CHAPTER 1

Introduction

1.1 Photochemical and photophysical processes

Photochemical and photophysical processes have been closely related to the development of human and environment. For example, photochemical reactions caused by the Sun's rays have generated organic molecules from the composition of the original atmosphere on the Earth. Photochemistry and photophysics both deal with the impact of energy in the form of photons on materials. Photochemistry process occurring in the chemical reactions involves the interaction of electromagnetic energy while photophysics process deals with physical changes that involves the absorption and emission of electromagnetic, light, energy without chemical reactions [1].

Photochemical and photophysical processes are at the basis of important applications such as photosynthesis in plants, plastic production initiated by radical polymerization and human skin from the damaging effect of sunlight, design of fluorescent compounds for a variety of sensing applications (biological markers, optical brighteners, molecular switches, pollutant detectors, and display devices), creation of photochromic materials used in sunglasses and optical memories, development of laser devices and development of light-powered molecular machines. Other interesting fields concern about photomedicine, multiphotonic processes, solar-powered green synthesis, and molecular photovoltaics [2].

Once the atoms or molecules absorb electromagnetic radiation or light. Light excitation with a photon of suitable energy promotes the atoms or the molecule from its ground state to an electronically excited state. The excited states are responsible for emission of light or involve energy loss processes. All these processes can be explained in the Jablonski diagram in the next section.

1.2 Jabonski diagram

The various processes that can occur upon excitation of a molecule are shown in the Jablonski diagram (Figure 1.1). As in the diagram shown, the molecule may be in a singlet or a triplet state. Once a molecule has absorbed energy and excited to excited state, there are several pathways by which it can return to ground state. The emission of photon occurring between excited and ground states of the same spin state (S_1–S_0) is called fluorescence. If the spin multiplicity of the initial and final states is different spin (T_1–S_0), the emission of the photon is called phosphorescence. Fluorescence is statistically much more likely to happen than phosphorescence for most molecules, the lifetimes of fluorescent states are very short (10^{-5} to 10^{-8} seconds) and phosphorescence somewhat longer (10^{-4} seconds). The deactivation processes of fluorescence and phosphorescence are also significant here: internal conversion (IC), intersystem crossing (ISC), and vibrational relaxation. The IC process is the radiationless transition between energy states of the same spin multiplicity, while ISC process is a radiationless transition between different spin states. Vibrational relaxation, the most common of the three process for most molecules, the lifetime of a vibrational excited molecule is less than 10^{-12} seconds. It is enhanced by physical contact of an excited molecule with other particles with energy, in which the form of vibrations and rotations, can be transferred through collisions.

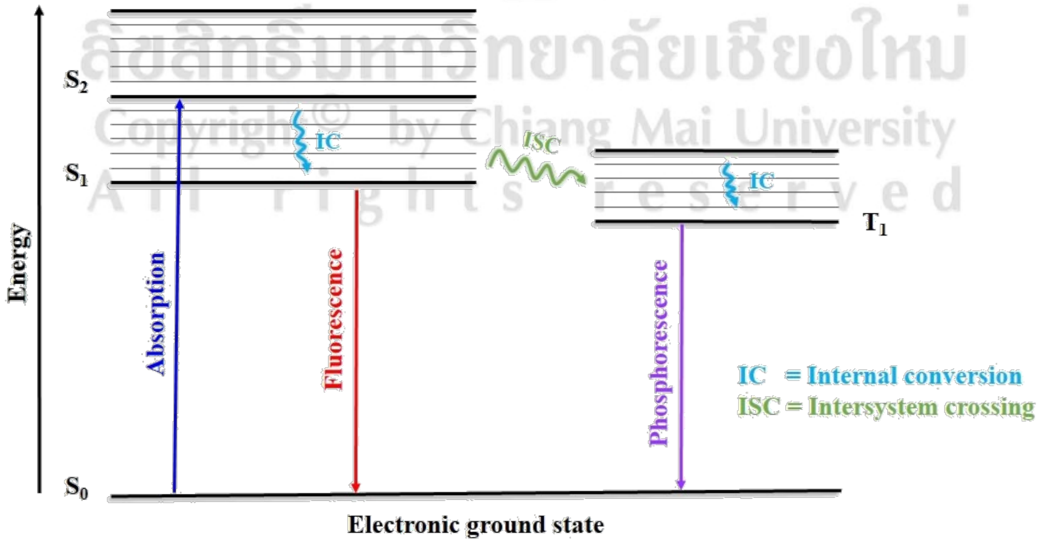

Figure 1.1 Jabonski diagram

This thesis is focused on only fluorescence process therefore phosphorescence will not be included. Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. The change in photon energy causes a shift of the fluorescence spectrum to longer wavelength and lower energy, relative to the absorption spectrum, this is referred to as the Stokes Shift. Fluorescence has many applications, such as fluorescent labelling [3] fluorescence sensors [4], fluorescence probe [5], laser dyes [6], organic light-emitting diodes [7]. Due to its unique photophysical properties, excited-state intramolecular proton transfer (ESIPT) is emerging as a new design principle for many applications such as fluorescence probe and laser dyes, and so on.

1.3 Background of excited-state intramolecular proton transfer reaction

Excited state proton transfer (ESPT) reaction represents one of the most fundamental processes involved in chemical reactions, which have been received considerable attention in recent years [8-10]. ESPT reactions are not as common as those chemical reactions occurring in the ground state. The fundamental approach to ESPT process has relied deeply on studies of excited-state intramolecular proton transfer (ESIPT) reactions, which is an important process in biological and chemical systems [11-16]. The molecule having ESIPT process generally involves transfer of a hydroxyl (or amino) proton which is a proton donor to a proton acceptor such as nitrogen or a carbonyl oxygen from a preexisting hydrogen-bonding configuration, forming a tautomer [17]. The four-level photocycle of tautomerization where the normal form (N) absorbs light and the ESIPT is occurred to yield the tautomer (T) is shown in Figure 1.2. First, the molecule of interest absorbs light to form an intramolecular molecular charge-transfer state (ICT), causing an electron redistribution that gives the driving force for ESIPT. Second, the proton transfer happens rapidly on the excited state surface. Third, the excited-state molecule is not stable and relaxes itself back to ground state, releasing its stored energy in an emitted photon called fluorescence. This fluorescence of the tautomer from the relaxed excited-state provides the driving force to complete the cycle through back proton transfer on the ground state surface. The difference between the absorption maximum wavelength of normal form and the emission maximum wavelength of tautomer form is called Stokes shift. Generally, the proton transfer process occurs in the ultrafast timescale of femtosecond or subpicosecond. The ultrafast nature of ESIPT molecules is normally accompanied by a large Stokes shift that can provide numerous opportunities for use in a variety of applications [18], such as fluorescent sensors [19, 20], laser dyes [21], ultraviolet stabilizers [22], proton and metal ion sensors [23, 24], probes for biological environment [25, 26], and materials for organic light-emitting diodes [12]. The important ESIPT molecules include 2-(2′-hydroxyphenyl)benzimidazole (HBI) [27], 2-(2′-hydroxyphenyl)benzoxazole (HBO) [28], 2-(2′-hydroxyphenyl)benzothiazole (HBT) [29], 10-hydroxybenzo[*h*]quinoline (HBQ) [30], 2′-hydroxychalcones [31], 2-(iminomethyl)phenol (IMP) [32], and their derivatives.

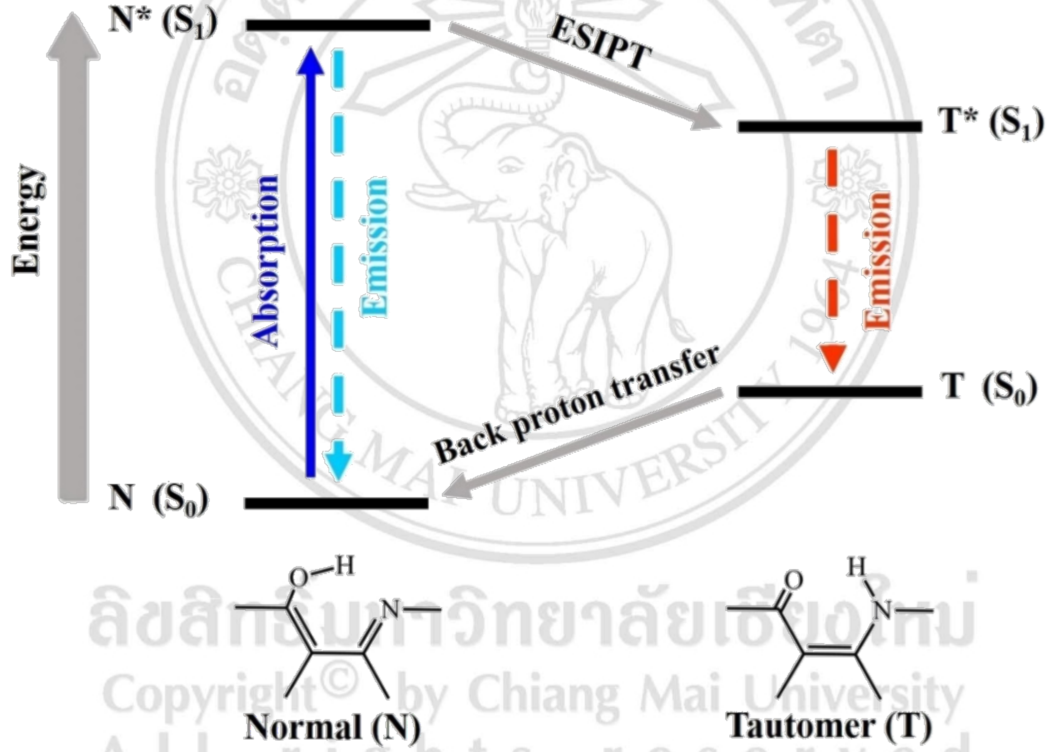

Figure 1.2 Mechanism of excited state intramolecular proton transfer (ESIPT) for HBQ

1.4 10-hydroxybenzo[*h*]quinoline (HBQ) and literature review

Among these ESIPT compounds, 10-hydroxybenzo[*h*]quinolone (HBQ), displayed in Figure 1.3, has been used to investigate the prototype example of excited state ESIPT process through hydrogen bond (H-bond). HBQ constitutes one of the fundamental heterocyclic systems. It possesses a rigid six-membered ring hydrogen bonding configuration, and a strong intramolecular hydrogen bonding is formed between the hydroxyl hydrogen and benzo-quinolinic nitrogen [33].

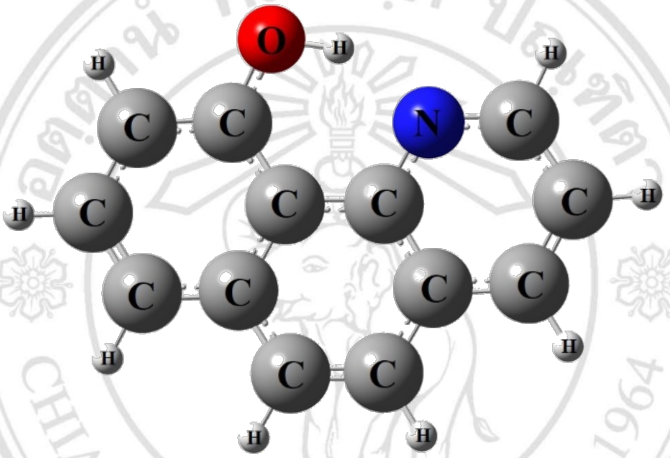

Figure 1.3 HBQ structure

The absorption of normal form appears at 400-600 nm region [34] while its tautomer emission appears at 580 nm [35] and the highly large Stokes-shifted emission and high photostability. HBQ has been used as a reagent in the preparation of optical filter agent in photographic emulsions for a long time [36] and as a chelating agent for gold cations [37]. The photophysical properties relevant to the proton transfer (PT) reaction are rather insensitive to solvent perturbation [17, 38]. Therefore, this molecule is considered to be one of the best systems that we can use to examine the vibrational coherence in the intrinsic proton-transfer process [34]. The enol-tautomeric form can be converted into its keto-tautomeric form via intramolecular PT reaction [39] as shown in Figure 1.4.

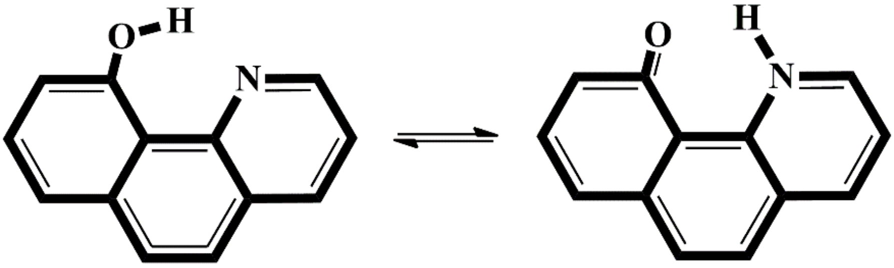

Figure 1.4 Simplified schematic of the ESIPT process in HBQ

Excited-state intramolecular proton transfer (ESIPT) has received considerable attention both experimentally and theoretically [40-46]. There have been several reports about ESIPT of HBQ and its derivatives. The first study of HBQ began with Martinez *et al*. in 1992, [35] reported a new ESIPT system. At room temperature, HBQ shows an absorption maximum peak of the normal form at 378 and 372 nm for methylcyclohexane (MCH) and ethanol respectively and the tautomer emission at 609 nm (MCH) and 580 nm (ethanol) leading to a large Stokes shift. These results revealed that the ESIPT in HBQ can effectively take place regardless of solvent. By comparison of the spectra of HBQ in MCH and ethanol, it was found that the intramoelcular hydrogen bond strength was decreased in protic polar solvent, supported by the blue-shifted of both absorption and emission spectra. Furthermore, at 77 K in MCH, the tautomer emissions were observed at 575 nm, suggested that the proton transfer barrier is small or barrierless. The strong hydrogen bonding in HBQ provides an ideal model to study the dynamics of intrinsic ESIPT independent from solvent perturbation. In 1995, Kubicki *et al*. [33] reported the crystal structure of HBQ (C13H9NO) with planarity and asymmetric part of the unit cell. It has a strong intramolecular O–N···N hydrogen bond forming a planar six-membered ring. The hydrogen atom is located almost at an equal distance from both N and O atoms, and the O–H···N angle becomes smaller compared to that of 2-(2'-pyridyl)phenol in order to help the proton transfer.

Photophysics of HBQ in aqueous solution was examined by Chou and Wei [38] in 1996. HBO shows absorption maximum peak of the normal form at 365 nm and the tautomer emission at 585 nm. ESIPT was proposed to be triggered by excited-state resonance charge transfer upon photoexcitation due to the stronger electron-accepting ability for the benzoquinolinic nitrogen than the carbonyl oxygen. This group further studied the spectroscopy and dynamics of ESIPT in HBQ and DBQ in 2001 [30] using steady-state absorption and fluorescence spectroscopy, femtosecond fluorescence upconversion in combination with pump-probe transient absorption experiments in nonpolar solvents. They reported the absorption maximum peaks of the normal form at 380, 377 and 370 nm for cyclohexane, benzene and acetonitrile, respectively and the tautomer emission peaks were also observed at 635, 630 and 625 nm in three different cases. Upon excitation energy at 385-400 nm, HBQ and DBQ underwent an ultrafast ESIPT and proton transfer barrier was proposed to be barrierless. Under the same condition of non-polar solvent and pump-probe absorption spectroscopy with Chou's group, Takeuchi and Tahara [34] in 2005 studied the ultrafast excited-state intramolecular proton transfer reaction of HBQ. The excited-state absorption of normal form appeared at 380 nm, and stimulated emission of tautomer form showed at ~ 600 nm. They estimated the proton-transfer time resolution of HBQ as good as 27 fs (25 ± 15 fs).

Furthermore, Schriever *et al*. [47] in 2008 reported ultrafast ESIPT of HBQ was investigated by means of combined experimental and theoretical method, namely transient absorption experiments, quantum wavepacket propagation, and classical dynamics simulation. They reported the ultrafast time scale on proton transfer of 25 fs for pump-probe experimental, for nuclear wavepacket dynamics time scale of 40 fs, and 30 fs for classical dynamics simulation. Their theoretical results agreed nicely with that of experimental data.

Many computational studies on ESIPT of HBQ have been reported by employing the Gaussian-09 program using the density functional theory (DFT) and time-dependent density functional theory (TD-DFT). In 2011, Higashi *et al*. [48] applied the electronically embedded multi-configuration Shepard interpolation and molecular mechanical (EE-MCSI/MM) molecular dynamics (MD) simulations to the ESIPT reaction and vibrational coherence of HBQ in cyclohexane. The time evolution of the distribution of the reaction coordinate (proton transfer) from the excited-state MD simulations was observed at 20 fs. Paul *et al*. [46] in 2011, described photophysical behavior of HBQ with particular emphasis on ESIPT phenomenon using a combined experiment and theory. The absorption band maximum of normal form (Theory) of HBQ appeared at 412 nm and its emission band maximum of tautomer form was found at 615 nm in gaseous phase. Their theoretical results agreed with that of experimental result. Furthermore, their molecular orbital (MO) calculations indicated that proton transfer cannot occur in the ground state, however the PT process can take place in the excited state. Their computational results are found to bear commendable consistency with experimental results. Lee *et al*. [49] in 2013, demonstrated the active role of the proton for the ESIPT reaction of HBQ in cyclohexane directly in time domain by employing extreme time-resolved fluorescence (TRF). ESIPT reaction of HBQ proceeds in the ultrafast manner at 12 ± 6 fs. This ultrafast PT process leads to the coherent excitation of the vibrational modes of the product state.

Moreover, substituent effect in different position of HBQ on its photophysical property and ESIPT reaction was investigated by Chai *et al*. [50] in 2014, They used the DFT and TD-DFT method at B3LYP with 6-311++G(d,p) basis set in the gas phase, acetronitrile and toluene. The potential energy curves (PEC) of HBQ-a (-CN) and HBQ-b (-NO2) were calculated as a function of O–H distance. The energy barrier of ESIPT reaction at excited-state of HBQ-a (3.73 kcal/mol) is less than HBQ-b (17.75 kcal/mol). It is mentioned that the occurrence of ESIPT reaction in HBQ-a is much easier than in HBQ-b, because of the substituent with the electron-withdrawing group in the hydrogen-accepting moiety. Zhou *et al*. [39] in 2015 studied the ESIPT of HBQ in different solvents using DFT and TD-DFT methods at B3LYP with TZVP basis set. The energy barriers of ESIPT reaction for HBQ in cyclohexane and HBQ in methanol complex are 13.54 kcal/mol and 17.58 kcal/mol, respectively. Their results suggested that ESIPT reaction of HBQ in cyclohexane occurs easier than in the methanol complex with HBQ. Parada *et al*. [51] in 2015 reported about influence of H-bond geometry on the dynamics of ESIPT and photoinduced tautomerization in a series of phenol-quinoline compounds. They demonstrated that a long distance between proton donor and proton acceptor (d_{DA}) correlates with a higher barrier for ESIPT, while a large dihedral angle induces highly efficient deactivation channels after ESIPT, preventing the formation of the fully relaxed tautomer photoproduct.

1.5 Objectives

From previous report by Parada *et al*. [51], it is clear that the structural modification of HBQ significantly affects their optical properties, especially the proton donor-acceptor distance and dihedral angle between the proton donor and acceptor moieties. Therefore, in this work, the effect of geometry changes of HBQ and its derivatives; (1a) HBQ, (1b) 9-hydroxy-3H-benzo[*g*]indole (HBID), (1c) 5H-indeno[1,2-*b*]pyridine-9-ol (IPDO), (1d) 3,4-dihydro indene[1,2-*b*]pyrrole-8-ol (IPRO), (1e) 2-(pyridin-2-yl)phenol (PDP), and (1f) 2-(4H-pyrrol-2-yl)phenol (PRP), as depicted in Figure 3.1 (differences of the pyridine and pyrrole rings, and the five and six membered ring in the center of molecules), on their photophysical properties and ESIPT process will be investigated using density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The geometries of all investigated molecules in S_0 and S_1 states will be optimized. Their vertical excitations, frontier molecular orbitals, absorption and emission spectra will be computed to investigate the photophysical properties. Moreover, their IR vibration spectra and potential energy curves corresponded to PT coordinate as well as dynamics simulations will be further carried out to provide the detailed PT mechanism.