

# **EXPLORING THE PROTON TRANSFER DYNAMICS OF SOME HYDROGEN BONDED HETEROCYCLIC MOLECULES IN DIFFERENT ENVIRONMENTS**

*Synopsis submitted in fulfillment of the requirements for the Degree of*

**DOCTOR OF PHILOSOPHY**

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February, 2014

## SYNOPSIS

Materials are ubiquitous. Each and every material are made up of small or big sized organic/inorganic molecules or molecular complexes such as water, amino acids, proteins, deoxyribonucleic acid (DNA), ribonucleic acid (RNA) where the basic building blocks are carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S), fluorine (F) [1]. The molecule/complex structures are the resultant of some chemical bonding due to different types of electrostatic interaction forces [2, 3]. Van der Waals bonding is one of the most significant types of bonding. This bonding arises from the coulombic attractive force (van der Waals force) between the oppositely charged ends of two or more dipoles [3]. A specific type of van der Waals' bonding exists between a positively charged H atom and a negatively charged atom or functional group [3], is known as hydrogen bonding. This bonding appears between partly exposed positively charged ( $\delta^+$ ) proton (H) [bound to an electron-withdrawing atom Z (O, N, F, etc.)] and a negatively charged ( $\delta^-$ ) lone pair of atom X (O, N, F, etc.) or functional group. Hydrogen bonding is very crucial for the existence of life. Water, which is a synonym of life, is one of the yields of hydrogen bonding [4]. Hydrogen bond defines the structures of protein ( $\alpha$ -helices,  $\beta$ -pleated sheets), DNA, RNA [5]. Most of our food items like carbohydrates (rice, wheat etc.), sugar [6], etc. are made of hydrogen bonded molecules. In the making of bio fuel gasoline [7] and ammonia based fertilizers (urea) [8], hydrogen bonding plays a vital role. In the area of crystal engineering hydrogen bonded interaction is used to produce different novel bulk and nano materials [9-11].

For hydrogen bonded system coulombic interaction can be expressed as  $Z^{\delta^-}-H^{\delta^+}\cdots X^{\delta^-}$  [3]. Z and X acts as hydrogen donor and acceptor atom. Acceptor X may or may not be bonded to another atom/functional group covalently but should contain at least one lone pair on it. Hydrogen bonding energy covers the range  $0.2 - 40 \text{ kcal mol}^{-1}$ . The bond length  $H\cdots X$  varies from  $\sim 1.5 \text{ \AA}$  to  $\sim 3.0 \text{ \AA}$ . The bonding is strongly affected by surrounding environments such as: local polarity, viscosity, acidity, basicity, organized assemblies (cyclodextrins, micelles) etc.

There are two types of hydrogen bonded molecular complexes: Intermolecular hydrogen bonded (**I<sub>er</sub>HB**) complexes and intramolecular hydrogen bonded (**I<sub>ra</sub>HB**) complexes. In **I<sub>er</sub>HB** complex, the hydrogen bond is formed between two different molecules ( $Z-H\cdots X \leftrightarrow Z\cdots H-X^+$ ), whereas in **I<sub>ra</sub>HB** complex hydrogen bond is formed within the same molecule. Due to its weak bonding force, the hydrogen bond can form/break easily with

the application of some external stimuli [12, 13]. There are mainly three types of external force fields which can affect hydrogen bonding. They are electric field, magnetic field, and electromagnetic field. Electric field can break or distort the hydrogen-bond by causing a reorientation of the charges and hence weaken or destroy the hydrogen-bonded network [12]. Whereas in presence of magnetic field hydrogen bonding strength used to enhance due to increased electron delocalization of the hydrogen-bonded molecules [13]. But the effect of electromagnetic field (electromagnetic radiation) can induce electronic redistribution of charges in the hydrogen bonded complexes, as a result of that molecules/complexes became more polar and so charge (proton,  $H^+$  ion) transfer can occur within the molecular system or with the surrounding environment. The process is known as **Proton transfer** (PT) where a proton gets transferred directly from the acidic site to the basic site [14-16] of a molecular network. So hydrogen bonding is an important intermediate in proton transfer reaction. The site from where proton is transferred is called as the proton donor and the receiving site is called as proton acceptor. Proton transfer reaction is one of the most common and fundamental reaction in physics, chemistry, and biology [17] to observe. There are various types of proton transfer process appear in hydrogen bonded complexes. They are:

1. Intramolecular Proton Transfer ( $I_{ra}PT$ )
2. Intermolecular Proton Transfer ( $I_{er}PT$ )

If the proton transfer occurs within the same molecule, the process is known as *Intramolecular Proton Transfer* ( $I_{ra}PT$ ). If the proton transfer occurs between different molecules, the process is known as *Intermolecular Proton Transfer* ( $I_{er}PT$ ). In an organic bifunctional molecule, containing the hydrogen donor and acceptor groups in close proximity, an intramolecular hydrogen bond is generally formed in the ground electronic state [18]. A distance of  $< 2 \text{ \AA}$  between the donor and the acceptor atom favours the migration of the proton to produce a proton transferred tautomer [19] by  $I_{ra}PT$ . The  $I_{er}PT$  process depends on the nature of the probe molecules and the surrounding environment.  $I_{ra}PT$  and  $I_{er}PT$  play important role in many chemical and biochemical process [15, 17]. Proton transfer active probe system used to show dual minima in its potential energy surface due the formation of newly proton transferred (zwitterion and /or anion) complex.

The driving force of the proton transfer process comes from the drastic changes of acidity and basicity of the involved hydrogen bonded groups of the probe system both in ground and excited states. Both  $I_{ra}PT$  and  $I_{er}PT$  processes can appear in the ground state and excited states. *Ground State Proton Transfer* (GSPT) reaction is one of the simplest process

found in hydrogen bonded system. GSPT mainly occurs due to the hydrogen-bonding ability of the molecules with the environment. On the other hand *Excited State Proton Transfer* (ESPT) is much popular due to their unquestionable importance in fundamental and applied physics and chemistry. Acid-base property in the excited state differs considerably from the ground state due to extensive redistribution of electron densities [18-20]. Most of hydrogen bonded organic molecules which are more polar in the excited state, can donate a proton to a basic acceptor group (within a molecule or surrounding environment), which results a very fast proton transfer (PT) reaction in the excited state [15-17]. In *Excited State Intermolecular Proton Transfer* (ESI<sub>er</sub>PT) process, a proton (one or more) is transferred from one molecule (proton donor) to another (proton acceptor) molecule or complex. ESI<sub>er</sub>PT appears in complex form or in molecular clusters. The ESI<sub>er</sub>PT process depends upon the nature of molecules and its surrounding environment. Studies on ESI<sub>er</sub>PT with solvent participation enable us to define the fine structure of the solvation shell and give valuable information regarding the nature and mechanism of acid (donor)-base (acceptor) reactions in aqueous and non-aqueous medium [21]. Another most important proton transfer phenomenon is *Excited State Intramolecular Proton Transfer* (ESI<sub>ra</sub>PT). If the proton is transfer from one moiety to another moiety within a single molecule [22] in the excited state that is known as ESI<sub>ra</sub>PT. The transfer of a proton between two groups of an aromatic molecule causes large electronic and structural rearrangements with the formation of zwitterionic species, which are associated with significant changes in dipole moments and molecular geometry and quite large (<10000 cm<sup>-1</sup>) fluorescence shifts [23]. The fields of ESI<sub>er</sub>PT and ESI<sub>ra</sub>PT reaction are expanding rapidly due to their potential applications in different areas of science, technology and industries like energy/data storage devices, optical switches [24], Raman filters, hard scintillation counters, polymer photostabilizers, conductive wires [25], lasers, organic light emitting diodes etc [26]. The newly observed most attractive applications of some specific organic ESI<sub>er</sub>PT and ESI<sub>ra</sub>PT systems are as white light generators in the optoelectronics industry. The large variation in energy level has led these systems to be used as ideal candidates for a white light generation [27], fluorescent sensors [28], organic conductor and superconductor, memory storage devices [24, 25] etc.

Recently the solvent polarity sensitive organic proton donor-acceptor (Z-X) compounds have been claiming increased interest and are being used as the fluorescent probes to study different microenvironments [29, 30]. The reactions have been employed as a mechanistic tool in the study of proton hydration dynamics [31, 32]. Reactants accommodated

in molecular assemblies like protein [33], micelles [34], reversed micelles [35] and cyclodextrins media [36] vesicles, etc. often achieve a greater degree of organization compared to their geometries in homogeneous solution. These reactions in bio-systems have potential use as energy storage [37]. The organized environment restricts the molecular motions inside the finite size assemblies, which influences the proton transfer process in a highly interesting way. One of these organic assemblies is cyclodextrin (CD). CDs are naturally occurring degraded starch formed by glycosyl transferases which are capable of embedding appropriate sized molecules. These resulting supramolecules can serve as excellent miniature models for enzyme–substrate complexes. CDs can sequester external guest molecules in their nano sized cavity by forming the annular structure [38]. CDs can act as host and can easily form inclusion complexes with a variety of guest molecules [39]. The complexation with the guest molecule occurs within the inner cavity where hydrophobic force stabilizes the formation of inclusion complex. Complexation can give a beneficial modification of the guest molecule's properties such as its solubility enhancement, physical isolation, volatility, sublimation control, stabilization for the protection of color, odor, flavor [40] etc. which has potential applications in drug delivery, catalysis [41], photochemistry, paint industry etc.

Fluorescent hydrogen bonded organic molecules revealing IPT dynamics, such as Anthraquinones, Pyridyls, Flavones are used in different optoelectronic applications such as organic light-emitting diodes (OLEDs) [27], organic light-emitting field-effect transistors (OLEFETs), organic solid-state lasers, organic fluorescent sensors, etc. Often materials that are strongly fluorescent in liquid solution become non-fluorescent in the solid form and vice versa. So the materials which fluoresce in both forms have a wide range of applications in all above fields. In view of all above mentioned applications today's scientific researchers are extensively using different biodegradable organic hydrogen bonded IPT active molecules. Two of such interesting systems are five member hydrogen bonded organic heterocyclic Indole and Pyrrole group systems like Benzoxazoles [42], 2-(2'-Phenylureaphenyl) benzoxazole [43], 2-(2'-Hydroxyphenyl) benzoxazole, Polypyrrole [44] etc. which are actively participating in all above mentioned optoelectronic applications. These Indole and Pyrrole derivatives are also used as a subject of extensive research for their interesting biological activities like antitumor, anti diabetic drugs [45]. Indole systems are significant players in a diverse array of markets such as dyes, plastics, agriculture, vitamin supplements, drugs, and perfumery. Similarly Pyrrole and its derivatives are widely used as an intermediate

in the synthesis of pharmaceuticals, medicines, agrochemicals, dyes, photographic chemicals, perfumes, and other organic compounds [45]. Highly functionalized Pyrroles are subunits of chlorophyll, vitamin B12, etc. Pyrrole is also used in drugs, eg. Atrovastatin (Lipitor) which is used for lowering cholesterol [46].

In the work plan of my present thesis I have chosen some organic heterocyclic hydrogen bonded molecules from Indole family such as: Indole (I), Indole-3-carboxaldehyde (I3C), Indole-7-carboxaldehyde (I7C) etc. and from Pyrrole family like Pyrrole-2-carboxaldehyde (PCL), 2-Acetyl pyrrole (2AP) as my probe systems. Indole (I) and its other carbonyl substituted derivatives like I7C, I3C are known as tryptophan residues of DNA photolyse which can be envisaged as a chemotherapy drug to bring DNA cleavage [47]. PCL is one of the basic structures of DNA base pairs. 2AP is found in many baked foods as a flavoured component like different types of fried and roasted flavourings since it is responsible for the roasted flavour of pumpkin oil. All these molecules have the capability to form intramolecular/intermolecular hydrogen bonding with themselves and surrounding environments. The aim of the present thesis is to investigate the dynamics of these molecules experimentally and theoretically in different environments in view of their enormous applications in industry. All of these molecules are involving themselves in charge (proton) transfer activities in different phases and environments. We have studied the existence of hydrogen bonding and proton transfer behaviour of these probe systems in different phases such as liquid, solid, gas etc. and in presence of different perturbed environments like polar and nonpolar solvents, acid, base, restricted organized assemblies, metal ions, etc. We have studied in detail the optical and electrical properties for these organic materials experimentally and theoretically in view of their active participation in various optoelectronic devices.

The whole thesis is divided into nine chapters which are organized as follows:

**Chapter 1** provides a general introduction to hydrogen bonding (definition, properties and characteristics) and its participation in different charge transfer processes. As the hydrogen bonded organic molecules are our subject of interest of this thesis, this chapter covers the detail review of hydrogen bonding and describes charge (proton) transfer processes in different hydrogen bonded molecular complexes. A section of this chapter is devoted to the proton transfer mechanism between different electronic ground state ( $S_0$ ), excited states ( $S_1$ ,  $S_2$ ,  $S_3$  etc.), and vibrational states. In the middle section, the current trends of proton transfer

dynamics in different phases (solid, liquid, gas) and environments (solvents, acidic and basic medium, restricted organized assemblies) have been discussed. In the last section, the applications of different proton transfer active organic/inorganic systems in the field of different optoelectronic devices: fluorescence sensors, proton transfer laser, OLEDs, WOLEDs, fluorescence imaging, memory devices, etc. have been discussed in detail.

**Chapter 2** describes the details of different computational and experimental techniques used in the whole thesis work. Computational techniques include quantum chemical methods based on famous Schrodinger equation with different approximation techniques like: Semi empirical [Parameterized Model number 3 (PM3)], restricted & unrestricted Hartree Fock (RHF, UHF), density functional theory (DFT), configuration interaction singles (CIS), time dependent density functional theory (TD-DFT), which have been used for material simulation in this thesis. This chapter also covers a comprehensive discussion of different experimental techniques used for the synthesis and characterization of materials in the present work. The characterization techniques used in the present study include, UV-Vis absorption and emission spectroscopy, Fourier transform infrared (FTIR) absorption spectroscopy, Nuclear magnetic resonance (NMR) spectroscopy, Impedance spectroscopy, Raman spectroscopy, PE-Loop tracer, Raman spectroscopy.

**Chapter 3** reports the results of our study on one of the Indole derivatives: Indole-7-carboxaldehyde (I7C) which is known to have cytotoxic effects on cancer cells. I7C is used as one of the components of chemotherapy drug for the cancer treatment due to its potential interface with cancer cells. In this chapter the reaction dynamics of I7C have been studied with theoretical results and experimental observations. In I7C existence of intramolecular hydrogen bonding and ESI<sub>ra</sub>PT have been studied in electronic ground ( $S_0$ ) and excited ( $S_1$ ,  $S_2$ ,  $S_3$  etc.) states in the gaseous phase and in liquid phase. DFT, TDDFT, CIS theories with B3LYP/6-311++G (d, p), etc. basis set have been used to obtain structural parameters and energies of I7C in the ground state, excited states for cis ( $N_c$ ), trans ( $N_t$ ) and zwitterionic ( $Z^*$ ) conformer. Computed and experimental results show that conformer  $N_c$  is more stable as compared to conformer  $N_t$ . With photo excitation I7C is transferred to its  $S_0 \rightarrow S_1, S_2, S_3$  excited states by absorbing 344 nm, 323 nm and 318 nm wavelengths. Experimentally the same phenomenon is verified with the 342 nm, 328 nm and 317 nm wavelengths obtained by UV-Vis absorption spectrometer. Photo-physical pathway through asymmetric dual minima (459 nm, 944 nm) in potential energy surface involves ESI<sub>ra</sub>PT from  $N_c^*$  to  $Z^*$  due to transfer

of proton ( $H^+$ ) from donor acidic ( $-N-H$ ) to acceptor basic ( $>C=O$ ) moiety. ESI<sub>ra</sub>PT is verified by different geometrical parameters, molecular orbitals in different energy states. Experimentally the phenomenon is verified with the dual fluorescence emission at  $\sim 451$  and  $\sim 862$  nm obtained by UV-Vis emission spectrometer. Asymmetric double minima in the excited state pathway shows the path of the proton transfer along the reaction coordinate ( $-N_{15}-H_{12}$ ) of donor moiety. Results discussed in this chapter are already published in *Chemical Physics Letters* [48].

In **Chapter 4** a detail theoretical study has been performed using density functional theory (DFT) and time dependent DFT (TDDFT) to investigate molecular structure, characteristics of I<sub>ra</sub>HB and I<sub>ra</sub>PT mechanism for I7C. Sometimes experimental approaches are insufficient to verify what extent the molecular structure and configuration affected by hydrogen bonds. So theoretical understanding of the inherent chemistry of hydrogen's ability to make bond can lead to further understanding of behaviour of proton transferred complex. Structural parameters and relative energies in the ground state ( $S_0$ ) and excited state ( $S_1$ ) reveal that I7C exists in two forms normal ( $I/I^*$ ) and zwitterion ( $II/II^*$ ). Charge analysis by natural bond orbitals (NBOs) and Mulliken methods shows the existence of strong dipole-dipole interaction in  $S_0$  state. A single minimum in the potential energy surface scans neglects the  $I \rightarrow II$  transformation in  $S_0$  state, whereas transition state ( $TS$ ) with dual minima in the potential energy surface (PES) confirms  $I^* \rightarrow TS \rightarrow II^*$  transition due to excited state intramolecular proton transfer (ESI<sub>ra</sub>PT). Atoms in Molecules (AIMs) analysis certify I<sub>ra</sub>HB and possibility of IPT from acidic ( $N_{15}-H_{12}$ ) to basic ( $>C_{16}=O_{18}$ ) group and creation of  $II^*$  with the help of electron density ( $\rho$ ) value at Bond critical points (BCPs) on a hydrogen bridge ( $N_{15}-H_{12} \cdots O_{18}$ ). NBOs analysis also proves the formation of  $II^*$  due to IPT. Results discussed in this chapter have been published in *Journal of Molecular Structure* [49].

**Chapter 5** deals with the optical, chemical, and electrical aspects of the proton transfer mechanism of Indole (I) and some carbonyl substituted Indole derivatives: Indole-3-carboxaldehyde (I3C) and Indole-7-carboxaldehyde (I7C). Often materials that are strongly fluorescing in liquid solution become non-fluorescent in the solid form and vice versa, but I7C is one of the rarest material which shows very strong fluorescence both in solid (powder) and liquid solution. In I3C and I, there is no other molecular interaction besides carbonyl association. Presence of IHB favours the existence of intra/intermolecular charge transfer in I7C. Weak absorbance for I at  $\sim 270$  nm ( $S_0 \rightarrow S_2$ ) and red shifted stronger absorbance for I3C

and I7C for  $S_0 \rightarrow S_1$  ( $^1L_b$ ) electronic transition at  $\sim 300$  nm (30 nm) and  $\sim 335$  nm (70 nm) indicate the increased molecular weight of I3C and I7C than I. Though I3C and I7C have the same molecular weight still the larger shift in I7C absorbance is due to its long range  $I_{ra}HB$  effect which is unavailable in I and I3C.  $^1H$  and  $^{13}C$  NMR, molecular vibrational frequencies (FTIR, Raman) of the fundamental modes, and P-E Loop measurement further established the above mentioned results. In I7C,  $ESI_{er}PT$  occurs between solute and solvent with the creation of new species Anion ( $A^*$ ) (520 nm) due to  $N_t^* \rightarrow A^*$  transition. Computed/experimental studies reveal the creation of new species: zwitterion ( $Z^*$ ) and anion ( $A^*$ ) in the excited state ( $S_1$ ) due to  $ESI_{ra}PT$  and  $ESI_{er}PT$  in I7C. Electrical conductivity ( $\sigma_{ac}$ ) with temperature and ferroelectric polarization at varying field verifies proton transport properties and establishes the sensing capability of I7C. In this chapter we have discussed the potential application of I7C as a white light generator for the new optoelectronic devices due to its wide range (violet, blue, green, and red) of fluorescence emission. Results discussed in this chapter are already published in *Journal of Physical Chemistry* [50].

In **Chapter 6** we have investigated the possibility of using I7C as fluorescent chemosensor for different environmentally hazardous metals ( $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cr^{3+}$ ) in aqueous medium. In this chapter we have established the candidature of I7C as an efficient metal ion sensor for  $Zn^{2+}$ ,  $Pb^{2+}$  due to its better complexation with these metals. Global chemical reactivity descriptors: chemical hardness ( $\eta$ ), electrophilicity ( $\omega$ ) and electronic chemical potentials ( $\mu$ ) confirm the selective reactivity of I7C ( $N_c$  and  $N_t$  conformers) in the presence of metal ions. Both conformers are found to form (1:1) metal ion: I7C complex ( $M_X$ ,  $M_X^*$ ) in  $S_0$  and  $S_1$  energy states. Creation of  $M_X$ ,  $M_X^*$  are witnessed via computed and experimental studies. Among all metal ions I7C is found to display excellent sensing capability for  $Zn^{2+}$  and  $Pb^{2+}$  ions. Appearance of UV-Vis absorption band at 350 nm, FTIR vibrational modes at  $1042\text{ cm}^{-1}$ ,  $1300\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  confirm the complex formation ( $M_{Zn}$ ). Computed results (absorption band at 359 nm, vibrational modes at  $1153\text{ cm}^{-1}$ ,  $1348\text{ cm}^{-1}$  and  $1416\text{ cm}^{-1}$ ) validate the experimental facts.  $^1H$  NMR of I7C in presence of  $Zn^{2+}$  verifies the  $M_{Zn}$  formation.  $\delta_{Cal}$  verifies the experimental observation by its obtained correlation value ( $R^2 = 0.97$ ). Fluorescence “Turn-On” response for  $Zn^{2+}$  is observed through the appearance of a new enhanced fluorescence at  $\sim 430$  nm. Fluorescence “Turn-Off” response is observed for  $Pb^{2+}$  through the quenching of existing fluorescence peak. I7C also establishes its strong candidature to be used as blue emitter.

In **Chapter 7** we have studied the inclusion behaviour of I7C inside  $\alpha$ -,  $\beta$ -,  $\gamma$ -cyclodextrin (CD) cavities. Caging of I7C within nano sized cyclodextrin ( $\alpha$ -,  $\beta$ -,  $\gamma$ -) cavities have been studied in detail with the help of detailed quantum chemical calculations: PM3, HF, DFT, ONIOM, and experimental (spectral) facts. Comparison of different complex structures suggests that I<sub>er</sub>HB interactions play a dominant role in the binding of I7C inside CD cavity. Out of all  $\alpha$ -,  $\beta$ -,  $\gamma$ -cyclodextrin (CD) cavities,  $\beta$ -CD shows better ability to accommodate I7C and form (I7C:  $\beta$ -CD) inclusion complex with 1:1 stoichiometry. Both  $N_c$  and  $N_t$  conformers of I7C with ring down ( $P$ :  $P_c, P_t$ ) and ring up ( $Q$ :  $Q_c, Q_t$ ) orientations form complexes with  $\beta$ -CD. Dipole moment, complexation energy ( $\Delta E_{1:1}$ ) and deformation energy ( $\Delta E_d$ ) values show the better stability of  $P$  orientation than  $Q$ . Calculated stabilization energy ( $E^2$ ) values from NBO analysis show that the main driving force in the process of I7C ( $P_c, P_t$ ):  $\beta$ -CD complex is strong I<sub>er</sub>HB interaction. New absorption peaks at ~255 nm and ~317 nm and fluorescence peaks at ~420 nm and ~447 nm confirm the presence of I<sub>er</sub>HB between I7C and  $\beta$ -CD. Characteristics of IR modes provide a prominent signature of the better complexation of  $P$  form of I7C with  $\beta$ -CD cavity. This work will contribute to the medical industry of some chemotherapy drug carriers based on CDs.

In **Chapter 8** we have chosen a set of molecules from the Pyrrole family: Pyrrole-2-carboxaldehyde (PCL) and 2-Acetyl pyrrole. Pyrroles and their derivatives are one of the most important classes of heterocyclic compounds. They exhibit extensive biological and pharmacological activities such as antibacterial drugs, antioxidant drugs, etc. PCL is one of the major components of DNA base. We have studied the excited state behaviour of Pyrrole-2-carboxaldehyde (PCL) theoretically and experimentally. Pyrrole-2-carboxyldehyde (PCL) is a heterocyclic molecule having a five member ring with both acidic (-NH) and basic (>C=O) moieties in close proximity. It is capable of establishing an intramolecular hydrogen bond between H<sub>12</sub> and O<sub>11</sub>. So PCL yield possible signatures of I<sub>ra</sub>PT and I<sub>er</sub>PT in an excited state. Ground state and excited state geometries such as single point energy, dipole moment, electron density, etc. show that PCL can exist in two form cis ( $E$ ) and trans ( $T$ ) form but  $E$  is more stable as compared to  $T$ . Dual emission (~325 nm, ~375 nm) on photo excitation indicates the existence of more than one species in an excited state. Computed reaction pathway and two-dimensional potential energy profile in the ground state reveals a single minimum corresponding to normal form ( $E$ ). Dual minima in excited state energy profile shows the existence of two species, one normal, and other zwitterionic ( $Z^*$ ) species. A large Stoke shifted emission at ~375 nm in hydrocarbon medium reveals the existence of

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zwitterionic species due to ESI<sub>ra</sub>PT, whereas ESI<sub>er</sub>PT is observed in a hydroxylic environment around 430–490 nm. pH variation in hydroxylic medium suggests the formation of anion ( $A^{(-)}$ ) from  $Z^*$ . Results discussed in this chapter are already published in *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* [51].

For 2-Acetyl pyrrole (2AP), it is the first time that we have observed the ground state intramolecular proton transfer (GSPT). 2AP also shows its active participation in the mechanism of intra- and intermolecular proton transfer reaction both in ground and excited electronic states. Existence of room temperature phosphorescence from triplet state species makes 2AP a better candidate for white light generation.

In **chapter 9** we have summarized all our experimental and theoretical results reported in the thesis. According to our work plan for thesis we have investigated some organic hydrogen bonded probe systems from Indole and Pyrrole family: Indole, Indole-3-carboxaldehyde (I3C), Indole-7-carboxaldehyde (I7C), Pyrrole-2-carboxaldehyde (PCL), and 2-Acetyl pyrrole (2AP) based on their enormous applications in industry. These hydrogen bonded organic systems are drawing great attention due to their unique ground and excited state intra/inter molecular proton transfer photo physical properties, which contribute to many optoelectronic and biomedical applications. The results we obtained through our computational and experimental approaches will definitely provide a breakthrough for challenging issues in optoelectronic applications such as chemical sensors, fluorescence imaging, proton transfer lasers, WOLED etc., and in biomedical applications such as some chemotherapy drugs and as antitumor, antioxidant drugs carriers. Focusing at the results of our present works we have set a goal and scopes for our application based future work which will definitely benefit the industry and society. We are also interested to fabricate some chemical sensing devices based on proton transferred probe systems of our interest which can work in different environments and contribute to industrial or domestic use.

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## ***Chapter in Book***

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