CHAPTER 1

Introduction

Nowadays, developments of technology and innovation have rapidly increased for which many scientists are interested in researching focuses on benefits to the human kind. Moreover, scope and type of research with more important to the whole community will be firstly considered. The popular topic for development in chemistry is luminescence which has many applications involving light such as light-emitting devices and fluorescent probes and so on. When a molecule is excited by light then it absorbs light and goes to excited state forming excited species after that it will return to a ground state giving luminescence. Luminescence is an emission of ultraviolet, visible or infrared photons from an electronically excited species. Fluorescence and phosphorescence are two cases of luminescence. The emission of photons accompanying de-excitation is then called *photoluminescence*, which has many other pathways and for de-excitation there are also possible physical effects resulted from interaction of light with matter (see in Figure 1.1) [1]. However, this thesis will concentrate on occurrence of fluorescence of molecule excited state proton transfer (ESPT).

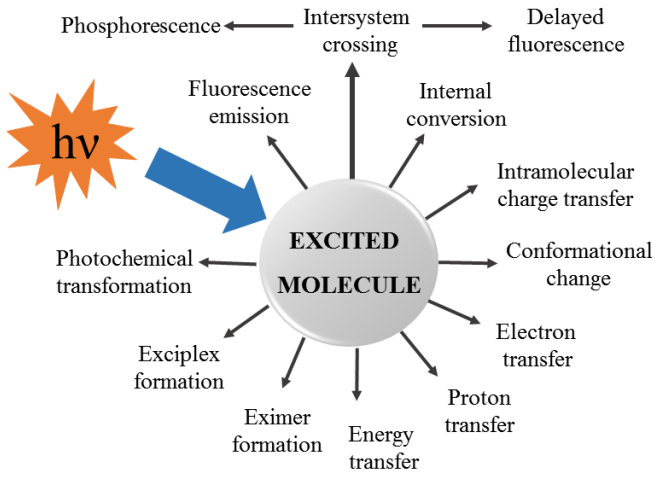

Figure 1.1 Possible de-excitation pathways of excited molecule adapt [1].

1.1 Phenomena of fluorescence

Luminescence is the emission of light or photon from any substance arising from electronically excited state of a considered system. Types of emission of photons are categorized into two types: fluorescence and phosphorescence based on the nature of the excited states [2]. When a molecule is excited by absorption of photons, the electron in the excited orbital is paired (by opposite spin) to the second electron in the ground state orbital. The molecule returns to the ground state is spin-allowed (e.g., $S_1 \rightarrow S_0$) called *fluorescence*. Another type of emission is *phosphorescence* in which after molecule is excited and then goes down into lowest state which alters spin of electron after that emits light from triplet excited state to ground state (e.g., $T_1 \rightarrow S_0$).

The processes of absorption and emission light are generally illustrated by the *Jablonski diagram*. This is frequently used as beginning for discussing light absorption and emission illustrating various molecular processes that can occur in excited states. A general Jablonski diagram is displayed in Figure 1.2. The singlet ground, first and second electronic states are denoted by S_0, S_1 and S_2, respectively. At each of these electronic energy levels the fluorophores can exist in a number of vibrational energy levels, denoted by 0, 1, 2, etc. The transitions between states are shown as vertical lines to represent the nature of light absorption. Transitions from ground states to excited states occur in about 10^{-15} s which is called the Franck-Condon principle.

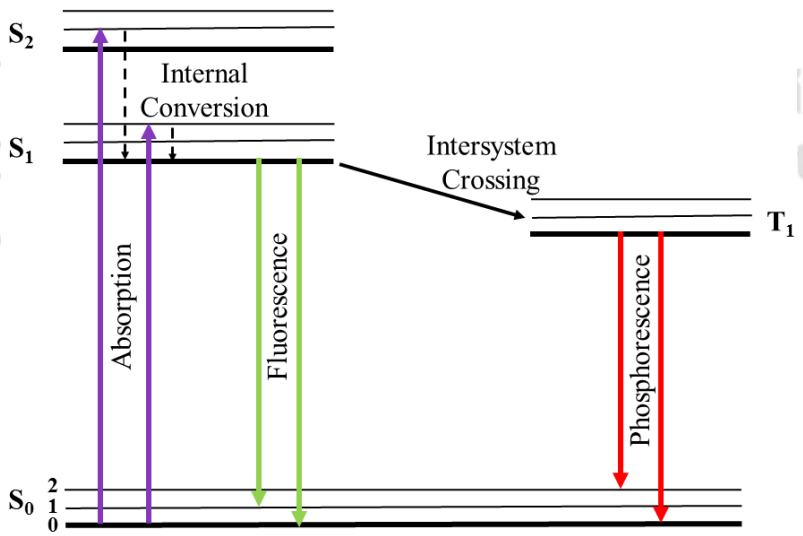

Figure 1.2 Jablonski diagram

Following light absorption, a fluorophore is normally excited to some higher vibrational levels of both S_1 and S_2 (violet lines). With a few rare exceptions, molecules in condensed phases rapidly relax to the lowest vibrational level of S_1 (dashed lines). This process is called internal conversion. Since fluorescence lifetimes are typically near 10^{-8} s, internal conversion is generally complete prior to emission and then a molecule usually returns to the ground state to a higher vibrational ground state level, which then quickly (10^{-12} s) reaches thermal equilibrium. An interesting consequence of emission to higher vibrational ground states is that the emission spectrum is typically a mirror image of the absorption spectrum of the $S_0 \rightarrow S_1$ transition.

Understanding of fluorescence process in the molecular level is very important if one wants to effectively use this molecule as various applications such as fluorescence probe, fluorescence sensor, fluorescence image and fluorescence dye. Among a variety of applications, fluorescent sensor applied extremely for food analysis, environmental monitoring and medical diagnostic has become important for human being.

1.2 Fluorescent sensing

The sensing process, in a general acceptation, utilizes one or more chemical-physical phenomena to notice the external environment (sensing domain), and converts the analytes of the sensed phenomenon and species into a signal that can be understood and manageable.

To obtain the detection of the target analyte, consequently, two integrated components are needed; molecular recognition and signal reporting**.** This means that the starting point is always the design of single molecules, or of arrays of molecules, that can specifically recognize an ion or a chemical species in a reversible manner (not always) and in a given concentration range. Molecules of abiotic origin of this kind are called chemosensors and, following a supramolecular approach, they can usually be schematized as made of different components (Figure 1.3): (i) a receptor (responsible for the selective analyte binding), (ii) an active unit (whose properties should change upon recognition) and, in some cases, (iii) a spacer that can change the geometry of the system and tune the electronic interaction between the two former moietyes [1].

A valuable feature of chemosensors is that they allow to monitor the analyte presence and concentration fluctuations in real-time and real space. Moreover, nowadays, single analyte sensing has been paralleled by a new kind of systems that are able to detect classes or mixtures of chemicals in a similar manner to which nature has developed human taste or smell. There are different principles of chemosensors available but the new emerging one involving the fluorescent probes is presented in the next section.

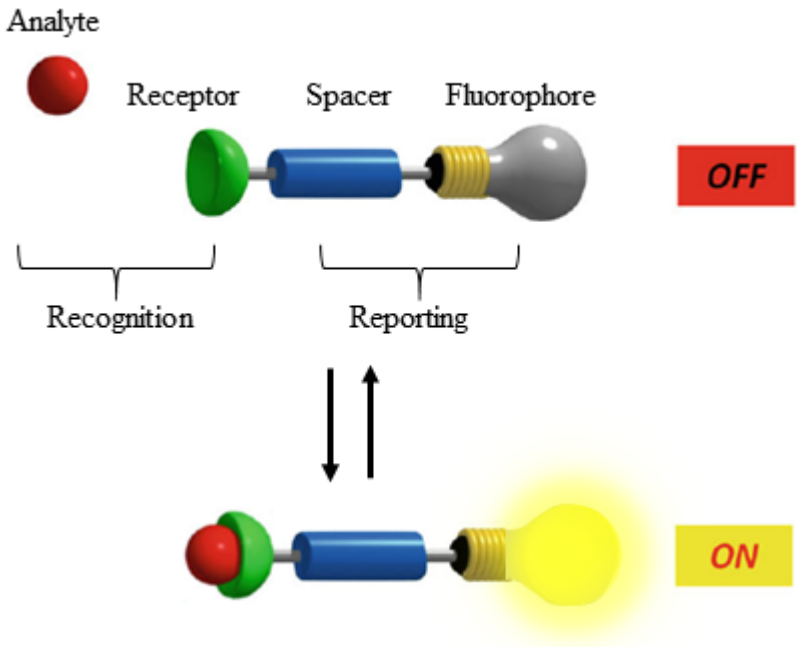

Figure 1.3 Schematic representation of a luminescent chemosensor.

1.3 Excited state proton transfer

The excited state proton transfer (ESPT) is one of the most important reactions in chemistry and biology [3-5]. Generally, ESPT process requires hydrogen bond between a proton donor group (–OH, $–NH_2$) and an acceptor group (–C=O, –N=) in the same molecule [6, 7]. Proton transfer (PT) process can be categorized into excited state intramolecular proton transfer (ESIntraPT) and excited state intermolecular proton transfer (ESInterPT) cases depending on the distance between the proton donor and the proton acceptor moieties [8], in which polar solvent molecules such as methanol, water and ammonia are needed to form hydrogen bonded wire prior to the ESPT reaction. The energetic driving force for the reaction is provided by a change in the acid-base properties of the donor and the acceptor with electronic excitation, so, the distribution of electronic

charge occurs, which increase in acidity of proton donor and the basicity of the proton acceptor. Subsequently, occurrence of PT is fast reaction from the proton donor to the proton acceptor in sub-picosecond time scale leading to tautomeric transformation from the excited enol form (E*) to the excited keto form (K*). After that decaying radiatively to the ground state provides fluorescence and then back proton transfer occurs to the initial position E form (see in Figure 1.4)

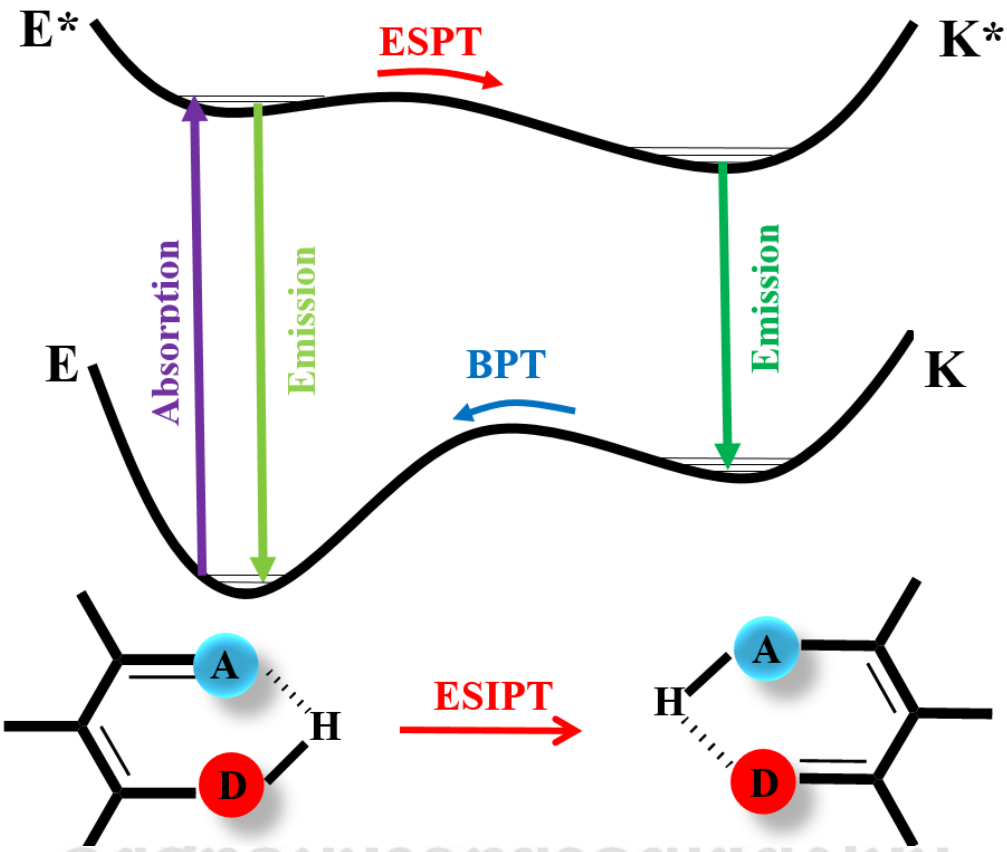

Figure 1.4 Four-level photocycle.

ESPT reaction has been observed in a variety of chemical compounds, such as 2-(2'-hydroxyphenyl)-benzoxazole (HBO) [9, 10], 2-(2'-hydroxyphenyl)-benzothiazole (HBT) [11, 12], 2-(2'-hydroxyphenyl)-benzimi-dazole (HBI) [12], 10-hydroxy-benzo[h]quinolone (HBQ) [13], 2-(2'-hydroxy-50-methylphenyl- benzotriazole (Tinuvin-P) [14], 3-hydroxyflavoes (3HF) [15, 16]. The applications of ESPT are found in many applications such as fluorescent probe [17-19], fluorescent sensor [20, 21] and organic light emitting diodes [22, 23].

1.4 3-hydroxyflavone

Among various molecules that exhibit the ESIntraPT, 3HF, a unique class of flavonoids, is composed of fused phenyl and γ-pyrone ring and phenyl ring [24] (Figure 1.5). It is abundantly found in a wide variety of natural sources and known to affect various biological processes [18, 25]. 3HF has long been interested as a model compound for studying the ESIntraPT process.

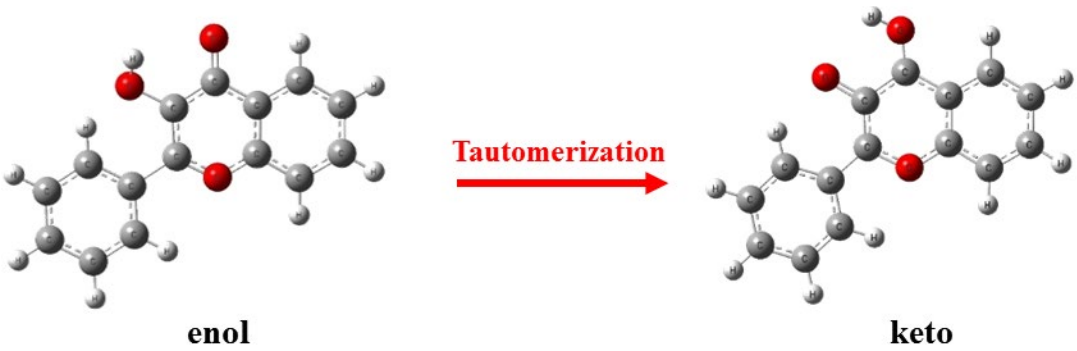

Figure 1.5 Enol-keto tautomerization of 3HF

Its four-level photocycle process of 3HF is displayed in Figure 1.6. Upon photoexcitation, however, the redistribution of electronic charge takes place, causing an increase in acidity of proton donor and basicity of proton acceptor [26]. As the result, fast proton transfer reaction from proton donor to proton acceptor occurs along the excited state potential energy surface via the intramolecular hydrogen bond, leading to a tautomeric formation from the excited enol form (E*) to the excited keto form (K*) in sub-picosecond time scale and then the molecule returns to the electronic ground state by fluorescence, finally the proton is transferred back to the initial position (E) [3-6]. In polar and protic solvent, both proton donor and proton acceptor groups of 3HF molecules can competitively form intermolecular hydrogen bonds with solvent molecule, instead of only forming intramolecular hydrogen bond between them, resulting in the dramatical increase of the E* emission band at the cost of suppressed K* emission band. As reported by several groups [27-30], the absorption and emission bands of 3HF were observed at 335 and 520 nm with exhibiting large Stokes shifted in non-polar solvent, however, 3HF in protic solvent such methanol was found to show both E* emission at 405 nm and K* emission at 528 nm. The photophysical change of 3HF affected by intermolecular

hydrogen bonded with protic solvent is of great importance to effectively use as a fluorescent probe.

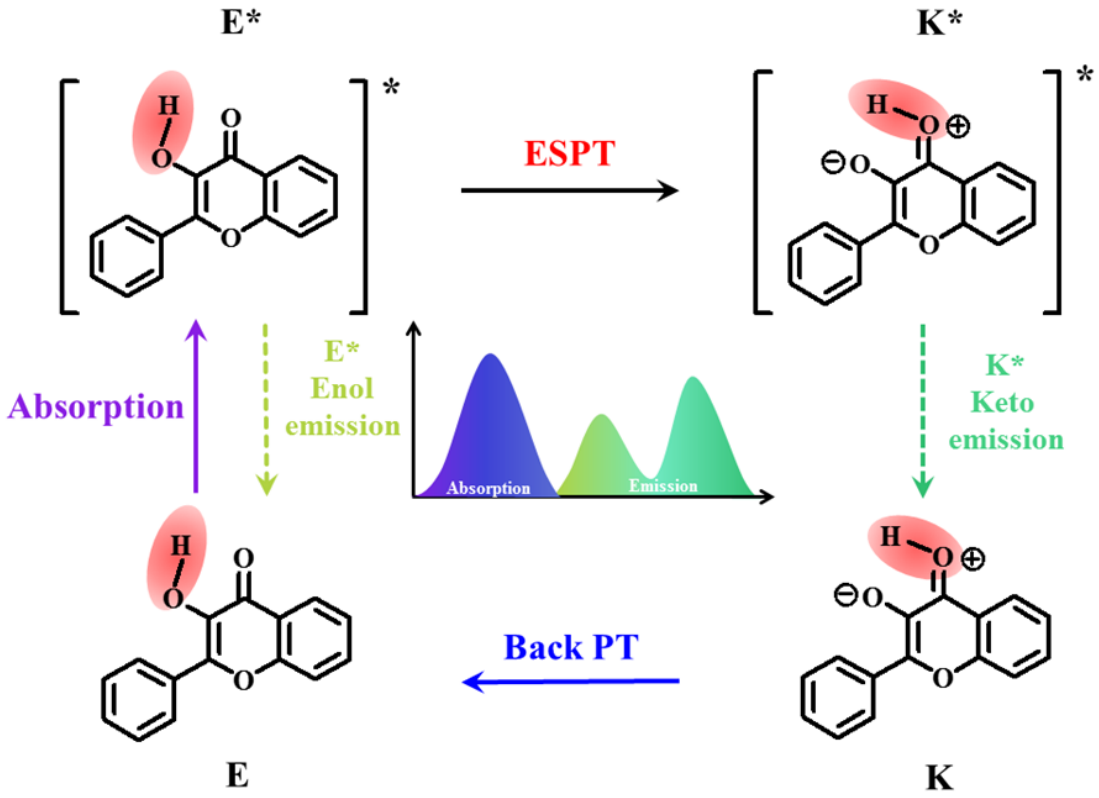

Figure 1.6 Excited state intramolecular proton transfer (ESIntraPT) of 3HF process.

3HF exhibiting ESPT has been extensively investigated both experimental and theoretical studies. ESPT has been considered as one of the great important photoreactions in chemical and biological systems such as acid-base neutralization, and enzymatic reactions. In addition to its important biological properties, 3HF is environmentally sensitive (solvatochromic) fluorescent dyes, which make it attractive as molecular fluorescent sensors, especially for monitoring biomolecular interactions.

The effect of solvent appears through properties like polarity, hydrogen bonding strength, and so forth. ESPT reaction of 3HF in protic solvents takes place without assistance of solvent molecule, the proper hydrogen bonded between 3HF and a solvent partner may influence the favorable conformation prior to proton transfer either intermolecular or intramolecular proton transfer reactions. Apart from ESPT of 3HF, the 4-carbonyl and the 3-OH groups of 3HF can also engage in intermolecular hydrogen bonding with appropriate solvents. When adding protic solvent molecules such as

methanol, water, and ammonia into 3HF, intramolecular hydrogen bond (dashed line) as depicted in Figure 3.1a can be perturbed and intermolecular hydrogen bond can be formed as represented by the dashed lines in Figure 3.1b-d. Such intermolecular hydrogen bond might prevent the formation of keto, resulting in the low quantum yield in protic solvents [24, 25]. However, proton transfer process might still occur but the mechanism will be altered and the proton transfer time may be slower than in non-polar solvents. Moreover, different types of solvents might also have different effects on hydrogen bond strength; as consequence of the proton transfer time might be different depending on the nature of the solvent.

Starting in 1979, Sengupta and Kasha [16] reported dual fluorescence of 3HF for the first time. 3HF as a unique group of flavonoids, which are responsible for the yellow color of petals of genus *Hemerocallis*, is composed of fused phenyl and pyrone ring. 3HF exhibits ESPT giving enol and keto forms with unique absorption and emission properties. It is known to exhibit fluorescence band "enol" blue fluorescence at 410 nm and "keto" green fluorescence at 525 nm depending on the solvent, but ESPT time constants differ significantly. In 1981, Woolfe and Thistlethwaite [15] presented a direct observation of ESPT kinetic in 3HF, and their results have revealed that the occurrence of proton transfer was strongly dependent on solvent. In non-polar solvents (hydrocarbon) the proton transfer occurred across pre-existing intramolecular hydrogen bond, however, in alcohol and solid poly (methyl methacrylate) (PMMA), the proton transfer was interrupted and ESPT may take place through intermolecular hydrogen bond with alcohol. Their results were in agreement with the work of Sengupta and Kasha but inconsistent about viscosity dependence.

Itoh et.al [27] described about ESPT in 3-hydroxychromone (3HC) and 3HF with two differential solvents (2-methyltetrahydrofuran (MTHF) and 3-methylpentane (MP)). 3HC in MTHF did not exhibit fluorescence (indication of no ESIPT) but 3HC in MP solvent showed fluorescence however the reaction was too fast to be determined by nanosecond pulse excitation. For 3HF in MTHF, the rise time of fluorescence was observed to be 1.8 ns at below 150 K and in MP, the rise time was observed to be 1-0.5 ns at 160-195 K. A comparison of fluorescence behavior of 3HC having no phenyl group with that of 3HF was proposed to be caused by the effect of torsional motion of phenyl

group of 3HF. The ESPT was concluded to be faster in 3HC than in 3HF due to the increasing basicity of the carbonyl oxygen in 3HF.

McMorrow and Kasha [28, 29] investigated effect of solvents of ESIPT reaction of 3HF. They reported the impurities present in hydrocarbon solvent causing dual fluorescence from two species (enol forming H-bonding with solvent and keto. With traces of water presented, three regions of fluorescence of 3HF in methylcyclohexane (MCH) could be observed which was different from their previous work [16]. There are three regions: first from tautomer with yellow-green fluorescence (at 523 nm), second with green fluorescence (at 497 nm) attributed to solute anion, and last region form normal was blue-violet fluorescence (at 400 nm) attributed to normal form. After that, Strandjord and Barbara [31] reported effect of alcoholic solvents on ESIPT reaction of 3HF using kinetic reaction. The rate constant of slow proton transfer component k_{slow} was observed depending on donating of H-bond of alcohol. A comparison of k_{slow} between strongly donating alcohol (2, 2, 2, trifluoroethanol and 2-cholo ethanol) and less donating alcohol (methanol and ethanol) showed that the k_{slow} would be diminished in the case of strongly donating.

In 1992, Schwartz et al. [32] investigated the ESIPT time constant of 3HF. They reported ESIPT dynamics of 3HF in hydrocarbon (non-polar) and alcohol (polar) solvents on ultrafast time scale using femtosecond time resolved absorption (at 620 nm), in which ESIPT could be studied by transient absorption. The fast ESPT times in methylcyclohexane (MCH) and in methanol (MeOH) were observed at 240±50 and 125 fs, respectively. And then, Ameer-Beg et al. [33] used femtosecond laser to investigate ESIntraPT reaction in 3HF with time constant around 60 fs component in ethanol which is more accurate than the results reported by Schwartz et al. [32]. In non-polar and aprotic solvents such as methylcyclohexane (MCH) and acetonitrile, the time constants of ESIPT process were found at 35 fs. After that, Bader et al. [34] used laser-excited Shpol's kii femtosecond to determine the ESIntraPT process of 3HF in *n*-octane. The time constant for ESIntraPT was evaluated to be 39 ± 10 fs. Later on they [35] investigated the substitution effect on ESPT rates in 3HF and it derivatives in *n*-octane. They found that time constant for ESIntraPT of 3HF was indicated to be 93 fs and those of its derivatives were slower than that of 3HF. Then, Chevalier et al. [36] in 2012 used transient IR

spectroscopy and ab initio calculations on ESIntraPT in 3HF solvated in acetonitrile. The ESIntraPT time was found to be less than 120 fs which was slower than the previous value. This slow ESIntraPT was proposed to be mediated by solute-solvent interaction which is induced with hydrogen bond between the hydroxyl group of 3HF and acetonitrile.

In 2012, Gunduz et al. [24] synthesized and photophysical properties of 3HF and its derivatives in various solvents. The absorption spectra of synthesized compounds were found to be 317-357 nm and their emission spectra were in the range of 496-580 nm depending on solvents. Furthermore, solvent effect on the photophysical and photochemical properties of 3HF in six different solvents was reported by Protti et al. [37] using a combined spectroscopic and kinetic study. The UV-Vis absorption spectra and the emission spectra of 3HF were strongly influenced by the polarity of solvents and their ability to interact with 3HF by donating and accepting hydrogen bond. After that, Ni et al. [38] used experimental luminescence to convey the difference in intramolecular and intermolecular hydrogen bonding in ground state and ESPT in excited state as a naked-eye study for students to better understand the concept of intra- and inter-hydrogen bonding and the interaction between 3HF and solvents. At room temperature, fluorescence of 3HF was observed with one band at 530 nm in non-polar solvent (hexane), and two bands: first band at 400 nm, second band at 530 nm in polar solvent (ethanol).

Photophysical property of ESIntraPT of 3HF was first theoretically investigated by Casadesús et al. [39] both in the ground-state and first excited state using B3LYP method. They showed that the proton transfer process in ground state was endoergic and has a quite high energy barrier. Optimized geometries at the TD-DFT level revealed a small barrier but non-negligible energy barrier for the proton transfer reaction in S_1 which was agreed well with experimental data obtained with femtochemistry spectroscopy. And then, Jiang et al. [40] investigated intramolecular proton transfer mechanism of 3HF in non-polar solvent in ground and excited states using DFT and time-dependent density functional theory (TD-DFT) method. Calculated enol absorption and emission spectra were located at 353 and 402 nm, respectively and keto emission spectrum was found at 545 nm. Hydrogen bonding dynamics could be evaluated by peak shift of IR vibration spectra with red shift of O–H vibrational mode. The potential energy curve barriers in ground-state and

excited-state were estimated at 13.045 and 2.06 kcal/mol, respectively, indicating that proton transfer process was likely to proceed in excited-state.

The most recent study on ESIntraPT mechanism of 3HF and its derivatives has been theoretically investigated by Dai et al. [41] using DFT and TD-DFT at B3LYP/TZVP. An analysis of absorption and emission spectra agreed nicely with experimental result. The potential energy curve indicated that the occurrence of proton transfer was not possible in ground state but possible in excited state with energy barrier lower than 6 kcal/mol.

From above literature review on 3HF and its derivatives, it is obviously seen that most previous reports on computational calculations have been focused only on their photophysical properties, however its information on hydrogen bonding with protic solvents is not well understood, especially the dynamic information of proton transfer time-constant and intermolecular proton transfer mechanism. Therefore, the goal of this work is to understand effect of protic solvents on dynamics of the ESPT in free 3HF and 3HF with solvent by using the computational calculations which has become a power tool nowadays.

1.5 Objectives

To answer the effects of protic solvents on ESPT process in 3HF for hydrogen-bond strength, photophysical properties and proton transfer mechanism, we use DFT and TD-DFT in quantum chemistry. Therefore, static and dynamics simulations are required to investigate the effect of protic solvents on PT process. Static calculations will provide optical properties, hydrogen-bond strength, potential energy curves for proton transfer mechanism. Dynamics simulations will provide a detail picture of pathway proton transfer between hydrogen bond of 3HF and solvent, as well as a proton transfer time, reaction pathways, reaction probabilities of the ESPT.