)$	DI	$V(r)$	E_{HB}
3HF	0.038	-0.0025	0.034	0.125	0.092	-0.036	0.018
3HQ	0.035	-0.0011	0.031	0.120	0.086	-0.032	0.016
3HTF	0.049	-0.0083	0.043	0.138	0.112	-0.051	0.026
3HSO	0.056	-0.0146	0.050	0.142	0.129	-0.055	0.028

Fig. 4. Simulated enol absorption (black line) and keto emission spectra (blue line) of 3HF, 3HTF, and 3HSO in cyclohexane and 3HQ in toluene computed at TD-B3LYP/TZVP level. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)**Table 4**Simulated enol absorption maximum wavelengths ($\lambda_{\max}$), keto emission maximum wavelengths (λ_{emiss}), oscillator strength (f), molecular orbitals (MOs) contribution, and Stokes shifts of 3HF, 3HTF, and 3HSO in cyclohexane and 3HQ in toluene computed at TD-B3LYP/TZVP level.

Molecule	Enol Absorption			Keto Emission		Stokes shift (nm)
	$\lambda_{\max}$ (nm)	f	MOs (%) Contribution	λ_{emiss} (nm)	f	
3HF	343	0.513	HOMO $\rightarrow$ LUMO (98%)	528	0.446	185
3HQ	362	0.228	HOMO $\rightarrow$ LUMO (97%)	538	0.302	176
3HTF	371	0.264	HOMO $\rightarrow$ LUMO (97%)	638	0.282	267
3HSO	377	0.189	HOMO $\rightarrow$ LUMO (98%)	791	0.156	414

3HQ. Sulfone heteroatom substitution of 3HF, namely 3-hydroxy-2-phenyl-4H-thiochromen-4-one 1,1-dioxide (3HSO) was reported to have a longer wavelength of enol absorption compared with that of 3HF however, its keto emission was not observed, implying that the ESIPT process might not take place [44].

Following the requirement of fluorescent probes as longer wavelength of enol absorption and near IR keto emission leading to a larger Stokes shift and high intensity of keto emission, most of the reports have only dealt with the photophysical properties of 3HF derivatives. Whereas the in-depth insights into the effects of the heteroatom substitution on the electronic structures, photophysical properties, and the chance of the ESIPT process, as well as the PT time of 3HQ, 3HTF, and 3HSO, have not been systematically studied. Nowadays, computational chemistry has become an effective tool not only for obtaining deep information on the electronic and photophysical properties but also predicting useful information where it cannot be accessible by means of experimental methods. Therefore, in this study, we systematically investigate the effect of different heteroatom

Fig. 5. Diagram of calculated HOMO and LUMO energy levels, HOMO-LUMO gaps (eV), and frontier molecular orbital of the enol and keto forms of 3HF, 3HTF, and 3HSO in cyclohexane and 3HQ in toluene computed at TD-B3LYP/TZVP level.

Fig. 6. The potential energy curves (PECs) of PT reactions both in S_0 and S_1 states of 3HF, 3HTF, and 3HSO in cyclohexane and 3HQ in toluene computed at TD-B3LYP/TZVP level.

Table 5

The relative PT barriers and PT reaction energy (ΔE_{rxn}) both in S_0 and S_1 states of 3HF, 3HTF, and 3HSO in cyclohexane and 3HQ in toluene computed at TD-B3LYP/TZVP level.

Molecule	PT barrier (kcal/mol)		ΔE_{rxn} (kcal/mol)	
	S_0 state	S_1 state	S_0 state	S_1 state
3HF	13.13	2.88	10.89	-4.81
3HQ	11.65	3.62	8.45	-4.05
3HTF	12.56	1.99	11.76	-7.25
3HSO	21.06	0.87	20.95	-10.26

substitutions on the electronic structures, photophysical properties, and the chance of ESIPT processes of all molecules (3HF, 3HQ, 3HTF, and 3HSO) and particularly why 3HSO does not exhibit keto emission in the experiment. By using density functional theory (DFT) and time-dependent DFT (TD-DFT), the electronic structures and the potential energy curves (PECs) along the proton transfer (PT) process of 3HF and its analogues both in the ground state (S_0) and the excited-state (S_1) will be analyzed. Furthermore, the details of dynamics simulations such as PT time, PT probability, and the change of interested dihedral angle during the simulation time, will be also carried out using on-the-fly dynamic simulations.

2. Computational details

2.1. Static calculations

The S_0 state optimizations of enol form of all molecules were carried out using seven DFT methods with various exchange-correlation functionals, which consist of three hybrid functionals (B3LYP [46], PBE0 [47], and M06-2X [48]) and four long-range corrected hybrid functionals (CAM-B3LYP [49], LC-BLYP [50], LC-BLYP

($\mu=0.200$) [51], and LC- ω PBE ($\mu=0.141$) [52,53]) with triple- ζ valence quality with one set of polarization functions (TZVP) basis set [54]. For the hybrid functional, the B3LYP is Hybrid Becke, 3-parameter, Lee-Yang-Parr gradient-corrected correlation potential with 20% Hartree-Fock (HF) exchange energy. The PBE0 is the mixed functional between Perdew-Burke-Ernzerhof and 25% HF exchange energy. The M06-2X are the hybrid functional of Truhlar and Zhao and 54% HF exchange energy. Four long-range correlated hybrid functionals include the CAM-B3LYP, the LC-BLYP, the LC- ω PBE, which are Handy, Hirao, and Henderson. The LC-BLYP and the LC- ω PBE, the damping parameter μ is set to 0.330 and 0.200 bohr^{-1} for the LC-BLYP and 0.141 bohr^{-1} for the LC- ω PBE which μ parameter is the term for correcting long-range interaction to describe via HF exchange. The effect of solvents such as cyclohexane and toluene, corresponding to the experiment [25,43,44], was taken into account by SCRF method through the non-equilibrium and equilibrium polarizable continuum model calculations using the polarizable continuum model (PCM) for all calculation [55]. All optimized structures were confirmed to be local minima by normal mode analysis with all positive frequencies. To reveal the influence of DFT functional on the absorption spectra associated with the electronic transition of the enol form of all molecules, the enol absorption spectra were performed using various TD-DFT methods. The absorption and emission spectra as well as the orbital contributions were generated with GaussSum package [56]. From the method of choice, among seven tested functionals, the most suitable method for reproducing the enol absorption spectra of all molecules is the B3LYP because this method provides the most satisfactory agreement with the experimental data. Moreover, previous studies have been proven that the B3LYP and TD-B3LYP functionals with TZVP basis set are suitable to describe electronic and photophysical properties as well as the PT process of ESIPT molecules [29,57-62]. Therefore, the B3LYP was further em-

Fig. 7. The potential energy curves (PECs) of PT reactions and the vertical energies both in the S₀ and S₁ states of all molecules computed at TD-B3LYP/TZVP level.

Table 6

Summary of the excited-state dynamics simulations performed at the TD-B3LYP/TZVP level.

Molecule	Reaction		PT time (fs)	Probability
	ESIPT	No PT		
3HF	19	6	60 (47–67)	0.76
3HQ	6	19	70 (51–150)	0.24
3HTF	12	13	55 (45–63)	0.48
3HSO	23	2	48 (42–55)	0.92

employed to optimize the enol form in the S₁ state and the keto form both in S₀ and the S₁ states of all molecules.

The S₀ and S₁ state optimizations of enol and keto forms of all molecules were carried out using B3LYP and TD-B3LYP, respectively. The strength of hydrogen bond of all molecules was investigated by the important parameters which involved the ESIPT process, including the O1–H1, O2...H1, and O1...O2 distances, the infrared (IR) spectra of the O–H bond both in S₀ and the S₁ states as

well as the topology analysis based on the theory of quantum theory of atoms in molecules (QTAIM) with the tool of Multiwfn [63] which was employed in previous studies [64,65]. Calculations of vertical excitation energies were done from the S₀ state optimized structure using TD-B3LYP with five low-lying singlet states absorbing transition. Moreover, the keto emissions of all molecules were simulated from the S₁ state. Furthermore, frontier molecular orbitals (MOs) of all molecules both the enol and keto forms were analyzed to provide information about the charge distribution upon photoexcitation. To further investigate the chance of PT process, the S₀ state energy curve (GS-PECs) and the S₁ state potential energy curves (ES-PECs) of all molecules along PT process coordinate were scanned by constraining optimizations with fixed the covalent (O1–H1) bond distance at a series of values. This approach was used in the previous studies and shown to be reliable in providing qualitative energetic pathways for PT process [62,66–70]. In addition, to obtain the thermodynamic information, the ESIPT reaction energies were calculated from the S₁ state optimization of keto forms of all molecules. All calculations were performed using Gaussian 09 program package [71].

Fig. 8. Snapshots along with the ESIPT dynamic simulations at a different time of 3HQ (left: front view, right: side view).

Fig. 9. Average values over all ESIPT trajectories of 3HQ (a) time evolution of breaking and forming bonds (b) average relative energies of the S_0 and S_1 states, and the energy difference between the S_1 and S_0 states (S_1-S_0), and (c-e) three different dihedral angles of 3HQ.

Fig. 10. Snapshots along with the ESIPT dynamic simulations at a different time of 3HTF (left: front view, right: side view).

2.2. Dynamics simulations

To obtain the information of the proton transfer, the S_1 state dynamic simulations of 3HF, 3HQ, 3HTF, and 3HSO were carried out using TD-B3LYP/TZVP level. Twenty-five trajectories as a representative set for each system were generated using a harmonic-oscillator Wigner distribution for each normal mode, as implemented in the NEWTON-X program [72,73] interfaced with the TURBOMOLE 6.3 program package [74]. Solving Newton's equation of nuclear motion was achieved by the Velocity-Verlet algorithm [22]. The Born-Oppenheimer energies and gradients were obtained at each time step by mean of the TD-B3LYP method, which has been tested and used in dynamic simulations in previous studies [60-62,66-68,75]. All trajectories for each complex were simulated with a time step of 1 fs with the maximal duration of 500 fs, which is long enough to cover the pre- and post-PT regimes. In addition, each trajectory was categorized into two types of process: (1) 'ESIPT' when the PT process is observed and (2) 'No PT' when the PT process cannot be observed within the given simulation time. To obtain the dynamic information such as PT time (determined by the intersection point of average $O1\cdots H1$ breaking and $O2\cdots H1$ forming bond as a function of time), energy difference between the S_0 and the S_1 states, PT probabilities,

and time evolutions in the S_1 state on PT process, all active ESIPT trajectories were analyzed.

3. Results and discussion

3.1. Effect of DFT functional

The suitable choice of DFT and TD-DFT is very important to accurately explain the electronic structures, photophysical properties, and the occurrence of ESIPT process of 3HF and its analogues (3HQ, 3HTF, and 3HSO). For choosing the suitable method, the structural optimization with seven different DFTs (B3LYP, PBE0, M06-2X, CAM-B3LYP, LC-BLYP, LC-BLYP ($\mu=0.200$), and LC- ω PBE ($\mu=0.141$)) with TZVP basis set were carried out to obtain the S_0 structures and to reveal the functional influence on the enol absorption spectra of 3HF, 3HQ, 3HTF, and 3HSO using TD-DFT. The suitable method must provide good simulated result in term of reproducing the enol absorption spectra from the experimental data. The comparison of various TD-DFT calculations in terms of absorption (λ_{max}), oscillator strength (f), and the deviation between the simulated and experimental absorption wavelength ($\Delta\lambda$) of all investigated molecules in enol forms are listed in Table 1 and plotted in Fig. S1 in Electronic Supplementary Information (ESI). For 3HF, TD-B3LYP provides most agreement simulated absorption spectra compared to

Fig. 11. Average values over all ESIPT trajectories of 3HTF (a) time evolution of breaking and forming bonds (b) average relative energies of the S_0 and S_1 states, and the energy difference between the S_1 and S_0 states (S_1-S_0), and (c-e) three different dihedral angles of 3HTF.

Fig. 12. Snapshots along with the ESIPT dynamic simulations at a different time of 3HSO (left: front view, right: side view).

the absorption spectra from the experimental data with the smallest $\Delta\lambda$ value whereas, other functionals provide larger $\Delta\lambda$ values. For 3HQ, the simulated enol absorption spectra from TD-B3LYP and TD-LC- ω PBE show good agreement with experimental data with small $\Delta\lambda$ values while other functionals show much larger values of $\Delta\lambda$. For 3HTF, the TD-B3LYP, TD-PBE0, TD-LC-B3LYP ($\mu=0.200$), and TD-LC- ω PBE provide a small $\Delta\lambda$ value. Whereas, other functionals provide larger $\Delta\lambda$ values. Overall for the performance of all TD-DFT functionals, normal hybrid functions, both TD-B3LYP and TD-PBE0 functionals can explain electronic structures and photophysical properties of 3HF and its analogues. Meanwhile, long-range-corrected functionals either with a small or medium fraction of HF exchange fail to reproduce the experimental results. Accordingly, the popular TD-B3LYP provides the lowest average value of $\Delta\lambda$ and better-computed results compared to TD-PBE0. Therefore, TD-B3LYP is the most suitable method to further be used as a method to investigate the electronic structures, photophysical properties, and the ESIPT process of 3HF and its analogues.

3.2. Optimized structure and H-bond strength supported by infrared spectra and topology analysis

The optimized enol and keto forms of all molecules with labelling of all atoms and distances involved in the hydrogen bonding of the PT process are illustrated in Fig. 2 and Fig. S2 in ESI, respectively. For the enol forms, the covalent bond distances (O1-H1), the in-

tramolecular hydrogen distances (O2...H1), the distances between heavy atoms (O2...O1) connecting the intramolecular hydrogen bond, and the selected dihedral angle of enol and keto forms of 3HF, 3HQ, 3HTF, and 3HSO both in S_1 and the S_0 states are summarized in Table 2 and Table S2 in ESI, respectively. For the enol form of all molecules, the covalent bond distances (O1-H1) of all molecules are lengthened from 0.978, 0.980, 0.981, and 0.978 Å in the S_0 state to 0.999, 0.995, 1.008, and 1.024 Å in the S_1 state, respectively. Whereas, the intramolecular hydrogen bond distances (O2...H1) of all molecules are shortened from 2.012, 1.994, 1.909, and 1.934 Å in the S_0 state to 1.847, 1.888, 1.730, and 1.648 Å in the S_1 state, respectively. In addition, the heavy atom distances (O1...O2) of all molecules are also shortened from 2.625, 2.620, 2.554, and 2.556 Å in the S_0 state to 2.541, 2.561, 2.473, and 2.433 Å in the S_1 state, respectively. Moreover, the bond angle $\delta(\text{O1-H1} \cdots \text{O2})$ of 3HF, 3HQ, 3HTF, and 3HSO increase from 118, 119, 121, and 119° in the S_0 state to 123, 122, 127, and 129° in the S_1 state, respectively. In addition, the selected dihedral angles of all molecules change in the S_1 state compared to those in the S_0 state. For example, O1C1C2X1 dihedral angles increase from 0.7, 1.5, 0.1, and 2.9° in the S_0 state to 1.1, 2.8, 10.6, and 13.5° in the S_1 state for 3HF, 3HQ, 3HTF, and 3HSO, respectively. O1C1C5O2 values of 3HF, 3HQ, 3HTF, and 3HSO also increase from 0.3, 0.6, 0.7, and 0.5° in the S_0 state to 0.5, 1.6, 8.2, and 8.3° in the S_1 state, respectively. The selected dihedral angles (C2C3C4C5) of all molecules decrease from 15.8, 40.2, 44.6, and 53.6° in the S_0 state to 0.06, 26.8, 23.6, and 30.1° in the S_1 state, re-

Fig. 13. Average values over all ESIPT trajectories of 3HSO (a) time evolution of breaking and forming bonds (b) average relative energies of the S_0 and S_1 states, and the energy difference between the S_1 and S_0 states (S_1-S_0), and (c-e) three different dihedral angles of 3HSO.

spectively. These might be the effect of the heteroatom substitutions of 3HF. Overall, the elongation of the covalent bond (O1–H1), the shortening of the intramolecular hydrogen bond (O2...H1) and the distance of the heavy atoms connecting proton donor and proton acceptor (O1...O2), and the decrease in bond angle δ (O1–H1...O2) indicate that the intramolecular hydrogen bonds are strengthened in the S_1 state. The strengthening of hydrogen bonds will be further confirmed by the IR spectra and topology analysis. Among 3HX analogues, 3HSO has the longest covalent bond distance, the shortest intramolecular hydrogen bond distance, and the shortest of the heavy atom distance both in S_0 and S_1 states, compared with other three molecules, these results suggest that the replacing of the SO_2 group at X position in 3HX might increase the strengthening of the intramolecular hydrogen bond in 3HSO more than the other 3HF analogues.

To prove that the intramolecular hydrogen bond becomes strengthened upon photoexcitation, the IR spectra of O1–H1 stretching vibrational mode corresponding to the PT reaction coordinate both in S_0 and S_1 states of all molecules are analyzed and shown in Fig. 3. The strengthening or weakening of the excited-state intramolecular hydrogen bond is considered through the red- or blue-shift of some important characteristic vibration modes, induced by the intramolecular hydrogen bond interactions which have been proposed by Han and co-worker [59,76]. For the enol form of 3HF in the S_0 state, the simulated IR frequency of O1–H1 stretching mode is located at 3571 cm^{-1} in the S_0 state and it decreased to around 3232 cm^{-1} in the S_1 state with 339 cm^{-1} red-shift. Similarly, the O1–H1 stretching bands of enol form of 3HQ, 3HTF, and 3HSO exhibit the red-shifts of 247, 446, and 716 cm^{-1} , respectively. These results confirm that the intramolecular hydrogen bond of all molecules is strengthened in the S_1 state. Among the four molecules, 3HSO shows the greatest red-shift of the O1–H1 stretching vibrational mode, which could be indicated that the replacing of the SO_2 group as the least electronegativity at the X position of 3HX can enhance the intramolecular hydrogen bond strength. The strengthening of the intramolecular hydrogen bond is further confirmed by the topology analysis.

To obtain the strengthening of the intramolecular hydrogen bond between proton donor and proton acceptor as a bond critical point (BCP [3,–1], type), the topological descriptors of the electron density $\rho(r)$, potential energy density $V(r)$, the Laplacian of the electron density $\nabla^2\rho(r)$, Lagrangian kinetic energy $G(r)$, Hamiltonian kinetic energy density $H(r)$, and the electron delocalization index between the proton acceptor and transferred proton (DI) of all molecules are analyzed and listed in Table 3. The value of $\rho(r)$ and the sign of $\nabla^2\rho(r)$ at BCP are closely related to the strengthening of the intramolecular hydrogen bond and bond type [77], respectively. The value of $V(r)$ at BCP is shown to be highly correlated with hydrogen bond energy [78]. The $H(r)$ can be recovered by integrating from definitions is as follows:

$$H(r) = -1/2 \sum \eta_i \phi_i^*(r) \nabla^2 \phi_i(r)$$

The value of $G(r)$ is the shortcoming of $H(r)$ which is not always positive and real. The definition that has more clear physical meaning is as follows:

$$G(r) = 1/2 \sum \eta_j |\nabla \phi_j(r)|^2$$

For another topological descriptor as DI, the larger the electron localization is in a region, the more likely the electron motion is confined within this value. If the electrons are completely localized, then they can be distinguished from the ones outside. The $V(r)$ is obtained from the relationships between the values of $\nabla^2\rho(r)$ and $G(r)$ as follows:

$$V(r) = 1/2 \nabla^2 \rho(r) - 2G(r)$$

In addition, the value of $V(r)$ at BPC highly correlates with the hydrogen bond energy which is described as the Espinosa's equation:

$$E_{\text{HB}} = 1/2 |V(r)_{\text{BCP}}|$$

The data in Table 3 indicate that the hydrogen bond energy of 3HSO is much higher than those of other 3HF analogues with the value of 0.028 a.u. The $V(r)$ of hydrogen bond becomes stronger gradually with the order of $3\text{HQ} > 3\text{HF} > 3\text{HTF} > 3\text{HSO}$. The bigger values of the topological descriptors, the stronger the hydrogen bond. Therefore, the values of $\rho(r)$, $H(r)$, $G(r)$, $\nabla^2\rho(r)$, and DI comply with the order of $3\text{HSO} > 3\text{HTF} > 3\text{HF} > 3\text{HQ}$, respectively. The results demonstrate that the intramolecular hydrogen bond of all molecules is strengthened in the S_1 state which provides the possibility of the ESIPT via the BCP (listed in Table S3 in ESI).

3.3. Electronic spectra and frontier molecular orbitals

The simulated enol absorption (black line) and keto emission spectra of all molecules using TD-B3LYP/TZVP level which is the most suitable method are plotted in Fig. 4 (the dash lines used to represent the corresponding experimental values). The maximum wavelengths with oscillator strengths (f), frontier molecular orbitals (MOs) contribution, and Stokes shifts of all molecules are summarized in Table 4.

From the data in Table 4, the simulated enol absorption maxima of 3HF, 3HQ, 3HTF, and 3HSO are located at 343, 362, 371, and 377 nm, respectively, which agree well with the experimental values of 340 [25], 371 [43], 380 [44], and 370 [44] nm. Moreover, the keto emission maxima of 3HF, 3HQ, 3HTF and 3HSO are located at 528, 538, 638, and 791 nm, respectively. The simulated keto emission spectra are just slightly overestimated, compared with the experiment, which was observed at 525, 505, and 590 nm for 3HF, 3HQ, and 3HTF, respectively. Therefore, we ensure that TD-B3LYP/TZVP level is acceptable to describe the electronic structures and photophysical properties of all molecules. The enol absorption and keto emission of 3HQ, 3HTF, and 3HSO are red-shifted, compared with those of 3HF. The deviations of 185, 176, 267, and 414 nm for 3HF, 3HQ, 3HTF, and 3HSO, respectively, between the enol absorption and keto emission peak, are described as a large Stoke shift. The results indicate that the heteroatom substitution obviously provides the red-shift of enol absorption and keto emission leading to larger Stokes shift. Nevertheless, the keto emission of 3HSO could be not observed in the experiment. The reason for the observation might be from nonradiative relaxation which is further investigated by dynamics simulation and potential energy curve of the important dihedral angle.

To explore the intrinsic reason for the red-shift of enol absorption and keto emission, the calculated highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy level, HOMO–LUMO gaps as well as frontier molecular orbitals (MOs) of enol and keto forms for all molecules are analyzed and illustrated in Fig. 5. Herein, the main electronic transition is associated with the orbitals in a range 97%–98% (HOMO $\rightarrow$ LUMO), which correspond to the dominant π to π^* transition or mixing with intramolecular charge transfer (ICT) transition depending on the heteroatom substitution. For the HOMO orbital, the electron density is distributed more on the phenyl moiety and partially on the pyran of 3HF, pyridine of 3HQ, thiopyran of 3HTF, and thiopyran-4-one 1,1-dioxide ring of 3HSO. Whereas, in the LUMO orbital, the electron density completely occupies the whole molecule. The HOMO and

LUMO energy levels of 3HQ and 3HTF are higher than those of 3HF. Meanwhile, the HOMO and LUMO energy levels of 3HSO are stabilized to be lower than those of 3HF because its nature of electronic transition upon photoexcitation is assigned to the combination of the π to π^* transition and ICT on the phenyl moiety and the thiopyran-4-one 1,1-dioxide ring which decrease dramatically the HOMO–LUMO gaps (see in Fig. 5).

Overall, the HOMO–LUMO gaps of enol and keto forms of 3HQ, 3HTF, and 3HSO are lower than that of 3HF, leading to the red-shifts of the enol absorption and keto emission spectra. Moreover, upon photoexcitation, the electron density of carbonyl ($\text{C}=\text{O}$) group increases, which become more basic, and that of hydroxy ($-\text{OH}$) group decreases, which become more acid, resulting in driving force to the ESIPT process through the intramolecular hydrogen bond between proton donor and proton acceptor groups.

3.4. Potential energy curves of ESIPT reactions

The PECs of PT reaction coordinates both in S_0 and S_1 states for all molecules are scanned and plotted in Fig. 6. The PT reaction energy (ΔE_{rxn}) in the S_0 and S_1 states is the energy differences between the optimized keto form (reactant) and enol form (product) without constraints. The PT barrier and ΔE_{rxn} of all molecules both in S_0 and S_1 states are summarized in Table 5 and plotted in Fig. S5 of the ESI. The PECs obtained from cost-effective B3LYP/TZVP level are reliable in providing qualitative energetic pathways for the ESIPT process, which has been used in the previous studies [62,70]. Moreover, the PECs from B3LYP and TD-B3LYP agree well with the PECs from higher level of calculation such as ADC(2)/cc-pVDZ (see Fig. S6 of the ESI). Therefore, TD-B3LYP method is suitable to describe the potential energy surface of the PT processes. The PT barriers in the S_0 state are 13.13, 11.65, 12.56, and 21.06 kcal/mol for 3HF, 3HQ, 3HTF, and 3HSO, respectively. While, the PT barriers of all molecules in the S_1 state are 2.88, 3.62, 1.99, and 0.87 kcal/mol for 3HF, 3HQ, 3HTF, and 3HSO, respectively. For the heteroatom substitution effect on the ESIPT process, the chance of ESIPT is found in this order: $3\text{HSO} > 3\text{HTF} > 3\text{HF} > 3\text{HQ}$. The SO_2 group in 3HX can greatly encourage the ESIPT process.

Moreover, to evaluate ESIPT and the possibility of dual emission, PECs calculated along the reaction path optimized in the S_0 and S_1 states, and the vertical energy computed along the minimum reaction path both in the S_0 and S_1 states are plotted in Fig. 7. The calculated PECs and vertical excitation results of all studied molecules are in accordance with available experimental data. Overall, from the PECs, the PT processes of all molecules are most likely not to occur in the S_0 state because the PT barriers are high with endothermic reaction. However, the PT processes of all molecules in the S_1 state are spontaneous to take place because of their kinetically and thermodynamically favorable character (exothermic reaction with PT barriers less than 3 kcal/mol). The possibility of the PT processes of all investigated molecules both in S_0 and the S_1 states will be confirmed by the excited-state dynamics simulations in the next section.

3.5. Dynamic simulations

The information of excited-state dynamics simulations, including the number of active trajectories, the probability of the PT process, the average time of the PT process of all molecules are performed and summarized in Table 6. Snapshots of average trajectories of 3HQ, 3HTF, and 3HSO dynamics showing the time evolutions of the ESIPT reaction via intramolecular hydrogen bond are displayed in Figs. 8, 10 and 12, respectively (Fig. S7 in ESI for 3HF). The time

evolution of the average distances of bond forming and breaking (shaded area as the average bonds referring to the time range of the proton being transferred), the potential energy of S_1 and S_0 , and the S_1 – S_0 energy difference, and three different dihedral angles of 3HQ, 3HTF, and 3HSO for all ESIPT trajectories are analyzed and displayed in Figs. 9, 11 and 13, respectively (Fig. S8 in ESI for 3HF). Since the dynamic simulation of the PT process of 3HF was already reported in our previous work [61], so we will not discuss the dynamics information in this present work but only the comparison to 3HQ, 3HTF, and 3HSO will be given.

3.5.1. 3-Hydroxyquinolone (3HQ)

Six trajectories out of all trajectories for 3HQ show the ESIPT process (PT probability of 24%) and 19 trajectories do not give PT process during the simulation time (500 fs). The results of dynamics simulations indicate that the PT time constant is found at 70 fs with the time range of 51–150 fs (Fig. 9a). The relative energy difference between the S_1 and S_0 (S_1 – S_0) states as a blue line in Fig. 9b is slightly decreased after the PT process (70 fs), this line decreases from above 3 to around 2 eV, implying that there is no skeleton change during the simulation time confirmed by no crossing between the S_1 and the S_0 states. The average values of the interested dihedral angles (O1C2C3N1 and O1C2C1O2) slightly rise from around 5 to just below 10° (Fig. 8c and d) while that of C2C3C4C5 gradually decrease from around 30 to around 20° (Fig. 9e). It is worth noting that once the PT process is complete within 70 fs, no major skeleton change of 3HQ is observed which is supported by the average S_1 – S_0 energy lying around 2 eV (no conical intersection between the S_1 and the S_0 states). Therefore, the keto emission will most likely to be observed, which is in accordance with the experimental data [44].

3.5.2. 3-Hydroxyhydroflavone (3HTF)

For 3HTF, twelve trajectories give the ESIPT process (PT probability of 0.48) and the other thirteen trajectories reveal no ESIPT process within the 500 fs. The PT time constant is found at 55 fs within the time range of 45–63 fs as shown in Fig. 11a. The relative energy difference between S_1 and S_0 states (S_1 – S_0) starts to gradually decrease in the first 100 fs and it is kept just below 2 eV during the simulation time as depicted in Fig. 11b. After the PT process, the average dihedral angles of O1C2C3S1 and O1C2C1O2 increase moderately from 0 up to around 15° (Fig. 11c and d) whereas that of C2C3C4C5 decreases gradually from 0 to about 25° (Fig. 11e). However, the overall dihedral angle changes do not effectively cause the crossing between S_1 and S_0 states. Like in the case of 3HQ, the keto emission is observed in the experimental study [44].

3.5.3. 3-Hydroxy-2-phenyl-4H-thiochromen-4-one 1,1-dioxide (3HSO)

For 3HSO, the ESIPT process of this molecule occurs in twenty-three trajectories (92%) and only two trajectories show no ESIPT process within 500 fs. The dynamics simulations indicate that PT time takes place at 48 fs with the time range of 42–55 fs (Fig. 13a). The energy difference between the S_1 and S_0 states (S_1 – S_0) is reduced from approximately 3 to just above 1 eV during the simulation time as shown in Fig. 13b. The S_1 – S_0 energy drastically drops to below 1 eV, approaching the conical intersection between the S_1 and S_0 states which is in accordance with the average O1C2C3S1 dihedral angle (Fig. S9 in ESI). This dihedral angle fluctuates from 0 to 10° depending on whether it is in the upward or downward direction (Fig. 13c). The O1C2C3S1 dihedral angle remains constant around 5° for the upward direction, however, that of the downward change slightly about 10° after the PT process. For the O1C2C1O2 and C2C3C4C5

dihedral angles, they gradually start to increase from 0 to 15° and decrease from around 50 to around 30° (Fig. 13d and e), respectively. Overall, the skeleton of 3HSO changes drastically during the simulation time and particularly after the PT has triggered, this leads to the crossing between the S_1 and S_0 states, resulting in the leaking of keto population in the S_1 state to S_0 (approaching conical intersection between the S_1 and the S_0 states) without giving any fluorescence even though the PT process of 3HSO occurs readily. This finding agrees well with the no observation of keto emission reported [44].

3.5.4. Comparative analysis

Overall, the results from dynamic simulations obviously show that the ESIPT processes of 3HQ, 3HTF, and 3HSO can take place and the PT time constants are found in this order; 3HSO (48 fs) > 3HTF (55 fs) > 3HF (60 fs) > 3HQ (70 fs). Considering different 3HX analogues, 3HF, 3HQ, 3HTF, and 3HSO with different heteroatoms at the X-position (X=O, N, S, and SO₂, respectively), the PT time of 3HSO is faster than other analogues because of the least electron-donating capability of the SO₂ compared to O, N, and S atoms. The Mulliken charges of all heteroatoms in the 3HX analogues both in S_0 and S_1 states are given in Figs. S2 and S3 of the ESI. The PT barriers attributing to the way of forming a keto form are well anti-correlated with PT probabilities. These PT barrier values assess the kinetically favorable direction of the reaction. The occurrence of ESIPT strongly depends on the electron-donating capacity of the heteroatom, the lesser electronegativity of heteroatom in the 3HX, the faster ESIPT process. Furthermore, the PT probability anti-correlates with the PT barrier. The PT probability is found in this order; 3HSO (92%) > 3HF (76%) > 3HTF (48%) > 3HQ (24%). The occurrence of the ESIPT process relates well with the ESIPT reaction energy, the more exothermic reaction, the higher PT probability, however, the rate of the ESIPT process is generally irrelevant to this value.

4. Conclusions

The influence of heteroatom substitutions on the electronic structures, photophysical properties, and ESIPT processes of 3HF and its analogues (3HQ, 3HTF, and 3HSO) were systematically investigated using DFT and TD-DFT with B3LYP/TZVP level, which was validated to be the most suitable method in term of good agreement of simulated maxima wavelengths of enol absorption of all molecules with the experimental data. The conclusion can be summarized into two parts; static calculations and dynamics simulations.

For the static results, the intramolecular hydrogen bond distances of all molecules are strengthened in the S_1 state, supported by the longer distances of the covalent bond (O1–H1) and the shorter distances of the intramolecular hydrogen bond (O2...H1) as well as the shorter distances of heavy atoms (O1...O2) connecting the intramolecular hydrogen bond. The strengthening of the intramolecular hydrogen bond was further confirmed by the red-shift of IR spectra of O1–H1 stretching mode in the S_1 state and the topology analysis. For the influence of heteroatom substitutions on the photophysical properties, the N and S substitutions raise the HOMO energy levels of 3HQ and 3HTF molecules more than their LUMO energy levels while the SO₂ substitution stabilizes the LUMO energy level more than its HOMO energy level, leading to decreasing of the HOMO–LUMO gaps of 3HF analogues. As a result, the simulated enol absorption and keto emission spectra of 3HF analogues are shifted to longer wavelengths and relatively larger Stokes shifts. Moreover, frontier molecular orbitals (MOs) indicate that the charge redistribution between the proton donor and proton acceptor groups upon the photoexcitation induces the ESIPT process. Furthermore,

the PECs of the PT process of all molecules reveal that the PT process in the S_0 is unfavorable due to high PT barrier and endothermic reaction, but favorable in the S_1 state because of low PT barriers and exothermic reaction.

For excited-state dynamics simulations, the results indicate that the ESIPT processes of all molecules easily occur via the intramolecular with the ultrafast time scale. The PT time values with the different heteroatoms in 3HX follow this order; 3HSO (48 fs) > 3HTF (55 fs) > 3HF (60 fs) > 3HQ (70 fs) which is found anti-correlated with the electron-donating capacity of heteroatom. In addition, all results of static calculations of all molecules are in accordance with the dynamics simulations. However, the PT barrier is somehow not relevant to the probability of the PT process. Among all 3HF analogues, the PT process of 3HSO is easily facilitated because the SO_2 group in 3HSO causes the strongest intramolecular hydrogen bond at the S_1 state on the account of its shortest bond length $O2 \cdots H1$, the greatest red-shift of the $O1-H1$ stretching band, the topology analysis. Furthermore, the lowest PT barrier in the S_1 state of 3HSO than those of O, N, and S-substituted molecules implies that the intramolecular charge transfer character (ICT), which is modulated by the SO_2 group in 3HX, can greatly contribute to the ESIPT process. Nevertheless, after ESIPT process is complete, the relative energy difference between S_1 and S_0 below 1 eV found in 3HSO has indicated that the conical intersection between the ground and excited states has approached, leading to no keto emission observed in the experiment.

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Appendix A. Supplementary data

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