

CHAPTER 1

Introduction

1.1 Photoluminescence

Photoluminescence is one of the light emission processes (luminescence) in which the excitation process is initiated by light absorption of a chromophore (Figure 1.1). This process includes fluorescence and phosphorescence. The molecule possessing fluorescence arising from an excited singlet state (S) is called fluorophore, while the molecule possessing phosphorescence arising from an excited triplet state (T) is called phosphorophore [1].

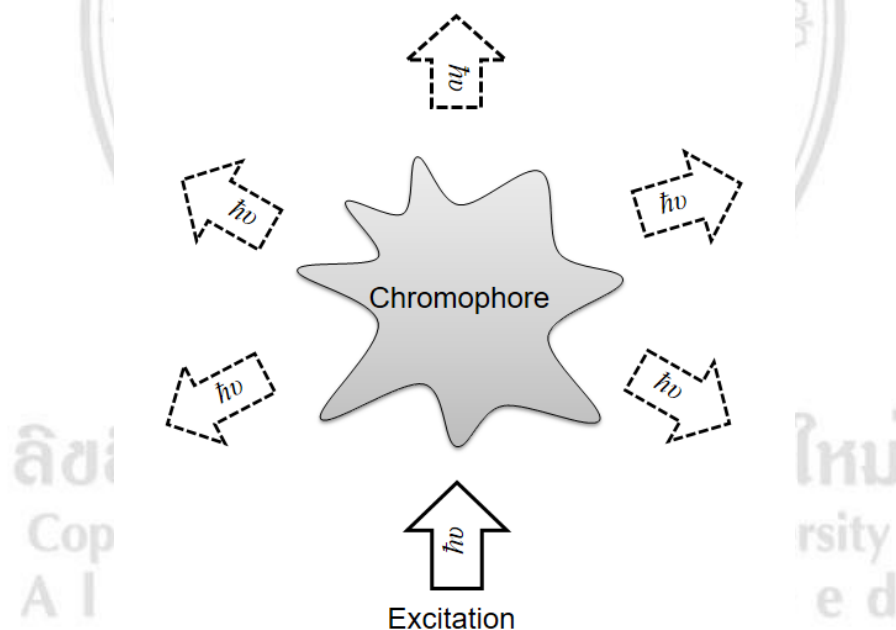


Figure 1.1 Diagram of photoluminescence of chromophore.

The photoluminescence of the chromophore is basically illustrated by a Jablonski diagram. The Jablonski diagram in Figure 1.2 shows the light absorption and emission processes of electrons of the chromophore. The ground singlet, first excited singlet, and second singlet states are depicted by S_0 , S_1 , and S_2 , respectively, while first excited

triplet state is represented by T_1 . Each line of these electronic states represents vibrational energy levels. The arrows directed upward are the absorption (excitation), while arrows directed downward are the light emission (fluorescence or phosphorescence) and non-radiation processes (internal conversion (IC), intersystem crossing (ISC), *etc.*). When the chromophore of a molecule absorbs light from the lowest vibrational energy level in the ground state (S_0), an electron is excited to the first excited singlet states (S_1) or higher excited singlet states (S_n $n>1$). This process is very fast within 10^{-15} s. The loss of vibrational energy in the excited state from excited state S_2 to excited state S_1 occurring within 10^{-14} to 10^{-11} s is called internal conversion (IC). Some molecules in the excited state may release energy as non-radiative decay to the ground state but some can emit photons. The process of photon emission from excited state S_1 to ground state is called fluorescence (within 10^{-9} to 10^{-7} s). In addition, electron of some molecules in the S_1 can undergo a spin conversion to the T_1 . The conversion of S_1 to T_1 called intersystem crossing (ISC), possibly occurs. The radiative decay from the T_1 going to the ground state is called phosphorescence that takes longer time than the fluorescence process. Time scale for the phosphorescence is 10^{-4} to 10^2 s [2].

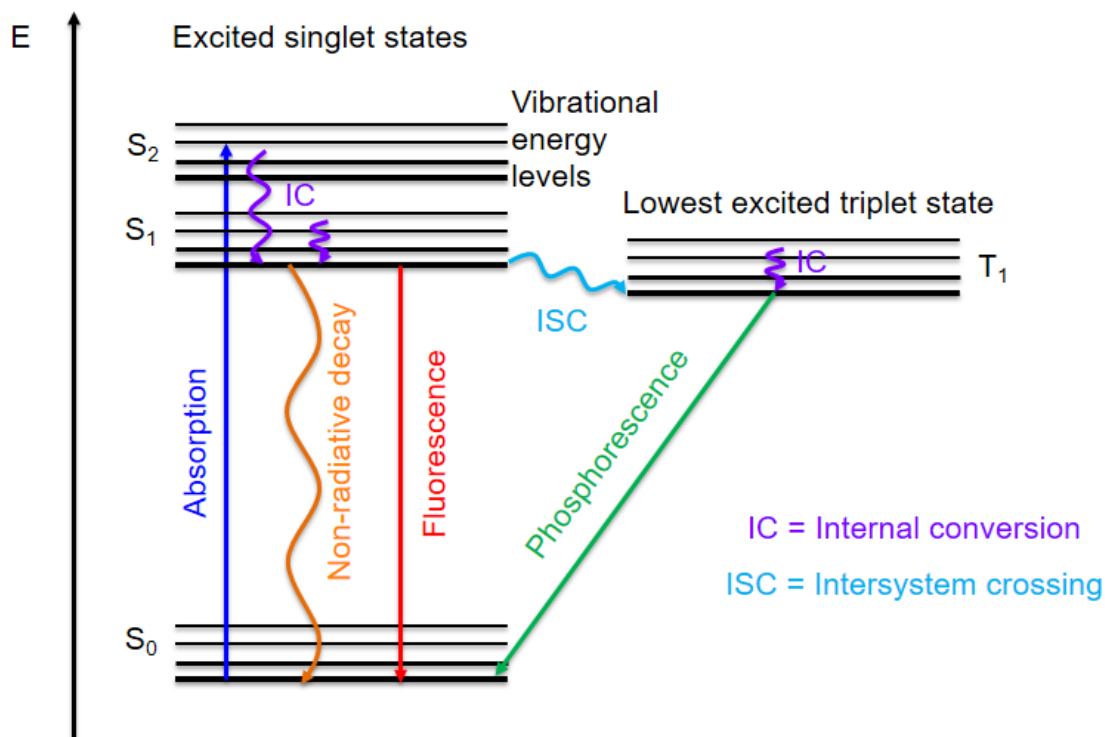


Figure 1.2 The Jablonski diagram describing light absorption and emission processes.

The fluorescence and phosphorescence are found at lower energy (longer wavelength) compared to the absorption. The loss of energy in the excited state of the fluorophore leads to deactivation processes resulting in its reducing fluorescence intensity and lifetime. The information from the fluorescence properties of the fluorophore is necessary for uses in various applications such as organic light emitting diodes [3], luminescent materials [4, 5], and fluorescent sensors [6, 7]. For fluorescence sensor, the optical characteristics (*e.g.*, fluorescence quantum yield, fluorescence lifetime and Stokes shift) are determined for the detection of change in photophysical properties of the fluorophore. Thus, this dissertation is focused on only fluorescence process.

1.1.1 Fluorescence Quantum Yield and Fluorescence Lifetime

The fluorescence quantum yield and lifetime are important characteristics of the fluorophore. The fluorescence quantum yield (Φ_F) is the efficiency of the fluorescence process. For simplicity, it is the ratio of a number of photons emitted to those photons absorbed by the fluorophore as shown in equation 1.1 [1]. Measurement of the time of the fluorophore spending in the excited state before the decay to the ground state is known as fluorescence lifetime (τ). It is useful to know how long that the molecule spends in the excited state before returning to the ground state.

$$\Phi_F = \frac{\text{Number of emitted photons}}{\text{Number of absorbed photons}} \quad (1.1)$$

The intensity of fluorescence can be decreased by many processes such as vibrational relaxation, non-radiative processes and interactions between the fluorophore and solvent molecules in solution phase. The decreasing intensity of fluorescence of the fluorophore is called quenching. Quenching may occur through thermal deactivation such as collision with solvent molecules or other external influences such as electron or energy transfer between the fluorophores.

1.1.2 Stokes Shift

General information of the absorption and emission spectra of the typical fluorophore is depicted in Figure 1.3. The maximum absorption spectrum (in solid

line) is found at the shorter wavelength (higher energy), whereas maximum emission spectrum (in dashed line) is found at the longer wavelengths (lower energy). The difference between the maxima of absorption band and emission band in the wavelength unit of the same electronic transition is called Stokes shift [8]. It is important to provide information of geometry change between the ground state and the excited state. Large Stokes shift shows obvious separation of absorption and emission peaks such as enol-keto tautomerization, *etc.* In addition, the large Stokes shift of a fluorescence species may indicate a large change of conformations. So, the information obtained from this characteristic of the spectrum can be used for the fluorescent sensor and will be explained in the next section.

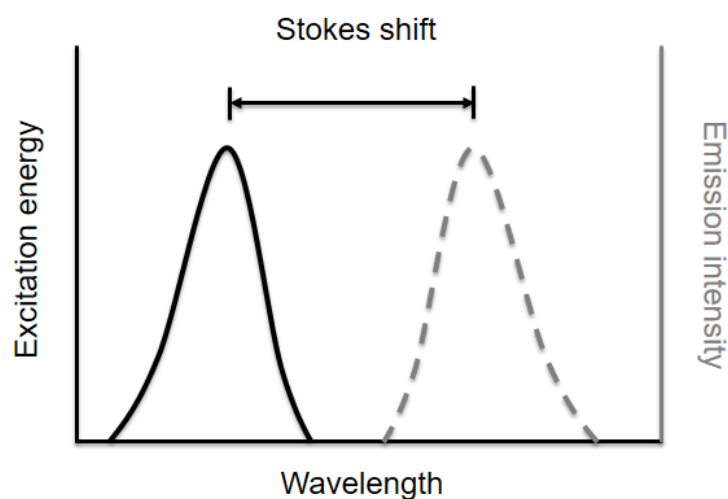


Figure 1.3 The difference between positions of the band maxima of the absorption and emission spectra of a typical fluorophore.

1.2 Chemical Sensing

Chemical sensing is one of the most important techniques in analytical chemistry and photochemistry [1, 9-11]. Chemical sensing refers to the detection of chemical species by using specialized devices such as a chemical sensor [12]. The chemical sensor is classified into different types according to operating principle of signal transducer, for example, optical, electrochemical, electrical, mass sensitive, magnetic, and thermometric principles. For optical devices, the chemical sensor uses optical properties to study changes in optical phenomena of the fluorophore including absorbance, reflectance, fluorescence, and light scattering [11]. Typically, it must be able to give a measurable signal in response to analyte recognition. It comprises two main components: a signaling part and a recognition part [1].

The chemical sensor using fluorescence property of the fluorophore is called a fluorescent sensor. It generally consists of the fluorophore (a signaling part) and the receptor (a recognition part) which is similar to chemical sensor. The fluorophore gives rise to a change in the photophysical properties and exhibits an optical response, while the receptor of the fluorophore binds to analyte in selective and efficient manner. A simple scheme of principle of the fluorescent sensor is shown in Figure 1.4. When the analyte interacts with the fluorophore at binding site, there are two possible “ON” or “OFF” signals of emission. Typically, the fluorophore can emit light after photoexcitation called “ON” but when it binds to analyte at the receptor side the fluorescence can be deactivated called “OFF” as shown in Figure 1.4a. On the other hand, the fluorophore binds with analyte as a complex and gives fluorescence called “ON” as shown in Figure 1.4b. For example, the fluorescent sensor for metals containing two essential features: a metal chelating or binding moiety and at least one fluorophore capable of absorbing and emitting light. The fluorophore may contain several units within its structure in which the receptor is separated from the fluorophore. In this case, a spacer is needed to connect the receptor with the fluorophore to make the fluorescent sensor function [1].

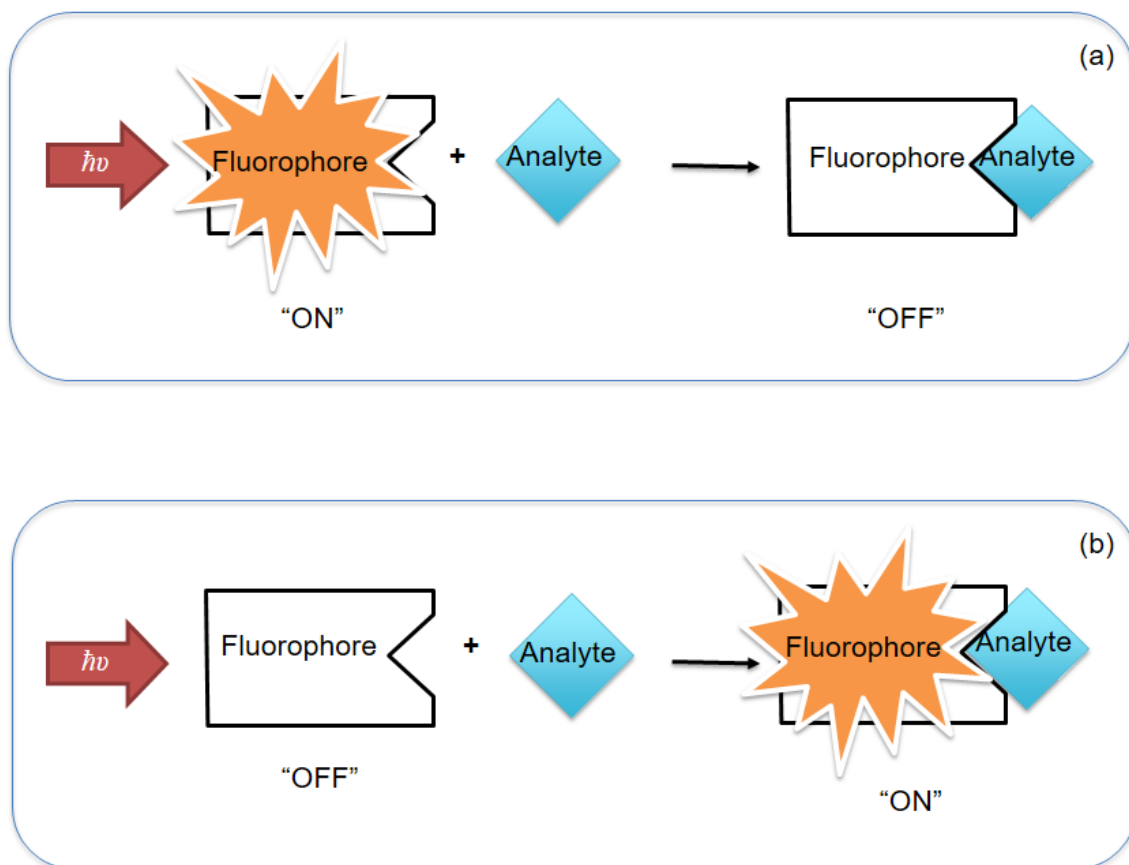


Figure 1.4 Schematic representation of principles of the fluorescent sensor.
 (a) “OFF” and (b) “ON” signals of fluorescence.

The fluorophore can emit many thousands of detectable photons that are fundamental to the high sensitivity of the fluorescence detection techniques. The main reason for the use of fluorescence sensing applications is a highly versatile spectroscopic method that employs the changes in fluorescence emission (wavelength, quantum yield, and lifetime). An understanding of the structural change at the molecular level upon the photoexcitation is important to help researchers develop the molecular design for uses as efficient fluorescent sensors [9]. The fluorescent sensors are used to detect a wide range of chemical species in different targets such as DNA [13], protein, [14] nucleic acid [15], sugar [16], metal ions such as Zn(II) [17]. The signal mechanisms have been developed based on photophysical processes, for example, intramolecular charge transfer (ICT) [18], metal-ligand charge transfer (MLCT) [19], and twisted intramolecular charge transfer (TICT) [20], *etc.* The enhancement or suppression of the ICT process of the ICT-based fluorescent sensor can lead to a redshift or blueshift in emission spectra. For MLCT, the charge transfer occurs from a

ligand to a transition metal. The MLCT energy level influenced by analyte is used for the design of the fluorescent sensor. In addition, TICT involving solvent relaxation around molecule gives a rotation of the proton donor part and the proton acceptor part up to 90° twist [9].

Fluorescent compounds normally contain π -conjugated and heterocyclic systems. They are classified into four categories: proteins and peptides, organic compounds, synthetic oligomers and polymers, and multi-component systems. Among them, the organic compounds such as fluorescent dyes have been intensively developed [21]. The commonly used fluorescent dyes such as BODIPYs [22], cyanines dyes [23], rhodamine analogues [24], squaraines [25], porphyrins [26] are utilized in many applications including tunable dye lasers, solar collectors, liquid crystal displays and electroluminescence displays [27]. Generally, the fluorescent dyes as a good fluorescent sensor used in the living systems should provide high intensity and large Stokes shift. Absorption and emission at longer wavelengths (lower energy) may result in less photodamage in the living systems [28]. It is an essential outcome to develop the fluorescent dyes with high efficiency and low toxicity for fluorescence bioimaging technology [26].

Moreover, fluorescent dyes exhibiting the excited-state intramolecular proton transfer (ESItraPT) or phototautomerization have been currently developed for various applications. The ESItraPT or phototautomerization is a reversible transformation process between two forms (enol and keto) of molecules by light absorption through an intrinsic intramolecular hydrogen bond. The ESItraPT molecules having large Stokes shift have been used as fluorescence probes [29]. The advantage of the large Stokes shift is less spectral overlap between absorption and emission. So this characteristic makes the ESItraPT dyes a promising candidate for use as a fluorescent sensor because of their appropriate photophysical properties including intense luminescence and large Stokes shift.

1.3 Excited-State Proton Transfer

The story of excited-state proton transfer (ESPT) started in 1950s, when the study of ESPT in salicylic acid was first reported by Weller [30], who noted that abnormally large Stokes shift compared to those of similar derivatives such as *o*-anisic acid. Most of the previous studies and reviews on ESPT have been focused on fundamental photophysical properties and proton transfer (PT) dynamics. ESPT is one of the most fundamental and important processes based on its photophysical properties [31-33]. Either excited-state intramolecular or intermolecular proton transfer (ESItraPT or ESInterPT) may occur depending on the nature of chemical structures. The ESItraPT exhibits in systems having an intrinsic hydrogen bond. However, some molecules do not have this intrinsic intramolecular hydrogen bond because the position of a proton donor is too far from a proton acceptor [34]. Therefore, PT can only occur through the assistance of solvent by forming the intermolecular hydrogen-bonded network between the solute and solvent molecules. The ESItraPT molecules with the intrinsic intramolecular hydrogen bond are of interest for many applications such as organic light emitting diodes [3], luminescent materials [4, 5], and fluorescent probes [6, 7]. The ESPT reaction has been investigated in many fundamental studies, for example, a model for hydrogen bonding in DNA bases and fluorescence emitting mechanism of green fluorescence markers in fluorescent probe [35]. Typically, this type of the PT process occurs along the hydrogen-bonded network. Most of the ESItraPT processes take place in molecules having a strong intramolecular hydrogen bond between O–H (or N–H) as a proton donor and C=N (or C=O) group as a proton acceptor [33]. The PT of these molecules is driven by an increase of the acidity of a proton donor group and also the basicity of proton acceptor group induced by photoactivation [36, 37]. In the ground state, the enol form is stable because the phenolic proton is not acidic enough to be deprotonated, implying that tautomerization does not occur in the ground state. Generally, the acidic and basic properties of the ESItraPT chromophore in the ground state differ from that in the excited state due to different electronic distributions of a molecule. PT from a proton donor group to proton acceptor group mostly proceeds in the excited state. In the excited state, the acidity of the molecule is higher than the ground state called photoacids. While, the basicity of an ESItraPT molecule usually increases in the excited state which is called photobases. Photoacidity is affected by

intramolecular charge rearrangement that is initiated by photoexcitation and also by intermolecular interactions with the solvent. Partial charge transfer to the aromatic ring may be important both in the photoacid and photobase sides. In the acid side this process is usually of a smaller magnitude than that in the photobase side and will make the acidic proton more positively charged and more susceptible to hydrogen bonding. In the photobase side charge transfer to the aromatic ring is considerable and contributes to increase the total photoacidity of the photoacid. So, the PT reaction from the excited enol can give the excited keto tautomer in subpicosecond timescale (Figure 1.5) [38]. This tautomerization in the ESIntraPT molecules results in a large Stokes shift between absorption and emission spectra [39].

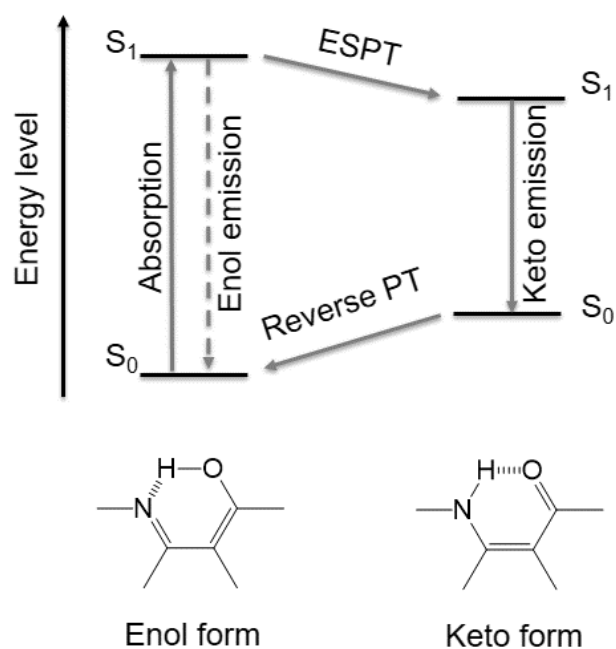


Figure 1.5 Schematic representation of excited-state intramolecular proton transfer (ESIntraPT) for four-level photocycle.

The appropriate position of the proton donor and acceptor is the most important point of PT reactions. Thus, the assistance by the solvents is necessary to trigger ESInterPT reactions. In presence of the solvent particularly the protic solvent, the formation of strong hydrogen bonds along the hydrogen-bonded network between solute and solvent can effectively reduce the reaction barrier and may induce intermolecular multiple-PT reactions to take place after the photoexcitation. Interesting compounds of ESInterPT molecules are 1*H*-pyrrolo[3,2-*h*]quinoline (PQ) [34, 40-43],

7-hydroxyquinoline (7HQ) [44-46], and 7-azaindole (7AI) [47-51]. The ESIntraPT reactions can spontaneously occur in some molecules through an intrinsic intramolecular hydrogen bond such as *o*-hydroxy Schiff base molecules [52-55]. Moreover, the ESIntraPT reactions have been studied theoretically and experimentally for several systems such as 2-(2'-hydroxyphenyl)benzoxazole (HBO) [37, 56, 57], 2-(2'-hydroxyphenyl)benzothiazole (HBT) [58, 59], 2-(2'-hydroxyphenyl)benzimidazole (HBI) [60, 61], 10-hydroxy-benzo[*h*]quinoline (HBQ) [62], and 2-(2'-hydroxyphenyl)benzotriazole (TIN-H) [63]. Among various molecules that exhibit the ESIntraPT, HBO is an interesting example of the ESIntraPT because its chemical structure can be easily modified [19]. Moreover, HBO has high quantum efficiency [64] compared to HBT and HBI. Therefore, HBO can be used as a prototype to study the ESIntraPT.



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1.4 2-(2'-Hydroxyphenyl)benzoxazole and Its Derivatives

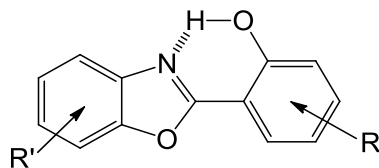
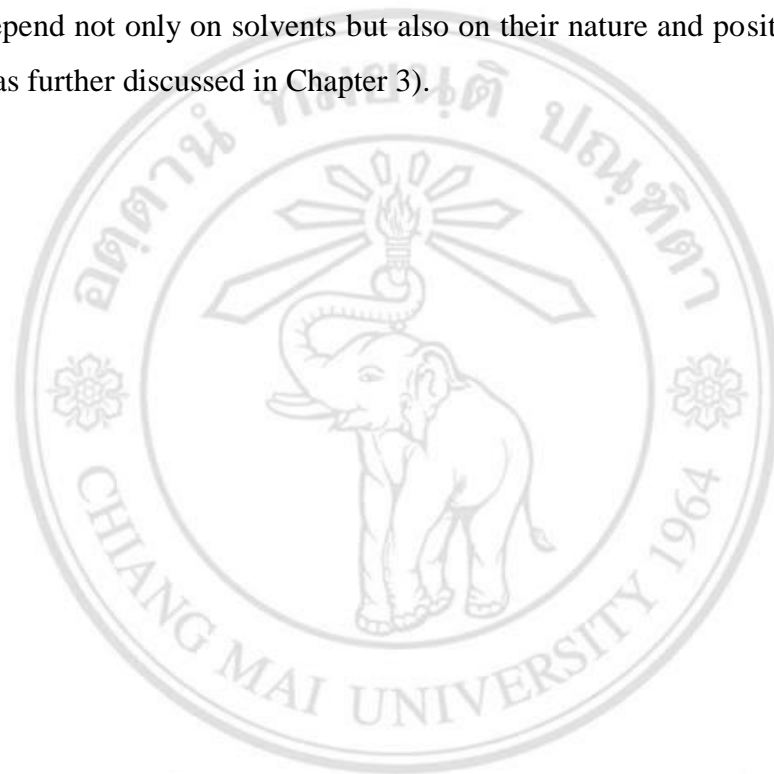


Figure 1.6 Structure of 2-(2'-hydroxyphenyl)benzoxazole (HBO) and its derivatives (where R and R' = H for HBO and other substituents for HBO derivatives).

2-(2'-hydroxyphenyl)benzoxazole (Figure 1.6) or HBO comprises the hydroxyl group (OH acting as the proton donor) and the benzoxazole group (nitrogen atom acting as a proton acceptor) [56]. The O–H group of a proton donor and the N atom of an acceptor in HBO form an intramolecular hydrogen bonding and exhibit a large Stokes shift arising from the ESIntraPT. To synthesize this desired HBO [65, 66], two methods are commonly used, for example, condensation of carboxylic acids with 2-aminophenols by dehydration, catalyzed by polyphosphoric acid (PPA) and oxidative cyclization of phenolic Schiff bases derived from condensation of 2-aminophenols and aldehydes. There have been several reports of HBO and its derivatives since 1953, for example, the investigation of the ESIntraPT in 2-(*o*-hydroxyphenyl)benzimidazole by Walter *et al.* [60] for detection of mercury. In 1970, stability studies, fluorescence spectra, quantum efficiencies, and excitation of the intramolecular PT reactions in HBO and its derivatives were reported by Heller and Williams [39]. In 1983, Woolfe *et al.* [67] studied the role of various *anti*-HBO and keto tautomer of HBO using time-resolved emission spectroscopy. Moreover, there is an intensive review of theoretical models for the singlet state of the ESIntraPT reported by Arnaut *et al.* [31] in 1993 as well as a study of photophysical properties of HBT and HBO reported by Chau *et al.* [68]. In 2005, the synthesis of HBO derivatives with the electron donor and acceptor substituents was studied by spectroscopic and theoretical methods by Seo *et al.* [69]. Recently, spectroscopic and theoretical studies of the ESPT molecules have been intensively reviewed [37, 70]. For HBO, the ESIntraPT occurs in ultrafast timescales of hundreds of femtoseconds. Femtosecond time-resolved spectroscopy is used to monitor this ultrafast dynamical behavior of hydrogen bonds in the electronic excited state [67]. For more information on the excited-state dynamics please see Chapter 2. Spectral features of absorption and emission of HBO show a large Stokes shift [71], indicating

the enol-keto tautomerization of HBO. Moreover, absorption and emission spectra of HBO strongly depend on solvent. In the gas phase and non-polar solvents, HBO shows its absorption peaks in the region 280-330 nm and only keto emission peak is found at ~480 nm [37], while in polar solvent, its absorption is blue-shifted compared to non-polar solvent but the enol emission peak is observed at ~360 nm and keto emission at ~475 nm [67, 72]. From these findings, solvent certainly plays an important role in absorption and emission spectra. The photophysical behaviors of HBO and its derivatives depend not only on solvents but also on their nature and position of various substituents (as further discussed in Chapter 3).



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1.5 Computational Chemistry

Computational chemistry is a mathematical approximation using computers to find the approximated solutions on the information of interesting chemical problems such as properties of molecules, predicted experimental results, *etc.* Most approximation methods of the computational chemistry is based on the Schrödinger equation [73, 74].

1.5.1 *Ab Initio* Theory

The term “*ab initio*” means “from the beginning”. The basis for *ab initio* methods is a differential equation derived from Schrödinger equation. The Schrödinger equation (1.2) is the fundamental equation for describing quantum mechanical behavior. The Schrödinger equation [75] represents a description of a molecular system in terms of a wavefunction (Ψ), Hamiltonian operator (\hat{H}) for a system of nuclei and electrons, and the energy (E).

$$\hat{H}\Psi = E\Psi \quad (1.2)$$

The wavefunction contains all information of the entire considered system. The wavefunction for the system of interest is solved by applying the appropriate mathematical operation to the Schrödinger equation [75]. The total wavefunction of the system can be written as the product of an electronic wavefunction and a nuclear wavefunction. This equation leads to an exact solution that can be obtained by using an expansion of the form:

$$\Psi(r, R) = \psi(r)\chi(R) \quad (1.3)$$

Here ψ is a wavefunction associated with solving the electron part of the Schrödinger equation for fixed nuclear coordinates, and χ is a wavefunction associated with nuclear motion. However, the wavefunction and energy of the system can be obtained by specified Hamiltonian operator (\hat{H}). The Hamiltonian operator consists of the kinetic (T) and potential (V) energies, in which Hamiltonian operator acts upon the wavefunction to give the evolution of the wavefunction. For simplicity, the Hamiltonian operator can be written as

$$\hat{H} = T_N(R) + T_e(r) + V_{eN}(r, R) + V_{NN}(R) + V_{ee}(r) \quad (1.4)$$

when $T_N(R)$ = kinetic energy of the nuclei
 $T_e(r)$ = kinetic energy of the electrons
 $V_{eN}(r, R)$ = electron-nuclei attractive Coulomb potential
 $V_{NN}(R)$ = nuclear-nuclear repulsive Coulomb potential and
 $V_{ee}(r)$ = electron-electron repulsive Coulomb potential.

The wavefunction is dependent on the electronic and nuclear positions. The nuclei are much heavier than the electrons implying that the nuclear motion is so much slower than that of electrons. The assumption that the electron motion and the nuclear motion in the molecule can be considered separately is known as Born-Oppenheimer approximation [73]. Thus, the Hamiltonian of the Schrödinger equation under Born-Oppenheimer approximation is

$$\hat{H}_{electron} = T_e(r) + V_{eN}(r, R) + V_{ee}(r) \quad (1.5)$$

In addition, the Schrödinger equation can be applied to the system of interest. Only energy of atom having one electron such as the hydrogen atom has been solved for exactly but multi-electron atoms require approximation methods. So, the Schrödinger equation requires the use of sophisticated techniques and mathematical methods to find the numerical solution. The calculations corresponding to *ab initio* theory are performed at several levels of theory. Initial investigations may start from Hartree-Fock approximation (HF) with the treatment of Coulombic electron-electron repulsion as an average effect of repulsion. For more accurately, the higher levels of theory concerning electron-electron correlation such as Møller-Plesset (MP) perturbation theory, configuration interaction (CI) calculation, coupled-cluster (CC) method, *etc.*

1.5.2 Hartree-Fock Approximation

In general, the many-electron wavefunction for Hartree model was written as a straightforward product of one-electron orbital ψ_i (when ψ_i represents α and β electron spin. From Fock's contribution to the field, it shows as a Slater determinant which is satisfied by the Pauli exclusion principle. For an N -electron

system, the HF equation for the spin-orbital, $\psi_i(N)$, where N assigned to electron N in the Slater determinant:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \dots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \dots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \dots & \psi_N(N) \end{vmatrix} \quad (1.6)$$

The approximation is derived from theoretical principle without inclusion of experimental data [76, 77]. The Coulombic electron-electron repulsion is treated in an average effect of repulsion. Each electron is considered to move in the electrostatic field of the nuclei and the average field of the other electrons. The most common approach of *ab initio* is called HF approximation. In addition, the step in HF calculation starts with an initial guess for the orbital coefficients. Calculations of energy and a new set of the orbital coefficients are finished then a new set will be recalculated until the energy and orbital coefficient remain constant (or convergence). This iterative calculation is called a self-consistent field (SCF) [76, 77]. The derivation of the HF equations can be solved in many ways. The common one is to look for an eigenvalue equation for the HF orbitals [75]:

$$\hat{f}\psi_i = \varepsilon_i\psi_i \quad (1.7)$$

where the Fock operator \hat{f} depends only on the coordinates of any one of the electrons, spin-orbital energy (ε_i) and spin-orbital (ψ_i).

1.5.3 Post Hartree-Fock Approximations

1.5.3.1 Møller–Plesset Perturbation Theory

MP improves on HF methods by introducing electron correlation effects. This calculation starts from an eigenfunction of the Fock-operator and the expressions produced by perturbation theory can be obtained as

$$\hat{H} = \hat{H}^{(0)} + \hat{V} \quad (1.8)$$

where $\hat{H}^{(0)}$ is known as the unperturbed Hamiltonian, while \hat{V} is termed the perturbation [78].

The ground-state energy is given by

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots \quad (1.9)$$

where superscript numbers are zeroth-order, first-order, second-order energy (E_{MP2}), etc.

Since $E^{(0)}$ is equal to the energy from HF (E_{HF}) and $E^{(1)}$ is zero. So, the lowest-order correlations energy can be obtained from second-order MP (MP2). The total electronic energy from MP2 is given by the HF energy and MP2 correction:

$$E = E_{HF} + E_{MP2} \quad (1.10)$$

1.5.3.2 Configuration Interaction Calculation

In HF equation, a single Slater determinant is employed for the approximation for the electronic wavefunction. For more accurately, a linear combination of all possible N -electron Slater determinants is necessary such as in CI. Single excitation configuration interaction (CIS) and all single and double excitation CI (CISD) calculations are probably the most common use to obtain excited-state energies. The exact electronic wavefunction for any states (ground and excited states) of the system in

$$\Psi_s = \sum_i^I C_{is} \psi_i \quad (1.11)$$

where the sum is over a finite number I of determinants ψ_i with expansion coefficients C_i for state s .

1.5.3.3 Coupled-Cluster Method

CC calculation is similar to CI calculations. The CI calculation wavefunction is a multiple-determinant wavefunction conducted by starting with the HF wavefunction and making new determinant by promoting electron from

the occupied to unoccupied orbitals. This CI calculation is very accurate, but the cost of computing is very high (N^8 time complexity). CC method introduces the cluster operator C which is related to the exact electronic wavefunction to HF wavefunction

$$\Psi = e^C \psi_0 \quad (1.12)$$

when e^C is the exponential operator.

The CC results are a bit more accurate than the equivalent size CI calculation results [76]. In the calculation, the resolution-of-the-identity (RI) with second-order approximate coupled-cluster model, RI-CC2 is used as a module for the calculation of excitation energies and response properties at a correlated *ab initio* level, in particular the CC2. In addition, the performance of the second-order methods for excitation energies is concerned in many systems. The approximation of CC2 is used to solve the excitation energies corrected through second-order in the fluctuation potential, the Jacobian \mathbf{A}^{CC2} . All calculations employed RI approximation for the electron repulsion integrals need the correlation treatment and the description of excitation processes. However, RI with the Algebraic Diagrammatic Construction through second order, RI-ADC(2), and is used in the calculations [79, 80]. A Hamiltonian similarly transformed with the exponential function of the single replacement part of the cluster operator. The secular used in ADC(2) is the symmetric or, in some cases, the Hermitian part of that for the iterative variant of the doubles correlation to CI singles, CIS(D_∞) in $\mathbf{A}^{\text{CIS}(D_\infty)}$. So, the Jacobian $\mathbf{A}^{\text{ADC}(2)}$ is

$$\mathbf{A}^{\text{ADC}(2)} = \frac{1}{2} (\mathbf{A}^{\text{CIS}(D_\infty)} + (\mathbf{A}^{\text{CIS}(D_\infty)})^*) \quad (1.13)$$

The above relations between CC2, CIS(D_∞), and ADC(2) provide a simple recipe to implement the latter two methods in an existing CC2 program: for CIS(D_∞), the only modification required is that the converged CC2 ground-state amplitudes are replaced by those from first-order perturbation theory.

1.5.4 Density Functional Theory

Density functional theory (DFT) [74] is one of the most widely used methods based on electron probability density, ρ . This method has become popular in recent years because it is less computational requirement than other methods with similar accuracy such as MP2. The general theoretical framework of DFT was originated by the Hohenberg and Kohn theorem. However, in practical applications, Kohn and Sham developed the theory that formulated a method similar in structure of HF method [2]. Instead of solving the problem using single electron wavefunction, this method uses one function to represent the entire electron density of the molecule, $\rho(r)$. The exact ground-state electron density is given by

$$\rho(r) = \sum_{i=1}^N |\psi_i(r)|^2 \quad (1.14)$$

Electronic energy as a function of electron density is represented by

$$E[\rho] = E_T[\rho] + E_V[\rho] + E_U[\rho] \quad (1.15)$$

where $E_T[\rho]$ is kinetic energy, $E_V[\rho]$ is potential energy, and $E_U[\rho]$ is external perturbation and Coulombic repulsive force between pairs of electrons. A simple form can be written as

$$E_T[\rho] = E_T[\rho] + E_V[\rho] + E_{XC}[\rho] \quad (1.16)$$

where the sum is overall energy of the occupied Kohn-Sham orbitals, the first term in the equation 1.16 represents the kinetic energy of the electrons; the second term is potential energy including electron-nucleus attraction and Coulomb repulsive interaction between electrons; and the last term is the exchange-correlation energy of the system. E_{XC} term is the functional of the electron density that can be split the exchange-correlation term into a sum of exchange effects and correlation effects.

$$E_{XC}[\rho] = E_X[\rho] + E_C[\rho] \quad (1.17)$$

Therefore, exchange-correlation potential, V_{XC} can be presented as the functional derivatives of the exchange-correlation energy:

$$V_{XC}[\rho] = \frac{\delta E_{XC}[\rho]}{\delta \rho} \quad (1.18)$$

Several exchange-correlation functionals have been developed for use in DFT calculations. For example, the most famous DFT for investigating the interesting system is hybrid three parameters of Beck and Lee-Yang-Parr correlation functional (B3LYP) [81, 82]. It notes that various approximations – local density approximation (LDA), Hartree-Fock (HF), Becke-1988 (B88), Lee-Yang-Parr 1988 (LYP88), and Vosko, Wilks, Nusair 1980 (VWN80) – are part of this hybrid functional:

$$E_{XC}^{Hybrid}[\rho] = C^{HF} E_{XC}^{HF} + C^{DFT} E_{XC}^{DFT} \quad (1.19)$$

From three parameters of B3LYP, it could give satisfied results on the organic molecules with experimental data. This functional spends 20% HF exchange and 75% correlation weighting [81, 82]. PBE0 or PBE1PBE [83] is a pure functional introduced by Perdew, Burke, and Ernzerhof since 1996. This functional spends 25% HF exchange and 75% correlation weighting. The following functionals include long range corrections such as CAM-B3LYP [84] proposed by Handy and coworkers' long range corrected version of B3LYP using the Coulomb-attenuating method. Head-Gordon and coworkers suggest ω B97XD method [85] including Grimme's dispersion. In addition, LC-BLYP [86] is added to any pure functionals to apply the long correction reported by Hirao and coworkers.

1.5.4.1 Time-Dependent Density Functional Theory

Time-Dependent Density Functional Theory (TD-DFT) is the generalization of stationary DFT to time-dependent potentials and electron densities, $\rho(r, t)$ [87]. TD-DFT is a very popular tool for electronic excitation energies and oscillator strength. It is a powerful tool in studying photochemistry because its computation

cost is not expensive compared to the post HF methods. The time-dependent Kohn-Sham equation in TD-DFT is

$$\rho(r, t) = \sum_{i=1}^N |\psi_i(r, t)|^2 \quad (1.20)$$

1.5.5 Frank-Condon Principle

According to the Born-Oppenheimer approximation, electronic transitions is very fast compared with nuclear motions. The analysis of vibronic transitions is based on the Frank-Condon principle that electronic transitions occurs between electronic states before nuclei have time to adjust. This electronic transition is most likely to take place without position changes of the nuclei. Vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates [88]. In Figure 1.7 showing a vertical transition, the greatest overlap of vibrational wavefunction is between the v_0 of the electronic ground state and v_2 on the first excited singlet state.

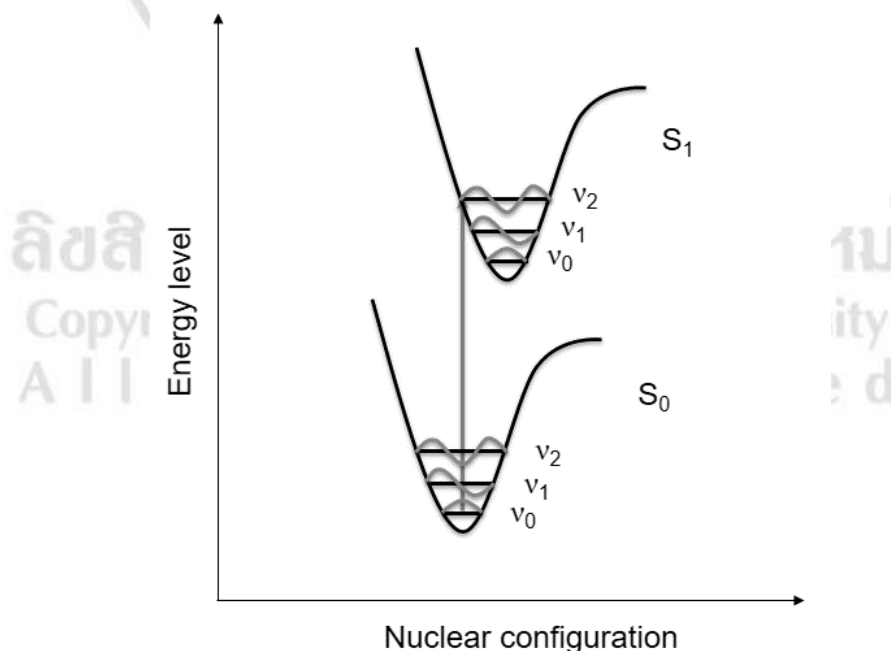


Figure 1.7 Frank-Condon energy diagram.

1.5.6 Adiabatic Dynamics

Time-dependent Schrödinger equation can be used to solve the basic problem in dynamics simulations of molecules for the complete molecular system,

$$\left(i\hbar \frac{\partial}{\partial t} - \hat{H} \right) \Psi(r, R, t) = 0 \quad (1.21)$$

where Ψ is the wavefunction depending on time (t), on the nuclear coordinates, R , and on the electronic coordinates, r , of the whole system. In this case Born-Oppenheimer expansion describes the nuclear motion as

$$\Psi(r, R, t) = \sum_i \psi_i(r; R) \chi_i(R, t) \quad (1.22)$$

A series of approximation performed for the simulations should be imposed. Reduced time-dependent Schrödinger equation is a set of first-order differential equation for the amplitudes c_k of each electronic state k :

$$i\hbar \frac{dc_k}{dt} + \sum_j (-V_k^c \delta_{kj} + i\hbar F_{kj}^c \cdot v^c) c_j = 0, \text{ noted as adiabatic [89]} \quad (1.23)$$

In this equation, V_k is the potential energy surface for state k , v is the nuclear velocity and F_{kj} is the nonadiabatic coupling vector between the states k and j .

Technically, we can solve this problem by generating a phase space distribution in the ground state and then exciting it to the excited states or to the higher level of energy. We prepared the ground-state trajectory simulation or sampling from a possibility for ground state distribution. However, this two methods may be slightly different. The ground-state potential energy surface near the minimum ($3N - 6$ internal coordinates) can be explained in term of the normal modes and the nuclear wavefunction can be approximated as that of a quantum harmonic oscillator. The classical phase space distribution can be approximated by a Wigner distribution (P^W). Sampling coordinates and momenta are in independent random values of the momentum (P^i) associated with the normal coordinate (Q^i).

$$P_w(Q^i, P^i) = |\chi_{OH}^0(Q^i)|^2 |\xi_{OH}^0(P^i)|^2, \quad (1.24)$$

where ξ_{OH}^i is the harmonic oscillator wavefunction in the momentum representation.

1.5.7 Basis Sets

A complete set of basis functions must be used to represent spin-orbitals [74]. The examples of basis functions are Slater-type orbitals (STOs) and Gaussian-type orbitals (GTOs). The simplest type of basis set is a minimal basis set in which one function is used to represent each of the orbitals of valence electron such as 1s-orbital, for hydrogen atom. In addition to the basis function in the minimal basis set, a double-zeta and triple-zeta basis sets are adopted to give full description of spin-orbitals. The accuracy of any calculations becomes more reliable when the flexibility in changing size and shape of molecular orbitals increases. This change in size and shape of molecular orbitals can be obtained from inclusion of a split-valence (SV) basis set and polarization and diffusion functions. The SV basis set provides two basis functions and one basis function for each valence orbital and inner-shell atomic orbital, respectively. Basis functions of *d*-type orbital is included for polarization functions of *p*-type basis function. Another addition to basis sets is the addition of diffuse functions [90] which is necessary for anions, Rydberg states, very electronegative atoms with a lot of electron density and for accurate polarizabilities or binding energies of van der Waals complexes (bound by dispersion). So, the evaluation of the basis functions needs to be considered due to the computational consumption and avoid basis-set superposition error.

1.6 Objectives

In this dissertation, the theoretical studies of ESPT processes and photophysical properties of HBO and its derivatives are investigated. To utilize the HBO and its derivatives as a fluorescent sensor, the detailed information of different conformers of HBO with and without interacting with water molecule are elaborately described using dynamics simulations at high accurate level of ADC(2). For use as screening tool and control desirable properties such as tunable and control fluorescence, DFT and TD-DFT calculations of HBO and its derivatives will be performed. These cost-effective methods of choices that provide precise photophysical properties with smallest deviation from the experiment are chosen to predict the spectra and large Stokes shift arising from the ESIntraPT through the intrinsic intramolecular hydrogen bond of HBO and its derivatives. The theoretical studies of ESPT processes and optical properties of HBO and its derivatives were performed using the computational approaches: excited-state dynamics simulations and TD-DFT calculations.

In the first part, we present both static and dynamics calculations for free HBO and its solvated clusters. In ground-state calculations, different conformers of free HBO in Figure 1.8 (*syn*, *anti*, and opened-HBO) and its hydrated clusters (intramolecular hydrogen-bonded, intermolecular hydrogen-bonded, and opened-HBO) are optimized to obtain the lowest energy (most stable) geometry. To provide more complete pictures of ultrafast PT of these systems, excited-state dynamics simulations are performed in the gas phase to explore reaction pathways, reaction probabilities and PT time. Moreover, the roles played by a water molecule in an ultrafast PT are discussed (in Chapter 2).

In the second part, in order to control desirable photophysical properties for the fluorescence applications, molecular design of HBO and its derivatives (Figure 1.9) is carried out to provide the best candidates for applications in fluorescent sensors. The properties of appropriate candidates of HBO derivatives include lowest excitation energy and high intensity for absorption. While in emission these candidates should have large Stokes shift and emit the fluorescence in the longer wavelength (low energy) because of less photodamage for further applications the living cells. We start from computing using various DFTs and TD-DFTs to find the suitable method of choice and to further study substitution effect on electronic and photophysical properties of HBO

and its derivatives using DFT and TD-DFT calculations to explain spectral shift corresponding to HOMO and LUMO energy gaps of HBO derivatives having electron donors and electron acceptor compared with HBO (as discussed in Chapter 3).

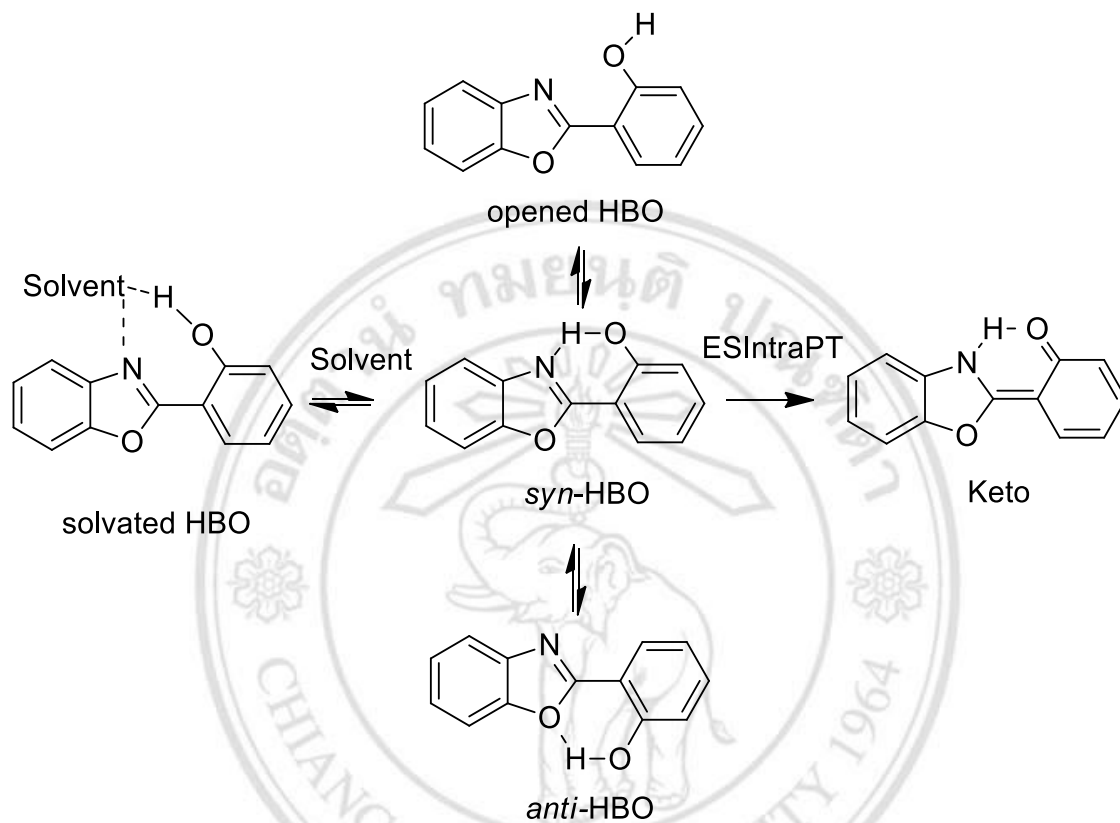


Figure 1.8 Different conformers of free HBO (*syn*, *anti*, and opened-HBO) and its hydrated cluster.

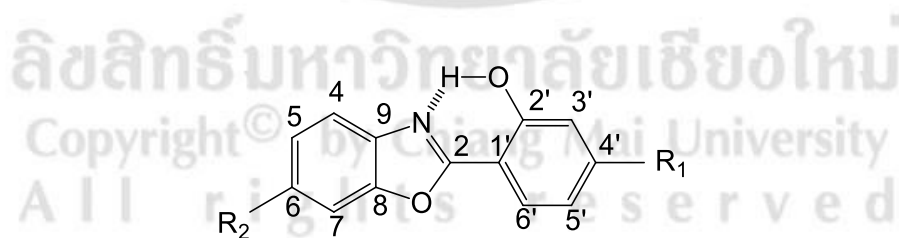


Figure 1.9 HBO and its derivatives with R₁ and R₂ substitutions.