ADIABATIC PROTON-COUPLED CHARGE-TRANSFER REACTIONS AND
PHOTOCHEMISTRY OF N,N-DIMETHYL-3-ARYLPROPAN-1-AMMONIUM SALTS

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ABSTRACT

The coupling of proton and electron transfers in concerted or sequential processes is of central importance to many biochemical and catalytic reactions. In this context, proton-coupled electron transfer reactions are typically described electrochemically, whereby the transfer of a proton is coordinated to a change in the oxidation state of the constituent donor/acceptor pairs. In the excited-state, intermolecular proton transfers are often facilitated through a redistribution of electron-density (charge-transfer) along the proton-transfer reaction coordinate without a corresponding change in the oxidation state of the donor/acceptor pair. Distinguishing charge-transfer from full electron-transfer reactions along the excited-state potential energy surface has received increased attention as advancements in engineering allow for the interrogation of the fastest molecular events. This dissertation seeks primarily to examine the confluence of charge-transfer, electron-transfer, and proton-transfer reactions which occur adiabatically in the excited-states of N,N-dimethyl-3-arylpropan-1-ammonium salts in solution. For these compounds, an excited-state intermolecular proton-transfer to the solvent is accompanied by intramolecular charge-transfer and the formation of either an emissive exciplex or a transient solvent-separated ion pair. The various electronic configurations have been interrogated through an array of spectroscopic techniques in order to more thoroughly understand the convergence of thermodynamic and kinetic factors affecting the proposed mechanism. In this regard, a range of temperatures, solvents, counterions, and lumophores have been explored. In addition, the ground-state equilibrium has been
investigated through targeted theoretical calculations and experiments. The summation of these experiments provide unique insights into a class of novel exciplex-mediated proton-coupled charge-transfer reactions.
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LIST OF IMPORTANT UNCOMMON ABBREVIATIONS

CT charge-transfer (incomplete electron-transfer)
Ae electron-acceptor
AnA N,N-dimethyl-3-(9-anthryl)propan-1-amine
AnCl N,N-dimethyl-3-(9-anthryl)propan-1-ammonium chloride
Ap proton-acceptor
ArA Generalized abbreviation for N,N-dimethyl-3-arylp propane-1-amines
ArS Generalized abbreviation for N,N-dimethyl-3-arylp propane-1-ammonium salts with varied counterions
ATP adenosine triphosphate
C ground-state closed conformation
C* excited-state closed conformation
D* deprotonated locally-excited state
Dc electron-donor
DFT density functional theory calculations
DLS dynamic light scattering
Dp proton-donor
EA elemental analysis
ESIPT excited-state intramolecular proton-transfer
eT electron-transfer
Ex exciplex
HAT hydrogen atom transfer
HPLC high-performance liquid chromatography
HPTS 8-hydroxypyrene-1,3,6-trisulfonic acid
InCl $N,N$-dimethyl-3-(1-indolyl)propan-1-ammonium chloride
InP uncharacterized indole photoproduct
IP solvent separated ion pair
KIE kinetic isotope effect
LE locally-excited state
Mel $N$-methylindole
mp melting point
NapA $N,N$-dimethyl-3-(2-naphthyl)propan-1-amine
NapCl $N,N$-dimethyl-3-(2-naphthyl)propan-1-ammonium chloride
O ground-state open conformation
O* excited-state open conformation
OEC oxygen evolving complex
PCCT proton-coupled charge-transfer
PCET proton-coupled electron-transfer
PSII photosystem II
PyA $N,N$-dimethyl-3-(1-pyrenyl)propan-1-amine
PyBr $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium bromide
PyCl $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium chloride
PyNO3 $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium nitrate
PyS Generalized abbreviation for $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium salts with varied counterions
PyTFA $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium trifluoroacetate
PyTSA $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium $p$-toluenesulfonate
<table>
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<th>Acronym</th>
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<tr>
<td>SCRF</td>
<td>solvent continuum reaction field DFT method</td>
</tr>
<tr>
<td>SPC</td>
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<td>time-dependent density functional theory calculations</td>
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1 **INTRODUCTION TO PROTON-COUPLED ELECTRON-TRANSFER REACTIONS**

1.1 **Ground-State Proton-Coupled Electron Transfer Reactions**

Proton and electron transfers are two of the simplest reactions of molecules in nature. However, these elementary processes are key components of the most complex mechanistic chemistry. The transfer of a proton and an electron as a hydrogen atom catalyzes the industrial production of ammonia in the Haber process, enabling global production of this key chemical.² Cell respiration, another example, relies upon cascades of electron and proton transfers in order to synthesize adenosine triphosphate (ATP), the biochemical energy source of life.³ Perhaps most importantly, photosynthesis, the process by which light is converted into chemical energy in plants, bacteria, and some animals, requires the efficient transport of electrons and protons within key enzymes.⁴ Thus a key challenge has been to harness proton and electron transfers in order to drive increasingly complex chemical transformations. A central aspect of this research involves probing the thermodynamic and kinetic relationships between donors and acceptors in varied environments. A multidisciplinary approach is required to meet these challenges. Targeted organic synthesis, theoretical calculations, and sophisticated instrumentation are all important tools in this endeavor.

A key mechanistic step in many naturally evolved processes is the proton-coupled electron-transfer (PCET), which links the acid-base and redox properties of a protein.⁵ One of the earliest detected PCET mechanisms was observed for a class of molybdenum containing enzymes.⁶,⁷ The redox chemistry of the active site is accompanied by a large change in the acidity of the coordinated ligands. Indeed, the catalytic abilities of these enzymes require the coupling of proton and electron transfers to the substrate. Increased research efforts have not just identified an abundance of naturally occurring PCET mechanisms, but have also utilized these processes for the development of photovoltaics,⁸ fuel cells,⁹ and artificial photosynthetic systems.¹⁰
A PCET reaction can loosely be defined as the coordinated transfer of a proton from a donor ($D_p$) to an acceptor ($A_p$) in conjunction with the transfer of an electron from a donor ($D_e$) to an acceptor ($A_e$).\textsuperscript{11} The transfers can occur in either a concerted or sequential manner. A concerted PCET mechanism requires the simultaneous transfer of a proton and an electron. A sequential mechanism involves two distinct transfer steps and is identified by the presence of a pseudo-stable intermediate. The transfers can occur either intermolecularly, as with the Mo enzymes, or intramolecularly where the donors and acceptors are part of a continuous molecular framework. An important class of PCET reaction, not discussed here, is the hydrogen atom transfer (HAT) reaction where a proton and electron are transferred simultaneously from one donor to one acceptor (i.e., $D_p = D_e$ and $A_p = A_e$).\textsuperscript{12} Definitive classification of PCET reactions is made difficult by the quantum mechanical behavior of both particles during the transfers.

Extensive experimentation\textsuperscript{13-16} and theoretical treatment of PCET reactions\textsuperscript{11,17} have revealed properties unique to this coupled process: namely, variable kinetic isotope effects (KIE), pH rate dependencies, and nonadiabatic transitions between mixed proton and electron vibronic wave functions.\textsuperscript{18} Initially, PCET reactions were described using a Marcus theory of electron transfer (eT). More recently, a unifying PCET theory was formulated using Marcus theory as a starting point and including an overlapping Frank-Condon proton vibrational wave-function.\textsuperscript{19} Hammes-Schiffer and others further generalized the treatment of PCET reactions by treating them as the nonadiabatic mixing of proton and electron vibronic states.\textsuperscript{18} Advancements in PCET theory have been invaluable to experimental efforts describing complex biochemical and catalytic mechanisms.

The greatest advantage of the PCET reaction to supporting fast processes is the avoidance of high-energy charged intermediates that typically accompany important redox reactions. As mentioned previously, photosynthesis requires cascades of proton and electron transfers in order to transform absorbed light into chemical energy. Much of the interesting chemistry occurs in Photosystem II (PSII). The absorption of light by chlorophyll subunits in PSII results in the transfer of electrons towards
plastoquinone acceptors within the reaction center\textsuperscript{5}. The oxidized chromophore is reduced by a proximal tyrosine subunit which is, in turn, reduced by a Mn\textsubscript{4}CaO\textsubscript{5} cluster, a key part of the oxygen evolving complex (OEC)\textsuperscript{6}. The OEC enzyme utilizes a PCET mechanism for water oxidation into protons and oxygen, a key prerequisite for animal life on the planet. A complete mechanistic understanding of the OEC remains elusive, but, increasingly, research has focused on mimicking key aspects of PSII for the development of novel technologies\textsuperscript{4,8}. A key example is the Nocera Co-catalyst\textsuperscript{10} (Scheme 1.1) which, similar to the OEC, utilizes a PCET mechanism to electrochemically oxidize water with a very low over-potential. More recently, ruthenium macrocycle catalysts have been developed for electrochemical water splitting\textsuperscript{20}. The discovery of the catalysts described above was made possible through research aimed at probing the mechanistic aspects of a fundamental chemical reaction, the PCET. A common attribute of these catalytic systems is that the acid-base and redox steps all occur in the ground-state. However, PCET reactions are not restricted to one potential energy surface. Indeed, many excited-state PCET reactions have already been identified.

![Scheme 1.1 Proposed mechanism for the 'Artificial Leaf' Co-catalyst. Electrochemical oxidation of the cobalt metal systems facilitates water oxidation through proton-coupled electron-transfer equilibrium which precedes the rate-determining O-O bond formation. Image Reprinted with Permission from Nocera\textsuperscript{10}.](image-url)
1.2 Excited-State Proton-Coupled Electron Transfer Reactions

Excited-state reactions differ from their ground-state counterparts in that they involve more than one potential energy surface. Reactions can occur adiabatically or non-adiabatically and are often limited by the lifetime of the participating excited-state. Within the sphere of PCET reactions, the excited-state intramolecular proton transfer (ESIPT) is by far the most common.\textsuperscript{21-23} This class of PCET reaction is driven by the absorption of light. Upon excitation of a chromophore, electron density is redistributed along the molecular framework leading to either an increase in the acidity of $D_p$ or basicity of $A_p$. These reactions are identified by large Stokes shifts and extremely rapid proton transfers ($k_{\text{ESIPT}} > 10^{12}$ s).\textsuperscript{21} Ordinarily, an organized ground-state structure provides the framework for the rapid proton transfer. An intramolecular hydrogen bond between $D_p$ and $A_p$ is typically a key feature of the ground-state.\textsuperscript{21} This structural motif facilitates the rapid transfer of a proton from $D_p$ to $A_p$ as after excitation; the rate is limited only by the quantum mechanical motion of the proton.

By far the most common application of this property is in the field of fluorescent chemosensors.\textsuperscript{24} Metal ions which complex with ground-state species and disrupt the intramolecular hydrogen bond ‘turn off’ the ESIPT pathway. This results in large changes to the steady-state fluorescence spectrum and detection limits approaching $10^{-9}$ M! Perhaps the most creative application of the ESIPT reaction was accomplished by Mukhina and Kutateladze who were able to perform an enantioselective synthesis of polyheterocyclic ketones.\textsuperscript{25} These reactions undergo an ESIPT reaction, forming a transient precursor, which then undergoes either [4+4] or [4+2] cycloaddition reactions. It was hypothesized that the enantioselectivity is controlled by a sterically hindered radical recombination step which terminates the reactions. This work provides an excellent example for how the controlled design of ground-state structures can lead to targeted photochemical outcomes. While this is a coveted goal in synthetic photochemistry, the interplay of ground and excited-state potential energy surfaces is an important aspect of all photochemical investigations.
Excited-state proton transfers are not restricted to intramolecular Dp/Ap frameworks. In fact, a wide variety of intermolecular excited-state proton transfers has been discovered with interesting applications. The most pertinent type of intermolecular excited-state proton transfer to the research of this thesis involves the transfer of a proton from an excited-state species to a proximal solvent molecule. In this case, the proton-donors are referred to as ‘photoacids’ because of the increased acidity (lower pKa) of the excited-state with respect to the ground-state species. Similar to their ground-state counterparts, photoacids dissociate from their acid form (HA) into a protonated solvent molecule (H3O+ in the case of water) and an excited-state conjugate base A′. Unlike ground-state acid-base chemistry, the parent species HA does not dissociate prior to the absorption of a photon of the appropriate energy. Excitation of the photoacid results in a redistribution of electron-density, promoting a rapid change in the pKa of HA. Numerous intermolecular excited-state proton transfers have been observed in natural systems. One of the most widely studied biochemical photoacids is the 4-hydroxybenzylidene-1,2-dimethylimidazolinone chromophore of the green fluorescent protein (GFP) pictured below (Scheme 1.2).
Another classic case of photoacidity is exhibited by 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS).\textsuperscript{30} In the ground-state, HPTS has a $pK_a$ of approximately 7.3. Upon excitation, the excited-state $pK_a^*$ decreases to approximately zero and transfers a proton to a water molecule ($A_0$) within 100 ps. This dramatic change in acidity is the result of an intramolecular charge-transfer state which stabilizes the excited-state conjugate base. Excited-state intermolecular proton transfers (photoacidity) and ESIPT reactions provide two examples of how the principles of PCET mechanisms can be extended across potential energy surfaces in both adiabatic and nonadiabatic chemical transformations.

In 2011, a unique adiabatic PCET process was discovered by Abraham and Weiss for a series of $N,N$-dialkyl-3-(1-pyrenyl)alkan-1-ammonium chloride salts in solution.\textsuperscript{31} While the photophysics of the
neutral amine, \(N,N\text{-dimethyl-3-(1-pyrenyl)alkan-1-amine (PyA)}\), have been extensively characterized\(^{32,33}\) the properties of the protonated salts had not yet been investigated. Unexpectedly, solutions of \(N,N\text{-dimethyl-3-(1-pyrenyl)propan-1-ammonium chloride (PyCl)}\), and other derivatives exhibited broad, red-shifted fluorescence consistent with the formation of an intramolecular charge-transfer complex (exciplex) between a neutral amine and an excited-state pyrenyl. Exciplexes formed between excited-state arenes (\(\text{A}_e\)) and amines (\(\text{D}_e\)) have been exhaustively characterized\(^34\) and solutions of PyA are known to form charge-transfer (CT) complexes and emit in this characteristic manner; however, the protonated nitrogen does not have the requisite lone-pair of electrons needed to form the exciplex. It was inferred that a rapid proton transfer must precede the formation of the exciplex. In order to test this hypothesis, quaternary ammonium salts were prepared with four alkyl substituents on the nitrogen. Solutions of these quaternary salts did not exhibit exciplex emission, implying that a protonated nitrogen was required for exciplex formation. Subsequent experiments determined the role of the alkyl spacer between the nitrogen (\(\text{D}_\text{F} \) and \(\text{D}_\text{E}\)) and the pyrenyl group (\(\text{A}_\text{F}\)). Consistent with previous investigations of PyA, a three carbon spacer maximized exciplex emission intensity\(^{32,35}\). This was rationalized in terms of the entropic and geometric constraints of bending the alkyl-linking chain over the pyrenyl to give sufficient overlap between \(\text{D}_e\) and \(\text{A}_e\). These investigations also revealed a dramatic effect of the ground-state conformation on the excited-state dynamics. As with many ESIPT reactions, the ground-state framework determined the extent to which this PCET process was operative. Additionally, the amphiphilic nature of these salts gave rise to significant aggregation at concentrations greater than \(10^{-4}\) M. Pyrenyl aggregates were identified by the presence of excimeric emission. At elevated concentrations (> \(10^{-4}\) M) pyrene has been observed to form intermolecular charge-transfer complexes (excimers) where pyrene molecules serve as both \(\text{D}_e\) and \(\text{A}_e\). The excimeric fluorescence is blue-shifted with respect to emission from the intramolecular exciplex. Nevertheless, dilute solutions of PyCl in low polarity solvents exhibited strong exciplex emission. The overall process is best described as a unique type of adiabatic PCET reaction. The
ammonium proton is transferred to an $A_\text{e}$, and after some minor nuclear rearrangements, electron density is transferred from the nitrogen to the excited-state pyrenyl. This donor-acceptor complex does not require the full transfer of an electron from the nitrogen to the pyrenyl. In fact, full electron transfer is believed to quench exciplex emission through the formation of a radical ion pair (IP). Thus, it is important to distinguish between proton-coupled electron-transfer and proton-coupled charge-transfer (PCCT) reactions, the latter of which is characterized by the partial redistribution of electron density from $D_\text{e}$ to $A_\text{e}$. To the best of our knowledge, this work is the first example of a PCET directly leading to the formation of an emissive charge-transfer complex, or put more simply, exciplex mediated photoacidity in low polarity media. Though specific investigative goals will be discussed in the following section, the general objective of this dissertation research is to provide information for a detailed understanding of the reasons for the initial observations through a meticulous examination of the PCCT mechanism utilizing targeted organic synthesis, theoretical calculations, and direct photophysical measurements.

![Scheme 1.3 Simplified Mechanism of PCCT Reaction Exhibited by N,N-Dimethyl-3-arylpinan-1-ammonium Salts in Proton-Accepting Solvents of Varied Polarities.](image_url)
1.3 Statement of the Problem

The body of work in this dissertation aims to answer the following the questions raised by the initial discovery of the PCCT mechanism outlined above:

1. *Which factors have the largest impact on the ground-state potential energy surface and to what extent are these effects manifested on the ground-state PCCT precursors?* As mentioned above, PyS has a propensity to aggregate at concentrations above $10^{-4}$ M in solvents ranging from 1,4-dioxane to acetonitrile. Aggregation complicates the analysis of the PCCT mechanism by introducing additional species (dimers, trimers, etc.) to the excited-state mechanism. Additionally, a ground-state conformational equilibrium has been hypothesized as a key component of the PCCT mechanism. Chapter 3 focuses on these ground-state processes. Steady-state fluorescence, time-correlated single photon counting (SPC), and dynamic light scattering (DLS) experiments are combined with density functional theory (DFT) calculations as a means to examine the ground-state effects.

2. *What are the thermodynamic relationships among the excited-state species and to what extent are these species influenced by external factors?* A unique aspect of the proposed mechanism is the coupling of photoacidity to exciplex formation. In order to understand better the thermodynamic relationship between the photoacid and its surrounding medium, a series of $N,N$-dimethyl-3-arylpropan-1-ammonium salts (ArS) were synthesized. These salts maintain the same aryl-propyl bridge-dimethylammonium structural motif and allow the influence of changes of the excitation energy, excited-state lifetime, anion, and excited-state reduction potential on the efficiency of the PCCT processes to be probed. Also, the photophysics of the ArS were probed in various media to better understand the role of the solvent as a proton acceptor ($A_0$). As will be discussed in Chapter 4, steady-state fluorescence, SPC, and transient absorption experiments provide insights into the relationship between locally excited-states, exciplexes, and radical ion pairs. Chapter 4 also addresses the role of the anion of the ArS salts.
Of course, an analysis of the thermodynamic relationships provide little insight without also considering kinetics aspects. This is especially true for excited-state processes which are limited by the lifetime of the excited species. Chapter 5 will address the kinetics of the PCCT mechanism in detail. SPC experiments are particularly important in this regard. Thus, temperature-dependent kinetic experiments provide insights into activation-barriers and kinetic restrictions along various reaction coordinates, including the proton-transfers and the decays of charge-transfer species.

3. To what extent do the ArS behave as photoacids in solution? After a discussion of thermodynamic and kinetic relationships, a broader analysis of ArS will be made in this regard. In order to address the photoacidity of the ArS, an empirical Förster cycle has been formulated using steady-state fluorescence data. Chapter 4 provides an analysis of the ArS as photoacids which, in many ways, is the best manner in which to discuss the confluence of thermodynamics (Chapter 4) and kinetics (Chapter 5).

Finally, N,N-dimethyl-3-(1-indolyl)propan-1-ammonium chloride (InCl) was synthesized with the intention to determine whether the PCCT process can be extended to heteroaromatic frameworks. Chapter 7 will discuss the photophysics of InCl which differ significantly from those of the homoaromatic ArS. Those results provide additional insights into the unusual photoprocesses of indoles.
2 General Experimental Methods

2.1 Experimental Instrumentation and Procedures

UV-vis spectra were collected using a Perkin-Elmer Lambda-6 spectrophotometer. $^1$H-NMR spectra were recorded on a Varian 400 MHz NMR spectrometer and analyzed using MestReNova software (v. 5.2.4-3924). HPLC experiments were performed using an Agilent Technologies 1220 Infinity LC with a Waters μBondpack C18 column (300 x 3.9 mm, 10 μm particle size). A ratio of 80:20 methanol:ethyl acetate was used as the mobile phase to elute each ArS at a flow rate of 1 mL/min. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer using acetanilide as a calibration standard.

Steady-state excitation and emission spectra at room temperature were obtained on a Photon Technology International Fluorimeter (SYS 2459) at excitation wavelengths of 344 nm (PyS), 369 nm (AnCl), 305 nm (NapCl), and 295 nm (InCl) unless otherwise specified. Multiple excitation wavelengths were used along the excitation spectrum to confirm that the shape and intensity of the emission spectra were independent of excitation wavelength. Temperature dependent fluorescence spectra of the PyS were collected using an Ocean Optics 1K series spectrometer with a 345 nm cut-off filter as the detector and a non-pulsed He-CD Kimmon laser operating at 325 nm as the excitation source. PyS temperature experiments were conducted in a 193 – 313 K temperature range by placing the samples, sealed in flattened capillaries (Vitrocom Glass, 0.4 mm i.d., 10 mm width), in a closed He-cycle cryosystem from APD Cryogenics. Fluorescence decay histograms of the PyS were obtained with a Hamamatsu single-photon counting system (model MCP-PMT r3809U-50) using the 340 nm output from a picosecond-pulsed light emitting diode (EPLD-340) from Edinburgh Instruments as the excitation source. Temperature-dependent, steady-state and dynamic experiments were performed at the Instituto de Química, Universidade Estadual de Campinas in Campinas, Brazil in collaboration with Dr. Marcelo Faleiros and Prof. Teresa Atvars. AnCl, NapCl, InCl, and ArA decay histograms were collected with an Edinburgh Analytical
Instruments single-photon counting system (model FL900) and a H$_2$ lamp operating at 40 KHz. “Instrument response functions” were recorded periodically using Ludox$^\text{©}$ as the scatterer at the excitation wavelength. Data were collected in 2046 channels for the PyS and 1023 channels for AnCl, NapCl, InCl, and ArA. They were treated by an exponential deconvolution method which minimizes $\chi^2$ using the FAST software supplied by Edinburgh Analytical Instruments. Fits were considered acceptable when $\chi^2 < 1.3$ and residual plots exhibited no systematic deviations from zero. Samples for photophysical measurements were flame-sealed in flattened glass capillary tubes after repeated freeze (liq N$_2$)-pump (~90 mTorr)-thaw cycles until no change in pressure was observed upon opening the tube with frozen contents to vacuum (typically 4-5 cycles).

Femtosecond pump-probe experiments to generate transient absorption spectra were performed on a modified ultrafast system (HELIOS) in combination with an ultrafast amplified laser system (Coherent) at the Department of Chemical Physics, Synergetic Innovation Center of Quantum Information and Quantum Physics at the University of Science and Technology of China in Hefei, China in collaboration with Mr. Shenlong Jiang, Mr. Lei Zhang, Professor Qun Zhang. All measurements were performed at room temperature (293 K) on samples in 1 cm quartz cuvettes with Teflon stoppers after bubbling N$_2$ for 5 min. The pump pulses (center wavelength at 320 nm; pulse energy ~100nJ at the sample cell) were delivered by an optical parametric amplifier (TOPAS-800-fs), which was excited by a Ti:sapphire regenerative amplifier (Legend Elite-1K-HE; center wavelength 800 nm, pulse duration 25 fs, pulse energy 3 mJ) seeded with a mode-locked Ti:sapphire laser system (Micra 5) and pumped with a 1-kHz Nd:YLF laser (Evolution 30) and 1.4 mm beam size. The probe pulses were provided by a stable white-light continuum (375 – 900 nm) that was generated by focusing the 800-nm beam (split from the regenerative amplifier by a portion of 10%) in a rotating CaF$_2$ or sapphire crystal. Difference spectra were measured using a high-speed CMOS spectrometer$^{36}$ over a 200 ns time window.
Cyclic voltammograms were recorded on a Radiometer 80 analyzer controlled by Voltamaster 4 software. The working electrode consisted of a BAS Pt disc electrode (1.6 mm diameter; MF-2013). The reference electrode was an Ag/AgCl electrode with 3M NaCl fill-soaking solution (BAS RE-5B; MF-2013). A platinum flag served as a counter electrode (approx. area: 3 cm$^2$; fabricated in-house). Electrodes were polished between sample runs using a BAS polishing pad and 0.3 micron alumina which was wetted with 18.3 MΩ water and then rinsed with the supporting electrolyte solution. An H-Type electrochemical cell was used with a glass frit between compartments to isolate the reference electrode from the working and counter electrode compartment containing the analyte. The reference compartment was filled with 0.1 M NaClO$_4$ in acetonitrile. All potentials were calibrated against ferrocene as an internal standard taking $E^\circ$ (Fc/Fc$^+$) +0.424V vs SCE.$^{37}$ Measurements of butyldimethylamine were obtained at a concentration of 4 mM in HPLC-grade acetonitrile (dried over 3Å molecular sieves) and containing 0.1 M NaClO$_4$ by Mr. Michael Bertocchi. The range chosen to encompass redox peaks of interest were 0 - 2 V. Scans were recorded four times per sample at a scan rate of 200 mV/s.

Energy-minimized structures were calculated using density functional theory (DFT) with the Gaussian 09 software suite (D.01)$^{38}$ at the M06/6-31G(d,p) level.$^{39}$ Energy minima were verified by frequency analyses revealing only real frequencies. The solvent continuum reaction field (SCRF) method was utilized to model dielectric field effects.$^{40}$ Structures were visualized using Chemcraft software (version 1.8).$^{41}$

Dynamic light scattering (DLS) experiments were performed on an LS Instruments spectrometer using a 633 nm single laser beam source. A solution of 10$^{-3}$ M PyCl was prepared in anhydrous 1,4-dioxane and then filtered three times through a PTFE filter (200 nm pore size) into a dust free DLS tube. Three measurements were made every 10° from 30° to 130°. Each measurement was comprised of three 20 s scans. A contin analysis was performed on each measurement using the LS Instruments software in order to determine the size distribution of particles in solution.
Counterion substitution was verified for MeInCl using a modified Perkin Elmer SQ300 quadrapole mass spectrometer with a plasma-assisted chemical ionization source. Flow injections of each solution were performed using a 20μL injection loop with a solvent (18 MOhm water) flow of 50 μL min\(^{-1}\). Solvent flow was provided by a Perkin Elmer Series 200 HPLC pump. Ion concentrations were compared against 1 μM solution of NaI and a 25 μM solution of chloramphenicol for iodide and chloride respectively. Fluorescence quantum yields of MeI, InCl, and MeInCl were calculated using 2-methylnaphthalene as the standard. The optical density was kept below 0.1 to prevent self-absorption. The relative fluorescence intensity was gathered by integrating the entire emission spectrum. Quantum yields were calculated under deoxygenated conditions.

2.2 List of Materials
Acetonitrile HPLC grade (EMD, 99.99%), 9-anthraldehyde (Sigma Aldrich, 97%), benzophenone (Sigma Aldrich, 99%), bromine (Acros Organics, 99+%), carbon tetrachloride (Fisher Scientific, 97%), chloroform (EM Science, 99.8%), chloroform-d (Cambridge Isotope Laboratories Inc., 99.9%), dichloromethane Chromasolv (Sigma Aldrich, 99.8%), 3-dimethylamino-1-propyl chloride hydrochloride (Sigma Aldrich, 96%), N,N-dimethylformamide (Alfa Aesar, 99.8%), dimethylsulfoxide-d\(_6\) (99.9%; Cambridge Isotope Laboratories, Inc.), 1,4-dioxane (Sigma Aldrich, 99.8%), diethyl ether (Sigma Aldrich, > 99%), ethyl acetate (Sigma Aldrich, 99.7%), glacial acetic acid (Baker, 99.8%), hydrobromic acid (Fluka, 99.8%), 12.4 N hydrochloric acid (Macron, 99 %), compressed hydrogen gas (GTS-Welco), indole (Sigma Aldrich, > 99%), iodomethane (Sigma Aldrich, 99%), lithium aluminum hydride (Sigma Aldrich, 95%), malonic acid (Alfa Aesar, > 99.5%), 2-naphthaldehyde (Sigma Aldrich, 98%), oxalyl chloride (Acros Organics, 98%), 10% palladium on carbon (Sigma Aldrich), piperidine (Sigma Aldrich, 99%), 1-pyrenebutyric acid (Acros Organics, 97%), 1-pyrenecarboxaldehyde (Lancaster, 99%), pyridine (Fisher, 98%), sodium (Sigma Aldrich, 99%), sodium sulfate (Fisher, 99.2%), silver nitrate (Fisher, 99.7%), 18 N sulfuric acid (Baker, 98%),
tetrahydrofuran (Sigma Aldrich, 99.9%), thionyl chloride (Sigma Aldrich, ≥ 99.9%), and trifluoroacetic acid (Alfa Aesar, 99%) were used as received. Tetrahydrofuran (Sigma Aldrich, 99.9%) and 1,4-dioxane (Sigma Aldrich, 99.8%) were dried over sodium and benzophenone and distilled under a flowing N₂ atmosphere. Dichloromethane (Fisher, 99.9%) was dried over calcium hydride (Acros Organics, 93%) and distilled under a flowing N₂ atmosphere for photophysical experiments.

2.3 Syntheses of the ArS

2.3.1 Preparation of N,N-Dimethyl-3-arylpropan-1-amines (ArA)

N,N-dimethyl-3-arylpropan-1-amines (ArA) were prepared by suspending 20 mg of the corresponding ArS in 10 mL diethyl ether and stirring with 20 mL 30% NaOH under flowing N₂ for 30 min. Each ArA was extracted with diethyl ether and washed with water to remove excess base. The solution of ArA was dried over Na₂SO₄ and concentrated on a rotary evaporator. HPLC analyses indicated greater than 99.5% purity for each ArA.

2.3.2 Synthesis of 4-(1-Pyrenyl)butan-1-amide

4-(1-Pyrenyl)butyric acid (0.50 g, 1.7 mmol) was placed in a three-neck round bottom flask with an affixed condenser under flowing N₂. Dichloromethane (30 mL) was added to the flask with 1 μL of dry DMF from a syringe. The suspension was stirred for 10 minutes before 160 μL (1.9 mmol) oxalyl chloride was added at room temperature. The solution was warmed refluxed under N₂ for 2 h. CaO was prepared by heating CaCO₃ with a Bunsen burner for 6 h. NH₃ gas was passed through a CaO tube and bubbled through the acyl-chloride solution for 1 h. The suspension was condensed through vacuum distillation at ~25 mtorr. The crude product was dissolved in 100 mL ethyl acetate and washed with distilled water. The aqueous phase was washed with 3x50 mL ethyl acetate. The organic layers were combined and washed with 3x50 mL distilled water. The organic layer was dried over NaSO₄ and condensed through vacuum
distillation at ~ 25 mtorr yielding 0.35 g of crude product. A silica column (17 cm x 3 cm) was prepared with an ethyl acetate mobile phase. 0.30 g (1.1 mmol) 4-(1-Pyrenyl)butan-1-amide was recovered from the column. The column purified material was recrystallized in ethyl acetate to give 0.23 g (47%) 4-(1-pyrenyl)butan-1-amide, mp 179 – 182 °C. δH (CDCl3, 400 MHz): 2.17 (3H, s, CH2CH2CH2CONH2), 2.25 (2H, m, CH2CH2CH2CONH2), 2.43 (2H, m, CH2CH2CH2CONH2), 3.43 (2H, m, CH2CH2CH2CONH2), 7.88 (1H, m, ArH), 8.00 (3H, m, ArH), 8.12 (2H, m, ArH), 8.17 (2H, m, ArH), 8.32 (1H, d, ArH).

2.3.3 Synthesis of Methyl-3-(1-pyrenyl)propyl Carbamate

Under a dry nitrogen atmosphere, a solution of sodium methoxide in methanol (2.5 mL) was prepared from sodium (100 mg, 4.4 mmol) in a three-necked flask with a reflux condenser and an addition funnel. The solution was cooled to -45 °C with a dry ice/acetone bath. Bromine (150 mg, 0.96 mmol) was added drop-wise with stirring, and stirring was continued until the bromine color disappeared. A solution of 4-(1-pyrenyl)butan-1-amide (250 mg, 0.87 mmol) in methanol (40 mL) was added slowly at 228 K. The temperature was raised to 333 K using a water bath and stirring was continued for 3 h. The solution was cooled to room temperature and acidified with acetic acid to pH 4. The solution was condensed using vacuum distillation at ~25 mtorr. The white residue was mixed with 20 mL water and extracted with dichloromethane (4x20 mL). The combined organic layers were washed with water, dried over anhydrous Na2SO4 and filtered. The solution was concentrated and the residue was purified by column chromatography using 17:3 hexane:ethyl acetate as the eluent to yield 120 mg (87 %) of methyl 3-(1-pyrenyl)propyl carbamate, mp 112-114 °C. δH (CDCl3, 400 MHz): 2.05-2.13 (m, 2H), 3.34-3.41 (m, 4H), 3.68 (s, 3H), 4.72 (s, 1H), 7.85-7.88 (d, 1H, J = 12 Hz), 7.97-8.03 (m, 3H), 8.10-8.18 (m, 4H), 8.23-8.26 (d, 1H, J = 12 Hz).
2.3.4 Synthesis of N-Methyl-3-(1-pyrenyl)propyl Carbamate

Under a dry nitrogen atmosphere, methyl-3-(1-pyrenyl)propyl carbamate (0.13 g, 0.40 mmol) in 5 mL dry DMF was placed in a three-necked flask with a reflux condenser. NaH (10 mg, 0.42 mmol) was added to the solution and it was stirred for 5 min. Iodomethane (22 mg, 0.16 mmol) was added drop-wise and the reaction was continued for 12 h. Excess NaH was quenched by adding water and the reaction mixture was extracted with dichloromethane (4x20 mL). The combined extracts were dried over anhydrous Na₂SO₄, concentrated, and the residue was purified by column chromatography using 17:3 hexane:ethyl acetate as eluent to yield 23 mg (87 %) of N-methyl-(3-(1-pyrenyl)propyl carbamate as a viscous liquid, > 98% purity by HPLC. δH (CDCl₃, 400 MHz), 2.05-2.12 (m, 2H), 2.87-2.93 (m, 3H), 3.30-3.46 (m, 4H), 3.70 (s, 3H), 7.84-7.86 (d, 1H, J = 12 Hz), 7.96-8.03 (m, 3H), 8.08-8.16 (m, 4H), 8.21-8.24 (d, 1H, J = 12 Hz).

2.3.5 Synthesis of N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium Chloride (PyCl)

Anhydrous THF (30 mL) and LiAlH₄ (51 mg, 1.3 mmol) were placed in a 100 mL three-necked round-bottom flask equipped with a stirrer, a nitrogen gas inlet, and an addition funnel. The flask was cooled in an ice bath (0 °C) and methyl N-methyl-3-(1-pyrenyl)propyl carbamate (90 mg, 0.27 mmol) in 20 mL THF was added drop-wise. The mixture was warmed to room temperature and then refluxed for an additional 12 h under a nitrogen atmosphere. The resulting mixture was quenched with ice and the crude product was extracted with dichloromethane (4x30 mL). The combined extracts were washed with water (30 mL), dried over anhydrous Na₂SO₄, and condensed under reduced pressure. The residue was dissolved in a mixture of 20 mL anhydrous diethyl ether and 10 mL dichloromethane. An excess of dry HCl gas (prepared by drop-wise addition of concentrated hydrochloric acid onto concentrated H₂SO₄ and dried by passing the gas through anhydrous CaSO₄) was bubbled through the solution to form a precipitate. The solid was filtered and washed with anhydrous ether (3x5 mL) to obtain 35 mg (45 %) of N,N-dimethyl-3-
(1-pyrenyl)propan-1-ammonium chloride (PyCl), mp 227 – 230 °C, and > 99.4% purity by HPLC. δH (CDCl₃, 400 MHz): 2.46 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 2.89 (6H, s, CH₂CH₂CH₂NH(CH₃)₂), 3.00 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 3.50 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 7.81 (1H, m, ArH), 8.01 (3H, m, ArH), 8.06 (5H, m, ArH), 12.73 (1H, s, NH). Elemental analysis calculated for C₂₁H₂₂NCl: C, 74.0; H, 7.1; N, 4.1. Found: C, 74.3; H, 6.9; N, 4.3.

2.3.6 Synthesis of N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium Bromide (PyBr)

N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium bromide (PyBr) was synthesized by dissolving N,N-dimethyl-3-(1-pyrenyl)propan-1-amine (0.13 g, 0.40 mmol) in 20 mL diethyl ether, under flowing N₂, in a one-neck round bottom flask. Three equivalents of concentrated acid (195 μL 48% hydrobromic acid) were added drop-wise at 0 °C. The precipitate that formed upon addition of the concentrated acid was recrystallized three times in dichloromethane and diethyl ether to give (70%) N,N-dimethyl-3-(1-pyrenyl)propan-1-ammonium bromide (PyBr), mp 224 – 226 °C, and > 99.3% purity by HPLC. δH (CDCl₃, 400 MHz), 2.50 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 2.71 (6H, s, CH₂CH₂CH₂NH(CH₃)₂), 3.05 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 3.51 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 7.85 (1H, m, ArH), 8.01 (3H, m, ArH), 8.18 (5H, m, ArH), 11.72 (1H, s, NH). Elemental analysis calculated for C₂₁H₂₂NBr: C, 66.9; H, 6.1; N, 3.7. Found: C, 67.2; H, 5.8; N, 3.8.

2.3.7 Synthesis of N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium Trifluoroacetate (PyTFA)

N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium trifluoroacetate (PyTFA) was synthesized by dissolving N,N-dimethyl-3-(1-pyrenyl)propan-1-amine (0.13 g, 0.40 mmol) in 20 mL diethyl ether, under flowing N₂, in a one-neck round bottom flask. Three equivalents of concentrated acid (408 μL trifluoroacetic acid) were added drop-wise at 0 °C. The precipitate that formed upon addition of the concentrated acid was recrystallized three times in dichloromethane and diethyl ether to give (62%) N,N-
dimethyl-3-(1-pyrenyl)propan-1-ammonium trifluoroacetate (PyTFA), mp 161 – 162 °C, and > 99.7% purity by HPLC. δH (CDCl₃, 400 MHz), 2.33 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 2.70 (6H, s, CH₂CH₂CH₂NH(CH₃)₂), 3.05 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 3.45 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 7.81 (1H, m, ArH), 8.04 (3H, m, ArH), 8.17 (5H, m, ArH), 12.01 (1H, s, NH). Elemental analysis calculated for C₂₃H₂₂N₁O₂F₃: C, 68.7; H, 5.5; N, 3.5. Found: C, 68.4; H, 5.5; N, 3.7.

2.3.8 Synthesis of N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium Nitrate (PyNO₃)

N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium nitrate (PyNO₃) was synthesized through anion substitution of PyBr with AgNO₃. A concentrated solution of AgNO₃ in methanol (64 mg in 5 mL) was prepared and added drop-wise to a solution of PyBr (0.04 g, 0.12 mmol) in 10 mL of methanol. Upon addition of the AgNO₃ solution, the clear solution turned cloudy and a precipitate formed. The PyNO₃ salt was extracted with chloroform and washed with water to remove excess AgNO₃. 0.03 g of crystalline N,N-dimethyl-3-(1-pyrenyl)propan-1-ammonium nitrate (71%) (PyNO₃), mp 158 – 160 °C, and > 99.4% by HPLC. δH (CDCl₃, 400 MHz), 2.37 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 2.79 (6H, s, CH₂CH₂CH₂NH(CH₃)₂), 3.10 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 3.48 (2H, m, CH₂CH₂CH₂NH(CH₃)₂), 7.84 (1H, m, ArH), 8.04 (3H, m, ArH), 8.17 (5H, m, ArH), 12.01 (1H, s, NH). Elemental analysis calculated for C₂₁H₂₂N₂O₃: ½ H₂O: C, 70.2; H, 6.5; N, 7.8. Found: C, 70.6; H, 6.4; N, 7.8.

2.3.9 Synthesis of N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium p-Toluenesulfonate (PyTSA)

N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium p-toluenesulfonate (PyTSA) was synthesized by dissolving N,N-dimethyl-3-(1-pyrenyl)propan-1-amine (0.13 g, 0.4 mmol) in 20 mL diethyl ether, under flowing N₂, in a one-neck round-bottom flask. Three equivalents of concentrated acid (0.20 g p-toluenesulfonic acid monohydrate in 20 mL ether) were added drop-wise at 0 °C. As the acid was slowly added, the yellow solution turned cloudy as a beige precipitate formed. The precipitate was filtered and
recrystallized three times with dichloromethane and diethyl ether to give (55%) \(N,N\)-dimethyl-3-(1-pyrenyl)propan-1-ammonium \(p\)-toluenesulfonate (PyTSA), mp 129 – 131 °C, and > 99.8% by HPLC. \(\delta\)H (CDCl\(_3\), 400 MHz), 2.32 (3H, s, CH\(_3\)(C\(_6\)H\(_4\))SO\(_3\)) 2.37 (2H, m, CH\(_2\)CH\(_2\)CH\(_2\)NH(CH\(_3\))\(_2\)), 2.70 (6H, s, CH\(_2\)CH\(_2\)CH\(_2\)NH(CH\(_3\))\(_2\)), 3.05 (2H, m, CH\(_2\)CH\(_2\)CH\(_2\)NH(CH\(_3\))\(_2\)), 3.45 (2H, m, CH\(_2\)CH\(_2\)CH\(_2\)NH(CH\(_3\))\(_2\)), 3.70 (2H, d, CH\(_3\)(C\(_6\)H\(_4\))SO\(_3\)), 7.13 (2H, d, CH\(_3\)(C\(_6\)H\(_4\))SO\(_3\)), 7.80 (3H, m, ArH), 8.05 (6H, m, ArH), 8.19 (2H, d, CH\(_3\)(C\(_6\)H\(_4\))SO\(_3\)), 11.22 (1H, s, NH).

Elemental analysis calculated for C\(_{28}\)H\(_{29}\)NSO\(_3\): ½ H\(_2\)O: C, 72.5; H, 6.3; N, 2.9. Found: C, 72.5; H, 6.3; N, 3.1.

2.3.10 Synthesis of \(N,N\)-Dimethyl-3-(9-anthryl)propan-1-ammonium Chloride (AnCl)

\(N,N\)-Dimethyl-3-(9-anthryl)propan-1-amide (0.60 g, 2.2 mmol) was dissolved in 10 mL anhydrous tetrahydrofuran and added dropwise to a stirred suspension of 0.39 g (10.2 mmol) LiAlH\(_4\) in 10 mL anhydrous tetrahydrofuran under a N\(_2\) atmosphere in a round-bottom flask. The suspension was stirred at room temperature under flowing N\(_2\) for 24 h with no detectable evaporation occurring. Two mL acetone was added carefully to quench the excess LiAlH\(_4\). 15 mL diethyl ether was added to the reaction flask and 2 mL deionized H\(_2\)O was then added and stirred to quench the remaining LiAlH\(_4\). The yellow solution was filtered and the lithium salts were washed with 30 mL diethyl ether. The mixture was concentrated under reduced pressure (~ 25 torr) 0.50 g of \(N,N\)-dimethyl-3-(9-anthryl)propan-1-amine was recovered. This was immediately dissolved in 15 mL diethyl ether and acidified with gaseous hydrogen chloride. Gaseous HCl was formed by adding concentrated hydrochloric acid dropwise to stirred concentrated sulfuric acid. The gas was passed through anhydrous calcium sulfate and bubbled through the solution of \(N,N\)-dimethyl-3-(9-anthryl)propan-1-amine for 20 min to give a brown precipitate that was filtered and recrystallized three times in dichloromethane/diethyl ether to give 0.38 g (59%) \(N,N\)-dimethyl-3-(9-anthryl)propan-1-ammonium chloride (AnCl), mp 189 – 190 °C, and > 99.8% purity by HPLC. \(\delta\)H (CDCl\(_3\), 400 MHz), 2.36 (2H, m, CH\(_2\)-CH\(_2\)-CH\(_2\)-NH(CH\(_3\))\(_2\)), 2.63 (6H, s, N(CH\(_3\))\(_2\)), 3.03 (2H, m, CH\(_2\)-CH\(_2\)-CH\(_2\)-NH(CH\(_3\))\(_2\)), 3.71 (2H, m, CH\(_2\)-
CH₂-CH₂-NH(CH₃)₂, 7.43 (4H, m, ArH), 7.96 (2H, d, ArH), 8.14 (2H, d, ArH), 8.32 (1H, s, ArH), 12.49 (1H, s, NH). Elemental analysis calculated for C₁₉H₂₂N₁Cl: C, 76.1; H, 7.4; N, 4.7. Found: C, 75.9; H, 7.4; N, 4.7.

2.3.11 Synthesis of N,N-Dimethyl-3-(9-anthryl)propan-1-amide

3-(9-Anthryl)propanoic acid (0.22 g, 0.88 mmol) was dissolved in 10 mL dry DMF in a round bottom flask and cooled to 0°C. 0.12 mL (1.7 mmol) thionyl chloride was added dropwise to the stirred solution under a static N₂ atmosphere. The temperature was then raised to 90 °C and stirred for 5 h. Excess DMF and thionyl chloride were removed through vacuum distillation at 2 torr. The crude product was then extracted with 3x50 mL dichloromethane. The organic layers were combined and washed with 3x50 mL distilled water. The solvent was removed by vacuum distillation at 25 torr to give 0.22 g (93%) of a red oil, N,N-dimethyl-3-(9-anthryl)propan-1-amide, > 99.9% purity by HPLC. δH (CDCl₃, 400 MHz), 2.68 (3H, s, NCH₃), 2.71 (2H, m, CH₂-CH₂-N(CH₃)₂), 2.90 (3H, s, NCH₃), 3.93 (2H, m, CH₂-CH₂-N(CH₃)₂), 7.43 (4H, m, ArH), 7.94 (2H, d, ArH), 8.21 (2H, d, ArH), 8.30 (1H, s, ArH).

2.3.12 Synthesis of 3-(9-Anthryl)propenoic Acid

3-(9-Anthryl)propenoic acid (3.47 g, 14.0 mmol) was added to a round-bottom flask with 0.35 g (0.32 mmol) 10% Pd/C and 15 mL dry DMF. The suspension was stirred in a flowing N₂ atmosphere for 30 min to displace O₂. A balloon of H₂ gas was then affixed to the round-bottom flask. The suspension was stirred for 48 h at room-temperature. The mixture was then filtered through diatomaceous earth to remove the catalyst and it was washed with acetone. The solvent was removed by vacuum distillation at 25 torr and the crude product was recrystallized three times in ethanol to give 2.20 g (81%) 3-(9-anthryl)propenoic, mp 189-190 °C, and > 95.0% purity by HPLC. δH (CDCl₃, 400 MHz), 2.85 (2H, m, CH₂-CH₂-COOH), 3.99 (2H, m, CH₂-CH₂-COOH), 7.52 (4H, m, ArH), 8.02 (2H, d, ArH), 8.26 (2H, d, ArH), 8.38 (1H, d, ArH).
2.3.13 Synthesis of 3-(9-Anthryl)propenoic Acid

9-Anthraldehyde (10.00 g, 48.5 mmol) was added to an open round bottom flask with 7.02 g (67.5 mmol) malonic acid, 45 mL pyridine and 6 mL piperidine. The solution was heated in an oil bath at 100 – 110 °C for 4 h. Then, a condenser was added and the solution was refluxed for 2 h at 120 °C. 220 mL distilled water was added to quench the reaction. The solution was acidified to a pH of 3 with concentrated HCl. The orange oil solidified and was filtered and washed with distilled water. The solid was dried by vacuum suction and heated uncovered in a beaker from 170 – 185 °C. The compound was washed with hexane. The crude product was recrystallized 5 times with 4% acetic acid in chlorobenzene to give 8.94 g (44%) 3-(9-anthryl)propenoic acid, mp 235 – 237 °C, and > 98.5 % purity by HPLC. δH (DMSO-d6, 400 MHz), 6.46 (1 H, d, J 16.3 Hz, vinyl-CH), 7.71 (4 H, m, ArH), 8.29 (4 H, dd, J 8.3, 18.3 Hz, ArH), 8.61 (1 H, d, J 16.2 Hz, vinyl-CH), 8.79 (1 H, s, ArH), 12.88 (1 H, s, COOH).

2.3.14 Synthesis of N,N-Dimethyl-3-(2-naphthyl)propan-1-ammonium Chloride (NapCl)

N,N-Dimethyl-3-(2-naphthyl)propan-1-amide (2.03 g, 8.93 mmol) was dissolved in 10 mL anhydrous THF and added dropwise to a stirred suspension of 1.90 g (31.3 mmol) LiAlH4 in 20 mL anhydrous THF under flowing N2 in a three-neck round-bottom flask. The reaction mixture was refluxed under flowing N2 for 26 h. The suspension was cooled to room temperature and 5 mL of acetone was added under N2. 30 mL diethyl ether was then added. Finally, 2 mL deionized water was added dropwise. The lithium salts were filtered and the organic solution was dried over Na2SO4 and condensed by vacuum distillation at 25 torr. N,N-Dimethyl-3-(2-naphthyl)propan-1-amine was dissolved in 50 mL diethyl ether and stirred. Gaseous HCl was formed by adding concentrated hydrochloric acid dropwise to stirred concentrated sulfuric acid. The gas was passed through anhydrous calcium sulfate and bubbled through the solution of N,N-Dimethyl-3-(2-naphthyl)propan-1-amine, quickly forming a beige precipitate. 0.94 g of amorphous solid was recovered and recrystallized with dichloromethane and diethyl ether to give 0.62 g
(28%) of N,N-dimethyl-3-(2-naphthyl)propan-1-ammonium chloride (NapCl), mp 175 – 176 °C, and > 99.9% purity by HPLC. δH (CDCl₃, 400 MHz), 2.28 (2H, m, CH₂-CH₂-CH₂-NH(CH₃)₂), 2.73 (6H, d, N(CH₃)₂), 2.90 (4H, m, CH₂-CH₂-CH₂-N(CH₃)₂), 7.29 (2H, m, ArH), 7.45 (2H, m, ArH), 7.61 (1H, m, ArH), 7.77 (2H, m, ArH), 12.67 (1H, s, NH(CH₃)₂). Elemental analysis calculated for C¹₉H₂₀N₁Cl: C, 72.1; H, 8.1; N, 5.6. Found: C, 72.0; H, 8.4; N, 5.7.

2.3.15 Synthesis of N,N-Dimethyl-3-(2-naphthyl)propan-1-amide

3-(2-Naphthyl)propanoic acid (1.82 g, 9.08 mmol) was dissolved in 10 mL anhydrous DMF and stirred under flowing N₂ in a three-neck flask. The solution was cooled to 0 °C and 1.37 mL (18.9 mmol) thionyl chloride was added dropwise. The solution was warmed to 90 °C and the reaction was stirred for 22 h. The solution was cooled to room temperature and excess DMF and thionyl chloride were removed by vacuum distillation at 2 torr as the temperature was warmed from 20 to 55 °C. The crude reaction mixture was dissolved in 200 mL dichloromethane and washed with 100 mL deionized H₂O. The aqueous layer was extracted with 3x50 mL dichloromethane. The organic layers were combined and washed with 5x100 mL deionized water. The organic layer was dried over Na₂SO₄ and condensed with vacuum distillation at 25 torr to give 2.03 g (98%) of a red oil (N,N-dimethyl-3-(2-naphthyl)propan-1-amide), >99.9% purity by HPLC. δH (CDCl₃, 400 MHz), 2.71 (2H, d, CH₂-CH₂-CON(CH₃)₂), 2.95, 3.14 (2H, d, CH₂-CH₂-CON(CH₃)₂), 7.39 (3H, m, ArH), 7.66 (1H, s, ArH), 7.79 (3H, m, ArH).

2.3.16 Synthesis of 3-(2-Naphthyl)propanoic Acid

3-(2-Naphthyl)propenoic acid (2.80 g, 14.2 mmol) was added to a one-neck round-bottom flask with 0.78 g 10% Pd/C and 30 mL anhydrous DMF. The suspension was stirred in a flowing N₂ atmosphere for 30 min to displace O₂. A balloon of H₂ gas was affixed to the flask to commence hydrogenation at ~ 1 atm of H₂. The solution was stirred under H₂ for 48 h. The reaction was quenched by displacement of the
H₂ with N₂. The suspension was filtered through celite to remove the catalyst. The filtrate was diluted with 100 mL ethyl acetate and washed 100 mL deionized water. The aqueous phase was extracted with 3x50 mL ethyl acetate. The organic layers were combined and washed with 5x100 mL deionized water. The organic layer was dried with MgSO₄ and condensed through vacuum distillation at 25 torr. 3.17 g pale yellow solid was recovered. Recrystallization in acetone and water gave 1.82 g (64%) 3-(2-naphthyl)propanoic acid, mp 134 – 135 °C, and > 98.5% purity by HPLC. δH (CDCl₃, 400 MHz), 2.74 (2H, d, CH₂-C₃H₂-COOH), 3.08 (2H, m, ArH), 7.30 (1H, m, CH₂-C₃H₂-COOH), 7.38 (2H, m, ArH), 7.61 (1H, s, ArH), 7.75 (3H, m, ArH).

2.3.17 Synthesis of 3-(2-Naphthyl)propenoic Acid

2-Naphthaldehyde (3.33 g, 21.3 mmol) was added to a single-neck round bottom flask with 2.45 g (23.6 mmol) malonic acid, 1.2 mL (12 mmol) piperidine, and 50 mL pyridine. A reflux condenser was affixed to the round-bottom flask and the solution was stirred and refluxed for 3 h under atmospheric conditions. The solution was cooled to room temperature and diluted by the addition of 100 mL of ethyl acetate. The solution was then washed with 3x50 mL 1N HCl. The aqueous layer was extracted with 3x50 mL ethyl acetate. The organic layers were combined and washed 3x50 mL with deionized H₂O. The organic layer was dried over MgSO₄ and condensed on a rotary evaporator to give 4.05 g yellow solid. The solid was recrystallized in ethanol to give 2.80 g (67%) 3-(2-naphthyl)propenoic acid, mp 208 – 210 °C, and > 95% purity by HPLC. δH (CDCl₃, 400 MHz), 6.54 (2H, d, CH=CH-COOH), 7.49 (2H, m, ArH), 7.66 (2H, d, CH=CH-COOH), 7.85 (5H, m, ArH).

2.3.18 Synthesis of N,N-Dimethyl-3-(1-indolyl)propan-1-ammonium Chloride (InCl)

A suspension of 3.8 g (160 mmol) NaH in 10 mL anhydrous THF was cooled to 0 °C. A solution of 3.0 g (26 mmol) indole in 10 mL anhydrous THF was added to it and it was stirred for 5 min under N₂. 4.2
g (27 mmol) 3-dimethylamino-1-propylchloride hydrochloride, suspended in 20 mL anhydrous THF, was added to the stirring suspension under N₂. The suspension was warmed to RT and then refluxed for 95 h. The conversion of indole to N,N-dimethyl-3-(1-indolyl)propylamine was monitored by HPLC. At 95% conversion, the reaction mixture was cooled to room temperature and excess base was deactivated through the dropwise addition of distilled water. The aqueous phase was extracted 3x50 mL with ethyl acetate. The organic layers were combined and washed with distilled water (3x50 mL) and then dried over anhydrous sodium sulfate. The dried organic layer was condensed using vacuum distillation at 25 torr. Approximately 0.50 g yellow oil was dissolved in 30 mL of diethyl ether. Anhydrous HCl gas was prepared by the slow addition of concentrated HCl into concentrated H₂SO₄. HCl gas was passed through a CaCl₂ drying tube and bubbled into the ether solution. A beige precipitate rapidly formed, filling the flask. 2.29 g crude solid was filtered and dried. The compound was recrystallized three times in ethanol to give 1.48 g (24%) N,N-dimethyl-3-(1-indolyl)propan-1-ammonium chloride (InCl), mp 145 – 148 °C, and > 99.9% purity by HPLC. δH (CDCl₃, 400 MHz), 2.45 (2H, m, CH₂-CH₂-CH₂-NH(CH₃)₂), 2.68 (6H, d, N(CH₃)₂), 2.81 (2H, m, CH₂-CH₂-CH₂-N(CH₃)₂), 4.36 (2H, m, CH₂-CH₂-CH₂-N(CH₃)₂), 6.52 (1H, m, ArH), 7.13 (1H, m, ArH), 7.20 (2H, m, ArH), 7.32 (1H, m, ArH), 7.62 (1H, m, ArH), 12.80 (1H, s, NH(CH₃)₂). Elemental analysis calculated for C₁₉H₂₀N₁Cl: C, 64.9; H, 8.6; N. 11.6. Found: C, 64.7; H, 8.8; N, 11.6.

2.3.19 Synthesis of N,N,N-Trimethyl-3-(1-indolyl)propan-1-ammonium Iodide (MeInI)

A suspension of 0.38 g (1.6 mmol) N,N-dimethyl-3-(1-indolyl)propan-1-ammonium chloride in 10 mL diethyl ether and 10 mL 3M aqueous NaOH was stirred for 30 min under flowing N₂ at room temperature. The aqueous layer was extracted 3x20 mL diethyl ether. The organic layers were combined and washed 3x20 mL with distilled water and dried over sodium sulfate. The dried organic layer was condensed using vacuum distillation at 25 torr. Approximately 300 mg of a yellow oil was dissolved in 25 mL acetonitrile and stirred under flowing N₂. Methyl iodide (0.20 mL, 3.2 mmol) was added to the solution
and the resulting mixture was stirred at room temperature under a static N\textsubscript{2} atmosphere at room temperature for 48 h. The solvent was removed with vacuum distillation at 25 torr to give 0.42 g (78%) \textit{N,N,N}-trimethyl-3-(1-indolyl)propan-1-ammonium iodide (MeInI), mp 41 – 44 °C, and > 99.4% purity by HPLC. δH (CDCl\textsubscript{3}, 400 MHz), 2.39 (2H, m, \textit{CH}\textsubscript{2}-\textit{CH}-\textit{CH}-N(\textit{CH}\textsubscript{3})\textsubscript{3}), 3.28 (9H, d, N(\textit{CH}\textsubscript{3})\textsubscript{3}), 3.71 (2H, m, \textit{CH}-\textit{CH}-\textit{CH}-N(\textit{CH}\textsubscript{3})\textsubscript{2}), 4.42 (2H, m, \textit{CH}-\textit{CH}-\textit{CH}-N(\textit{CH}\textsubscript{3})\textsubscript{2}), 6.53 (1H, m, ArH), 7.16 (1H, m, ArH), 7.20 (2H, m, ArH), 7.43 (1H, m, ArH), 7.63 (1H, m, ArH).

\textbf{2.3.20 Synthesis of \textit{N,N,N}-Trimethyl-3-(1-indolyl)propan-1-ammonium Chloride (MeInCl)}

\textit{N,N,N}-Trimethyl-3-(1-indolyl)propan-1-ammonium chloride was prepared through a counterion substitution of MeInI using Dowex 22 ion exchange column. The ion exchange column (24 cm x 4 cm) was first washed with distilled water and then activated with 3M HCl. The activated column was washed again with water and then with methanol. 200 mg MeInI was dissolved in methanol and eluted through the column. The solvent was removed through vacuum distillation at 25 torr to give 80 mg (55%) \textit{N,N,N}-trimethyl-3-(1-indolyl)propan-1-ammonium chloride (MeInCl) of > 99.8% purity by HPLC. Plasma-assisted chemical ionization mass spectroscopy indicated 99.4% counterion substitution. δH (CDCl\textsubscript{3}, 400 MHz), 2.38 (2H, m, \textit{CH}-\textit{CH}-\textit{CH}-N(\textit{CH}\textsubscript{3})\textsubscript{3}), 3.30 (9H, d, N(\textit{CH}\textsubscript{3})\textsubscript{3}), 3.71 (2H, m, \textit{CH}-\textit{CH}-\textit{CH}-N(\textit{CH}\textsubscript{3})\textsubscript{2}), 4.39 (2H, m, \textit{CH}-\textit{CH}-\textit{CH}-N(\textit{CH}\textsubscript{3})\textsubscript{2}), 6.52 (1H, m, ArH), 7.15 (3H, m, ArH), 7.37 (1H, m, ArH), 7.63 (1H, m, ArH).
3 THE ROLE OF THE GROUND-STATE

3.1 Introduction

To understand dynamic excited-state processes, it is first necessary to examine the structure and dynamics of the corresponding ground-states. The Frank-Condon principle for radiative transitions can be stated simply as a vertical transition (i.e., for excitation or emission) that occurs without nuclear motion and is more probable between vibronic states that conserve the initial nuclear geometry. In other words, electrons move much faster than the (much heavier) nuclei. Allowed electronic transitions occur on timescales in the femtosecond regime. Nuclear motion is typically much slower (i.e., in the picosecond regime). This large difference in the rates of electronic and nuclear motion allows one to separate the quantum-mechanical motion of electrons from the pseudo-Newtonian motion of the nuclei. In practice, this means that the initial excited-state species will resemble the ground-state structure which was excited. The motion of protons is oftentimes much less straightforward. The small size and low mass of a single hydrogen nucleus allows for quantum mechanical perturbations along a given reaction coordinate. These effects are best evidenced by observations of femtosecond proton transfer rates which can only be rationalized through ‘tunneling’ behavior outside the scope of this work. For the purpose of this research, Frank-Condon transitions will be discussed as distinct and independent electronic events which bridge identical ground and excited-state structures. As mentioned in the introduction, Chapter 6 will be almost entirely dedicated to expounding upon the excited-state proton transfer. Thus, in order to better understand the excited-state dynamics of ArS, Chapter 3 will first describe theoretical and experimental investigations of the ground-state potential energy surface.

This dissertation builds extensively upon the work of Abraham and Weiss which explored the properties of a series of $N,N$-dialkyl-3-(1-pyrenyl)alkan-1-ammonium chloride salts. Exciplex emission was observed for solutions of $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium chloride (PyCl), 3-(1-pyrenyl)propan-1-ammonium chloride, $N,N$-dimethyl-4-(1-pyrenyl)butan-1-ammonium chloride, and $N$-
hexyl-N-methyl-3-(1-pyrenyl)propan-1-ammonium chloride in THF. The strongest exciplex emission was observed for N-hexyl-N-dimethyl-3-(1-pyrenyl)propan-1-ammonium chloride and PyCl in THF. Abraham and Weiss posited that the excited-state proton-transfer was facilitated by a ground-state conformer (C) which resembled the exciplex geometry, with the propane chain bent, and the ammonium proton pointing towards the pyrenyl.\textsuperscript{31} The C conformation is disfavored entropically in comparison to an open conformation (O) where the ammonium group is solvated and extended away from the pyrenyl (Figure 3.1). These conformations presumably represent two extrema in a distribution of ground-state conformations where the equilibrium between O and C is dictated by an equilibrium constant ($K_{OC}$). It was hypothesized by Abraham and Weiss that polar solvents (acetonitrile and ethanol) could better solvate the ammonium group and thus favored conformations resembling O.\textsuperscript{31} On the other hand, lower polarity solvents (THF), which cannot effectively solvate the ionic ammonium group, promote conformations resembling C which is stabilized through an intramolecular hydrogen-$\pi$ bond between the ammonium proton and the $\pi$-cloud of the pyrenyl. A mechanism was proposed describing the above ground-state relationships and also excited-state dynamics discussed in subsequent chapters (Scheme 3.1). While this mechanism was originally proposed for the pyrenyl-salts, subsequent analysis of $N,N$-dimethyl-3-(9-anthryl)propan-1-ammonium chloride (AnCl) and $N,N$-dimethyl-3-(2-naphthyl)propan-1-ammonium chloride (NapCl) indicate that the relationships described by Scheme 3.1 can reasonably attributed to all three ArS.
Scheme 3.1 Proposed Mechanism for Deprotonation of and Exciplex Formation by PyS in Solutions of ‘Intermediate Polarity’. X refers to any of the anions examined with the ammonium cation.

3.2 Ground-State Conformational Equilibria of the ArS

Density functional theory (DFT) calculations have been used extensively to probe the ground-state equilibrium between O and C. M06 was selected as the level for these calculations based on its success in modeling weak hydrogen bonds. The basis set (6-31G(d,p)) was selected for its diffuse functionals, necessary for approximating weak hydrogen bonds. As noted above, a hydrogen-π bond is hypothesized to exist between the ammonium proton and the π-electrons of pyrenyl. These calculations excluded the anion from the structure in order to emphasize the attractive interaction between the ammonium group and the pyrenyl. Geometry optimizations were performed from two initial conformations with the propylene chain bent towards the aryl, but with the ammonium-proton at varied angles with respect to the aromatic plane. Energy minimization, starting from these conformations, resulted in the same final structure, corresponding to the C conformation in Figure 3.2. Two minima were observed on the ground-state potential energy surface corresponding to the O and C structures. A frequency analysis was performed at optimized geometries to ensure that a local minima had been reached. The energy difference between O and C (ΔE_{OC}) was arrived at by comparing the internal energies of the two
conformers. A negative $\Delta E_{\text{OC}}$ indicates a preference for the closed conformation. These calculations were also repeated for AnCl, NapCl, and InCl (Figure 3.2). The results are tabulated in Table 3.1. The strength of the hydrogen-$\pi$ bond can be approximated from both the conformational preference ($\Delta E_{\text{OC}}$) and the length of the hydrogen-$\pi$ bond ($r_{\text{NH}}$). The hydrogen-bond length was calculated as the distance between the proton and the closest aromatic atom ($r_{\text{CH}}$ and $r_{\text{NH}}$). The hydrogen-$\pi$ bond length is best compared to the summation of the van der Waals radii ($r_{\text{vdW}}$). When $r_{\text{CH}}/r_{\text{NH}} < r_{\text{vdW}}$ an attractive interaction (bond) is assumed to be operative between the two constituents. In addition, the distance from the proton to the aromatic plane ($r_{\text{NH}}$) is tabulated below.

Figure 3.1 Ground-State Equilibrium between O and C for $N,N$-Dimethyl-3-(1-pyrenyl)propan-1-ammonium Salts (PyS) where the Anion $X^-$ is Chloride (PyCl), Bromide (PyBr), Trifluoroacetate (PyTFA), Nitrate (PyNO3), or $p$-Toluenesulfonate (PyTSA).

Table 3.1 Ground-State Gas-Phase DFT Calculations of Conformer Energy Difference ($\Delta E_{\text{OC}}$) and Hydrogen-$\pi$ Bond for ArS.

<table>
<thead>
<tr>
<th>ArS Cation</th>
<th>$\Delta E_{\text{OC}}$ (eV)</th>
<th>$r_{\text{CH}}$ or $r_{\text{NH}}$ (Å)</th>
<th>$r_{\text{vdW}}$ (Å)</th>
<th>$r_{\text{NH}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>-0.52</td>
<td>2.07</td>
<td>2.90</td>
<td>2.06</td>
</tr>
<tr>
<td>AnCl</td>
<td>-0.51</td>
<td>2.06</td>
<td>2.90</td>
<td>1.95</td>
</tr>
<tr>
<td>NapCl</td>
<td>-0.42</td>
<td>2.07</td>
<td>2.90</td>
<td>1.99</td>
</tr>
<tr>
<td>InCl</td>
<td>-0.64</td>
<td>2.25</td>
<td>2.75</td>
<td>1.96</td>
</tr>
</tbody>
</table>
Figure 3.2 Optimized Geometries (M06/6-31G(d,p)) of N,N-Dimethyl-3-(1-pyrenyl)propan-1-ammonium Chloride (PyCl), N,N-Dimethyl-3-(9-anthryl)propan-1-ammonium Chloride (AnCl), N,N-Dimethyl-3-(2-naphthyl)propan-1-ammonium Chloride (NapCl), and N,N-Dimethyl-3-(1-indolyl)propan-1-ammonium Chloride (InCl) Cations in their Open (O) and Closed (C) Conformations. Energy minima were verified with a frequency analysis which revealed no imaginary frequencies.
These calculations reveal a marked preference for the closed conformation in the ground-state based on the $\Delta E_{OC}$. In addition, the calculations predict, absent any other intermolecular interactions, the formation of an intramolecular hydrogen-$\pi$ bond between the ammonium proton and the aryl group. It is important to qualify these results with “absent any other intermolecular interactions” because, of course, the effect/presence of solvent is omitted. Solvation of the ArS is manifested through bulk effects such as the dielectric field ($\varepsilon$) of the solvent, and probably more importantly, through localized intermolecular interactions including dipole-dipole interactions, hydrogen-bonding, and dispersive interactions. In order to better understand the role of solvent on the ground-state conformation, a series of increasing dielectric fields were placed around the O and C conformers using the solvent continuum reaction field (SCRF) method. A second geometry optimization was performed within the dielectric fields to understand bulk solvent effects on the conformational equilibrium. The results of these calculations are listed in Table 3.2.

<table>
<thead>
<tr>
<th>ArS Cation</th>
<th>$\Delta E_{OC}$ ($\varepsilon = 1$) (eV)</th>
<th>$\Delta E_{OC}$ ($\varepsilon = 7$) (eV)</th>
<th>$\Delta E_{OC}$ ($\varepsilon = 78$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>-0.52</td>
<td>-0.16</td>
<td>-0.09</td>
</tr>
<tr>
<td>AnCl</td>
<td>-0.51</td>
<td>-0.15</td>
<td>-0.08</td>
</tr>
<tr>
<td>NapCl</td>
<td>-0.42</td>
<td>-0.13</td>
<td>-0.08</td>
</tr>
<tr>
<td>InCl</td>
<td>-0.64</td>
<td>-0.23</td>
<td>-0.15</td>
</tr>
</tbody>
</table>

When the bulk dielectric of the solvent is considered, the attraction between the positively charged ammonium group and the aromatic $\pi$-cloud is diminished. The corresponding increase in $\Delta E_{OC}$ indicates a growing preference for the O conformer in polar environments. However, the most important contribution to this equilibrium is undoubtedly the local solvation of the ammonium group. This was approximated in the case of PyCl by the inclusion of a THF solvent molecule within the SCRF for the C conformer. A geometry optimization under these conditions indicated the possibility of a shared hydrogen-bond between the $\pi$-cloud and the solvent molecule (Figure 3.3). Under these conditions $r_{CH}$ increased from 2.07 Å in the gas-phase to 2.47 Å, still remaining within the sum of the van der Waals
radii. More importantly, the distance between the proton-accepting oxygen and the proton ($r_{OH}$) is 2.08 Å, substantially less than the sum of the van der Waals radii (2.72 Å). As with the ammonium-π bond, the O-H hydrogen bond is likely overestimated by these calculations which fail to include competing intermolecular interactions present in solution. However, the inclusion of a proton-accepting solvent molecule provides a key insight into a possible ground-state structure operative in the PCCT mechanism.

Excited-state proton transfer reactions typically require the formation of a ‘proton-transfer complex’ prior to the reaction. In the simplest case, a proton-transfer complex is the proton-donor ($D_P$) linked through a hydrogen-bond to the proton-acceptor ($A_P$). The most rapid excited-state proton transfers require a precise alignment of $D_P$ and $A_P$ prior to excitation. Although the proton transfer dynamics of the ArS will be discussed much more thoroughly in subsequent chapters, Figure 3.3 is included here as an idealized picture of the ground-state proton-transfer complex. A shared hydrogen-bond between the ammonium ($D_P$), the pyrenyl π-cloud ($A_e$), and a solvent-molecule ($A_P$) is a reasonable precursor to the excited-state PCCT reaction.
3.3 Approximating the Ground-State Potential Energy Surfaces of the ArS

A central concern continually addressed by this research is whether the proton-transfer occurs in the ground- or excited-state. The $pK_a$ of triethylammonium perchlorate in THF is reported to be 14.07. Assuming a similar $pK_a$ for the ArS in THF, protonation is favored thermodynamically by 0.83 eV. That value corresponds to an equilibrium constant of $8.5 \times 10^{-15}$ or, for THF solutions at $10^{-5}$ M, a concentration of $<10^{-19}$ M $N,N$-dimethyl-3-arylp propane-1-amin es (ArA) at room temperature. Various reaction coordinates of the PyCl cation were also examined using M06/6-31G(d,p) to better understand the ground-state potential energy surface. The first reaction-coordinate examined was a rotation about the carbon-nitrogen bond. The goal of these calculations was to investigate whether rotation about this bond provides a viable method for liberating the proton from the intramolecular hydrogen-$\pi$ bond. After a geometry optimization, single-point calculations were performed at rotations about this bond ($\theta_{CN}$) at
intervals of 10°. Unsurprisingly, these calculations reveal a local minima at the initial optimized angle, and a second local minima at approximately 180° (Figure 3.4). The same was observed along the first excited-state potential energy surface, calculated using a time-dependent method with the same calculation model. The DFT calculations reveal a 13.4 eV barrier in the ground-state and an 11.0 eV barrier in the excited-state, effectively preventing any complete rotation about the C-N bond. However, smaller rotations of about 40° from the minimum have a calculated barrier of only ~0.1 eV. The resulting calculations agree with our understanding of the C conformer; that is to say, it is entropically constrained, and access to the proton is limited to a very specifically oriented solvent molecule and only minor conformational changes to the ammonium group are energetically feasible (Figure 3.3). These energetic constraints remain in the first excited singlet-state. As expected, redistribution of the π-electrons has no influence on the steric-constraints limiting rotation about the C-N bond. The single-point rotation calculations did not include relaxation of the nuclei around this angle. Because the nuclear coordinates are not relaxed at each angle, the rotational barriers are likely overestimated. Nevertheless, it is clear that significant rotation about this bond is not feasible without also extending the propane chain.
Using the optimized geometry of the PyS cation and a THF molecule as a starting point, we examined the presumed reaction coordinate of the proton transfer from \( D_F \) to \( A_F \). To probe this coordinate, the proton was translated from the nitrogen atom to the oxygen atom in intervals of 0.05 Å. Single-point energy calculations were performed at each step (Figure 3.5). These calculations provide a rough approximation for the proton-transfer along the proton-transfer complex. Two local minima are observed along this reaction coordinate. The first is the optimized geometry of the C conformer with a THF molecule, which predicts a protonated nitrogen participating in a shared hydrogen bond. The second minimum corresponds to a protonated oxygen in a hydrogen bond with the neutral amine. The energy difference between these two minima in the ground-state is 1.36 eV. Because these single-point
calculations *did not* include relaxation of the nuclei outside the reaction coordinate, they necessarily overestimate the energy difference between the two protonated species. Yet, even without performing the more accurate constrained optimizations, the energetic cost of transferring the proton in the ground-state approaches the experimentally observed 0.83 eV of triethylammonium perchlorate in THF.

![Potential Energy Surfaces](image)

**Figure 3.5** Calculated Potential Energy Surfaces for $S_0$ and $S_1$ States of the PyCl Cation and a THF Molecule in a SCRF ($\varepsilon = 7$) with Translation of the Proton from $D_r$ to $A_r$ as Calculated Using M06-6-31G(d,p).

Although this chapter seeks to primarily describe ground-state phenomena, the first excited-state potential energy surface was also examined along these reaction coordinates. The $S_1$ surface along the rotation coordinate has already been addressed. A redistribution of $\pi$-electron density in the pyrenyl is
far outweighed by the steric repulsion of the methyl-groups, which is reflected in the large activation barriers to rotation. The same cannot be said of the proton-transfer coordinate. The above TD-DFT single-point calculations represent vertical Frank-Condon excitations from a static ground-state differing only in the relative position of the proton. The resulting calculations predict no significant change to the excitation energy as the proton is translated away from the shared hydrogen-bond. This conclusion is consistent with experimental results. The excitation spectrum of PyCl does not shift dramatically as a function of solvent, although solvent presumably shifts $K_{OC}$ and thus, the amount of PyCl participating in an intramolecular hydrogen-bond. Increasingly, TD-DFT calculations have become an attractive alternative to more expensive configuration interaction (CI) calculations for probing excited-state potential energy surfaces. However, the success of TD-DFT methods for predicting vertical excitations is mitigated by their underestimation of charge-transfer energies. In order to describe the PCCT reactions exhibited by ArS, calculations must include not just the $S_0$ and $S_1$ states, but also the interplay of charge-transfer (CT) interactions from the nitrogen coinciding with the transfer of the proton. Indeed, there are excellent examples of this in the literature for different PCET systems.

3.4 Ground-State Aggregation of ArS in Solution

There is an additional ground-state effect that must be considered in the discussion of the ArS. The amphiphilic structure of the ArS increases the probability of aggregation in concentrated solutions. Aggregation was first observed by Abraham and Weiss for a series of pyrenyl salts. Ammonium salts substituted with long alkyl chains on the nitrogen have the strongest propensity for aggregation. The ArS studied in greatest detail in this regard, $N$-dodecyl-$N$-methyl-3-(1-pyrenyl)propan-1-ammonium chloride, was observed to aggregate in solvents of varying polarity at concentrations as low as $10^{-4}$ M. Evidence for aggregation was found in a red-shifted, unstructured emission centered at 485 nm, consistent with the formation of pyrenyl excimers. Single-crystal X-ray diffraction revealed that molecular packing was
dominated by extensive hydrogen bonding between ammonium groups, dispersive interactions along the dodecyl chains, and $\pi-\pi$ stacking between pyrenyl groups. $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium chloride (PyCl) may pack in a similar fashion, albeit without the dispersive interactions of the dodecyl chain. In fact, Abraham and Weiss observed a comparable excimer between PyCl and $N$-dodecyl-$N$-methyl-(1-pyrenyl)propan-1-ammonium chloride in solutions of THF at concentrations of $10^{-3}$ M.\textsuperscript{31} Aggregation complicates analysis of the PCCT mechanism at almost every step. Fortunately, at more dilute concentrations ($10^{-5}$ M), there was no evidence of PyCl aggregation in every solvent examined, except in dichloromethane. In the case of dichloromethane, dilution to $10^{-6}$ M prevented aggregation.

The main experimental evidence for aggregation is spectroscopic. Changes in the UV-vis absorption spectra or the appearance of excimeric emission ($\sim 485$ nm) are key indicators of aggregates in solution. Aggregation of PyCl in 1,4-dioxane was investigated spectroscopically as well as by dynamic light scattering (DLS) experiments. The steady-state fluorescence spectra of PyCl in 1,4-dioxane at $10^{-3}$ M, $10^{-4}$ M, and $10^{-5}$ M are shown in Figure 3.6. As was observed by Abraham and Weiss, at higher concentrations the PyCl emission spectrum in THF contains an excimeric emission (centered at 480 nm). As the concentration is reduced, this band is replaced by a further red-shifted exciplex emission centered at 495 nm. Both the excimer and exciplex emissions in 1,4-dioxane are blue-shifted with respect to the THF solutions because the lower polarity 1,4-dioxane increases the energy of the CT state. These effects will be described in much greater detail in the subsequent chapter. Suffice it to say, it is clear that PyCl will aggregate at sufficiently high concentrations, but that these effects can be mitigated by sufficient dilution.
Figure 3.6 Normalized Emission Spectra ($\lambda_{\text{excitation}} = 344$ nm) of PyCl in 1,4-Dioxane at 293 K at Concentrations of $10^{-3}$ M (Black), $10^{-4}$ M (Red), and $10^{-5}$ M (Blue). The spectra were normalized with respect to emission from the locally excited state ($\lambda_{\text{LE}} = 377$ nm).

Further evidence for aggregation at higher concentrations is gained through DLS measurements. At $10^{-3}$ M, aggregation of PyCl in 1,4-dioxane was presumed from strong excimeric emission. A filtered solution of PyCl at this concentration was scanned at multiple angles using dynamic light scattering (DLS) to measure the size and shape of these aggregates. A contin analysis of these scans revealed objects with high polydispersity (Figure 3.7). The average calculated hydrodynamic radius was 110 nm and the measured polydispersity varied with the measurement angle. Analysis was complicated by low signal-to-noise at this concentration of PyCl. So, while the DLS measurements confirm aggregation at $10^{-3}$ M, these experiments cannot report on more dilute concentrations, though the steady-state spectra indicate moderate excimer emission even at $10^{-4}$ M. Thus, in order to greatly simplify the investigation of the PCCT mechanism, all experiments were carried out at < $10^{-4}$ M. While we cannot definitely claim that there is
no aggregation at 10⁻⁵ M, there is no evidence to support the presence of aggregates for any of the ArS at these dilute concentrations. The absence of substantial aggregation is corroborated by SPC experiments which do not reveal any fluorescent states which cannot be attributed to mechanism proposed in Scheme 3.1.

Figure 3.7 Contin Analyses from DLS Experiments on 10⁻³ M PyCl in 1,4-Dioxane. The calculated size distribution of aggregates in solution is calculated from multiple scattering angles.

3.5 Conclusions on Ground-State Dynamics of ArS Salts

The ground-state structures of the ArS provide the foundation for subsequent excited-state processes, specifically, the PCCT reaction. The DFT calculations, steady-state emission spectra, and time-correlated single photon counting experiments presented in this chapter validate the ground-state conformational equilibrium initially proposed by Abraham and Weiss. The SPC results in dichloromethane are consistent with two distinct emissive species in solution. An idealized proton-transfer complex has been approximated through DFT calculations positioning a lone THF molecule (A₀) in proximity to the ammonium group of the closed conformation (D₀). From these calculations, a ground-state proton-
transfer along the reaction coordinate from the nitrogen to the oxygen is predicted to be endothermic. Higher-level calculations may be able to provide additional insights into the PCCT mechanism provided the various participating states are accounted for. Finally, DLS experiments have further verified the existence of PyCl aggregates at $10^{-3}$ M, consistent with excimeric emission observed in the steady-state fluorescence spectra. At more dilute concentrations ($10^{-5}$ M in 1,4-dioxane, THF, ethyl acetate, and acetonitrile and $10^{-6}$ M in dichloromethane), the effects of aggregation are not observed in either the steady-state spectra or fluorescence decays measured through SPC measurements. AnCl, NapCl, and InCl do not exhibit evidence of intermolecular complexation in their fluorescence spectra, and generally, are less prone to aggregation than are the pyrenyl derivatives because of the weaker π-stacking interactions experienced by these salts.
4 THERMODYNAMIC RELATIONSHIPS ALONG THE EXCITED STATE POTENTIAL ENERGY SURFACE

4.1 Introduction

Irradiated solutions of ArS highlight the importance of the ground-state structure to subsequent photophysical processes. Frank-Condon excitations of the ground-state ArS result in excited-state structures with identical nuclear configurations but vastly different electronic character. It is primarily the redistribution of electron density in the excited-state and the potential energy gained from excitation which give rise the unusual PCCT mechanism described in the Introduction. A key feature of the PCCT mechanism is the formation of an emissive intramolecular exciplex (Ex). An exciplex is defined as an excited molecular complex of definite stoichiometry, but which is dissociated in its ground state. Complexes which fit this definition, but for which the donor and the acceptor are the same molecule, are generally referred to as excimers. It is difficult to discuss exciplexes, which are stabilized through a mixture of charge-transfer and locally-excited states, without also discussing excited-state electron transfer. The foundations of excited-state electron transfer were laid by Marcus, and later, by Rehm and Weller. This led to the development of the Rehm-Weller equation for excited-state electron-transfer:

\[ \Delta G_{et} = \frac{1}{2} E_{Ox}^1 - \frac{1}{2} E_{Red}^1 - E_{Ex} - \frac{e^2}{r\epsilon} \]  

(4.1)

In this equation, \( E_{Ox}^{1/2} - E_{Red}^{1/2} \) is the difference between the half-wave oxidation and reduction potentials of \( D_e \) and \( A_e \), respectively, \( E_{Ex} \) is the Frank-Condon excitation energy, \( e \) is the elementary charge, \( r \) is an approximation to the distance between \( D_e \) and \( A_e \) when they are nearest neighbors, and \( \epsilon \) is the dielectric constant of the solvent. This first-principles approach to electron-transfer approximates the free energy of excited-state electron transfer (\( \Delta G_{et} \)) using easily obtained empirical data. Weller later
extended this equation to explore excited-state electron-transfer processes in solvents of different polarities:\textsuperscript{51}

$$\Delta G_{\text{rip}}^e = (E_D^{\text{ox}} - E_A^{\text{red}}) + \frac{e_0^2}{\epsilon} \left( \frac{1}{r} - \frac{1}{a} \right) - \frac{e_0^2}{37r} - E_{0,0}$$ \hspace{1cm} (4.2)

$\Delta G_{\text{rip}}^e$ is the free energy needed to form a solvent-separated ion pair (IP) and $E_D^{\text{ox}} - E_A^{\text{red}}$ are the oxidation and reduction potentials here of the donor nitrogen and aromatic acceptor, respectively. $\frac{e_0^2}{\epsilon} \left( \frac{1}{r} - \frac{1}{a} \right) - \frac{e_0^2}{37r}$ is the solvation energy of the ion pair (relative to acetonitrile), where $r$ is the distance between the D$_e$ and the A$_e$ as defined above, $a$ is the assumed center-to-center distance of the ion-pair components separated by one solvent molecule,\textsuperscript{51} $e_0$ is the permittivity of free space, and $E_{0,0}$ is the vertical excitation energy (calculated from the wavelength at the overlap point between intensity-normalized absorption and emission spectra). The free energy of ion pair formation ($\Delta G_{\text{rip}}^e$) was calculated for PyS, AnS, and NapS, using the half-wave reduction potential of pyrene (-2.22 V),\textsuperscript{52} anthracene (-2.10 V),\textsuperscript{52} and naphthalene (-2.66 V),\textsuperscript{52} the half-wave oxidation potential of butyldimethylamine (1.25 V), $<r> = 3$ Å, and $<a> = 5$ Å.\textsuperscript{51} These energies provide an important reference for subsequent discussions of excited-state electron-transfer exhibited by the ArS in solutions of varying polarity.
Table 4.1 Free Energy Parameters Used in the Calculation of $\Delta G_{ritp}^e$ for ArS in Solvents of Varying Dielectric Constants ($\varepsilon$) Using $<r> = 3$ Å, and $<a> = 5$ Å, the Half-Wave Oxidation Potential of Butyldimethylamine ($E_{D}^{ox} = 1.25$ V), and the Half-Wave Reduction Potentials of Pyrene, Anthracene, and Naphthalene, Respectively.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_{D}^{ox} - E_{A}^{red}$ (eV)</th>
<th>$\frac{e^2}{\varepsilon} \left( \frac{1}{r} - \frac{1}{a} \right) - \frac{e^2}{37r}$ (eV)</th>
<th>$E_{0,0}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>3.47</td>
<td></td>
<td>3.43</td>
</tr>
<tr>
<td>AnCl</td>
<td>3.35</td>
<td>$\frac{2.6}{\varepsilon} - 0.13$</td>
<td>3.17</td>
</tr>
<tr>
<td>NapCl</td>
<td>3.91</td>
<td></td>
<td>3.78</td>
</tr>
</tbody>
</table>

Table 4.2 Predicted Free-Energies in eV for Ion Pair Formation ($\Delta G_{ritp}^e$) of the ArS in Various Solvents, as Calculated with eq 4.2.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PyCl</th>
<th>AnCl</th>
<th>NapCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile ($\varepsilon = 37$)</td>
<td>-0.03</td>
<td>0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>Tetrahydrofuran ($\varepsilon = 7$)</td>
<td>0.24</td>
<td>0.39</td>
<td>0.33</td>
</tr>
<tr>
<td>1,4-Dioxane ($\varepsilon = 2$)</td>
<td>1.05</td>
<td>1.21</td>
<td>1.15</td>
</tr>
<tr>
<td>Gas-phase ($\varepsilon = 1$)</td>
<td>2.50</td>
<td>2.65</td>
<td>2.59</td>
</tr>
</tbody>
</table>

4.2 Steady-State Fluorescence of ArS in Solution

As mentioned previously, this research was instigated by observations of exciplex emission by Abraham and Weiss for a class of $N,N$-dialkyl-3-(1-pyrenyl)alkan-1-ammonium chloride salts in THF. Exciplexes are the result of coupling between locally-excited (LE) and charge-transfer (CT) states and these complexes require orbital overlap between $D_e$ and $A_e$. The characteristics of the exciplex are determined primarily by the thermodynamic driving force of electron transfer ($\Delta G_{ritp}^e$), the overlap integrals between the CT state and pertinent LE states, and the dipole moment of the exciplex. Recent transient infrared absorption experiments by Vauthey et al. indicate that the exciplex serves as an intermediate between the LE state and the solvent separated ion pair (IP) and thus can be thought of as the product of incomplete charge separation. The neutral $N,N$-dimethyl-3-arylprom-1-amines (ArA) derived from neutralization of the PyS, AnCl and NapCl, provide an important comparison to the photophysics of ArS.
For ArA, the lone-pair on the nitrogen is free to participate in CT interactions with the LE state, and it is not restricted by the proton-transfer required for solutions of ArS. Fortunately, the photophysics of ArA have been described in detail by Mataga, DeSchryver, and Van derAuwereraer.\textsuperscript{32,35} Solutions of ArA are known to exhibit moderate to strong exciplex emission, and both the energy and intensity of Ex emissions depend on solvent polarity. The effect of solvent polarity on the emission spectra of the exciplexes is primarily dictated by the large dipole moments of the exciplexes which closely resemble tight ion pairs because of the extent of CT interactions. In the case of \textit{N,N}-dimethyl-3-(1-pyrenyl)propan-1-amine (PyA), exciplex formation was observed to occur from both excited singlet-state conformations (O* and C*) due to the long lifetime of the LE state. The excited-state equilibrium between open and closed conformations ($K_{OC}$) may also be contributing to the photophysics of PyS, but it is unlikely that AnCl or NapCl interconvert between O* and C* because of their shorter-lived excited singlet-states. In any case, $K_{OC}$ is the first relationship between excited-states that must be considered in the PCCT mechanism. A more detailed mechanism for the complete PCCT mechanism is given below (Scheme 4.1).

\textbf{Scheme 4.1 Proposed PCCT Mechanism Exhibited by Irradiated Solutions of \textit{N,N}-Dimethyl-3-arylpropan-1-amine Salts (ArS).}
Irrespective of the value of \( K_{OC*} \), much of the interesting chemistry occurs from C*. Excitation of C* results in the transfer of a proton from the ammonium group (D\( \text{P} \)) to a proximal solvent molecule (A\( \text{P} \)). The ground-state conformational analysis presented in the previous chapter indicates that the proton acceptor can form a shared hydrogen bond between the ammonium group and the aromatic \( \pi \)-cloud. This configuration (Figure 3.3) is our best representation of the proton-transfer complex. As will be discussed in Chapter 5, the formation of the exciplex is limited by the rate of proton-transfer ([B]\( k_{CE*} \)). Rehybridization of the molecular orbitals on the nitrogen accompanies the transfer of electron-density from the lone pair to the excited-state aryl. Reorganization of electron density and nuclei leads to the formation of an intramolecular exciplex (Ex) which can exist in equilibrium between a decomplexed LE state (D\( * \)) and a charge-separated ion pair (IP). The interplay between these states is determined by the driving force of electron transfer (\( \Delta G^f_{ri,p} \)) and the solvent, which both dictates the equilibrium between O and C and accepts the proton. The steady-state emission spectra of PyCl, AnCl, and NapCl (Figure 4.1) demonstrate the aforementioned solvent effects.

Figure 4.1 Normalized Steady-State Fluorescence Spectra of 10\(^{-5}\) M ArS at 293 K in 1,4-Dioxane (Red), Tetrahydrofuran (Magenta), Acetonitrile (Blue), and Dichloromethane (Black): a) PyCl (\( \lambda_{\text{excitation}} = 344 \) nm), b) AnCl (\( \lambda_{\text{excitation}} = 369 \) nm), and c) NapCl (\( \lambda_{\text{excitation}} = 305 \) nm).
As the solvent polarity was increased from 1,4-dioxane ($\varepsilon = 2$), to THF ($\varepsilon = 7$), and to acetonitrile ($\varepsilon = 37$), the intensity of Ex emission decreased and became progressively red-shifted as a result of both ground and excited-state effects. First, as solvent polarity is increased, the open conformation is stabilized with respect to the closed conformation. This shifts $K_{OC}$, favoring a larger population of O* which limits Ex formation. In addition, contributing CT states are stabilized in solvents with larger dielectric fields (eq 4.2). Because the exciplexes formed from solutions of ArA resemble a tight ion pair, stabilization of the CT state red-shifts Ex emission. Finally, these exciplexes are believed to decay primarily through the formation of an IP, charge recombination, and internal conversion to the ground-state.\textsuperscript{33} Therefore, while the Ex is stabilized to a larger extent in polar solvents, so too, is the IP which ultimately quenches Ex fluorescence. In acetonitrile, for example, Ex emission is not observed for PyCl, AnCl, or NapCl. It is reasonable to attribute the lack of Ex emission to both changes to the ground-state equilibrium and to stabilization of the ‘dark’ ion pair. Here, a distinction can likely be made between the photophysics of PyCl and those of AnCl and NapCl.

4.3 Transient Absorption Spectra of ArS in Solution

In order to distinguish between ground-state and excited-state effects, transient absorption experiments were performed in solvents of different polarities (Figure 4.2). The anion radicals of pyrene, anthracene, and naphthalene have been exhaustively characterized, and they are easily observed by transient absorption spectroscopy.\textsuperscript{55} Although pulsed irradiations of AnCl and NapCl exhibited no significant transient absorptions, an absorption characteristic of the pyrenyl radical anion was observed from PyCl in THF and in acetonitrile.
Figure 4.2 Transient Absorption Spectra of $10^{-5}$ M a) NapCl, b) AnCl, and c) PyCl in 1,4-Dioxane (Black), Tetrahydrofuran (Red), and Acetonitrile (Blue) Collected at 1.4 ns after Excitation at 320 nm. The absorptions at 640 nm are attributed to light leakage from the second order harmonic of the excitation source to the detector.

The transient absorption results are consistent with $\Delta G^r_{ri}$ as calculated from eq 4.2. Solutions of PyCl in the more polar acetonitrile exhibit moderate transient absorption from 440 – 520 nm that is consistent with the formation of the pyrenyl radical anion. In the lower polarity solvent, THF, the signal is broadened and red-shifted. Because the calculated $\Delta G^r_{ri}$ of PyCl in THF is endothermic by 0.24 eV, we hypothesize that this signal is from a tight ion pair that closely resembles the exciplex. Consistent with the extraordinary thermodynamic barrier to IP formation in 1,4-dioxane ($\Delta G^r_{ri} = 1.05$ eV), there is no transient absorption that can be attributed to the pyrenyl radical anion. These results indicate that PyCl exhibits a more typical PCET mechanism in acetonitrile, in which the transfer of a proton is coupled to the full transfer of an electron from the nitrogen lone pair ($D_e$) to the excited singlet-state of pyrenyl ($A_e$). The transient absorption results for PyCl are in stark contrast to results from pulsed irradiations of solutions of AnCl and NapCl, which do not form ion pairs in solution, yet clearly must transfer a proton in order to form the exciplexes whose emissions are clearly observable in Figure 4.1. In summary, Ex emission is absent for all three ArS in acetonitrile. For PyCl, exciplex emission is quenched through full electron-transfer and the formation of a solvent separated ion pair. In the case of AnCl and NapCl, the more polar solvent shifts $K_{eq}$ favoring the O conformation and hindering Ex formation.
4.4 Comparing the Excited-States of ArS to ArA in Solution

Additional support for the PCCT mechanism is found through a comparison of the steady state spectra of ArS with those of ArA in dichloromethane (Figure 4.3). Dichloromethane has a dielectric constant of ~9, similar to that of THF (ε = 7). At least with regard to bulk field effects, these solvents provide a similar dielectric field for the photophysics of ArS. However, the local solute-solvent interactions, particularly with regard to proton-accepting ability, are markedly different. The basicity of a solvent can roughly be described by the Kamlet-Taft β parameter,\textsuperscript{56} which quantifies the proton accepting ability of a solvent. While 1,4-dioxane\textsuperscript{56} (β = 0.36), THF\textsuperscript{56} (β = 0.52), and acetonitrile\textsuperscript{57} (β = 0.37) are all moderately basic, dichloromethane\textsuperscript{58} (β = -0.01) is not an efficient or even a poor proton acceptor, and, thus, the PCCT reaction is not viable. The difference in basicity is manifested in the steady-state fluorescence spectra of ArS and ArA in dichloromethane: while moderate intensities of exciplex emission are observed for each ArA, there is no discernible exciplex emission from the ArS.

![Figure 4.3 Normalized Steady-State Fluorescence Spectra](image)

Figure 4.3 Normalized Steady-State Fluorescence Spectra of a) 10^{-5} M PyCl (Black) and 10^{-4} M PyA (Red) (λ_{excitation} = 344 nm), b) 10^{-5} M AnCl (Black) and 10^{-4} M AnA (Red) (λ_{excitation} = 369 nm), and c) 10^{-5} M NapCl (Black) and 10^{-4} M NapA (Red) (λ_{excitation} = 305 nm) at 293 K in Dichloromethane.

Furthermore, while it is clear that the dichloromethane solutions of ArS do not exhibit exciplex emission, time-correlated singlet photon counting (SPC) experiments, measuring the decay of the LE fluorescence, can be resolved into two distinct decay components representing two different fluorescent species (Table 4.2). For each of the ArS, the (much) shorter decay component, τ_{LE, s}, is indicative of an
excited-state population which experiences non-radiative decay processes in addition to those found in aromatic moieties that do not contain a tethered ammonium group. The C conformations of the electronically excited ArS offer a simple and reasonable attribution to the shorter decay components: although dichloromethane, like THF, is presumed to promote significant amounts of the ground-state C conformations, its molecular properties are incompatible with an excited-state proton-transfer as a result of different, specific local solute-solvent interactions (like the ones needed for the excited-state proton-transfers from an ArS to a solvent molecule).

Table 4.3 Decay Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from LE Emissions of 10^{-6} M PyCl, 10^{-5} M AnCl, and 10^{-5} M NapCl in Dichloromethane at 293 K.

<table>
<thead>
<tr>
<th>ArS</th>
<th>( \tau_{\text{LE} 1} )</th>
<th>( \tau_{\text{LE} 2} )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl(^a)</td>
<td>24.4 (0.24)</td>
<td>114.6 (0.86)</td>
<td>1.0</td>
</tr>
<tr>
<td>AnCl(^b)</td>
<td>3.6 (0.05)</td>
<td>7.3 (0.95)</td>
<td>1.1</td>
</tr>
<tr>
<td>NapCl(^c)</td>
<td>16.5 (0.29)</td>
<td>33.8 (0.71)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a) \( \lambda_{\text{LE}} = 377 \text{ nm}, \lambda_{\text{Excitation}} = 344 \text{ nm} 

b) \( \lambda_{\text{LE}} = 391 \text{ nm}, \lambda_{\text{Excitation}} = 369 \text{ nm} 

c) \( \lambda_{\text{LE}} = 350 \text{ nm}, \lambda_{\text{Excitation}} = 305 \text{ nm} 

4.5 Role of the Counterion in the PCCT Mechanism Exhibited by PyS in Solution

After the initial discovery of the PCCT mechanism by Abraham and Weiss,\(^{31}\) the role of the counterion, a chloride anion in the preliminary experiments, was unknown. In fact, there was no definitive evidence as to whether the excited-state proton-transfer was occurring to the solvent or to the anion. In order to investigate the role of the counterion and clarify the nature of the proton acceptor, a series of \( N,N\)-dimethyl-3-(1-pyrenyl)propan-1-ammonium salts were synthesized in which the counterion was chloride (PyCl), bromide (PyBr), trifluoroacetate (PyTFA), nitrate (PyNO3), or \( p \)-toluenesulfonate (PyTSA). Irradiated solutions of these salts (PyS) revealed varying intensities of exciplex emission (Figure 4.4), yet importantly, in dichloromethane they did not exhibit any discernible emission from the CT complex. If the anion were participating as a proton-acceptor, one would expect exciplex emissions correlated to the
basicity of the counterion. The absence of exciplex emission in dichloromethane for any of the PyS, in conjunction with similar results for AnCl and NapCl, indicate that the proton is abstracted exclusively or nearly exclusively by the solvent. Importantly, variations in the counterion do result in varied exciplex emission in solvents which can abstract a proton (i.e., 1,4-dioxane, THF, and ethyl acetate). Nevertheless, the exciplexes formed from irradiated solutions of PyS decay with a narrow distribution of lifetimes ranging from 14.4 – 15.0 ns and form with time constants of 1.1 – 1.6 ns. Thus, the decay and formation of exciplexes from solutions of PyS are nearly unaffected by the identity of the counterion. Therefore, we ascribe the relative differences in Ex emission across PyS to specific ground-state conformational effects on the $K_{oc}$ equilibrium.
Figure 4.4 Steady-State, Intensity-Normalized (at 377 nm) Emission Spectra ($\lambda_{ex} = 344$ nm) of Solutions of PyCl (—), PyBr (· · ·), PyTFA (· · ·), PyNO3 (· · ·), and PyTSA (· · ·): (a) $10^{-5}$ M in Tetrahydrofuran, (b) $10^{-5}$ M in 1,4-Dioxane, (c) $10^{-5}$ M in Ethyl Acetate, and (d) $10^{-6}$ M in Dichloromethane.

4.6 Conclusions Concerning Excited-State Thermodynamic Relationships

The excited-state species which participate in the PCCT mechanism depend on the ground-state precursors of the ArS. The ground-state equilibrium between O and C primarily dictates the respective populations of O* and C*. While interconversion between O* and C* cannot be completely excluded for the long-lived excited singlet state of PyS, it is unlikely that $K_{OC*}$ plays a large role in the excited-state dynamics. Locally-excited ArS in the correct conformation (C*) can participate in the PCCT mechanism provided that the solvent is sufficiently basic. In dichloromethane, exciplex emission is not observed for
NapCl, AnCl, or any of the PyS, despite the observation of two distinct conformations (Table 4.2). These steady-state and dynamic observations indicate that the counterion does not participate in the proton transfer. Under the correct conditions, the proton-transfer is directly coupled to the formation of an intramolecular exciplex. Charge-transfer species have been observed in multiple proton-accepting solvents (i.e., acetonitrile, THF, ethyl acetate, and 1,4-dioxane) for all of the ArS. The degree of electron-transfer has a large effect on the exciplex population. In acetonitrile, full electron-transfer was observed for PyCl, consistent with the free energy of ion pair formation, \( \Delta G_{\text{ip}}^\Sigma \). AnCl and NapCl do not exhibit exciplex emission or transient absorption (from the ion pair) in acetonitrile. In low polarity 1,4-dioxane, exciplex emission is observed for each ArS. The position of the exciplex emission maxima correlates strongly with solvent polarity and is consistent with the emissions of irradiated solutions of the neutral ArA. The dynamic relationships among the excited-state species described above are discussed at length in Chapter 5.
5 PCCT DYNAMICS EXHIBITED BY SOLUTIONS OF ARS

5.1 Introduction

The interplay of thermodynamics and kinetics is an important aspect of excited-state electron-transfer reactions. The foundational work presented by Rehm and Weller in 1970 first demonstrated that fluorescence quenching rates are directly correlated to the thermodynamic oxidation and reduction potentials of $D_e$ and $A_e$, respectively.\(^5\) The rate of bimolecular electron-transfer quenching ($k_Q$) is traditionally predicted using a Stern-Volmer analysis\(^6\) (eq 5.1), where $I$ is the fluorescence intensity at a specific concentration of quencher [$Q$], $I_0$ is the fluorescence intensity in the absence of a quencher ([Q] = 0), and $\tau_0$ is the lifetime of the fluorophore in the absence of a quencher.

$$\frac{I_0}{I} = 1 + K_{SV} [Q] = 1 + k_Q \tau_0 [Q] \quad (5.1)$$

The rate of electron-transfer ($k_{ET}$) was initially measured for a wide variety of donor/acceptor systems in acetonitrile, with thermodynamic driving forces ranging from approximately -0.2 to +2.6 eV, where a positive driving force corresponds to an exothermic free energy of electron transfer ($-\Delta G_{ET}$). The original “Rehm-Weller plot” is reproduced below with the X-axis modified to be in eV (Figure 5.1). The most interesting feature of this plot is the plateau values at large driving forces corresponding to the rate of self-diffusion of acetonitrile. The dashed line represents the predicted kinetics of electron-transfer from Marcus theory, including the Marcus ‘inverted region’ where large thermodynamic driving forces are predicted to slow the rate of electron-transfer as a result of overlapping potential energy surfaces.\(^5\)\(^1\)\(^4\)\(^8\) In bimolecular quenching experiments, electron-transfer is limited by the diffusion of the solvent, even for photochemical electron-transfer reactions possessing large thermodynamic driving forces (> 0.86 eV). It was not until 1984 that the Marcus inverted region was observed by Closs and Miller by covalently bridging $D_e$ and a series of electron acceptors with varied excited-state reduction potentials.\(^6\) Thus, the
theories of electron-transfer have been modified with continuing advancements in technology and experimentation. This tradition has been continued through the work of Farid, Vauthey, and others. Recent experiments by Farid et al. have sought to improve upon the Rehm-Weller model by including an exciplex as an intermediate for full electron-transfer between aromatic donors and cyanoaromatic acceptors. It was assumed by Rehm and Weller that exciplexes could not form in the polar solvent, acetonitrile; however, the experiments by Farid et al. have demonstrated that exciplexes do form in the original Weller series, particularly in the case of donor/acceptor pairs with weakly exothermic or even endothermic thermodynamic driving forces. Similar conclusions have been drawn by Vauthey et al. who have modulated the extent of electron-transfer by varying the polarity of the solvent so as to deconvolute exciplexes from their electronically related ‘tight ion pairs’. For some bimolecular systems, interconversion between exciplexes and the corresponding ion pair was found to occur on a picosecond timescale as measured by transient infrared absorption spectroscopy. Because exciplexes and tight ion pairs are very similar in both their structure and electronic character, it is difficult to differentiate these species through transient UV-vis absorption spectroscopy alone. Transient infrared absorption measurements may not be helpful in differentiating tight ion pairs from the exciplexes of ArS because the complexes are not conjugated to specific IR active modes. However, the transient UV-vis absorption spectra of PyCl, presented in Chapter 4, do broaden in response to decreasing solvent polarity, indicative of the relationship between the ion pair and the exciplex.
Figure 5.1 Original Rehm-Weller Plot (Reproduced with Permission\textsuperscript{50}) of Quenching Rate Constants as a Function of the Free Energy of Electron-Transfer.

5.2 Temperature Dependent Steady-State and Dynamic Fluorescence of ArS in Solution

Excluded from the discussion on PCCT reactions thus far has been the kinetic relationships between the excited-state species. For photochemical processes, generally, kinetics often play as large a role as thermodynamics because of the often short-lived excited-states involved. As mentioned in previous chapters, the ability of ArS to participate in the PCCT mechanism is primarily dictated by the ground-state equilibrium between O and C. The ground-state equilibrium is important precisely because conformational changes in the excited-state (between O* and C*) are not easily attained given the excited singlet lifetimes of the ArS. Only for the pyrenyl salts should $K_{OC^*}$ be considered as a mechanistic possibility, but even for these salts there is no evidence to support large interconversion between O* and C*.\textsuperscript{65} Aside from this equilibrium, the rate of proton transfer and the lifetimes of the exciplex, ion pair, and decomplexed locally-excited state are all germane to the discussion of the PCCT mechanism. Key insights into this mechanism were gleaned from temperature-dependent fluorescence and SPC experiments for PyS.
Scheme 5.1 Proposed PCCT Mechanism Exhibited by Irradiated Solutions of N,N-Dimethyl-3-arylpropan-1-amine (ArS).

As stated above, the solutions of PyS in dichloromethane demonstrate that a good proton-accepting solvent and not the anion of the PyS salt is required for proton transfer. Thus, in THF, the broad peak attributed to Ex fluorescence increased in intensity (relative to the LE emission) and narrowed as temperature was increased for all of the PyS examined. The relative importance exciplex fluorescence at a given temperature can be described by the ratio of its peak intensity at ~515 nm to the LE emission intensity at 377 nm ($I_{Ex}/I_{LE}$). This ratio was multiplied by the full width at half-maximum of the Ex emission band to account for changes in its shape as a function of temperature. The “adjusted $I_{Ex}/I_{LE}$ ratio” provides an indication of the conformational equilibrium in the ground state and the dynamic processes occurring along the excited state potential energy surface. In the 243–313 K temperature range, time-correlated single photon counting histograms for PyCl in THF, monitored at 377 nm (pyrenyl emission), could be fitted satisfactorily to three time constants (Table 5.1), while emission at 515 nm (exciplex emission) required only two constants (Table 5.2). One of the time constants at 515 nm ($\tau_{Ex,1}$) has an associated negative pre-exponential, indicative of formation of the exciplex. It decreased from 4.4 to 1.2 ns as the temperature was raised from 243 to 313 K. The other decay constant, $\tau_{Ex,2}$, increased from 8.8 ns at 243 K to 17.5 ns at 313 K; it is ascribed to the decay of Ex. These attributions can similarly be made for the other PyS (Table 5.3).
Table 5.1 Time Constants (ns) and Pre-Exponential Factors, Normalized to an Absolute Value of One (in Parentheses), from LE Emissions of $10^{-5}$ M PyCl in THF at 377 nm ($\lambda_{ex} = 325$ nm) as a Function of Temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\tau_{LE 1}$</th>
<th>$\tau_{LE 2}$</th>
<th>$\tau_{LE 3}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>1.5 (0.84)</td>
<td>15.9 (0.15)</td>
<td>143.4 (0.02)</td>
<td>1.1</td>
</tr>
<tr>
<td>298</td>
<td>1.8 (0.87)</td>
<td>12.8 (0.11)</td>
<td>156.6 (0.02)</td>
<td>1.1</td>
</tr>
<tr>
<td>283</td>
<td>1.9 (0.91)</td>
<td>11.5 (0.07)</td>
<td>154.9 (0.02)</td>
<td>1.3</td>
</tr>
<tr>
<td>263</td>
<td>2.7 (0.94)</td>
<td>9.0 (0.05)</td>
<td>165.2 (0.01)</td>
<td>1.1</td>
</tr>
<tr>
<td>243</td>
<td>3.5 (0.88)</td>
<td>8.4 (0.10)</td>
<td>168.5 (0.02)</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 5.2 Time Constants (ns) and Pre-Exponential Factors, Normalized to an Absolute Value of One (in Parentheses), from Ex Emissions of $10^{-5}$ M PyCl in THF at 515 nm ($\lambda_{ex} = 325$ nm) as a Function of Temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\tau_{Ex 1}$</th>
<th>$\tau_{Ex 2}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>1.2 (-0.50)</td>
<td>17.5 (0.50)</td>
<td>1.1</td>
</tr>
<tr>
<td>298</td>
<td>1.6 (-0.51)</td>
<td>14.4 (0.49)</td>
<td>1.1</td>
</tr>
<tr>
<td>283</td>
<td>1.9 (-0.40)</td>
<td>12.7 (0.60)</td>
<td>1.0</td>
</tr>
<tr>
<td>263</td>
<td>2.8 (-0.48)</td>
<td>10.5 (0.52)</td>
<td>1.0</td>
</tr>
<tr>
<td>243</td>
<td>4.4 (-0.39)</td>
<td>8.8 (0.61)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 5.2 Steady-State, Intensity-Normalized (at 377 nm) Fluorescence Spectra of $10^{-5}$ M a) PyCl, b) PyBr, c) PyTFA, d) PyNO3, and e) PyTSA in THF at 193 – 313 K in 20 °C Increments. f) Adjusted Relative Exciplex Emission ($I_{Ex}/I_{LE}$), for $10^{-5}$ M PyCl, PyBr, PyNO3, PyTFA, and PyTSA in THF, from 193 – 313 K. Note that the apparent structure in the emission in the 500 – 625 nm region is due to an artifact associated with the Ocean Optics spectrometer.
Table 5.3 Time Constants (ns) and Pre-Exponential Factors Normalized to an Absolute Value of One (in Parentheses) from LE Emissions of $10^{-5}$ M PyS in THF at 377 nm ($\lambda_{ex} = 325$ nm) Collected at 298 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau_{LE 1}$</th>
<th>$\tau_{LE 2}$</th>
<th>$\tau_{LE 3}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>1.77 (0.87)</td>
<td>12.8 (0.11)</td>
<td>156.6 (0.02)</td>
<td>1.1</td>
</tr>
<tr>
<td>PyBr</td>
<td>2.41 (0.90)</td>
<td>13.0 (0.08)</td>
<td>126.5 (0.02)</td>
<td>1.3</td>
</tr>
<tr>
<td>PyTFA</td>
<td>2.06 (0.94)</td>
<td>9.9 (0.05)</td>
<td>122.3 (0.01)</td>
<td>1.2</td>
</tr>
<tr>
<td>PyNO3</td>
<td>1.86 (0.91)</td>
<td>12.0 (0.07)</td>
<td>171.7 (0.02)</td>
<td>1.3</td>
</tr>
<tr>
<td>PyTSA</td>
<td>0.87 (0.92)</td>
<td>12.0 (0.03)</td>
<td>186.7 (0.06)</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 5.4 Time Constants (ns) and Pre-Exponential Factors Normalized to an Absolute Value of One (in Parentheses) from Ex Emissions of $10^{-5}$ M PyS in THF at 515 nm ($\lambda_{ex} = 325$ nm) Collected at 298 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau_{Ex 1}$</th>
<th>$\tau_{Ex 2}$</th>
<th>$\tau_{Ex 3}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>1.6 (-0.51)</td>
<td>14.4 (0.49)</td>
<td>14.4 (0.49)</td>
<td>1.1</td>
</tr>
<tr>
<td>PyBr</td>
<td>1.6 (-0.42)</td>
<td>14.5 (0.58)</td>
<td>14.5 (0.58)</td>
<td>1.2</td>
</tr>
<tr>
<td>PyTFA</td>
<td>1.1 (-0.69)</td>
<td>14.7 (0.31)</td>
<td>14.7 (0.31)</td>
<td>1.0</td>
</tr>
<tr>
<td>PyNO3</td>
<td>1.6 (-0.48)</td>
<td>14.8 (0.52)</td>
<td>14.8 (0.52)</td>
<td>1.1</td>
</tr>
<tr>
<td>PyTSA</td>
<td>0.77 (-0.81)</td>
<td>17.8 (0.19)</td>
<td>17.8 (0.19)</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The temporal decay of the LE emission at 377 nm can be deconvoluted into three components that reflect the fates of the various species along the excited-state potential energy surface. The longest-lived emission ($\tau_{LE 3}$) appears to be related to the population of O* molecules; the more rapid decay of O* at elevated temperatures (Table 5.1) is attributed to increased rates of non-radiative decay, although minor contributions from the excited state equilibrium ($K_{OC^*}$) cannot be excluded completely. The similarity between the fastest LE decay component ($\tau_{LE 1}$) and $\tau_{Ex 1}$ implies that this LE state is closely related to Ex formation. The rate of exciplex formation ($k_{CE^*}$) will be governed by the rate of the proton transfer ($k_{CD^*[B]}$, where B is a solvent molecule), the rate of the reverse reaction ($k_{DC^*[BH^+]})$, the rate of complexation of D* ($k_{DC^*}$), and the rate of Ex decay ($1/\tau_{Ex 2}$) (Scheme 5.1). Analogous to a previous analysis of the photodynamics of PyA, the equilibrium between D* and Ex is hypothesized to occur on a much faster timescale than the rate-limiting proton transfer. Thus, $\tau_{LE 1}$ is governed by the establishment of an equilibrium between the proton acceptor and the exciplex precursor, C*. Consistent with this
explanation, the third decay component in the LE emission ($\tau_{LE\,2}$) can be ascribed to emission from the ‘decomplexed’ species, D*. The rapid equilibrium between Ex and D* results in a shared decay constant between these two states (i.e., for $\tau_{LE\,2}$ and $\tau_{Ex\,2}$). The attributions and behavior of the decay constants at both 377 nm and 515 nm are in complete agreement with previous investigations of $N,N$-dimethyl-3-(1-pyrenyl)propan-1-amine (PyA) in ethyl acetate.$^{32}$ As a comparison, SPC data for $2 \times 10^{-5}$ M PyA in THF were also collected as a function of temperature at 291 – 330 K (Table 5.5).
Table 5.5 Time Constants (ns) and Pre-Exponential Factors Normalized to an Absolute Value of One (in Parentheses) from Ex Emissions of $10^{-5}$ M PyA and PyS in THF at 515 nm ($\lambda_{\text{ex}} = 325$ nm) as a Function of Temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (K)</th>
<th>$\tau_{\text{Ex}1}$</th>
<th>$\tau_{\text{Ex}2}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>243</td>
<td>4.4 (-0.50)</td>
<td>8.8 (0.50)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>2.8 (-0.51)</td>
<td>10.5 (0.49)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>1.9 (-0.40)</td>
<td>12.7 (0.60)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.6 (-0.48)</td>
<td>14.4 (0.52)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.2 (-0.39)</td>
<td>17.5 (0.61)</td>
<td>1.1</td>
</tr>
<tr>
<td>PyBr</td>
<td>223</td>
<td>5.5 (-0.48)</td>
<td>9.6 (0.52)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>4.2 (-0.49)</td>
<td>9.3 (0.51)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>2.4 (-0.29)</td>
<td>11.5 (0.71)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>2.0 (-0.44)</td>
<td>12.8 (0.56)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.6 (-0.43)</td>
<td>14.5 (0.57)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.1 (-0.39)</td>
<td>17.5 (0.61)</td>
<td>1.1</td>
</tr>
<tr>
<td>PyTFA</td>
<td>263</td>
<td>2.1 (-0.42)</td>
<td>11.5 (0.58)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>1.6 (-0.53)</td>
<td>12.8 (0.47)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.1 (-0.69)</td>
<td>14.7 (0.31)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.9 (-0.53)</td>
<td>17.2 (0.47)</td>
<td>1.0</td>
</tr>
<tr>
<td>PyNO3</td>
<td>263</td>
<td>2.4 (-0.49)</td>
<td>11.7 (0.51)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>2.0 (-0.43)</td>
<td>12.9 (0.57)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.6 (-0.48)</td>
<td>14.8 (0.52)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.3 (-0.48)</td>
<td>17.0 (0.52)</td>
<td>1.1</td>
</tr>
<tr>
<td>PyTSA</td>
<td>263</td>
<td>2.4 (-0.50)</td>
<td>11.8 (0.50)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>1.9 (-0.47)</td>
<td>13.3 (0.53)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.3 (-0.56)</td>
<td>15.0 (0.44)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.8 (-0.81)</td>
<td>17.8 (0.19)</td>
<td>1.1</td>
</tr>
<tr>
<td>PyA</td>
<td>291</td>
<td>1.5 (-0.52)</td>
<td>14.6 (0.48)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.4 (-0.50)</td>
<td>15.9 (0.50)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>306</td>
<td>1.0 (-0.54)</td>
<td>16.8 (0.46)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0.7 (-0.53)</td>
<td>17.8 (0.47)</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>317</td>
<td>0.7 (-0.52)</td>
<td>19.2 (0.49)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>321</td>
<td>0.6 (-0.52)</td>
<td>20.0 (0.48)</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>324</td>
<td>0.4 (-0.56)</td>
<td>20.4 (0.44)</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>0.3 (-0.58)</td>
<td>21.1 (0.42)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
After the proton transfer, species derived from the excited singlet states of PyS behave kinetically like those of PyA. Arrhenius and Eyring plots were constructed for $1/\tau_{Ex_1}$ and $1/\tau_{Ex_2}$ (Figures 5.3 and 5.4) to estimate the activation parameters for exciplex formation ($k_{CEx}$) (Table 5.8). Within the precision limits of the data, the activation energies for all of the salts are the same. Their similarity supports our earlier contention that the proton is being transferred from the closed conformations of the electronically excited PyS to solvent molecules rather than to the anions. However, the activation energy and enthalpy of Ex formation from PyA are significantly larger than for the PyS. As noted above, PyA lacks the attractive intramolecular hydrogen-π bonding available to PyS. For that reason, the higher activation energy upon direct excitation of PyA is a consequence of starting principally from excitation of open conformations. Bending the propylene spacer separating the dimethyl amino and pyrenyl groups of PyA is enthalpically and entropically disfavored due to the lack of a ground-state interaction that enhances the stability of the C conformation.
Figure 5.3 Arrhenius Plots for $10^{-5}$ M PyS and PyA in THF Using the Time-Correlated Single Photon Counting Decay Components, a) $\tau_{Ex1}$ and b) $\tau_{Ex2}$ at 515 nm as a Function of Inverse Temperature.

Table 5.6: Activation Parameters Associated with the Best Linear Fits of the Data from Arrhenius Plots in Figure 5.3 for $10^{-5}$ M PyS and PyA in THF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Arrhenius slope ($\tau_{Ex1}$) (K$^{-1}$)</th>
<th>Arrhenius slope ($\tau_{Ex2}$) (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>$-1400 \pm 50$</td>
<td>$730 \pm 60$</td>
</tr>
<tr>
<td>PyBr</td>
<td>$-1370 \pm 130$</td>
<td>$640 \pm 60$</td>
</tr>
<tr>
<td>PyTFA</td>
<td>$-1480 \pm 200$</td>
<td>$660 \pm 100$</td>
</tr>
<tr>
<td>PyNO3</td>
<td>$-1050 \pm 150$</td>
<td>$610 \pm 90$</td>
</tr>
<tr>
<td>PyTSA</td>
<td>$-1860 \pm 370$</td>
<td>$660 \pm 100$</td>
</tr>
<tr>
<td>PyA</td>
<td>$-2770 \pm 325$</td>
<td>$1030 \pm 90$</td>
</tr>
</tbody>
</table>
Figure 5.4 Eyring Plots for 10^{-5} M PyS and PyA in THF Using Time-Correlated Single Photon Counting Decay Components a) $\tau_{\text{Ex}1}$ and b) $\tau_{\text{Ex}2}$ at 515 nm as a Function of Inverse Temperature.

Table 5.7 Parameters Associated with the Data from Eyring Plots in Figure 5.4 for 10^{-5} M PyS and PyA in THF to Linear Fits.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Eyring Slope ($\tau_{\text{Ex}1}$) (K^{-1})</th>
<th>Eyring Intercept ($\tau_{\text{Ex}1}$)</th>
<th>Eyring Slope ($\tau_{\text{Ex}2}$) (K^{-1})</th>
<th>Eyring Intercept ($\tau_{\text{Ex}2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>-1120 ± 50</td>
<td>-23.1 ± 0.2</td>
<td>1000 ± 60</td>
<td>-32.5 ± 0.2</td>
</tr>
<tr>
<td>PyBr</td>
<td>-1090 ± 130</td>
<td>-23.1 ± 0.5</td>
<td>910 ± 70</td>
<td>-32.2 ± 0.2</td>
</tr>
<tr>
<td>PyTFA</td>
<td>-1200 ± 200</td>
<td>-22.5 ± 0.7</td>
<td>940 ± 100</td>
<td>-32.3 ± 0.4</td>
</tr>
<tr>
<td>PyNO3</td>
<td>-770 ± 140</td>
<td>-24.3 ± 0.5</td>
<td>900 ± 100</td>
<td>-32.1 ± 0.3</td>
</tr>
<tr>
<td>PyTSA</td>
<td>-1570 ± 360</td>
<td>-21.3 ± 1.3</td>
<td>950 ± 100</td>
<td>-32.3 ± 0.4</td>
</tr>
<tr>
<td>PyA</td>
<td>-4530 ± 400</td>
<td>-11.7 ± 1.3</td>
<td>1490 ± 110</td>
<td>-34.1 ± 0.3</td>
</tr>
</tbody>
</table>
Table 5.8 Activation Energies ($E_a$), Transition State Enthalpies ($\Delta H^\dagger$), and Entropic Term at 298 K ($T\Delta S^\ddagger$) of Ex Formation and Decay for the PyS and for PyA in THF as Calculated from Arrhenius and Eyring plots of $1/\tau_{Ex}$.

<table>
<thead>
<tr>
<th>PyS or PyA</th>
<th>$E_a$ (eV)</th>
<th>$\Delta H^\dagger$ (eV)</th>
<th>$T\Delta S^\ddagger$ at 298 K (eV)</th>
<th>$\Delta S^\ddagger$ (eV K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>0.12 ± 0.01</td>
<td>0.10 ± 0.01</td>
<td>-0.52 ± 0.08</td>
<td>1.7 x 10$^{-3}$</td>
</tr>
<tr>
<td>PyBr</td>
<td>0.12 ± 0.01</td>
<td>0.10 ± 0.01</td>
<td>-0.52 ± 0.09</td>
<td>1.7 x 10$^{-3}$</td>
</tr>
<tr>
<td>PyTFA</td>
<td>0.13 ± 0.02</td>
<td>0.10 ± 0.01</td>
<td>-0.51 ± 0.09</td>
<td>1.7 x 10$^{-3}$</td>
</tr>
<tr>
<td>PyNO3</td>
<td>0.09 ± 0.01</td>
<td>0.07 ± 0.01</td>
<td>-0.55 ± 0.09</td>
<td>1.8 x 10$^{-3}$</td>
</tr>
<tr>
<td>PyTSA</td>
<td>0.16 ± 0.03</td>
<td>0.13 ± 0.03</td>
<td>-0.47 ± 0.10</td>
<td>1.6 x 10$^{-3}$</td>
</tr>
<tr>
<td>PyA</td>
<td>0.24 ± 0.03 (0.18$^a$)</td>
<td>0.39 ± 0.04</td>
<td>-0.23 ± 0.10</td>
<td>0.8 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

$^a$in ethyl acetate$^{32}$

Consistent with this interpretation of the data, the entropy of activation is much lower for PyA than for PyS. This is also consistent with the proposed mechanism in Scheme 5.1, which makes proton-transfer ($k_{CD^*}$) the rate-determining step in Ex formation ($k_{CEx^*}$). Although the excited-singlet state of PyA can undergo charge-transfer and complexation when in the correct conformation ($k_{DEx^*}$), exciplex formation for PyS is limited by the establishment of an equilibrium between C* and D*. This requires a proximal solvent molecule to act as a proton-acceptor and, thus, is a much more entropically demanding process. The calculated entropy of the rate-determining proton-transfer is consistent with the DFT calculations discussed in Chapter 3, which identified a highly organized local minimum, positioning a solvent molecule in close association with the ammonium group in what can be described as a ‘shared’ hydrogen bond between the solvent, the ammonium proton, and the π-cloud of the pyrenyl group. In solution, deviations from this conformation can be expected, although precise alignment along this reaction coordinate would be required to facilitate the proton-transfer.

The comparison of Ex formation between PyS and PyA provides a useful foundation to analyze the more general kinetic steps exhibited by ArS. As discussed in the Chapter 5, the steady-state fluorescence spectra collected for 10$^{-5}$ M $N,N$-dimethyl-3-(9-anthryl)propan-1-ammonium chloride (AnCl) and $N,N$-dimethyl-3-(2-naphthyl)propan-1-ammonium chloride (NapCl) exhibit exciplex emission in low
polarity solvents that are potential proton acceptors, similar to what is found in the emission spectra of $N,N$-dimethyl-3-(1-pyrenyl)propan-1-ammonium chloride (PyCl) (Figure 4.1). Solutions in 1,4-dioxane exhibit red-shifted, unstructured fluorescence that is attributed to emission from the $N,N$-dimethyl-3-arylpropan-1-amine exciplexes (Ex). The weak exciplex emissions from AnCl and NapCl can be attributed to a mixture of both thermodynamic and kinetic constraints which inhibit the PCCT mechanism. 1,4-Dioxane is a low polarity solvent which presumably makes the closed ground-state conformation more favorable than do solvents of higher polarity; in addition, this solvent is also moderately basic, as measured by the Kamlet-Taft scale $^{56}$ ($\beta = 0.37$), and, thus, can facilitate the PCCT mechanism along the excited-state potential energy surface by acting as a potential proton acceptor. Finally, low-polarity solvents, such as 1,4-dioxane, facilitate exciplex emission by limiting the extent of electron transfer and the formation of a solvent-separated ion pair (IP).

The kinetics of the PCCT mechanism have been discussed extensively above for PyS, but there are some key differences for solutions of either AnCl or NapCl. Importantly, the lifetimes of the excited singlet states of these two salts are much shorter than that of the PyS. The mechanism proposed for PyS (Scheme 5.1) is first-order in each step except the bimolecular proton-transfer to a solvent molecule, and that is pseudo first-order. It is reasonable to assume that solutions of AnCl and NapCl follow analogous PCCT mechanisms. The LE emission can be deconvoluted into two distinct emitting species for AnCl and NapCl and three components for the PyS. For AnCl and NapCl, $\tau_{LE1}$ and $\tau_{LE2}$ are ascribed to excited species in the C* and O* conformations, respectively. As mentioned, the PyS exhibit an additional decay component that is attributed to the decomplexed, locally-excited-state in equilibrium with the exciplex and ion pair. $^{65}$ It is reasonable to assume that similar LE processes occur with AnCl and NapCl, but that deconvolution of the decomplexed LE state components is made difficult by the small Ex populations.

Analyses of the dynamic decays of the LE emissions provide insights into only a part of the total PCCT mechanism. Additional support for the PCCT mechanism can be found in the decays of the exciplex
emissions. Ex emission is strongest for each ArS in 1,4-dioxane. Information gained from their decays can, thus, be combined with the data from the LE states to obtain an assessment of most of the species in Scheme 5.1. The exciplex emissions are fit best by biexponential decay functions. The \( \tau_{\text{Ex}} \) have associated negative pre-exponential factors, indicating the dynamics of formation of the exciplex. Because the magnitude of \( \tau_{\text{Ex}} \) correlates well with the decay of the excited singlets of \( C^* \), \( \tau_{\text{LE}} \), a direct link between the loss of the LE species and the formation of the exciplex is inferred.

### Table 5.9 Time Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from LE Emissions of 10^{-5} M ArS in 1,4-Dioxane at 293 K.

<table>
<thead>
<tr>
<th>ArS</th>
<th>( \tau_{\text{LE}} ) (ns)</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl(^a)</td>
<td>2.0 (0.80)</td>
<td>1.1</td>
</tr>
<tr>
<td>AnCl(^b)</td>
<td>2.1 (0.09)</td>
<td>1.2</td>
</tr>
<tr>
<td>NapCl(^c)</td>
<td>6.7 (0.64)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a) \( \lambda_{\text{LE}} = 377 \text{ nm, } \lambda_{\text{Excitation}} = 344 \text{ nm} \)
b) \( \lambda_{\text{LE}} = 391 \text{ nm, } \lambda_{\text{Excitation}} = 369 \text{ nm} \)
c) \( \lambda_{\text{LE}} = 350 \text{ nm, } \lambda_{\text{Excitation}} = 305 \text{ nm} \)

### Table 5.10 Time Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from Ex Emissions of 10^{-5} M ArS in 1,4-Dioxane at 293 K.

<table>
<thead>
<tr>
<th>ArS</th>
<th>( \tau_{\text{Ex}} ) (ns)</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl(^a)</td>
<td>2.2 (-0.69)</td>
<td>1.2</td>
</tr>
<tr>
<td>AnCl(^b)</td>
<td>1.0 (-0.18)</td>
<td>1.3</td>
</tr>
<tr>
<td>NapCl(^c)</td>
<td>6.7 (-0.49)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a) \( \lambda_{\text{Ex}} = 500 \text{ nm, } \lambda_{\text{Excitation}} = 344 \text{ nm} \)
b) \( \lambda_{\text{Ex}} = 500 \text{ nm, } \lambda_{\text{Excitation}} = 369 \text{ nm} \)
c) \( \lambda_{\text{Ex}} = 450 \text{ nm, } \lambda_{\text{Excitation}} = 305 \text{ nm} \)

For comparison purposes, the photophysics of solutions of the deprotonated neutral amines (ArA) were also examined (Table 5.11). The intramolecular exciplexes of \( N,N\)-dimethyl-3-(2-naphthyl)propan-1-amine (NapA), \( N,N\)-dimethyl-3-(9-anthryl)propan-1-amine (AnA), and \( N,N\)-dimethyl-(1-pyrenyl)propan-1-
amine (PyA) have been studied in some detail,\textsuperscript{32,35,66} and their dynamic properties provide a benchmark
to compare the photophysics of the ArS. The only barrier to exciplex formation by the ArA is attainment
of an appropriate conformation (C*) during the lifetimes of their excited singlet states. Thus, longer-lived
excited states can facilitate intrinsically more Ex formation. For solutions of ArS, a proton-transfer to a
solvent molecule and attainment of an appropriate conformation, both entropically demanding steps,\textsuperscript{65}
must precede exciplex formation within the lifetime of the excited singlet-state. However, as with the PyS,
the eventually formed exciplexes, obtained upon irradiation of the ArS or the ArA, are the same
structurally and dynamically (Table 5.8).

Table 5.11 Time Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from Ex
Emissions of 10^{-5} M ArA in 1,4-Dioxane at 293 K.

<table>
<thead>
<tr>
<th>ArA</th>
<th>(\tau_{Ex}^1)</th>
<th>(\tau_{Ex}^2)</th>
<th>(\chi^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyA\textsuperscript{a}</td>
<td>1.4 (-0.04)</td>
<td>36.7 (0.96)</td>
<td>1.1</td>
</tr>
<tr>
<td>AnA\textsuperscript{b}</td>
<td>1.0 (-0.36)</td>
<td>7.7 (0.74)</td>
<td>1.2</td>
</tr>
<tr>
<td>NapA\textsuperscript{c}</td>
<td>4.9 (-0.19)</td>
<td>64.7 (0.81)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

a) \(\lambda_{Ex} = 500\ nm, \lambda_{Excitation} = 344\ nm\)
b) \(\lambda_{Ex} = 500\ nm, \lambda_{Excitation} = 369\ nm\)
c) \(\lambda_{Ex} = 450\ nm, \lambda_{Excitation} = 305\ nm\)

Table 5.12 Time Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from LE
Emissions of 10^{-5} M ArS in Tetrahydrofuran at 293 K.

<table>
<thead>
<tr>
<th>ArS</th>
<th>(\tau_{LE}^1)</th>
<th>(\tau_{LE}^2)</th>
<th>(\tau_{LE}^3)</th>
<th>(\chi^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl\textsuperscript{a}</td>
<td>1.8 (0.87)</td>
<td>12.8 (0.11)</td>
<td>156.6 (0.02)</td>
<td>1.1</td>
</tr>
<tr>
<td>AnCl\textsuperscript{b}</td>
<td>2.1 (0.09)</td>
<td>6.7 (0.91)</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>NapCl\textsuperscript{c}</td>
<td>4.1 (0.64)</td>
<td>31.7 (0.36)</td>
<td>-</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a) \(\lambda_{LE} = 377\ nm, \lambda_{Excitation} = 344\ nm\)
b) \(\lambda_{LE} = 391\ nm, \lambda_{Excitation} = 369\ nm\)
c) \(\lambda_{LE} = 350\ nm, \lambda_{Excitation} = 305\ nm\)
Table 5.13 Time Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from Ex Emissions of $10^{-5}$ M ArS in Tetrahydrofuran at 293 K.

<table>
<thead>
<tr>
<th>ArS</th>
<th>$\tau_{Ex,1}$</th>
<th>$\tau_{Ex,2}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl$^a$</td>
<td>1.6 (-0.51)</td>
<td>14.4 (0.49)</td>
<td>1.1</td>
</tr>
<tr>
<td>AnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NapCl$^b$</td>
<td>3.7 (-0.46)</td>
<td>71.0 (0.39)</td>
<td>1.3</td>
</tr>
</tbody>
</table>

a) $\lambda_{Ex} = 500$ nm, $\lambda_{Excitation} = 344$ nm  
b) $\lambda_{Ex} = 450$ nm, $\lambda_{Excitation} = 305$ nm

Table 5.14 Time Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from LE Emissions of $10^{-5}$ M ArS in Acetonitrile at 293 K.

<table>
<thead>
<tr>
<th>ArS</th>
<th>$\tau_{LE,1}$</th>
<th>$\tau_{LE,2}$</th>
<th>$\tau_{LE,3}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl$^a$</td>
<td>2.6 (0.74)</td>
<td>12.0 (0.24)</td>
<td>216.9 (0.02)</td>
<td>1.1</td>
</tr>
<tr>
<td>AnCl$^b$</td>
<td>6.7 (1)</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>NapCl$^c$</td>
<td>6.5 (0.97)</td>
<td>31.0 (0.03)</td>
<td>-</td>
<td>1.1</td>
</tr>
</tbody>
</table>

a) $\lambda_{LE} = 377$ nm, $\lambda_{Excitation} = 344$ nm  
b) $\lambda_{LE} = 391$ nm, $\lambda_{Excitation} = 369$ nm  
c) $\lambda_{LE} = 350$ nm, $\lambda_{Excitation} = 305$ nm

A correlation is observed between the exciplex fluorescence intensity and the lifetime of the corresponding LE state. Exciplex formation ($k_{CEx^*}$) in 1,4-dioxane required ~ 2 ns for PyCl and AnCl, and up to 7 ns for NapCl. By comparison, the lifetime of the locally-excited AnCl (i.e., in its O* conformation) is only 6.3 ns! Thus, the time available to excited singlets of AnCl in the C* conformation for any structural adjustments that might be required to bring a proton-accepting solvent molecule into the appropriate proximity and orientation for proton acceptance is extremely limited. The somewhat longer-lived excited singlet state of NapCl, 31.7 ns, allows the possibility of more structural adjustments and, thus, more exciplex formation (and fluorescence). As noted, the excited singlet lifetimes of the LE states of both of these salts are much shorter than that of PyCl, which exhibits much more intense exciplex emission. Thus, electron-transfer is more favored for excited singlets of PyCl than those of AnCl and NapCl both
thermodynamically, and because the intrinsic lifetime of the LE state of PyCl allows it to form a larger population of conformers and associated solvent molecules with the geometry necessary for proton-transfer and exciplex formation.

Table 5.15 Decay Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from Emissions of 10⁻⁵ M PyCl in Multiple Solvents at 293 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>τ_{LE 1}</th>
<th>τ_{LE 2}</th>
<th>τ_{LE 3}</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Dioxane</td>
<td>2.0 (0.80)</td>
<td>35.8 (0.17)</td>
<td>169.9 (0.03)</td>
<td>1.1</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>1.8 (0.84)</td>
<td>12.8 (0.11)</td>
<td>156.6 (0.02)</td>
<td>1.1</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>2.6 (0.74)</td>
<td>12.0 (0.05)</td>
<td>216.9 (0.21)</td>
<td>1.1</td>
</tr>
</tbody>
</table>

a) λ_{LE} = 377 nm, λ_{Excitation} = 344 nm
b) λ_{LE} = 377 nm, λ_{Excitation} = 344 nm
c) λ_{LE} = 350 nm, λ_{Excitation} = 344 nm

Table 5.16 Decay Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from Emissions of 10⁻⁵ M PyCl in Multiple Solvents at 293 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>τ_{Ex 1}</th>
<th>τ_{Ex 2}</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Dioxane</td>
<td>2.2 (-0.69)</td>
<td>36.2 (0.31)</td>
<td>1.1</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>1.6 (-0.18)</td>
<td>14.4 (0.82)</td>
<td>1.1</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>-</td>
<td>13.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

a) λ_{Ex} = 500 nm, λ_{Excitation} = 344 nm
b) λ_{Ex} = 500 nm, λ_{Excitation} = 344 nm
c) λ_{Excitation} = 344 nm, τ_{Ex 2} extrapolated from ΔA at 470 nm.

5.3 Kinetic Relationships among the Locally-Excited State, the Exciplex, and the Ion Pair

Previously, we suggested that the decay of Ex was governed by full electron transfer and the formation of an ion pair. Transient absorption experiments confirm the presence of ion pairs in polar solvents, and they indicate a consequential role for additional kinetic steps involving the formation of IPs and back electron-transfer, \( k_{ExIP^*} \) and \( k_{IPEx^*} \), respectively (Scheme 5.1). Such processes necessitate an equilibration among the locally excited state, the exciplex, and the ion pair. The transition from one
state to another requires very little nuclear motion and is controlled principally by changes in electronic distributions. For that reason, each of the states should exhibit similar rates of formation and decay. The fluorescence decays in Table 5.16 and Table 5.17 demonstrate such a relationship. The exciplexes in 1,4-dioxane and THF form with time constants corresponding to $\tau_{LE}$ and then decay at rates shared by the corresponding LE states. The LE fluorescence decay of PyCl in acetonitrile is fit best by a tri-exponential function (Table 5.16) despite the absence of Ex emission; in the more polar solvent, acetonitrile, full electron-transfer occurs, resulting in the formation of an IP (Figure 4.2). A kinetic fit of the PyCl transient absorbance at 470 nm in acetonitrile reveals an IP decay time of 13 ns (Figure 5.5), a number in good agreement with the decay time of the LE state ($\tau_{LE}$), 12 ns. Although the growth of the IP transient absorption in acetonitrile could not be deconvoluted from the excitation pulse signal, it reached a maximum absorbance at $\sim$ 1.5 ns after excitation. Again, this number is in good agreement with the decay time of the locally excited-state (1.8 ns).

To summarize, in the low polarity solvents, 1,4-dioxane and THF, the rate of Ex formation matches the rate of $C^*$ decay and Ex shares a lifetime with the LE state, $D^*$. In acetonitrile, the same behavior is observed between an LE state and an IP. Thus, by changing the solvent environment, the degree of electron transfer in the excited singlet manifold of PyCl can be controlled. However, the proton transfer appears to be unaffected by the extent of electron-transfer. That is, even in a low-polarity solvent like 1,4-dioxane, where full electron-transfer is inhibited by the low dielectric field of the medium ($\Delta G_{ri,p}^e = 1.05$ eV), the proton transfer occurs at approximately the same rate as in the higher polarity solvent, acetonitrile.
Figure 5.5 Transient Absorption Spectra of $10^{-5}$ M PyCl in Acetonitrile ($\lambda_{ex} = 350$ nm) Obtained over 200 ns.

Figure 5.6 Decay of Transient Absorbance ($\Delta A$) of $10^{-5}$ M PyCl in Acetonitrile as a Function of Probe-Delay Time: the $\Delta A$ Decay at 470 nm was Fitted with a Monoexponential Decay Function (Left); the $\Delta A$ Decay at 415 nm was Fitted with a Monoexponential Growth Function and Monoexponential Decay Function (Right).

Interestingly, previous investigations of PyA indicated that charge recombination and internal conversion were the primary modes of decay for the derived ion pairs.$^{32,33}$ Analyses of data from carefully performed laser-induced optoacoustic spectroscopy experiments indicated that intersystem crossing to
the triplet state occurred from both the LE and Ex states, as indicated by the observation of moderate T$_1$–T$_n$ absorption bands immediately after excitation.\textsuperscript{33} However, the temporal resolution of these experiments prevented direct observation of IP or triplet formation. Contrary to the aforementioned study, we observe a large increase in triplet absorption at 415 nm that coincides with the decay of the IP signal upon excitation of PyCl (Figure 5.6). A kinetic analysis of the absorption at 415 nm reveals that the triplet forms with a time constant of 13 ns, a value consistent with the decays of the exciplex and ion pair. Absorptions attributed to the triplet state persisted throughout the 200 ns time window of the transient experiment (Figure 5.6). Perhaps most importantly, although solutions of PyCl in 1,4-dioxane show strong exciplex emission (Figure 4.1), they do not exhibit discernible IP formation or any triplet-triplet absorption. These observations indicate that \textit{intersystem crossing occurs almost exclusively from the radical ion pair and not from the exciplex or locally excited singlet state.} From these data and those from the optoacoustic studies, we conclude that the PCCT mechanism in polar solvents is terminated by the formation of an IP state which, in turn, is lost either by charge recombination and internal conversion to the ground-state or through intersystem crossing to the triplet state. Analogous optoacoustic experiments performed on PyCl would be required to resolve completely this ambiguity.

For PyCl, termination of the PCCT process, with the formation of an IP, is consistent with the energies calculated by the Weller equation (eq 4.2). AnCl and NapCl, which exhibit weak exciplex emission in low polarity solvents, do not appear to undergo full electron transfer. Although eq 4.2 predicts that formation of a solvent-separated ion pair is energetically unfavorable for AnCl and NapCl, the calculated thermodynamic barriers are small compared to that of PyCl in THF (for which a moderate transient absorption signal is still observed).

The inconsistency above cannot be understood using arguments based solely on thermodynamic parameters. As discussed, the excited singlet-state lifetimes of the aromatic groups of PyCl, AnCl, and NapCl differ significantly. They and thermodynamic factors limit the fraction of excited singlet states of
each of the ArS which can undergo the PCCT mechanism. Thus, the amount of proton transfer is determined by the endothermicity of $\Delta G^e_{riip}$, the lifetime of C*, and how closely C* resembles the structure of Ex immediately after excitation of C. Despite the apparent constraints imposed on AnCl and NapCl, both produce moderate exciplex emission after excitation, even in low polarity solvents such as 1,4-dioxane where $\Delta G^e_{riip}$ is endothermic by $>1$ eV. The endothermicity is a result of the solvation term, $\frac{e^2}{\varepsilon} \left( \frac{1}{r} - \frac{1}{a} \right) - \frac{e^2}{37r}$, in eq 4.2. The attraction between opposing charges of the ion pair becomes the dominant factor in low polarity solvents, and pulls the ions closer to each other. It also makes full electron transfer more difficult for the excited singlet states of AnCl and NapCl. Because the major deactivation pathway for the exciplex, ion pair formation, is hindered, the lifetime of the excited-state complex is increased. The fluorescence spectra presented here indicate that full electron transfer is not a requirement for proton transfer to occur; partial charge transfer and the formation of the exciplex provide the driving force necessary for AnCl and NapCl to transfer a proton to a THF or 1,4-dioxane molecule. This behavior is analogous to that of solutions of PyCl in 1,4-dioxane, in which exciplex emission, without the formation of an IP, was observed (Figure 4.2). In higher polarity solvents, PyCl undergoes a more traditional PCET mechanism in which intermolecular transfer of a proton is coupled to an intramolecular electron transfer.

5.4 Conclusions Regarding PCCT Dynamics

The PCCT mechanism operating on solutions of excited-state ArS is highly susceptible to both thermodynamic and kinetic parameters. The temperature dependent steady-state and dynamic experiments indicate moderate activation barriers to Ex formation for the PyS ($E_a = 0.09 - 0.16$ eV). Perhaps more importantly, the entropy associated with the rate-determining proton-transfer is much larger than for similar solutions of the neutral PyA. The entropy associated with this step is consistent with ground-state DFT calculations which identified a highly specific configuration between a solvent (Ae), the ammonium group (Dp, De), and the aryl group (Ae). This orientation is our best approximation of the
proton-transfer complex. The methyl groups on the ammonium shield the proton from proximal solvent molecules, ensuring that the proton-transfer complex is oriented with high specificity. The activation energy and entropy of forming this complex directly affects the relative populations of Ex from AnCl and NapCl. Compared to the PyS, AnCl and NapCl have much shorter excited-state lifetimes with which to overcome these kinetic constraints. The result of these limitations is diminished exciplex formation with respect to the pyrenyl salts. Importantly, the longer-lived pyrenyl salts also have lower excited-state reduction potentials. Specifically in the case of PyCl, the formation of ion pairs in acetonitrile is consistent with eq 4.2 which predicts an exothermic $\Delta G_{\text{rip}}^E$. The radical ion pair shares a decay constant with a LE state ($D^*$) and appears to form with a decay constant corresponding to the lifetime of $C^*$. Thus, the PCCT mechanism can be tuned to a PCET mechanism, varying the extent of electron-transfer, by changing the dielectric of the solvent. The ion pairs can then decay through intersystem crossing to a triplet state as evidenced by the kinetic fits of $\Delta A$ at 415 nm. One of the most interesting aspects of this research is the relationship between thermodynamic driving force and the rates of proton-transfer exhibited by the ArS. Large changes in the thermodynamic driving force, as described by $\Delta G_{\text{rip}}^E$, have little effect on the rate of proton-transfer as illustrated by comparisons of the ArS in solvents of varying polarity. The relationship between thermodynamics and kinetics will be expounded upon further in Chapter 6.
6 PHOTOACIDITY

6.1 Introduction to Photoacidity

The proton-coupled charge-transfer reactions discussed in the previous chapters can be classified more specifically as intermolecular, adiabatic, excited-state proton-transfers. Species which participate in excited-state proton-transfers where the acceptor is a solvent molecule are generally referred to as photoacids. Photoacids exhibit large differences in their acidity ($pK_a$) between their ground and excited-states as a result of redistributed electron density upon photoexcitation. A classic case of photoacidity is exhibited by 2-naphthol which has a $pK_a$ of approximately 9.5 in the ground-state and a $pK_a^*$ of approximately 2.5 in the first excited singlet state in water. The increased acidity is the result of partial charge-transfer from the oxygen ($D_P$, $D_e$) to the excited-state naphthyl ($A_e$). Evidence for this electronic redistribution can be found through an analysis of the substituent effects on $pK_a^*$. For example, when an electron-withdrawing cyano group is placed at the 5 position, the $pK_a^*$ drops further to −0.8. Thus, for the majority of photoacids, including 2-naphthol, conjugation between $D_P$ and the excited-state facilitates the excited-state proton-transfer by stabilizing the conjugate base.

However, as was discussed above in Chapter 5, the kinetics of the proton-transfer can often dictate the extent of photoacidity, irrespective of the thermodynamic driving force. Excited-state intermolecular proton-transfers of this sort are dependent upon multiple kinetic factors including the lifetime of the photoacid, organization of the proton-transfer complex, solvent relaxation about the photoproducts, and diffusion of the proton-acceptor. Thus, temperature-dependence is observed for the rate of proton transfer ($k_{PT}$) for even ‘super’ photoacids such as N-methyl-6-hydroxyquinolinium (MHQ) which exhibits a $pK_a^*$ of approximately -7 in water.

Simkovitch et al. proposed four classes of photoacids, based on their $pK_a^*$s and rates of proton-transfer. These distinctions concern the overlapping effects of thermodynamics and kinetics which must also be considered in discussing the photoacidities of the ArS. The proton-transfer rates ($k_{PT}$) of strong
photoacids ($pK_a^* < -4$, in regimes III and IV) are limited only by solvent orientational dynamics ($k_{PT} \sim 10^{13}$ s$^{-1}$). Compounds exhibiting low or moderate photoacidities and relatively slow proton-transfer steps ($k_{PT} \sim 10^{10}$ s$^{-1}$) are placed in regimes I or II, respectively.$^4$ The rate of proton transfer in the weak photoacid classes is believed to be governed by specific covalent interactions in the ‘proton-transfer complex’, which includes the proton donor and acceptor and the first solvation shell.$^4$ Transient infrared absorption experiments$^7$ and theoretical calculations$^4$ of 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS) indicate that two steps are required for its proton transfer to occur. First, photoexcitation of HPTS weakens the bond between the proton and the donor and strengthens the hydrogen-bond between the proton and the eventual acceptor. Next, the proton-transfer occurs after appropriate reorganization of the solvent shell around the protonated-acceptor.$^7$ Only after the proton-transfer does electron density shift from the donor, resulting in a metastable charge-transfer state.$^7$ The ability to create a rapid drop in pH upon selective irradiation has led to the development of many applications for various photoacids. Perhaps the most popular application of photoacids is as photoinitiators for polymerization reactions.$^{73,74,75}$ Recent applications have also included modulation of material properties for opto-electronics in low polarity environments.$^{26}$ For example, HPTS has been used to facilitate photoconductivity in an organic polymer through the controlled release of ‘free’ protons.$^{27}$ Additional types of photoresponsive materials will require an extensive library of photoacids, with diverse and well-characterized photophysical properties. In that regard, the photoacidities exhibited by solutions of the ArS occur in a wide variety of environments. The confluence of thermodynamics and kinetics are discussed in the context of photoacidity below for solutions of ArS.
6.2 Förster Treatment of ArS Photoacidity

As discussed above, the photoacidities of ArS molecules in solution are driven by either charge-transfer or electron-transfer interactions that lead to large decreases in $pK_a^*$. Very little dissociation of the salt in the ground-state is expected based on the acidity of comparable trialkylammonium salts (e.g., $pK_as ≈ 14$ measured in THF\textsuperscript{76}). The high $pK_a$ translates to an endothermic free energy cost ($\Delta G_{PT}$) of 0.83 eV to protonate a solvent molecule in the ground-state. Therefore, it is reasonable to assume that both prior to excitation and after termination of the PCCT process, the nitrogen atoms of the ArS exist predominantly as protonated ammonium cations which are associated with nearby chloride counterions.

This ground-state approximation is the basis for a Förster treatment of the PCCT mechanism: the thermodynamic driving force for the excited-state proton transfer ($\Delta G_{PCCT}$) can be estimated to be the difference between the excitation energy of the chromophore ($E_{0,0}$) and the energies of ground-state deprotonation ($\Delta G_{PT}$) and exciplex fluorescence energy ($E_{Ex}$) (eq 6.1; Scheme 6.1).

$$\Delta G_{PCCT} = \Delta G_{PT} + E_{Ex} - E_{0,0} \quad (6.1)$$

$E_{0,0}$ can be measured spectroscopically from the intersection of intensity-normalized absorption and emission spectra, and $E_{Ex}$ can be estimated from the emission spectra (Figure 4.1). Then, the calculated $\Delta G_{PCCT}$ is related to the thermodynamic driving force for excited-state proton transfer from an ArS* to a THF solvent molecule and it can be converted into an excited-state $pK_a^*$. 

80
Scheme 6.1 Förster-Cycle for the PCCT Processes of ArS.

Table 6.1 Thermodynamic Parameters from Steady-State Emission Spectra and eq 6.1, where $\Delta G_{PT} = 0.83$ eV is Used for Calculation of the $pK_a^*$s in $10^{-5}$ M ArS in THF.

<table>
<thead>
<tr>
<th>ArS</th>
<th>$E_{0,0}$ (eV)</th>
<th>$E_{Ex}$ (eV)</th>
<th>$\Delta G_{PCCT}$ (eV)</th>
<th>$pK_a^*$</th>
<th>$k_{f/} (10^8$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyCl</td>
<td>3.43</td>
<td>2.41</td>
<td>-0.20</td>
<td>-3.4</td>
<td>5.5</td>
</tr>
<tr>
<td>AnCl</td>
<td>3.17</td>
<td>2.41</td>
<td>0.07</td>
<td>1.3</td>
<td>4.7</td>
</tr>
<tr>
<td>NapCl</td>
<td>3.78</td>
<td>2.76</td>
<td>-0.20</td>
<td>-3.3</td>
<td>2.4</td>
</tr>
</tbody>
</table>

a) Considered to be $1/\tau_{LE}$ in THF (Table 5.9)
Based upon their $pK_a^*$s, PyCl and NapCl belong to regime II ($-4 < pK_a^* < 0$) and AnCl is in regime I ($pK_a^* > 0$). However, proton-transfers in the excited singlet states of the ArS occur at a slower rate ($k_{PT} \sim 10^8$ s$^{-1}$) than would be predicted based on thermodynamic driving forces alone. We hypothesize that a two-step process, analogous to HPTS, is operative upon irradiation of solutions of the ArS. Charge-transfer and the formation of the exciplex are limited by the proton-transfer step (Tables 5.8 – 5.10). Somewhat unusual kinetics for proton-transfer are exhibited by the seven ArS in their solutions. For weak photoacids, $k_{PT}$ has been found to correlate strongly with $pK_a^*$ values.$^{70,30}$ We observe no such correlation within our limited series of salts. The photoacidity of AnCl is 4 orders of magnitude weaker than that of either PyCl or NapCl, although the $k_{PT}$ measured by SPC experiments ($1/t_{le}$) is similar for the salts in 1,4-dioxane (Table 5.8). Additionally, for PyCl, as the solvent is changed from 1,4-dioxane to acetonitrile, large changes in the extent of electron-transfer are observed spectroscopically. Despite large changes in the driving force, $\Delta G^E_{ript}$, in these solvents (Table 4.2), the rate limiting proton-transfer step varies only slightly, with decay times between 1.8 and 2.6 ns.

Chapter 5 discussed the role of temperature on the dynamics of exciplex formation for PyS in THF.$^{65}$ The Arrhenius plots reveal an activation barrier ranging from 0.9 – 0.16 eV. Because the same proton-donor group, a dimethylpropylammonium cation, is employed in PyCl, AnCl, and NapCl, it is reasonable to assume that AnCl and NapCl have similar activation energies for Ex formation. Thus, we ascribe the slow proton-transfer rates for the ArS to two principal factors. First, the strength of the N-H covalent bond creates a large kinetic barrier that must be overcome within the lifetime of C*. DFT calculations presented in Chapter 3 reveal a highly-ordered local minima for the PyS cation with an associated THF molecule. The shared hydrogen bond between a solvent molecule, the $\pi$-electrons, and the ammonium proton is thermodynamically favored by overly simplified DFT calculations; however, in solution, it is likely that a plethora of local minima exist, not all of which can support the proton-transfer. An Eyring analysis of the temperature dependent SPC experiments indicates a much larger transition state.
entropy for PyS than for PyA. These kinetic constraints must be overcome within the lifetime of the excited-state ArS, a particularly difficult task for solutions of short-lived AnCl. The kinetic constraints are manifest in the steady-state emission spectra, where a correlation between relative exciplex intensity and excited-state lifetime is evident across the limited series of PyCl, AnCl, and NapCl.

In addition, the structures of the ArS salts differ from many photoacids in the literature. The LE state and proton donor are not conjugated, and conformational changes are required to provide appropriate overlap between the nitrogen center and the excited aryl group to accommodate charge-transfer interactions. The through-space charge-transfer interactions are much more susceptible to subtle conformational perturbations than are conjugated photoacids. Thus, even for PyCl and NapCl (regime II photoacids if classified by \( pK_{a}^{*} \) alone), the rates of proton-transfer are limited by both relatively large activation barriers and needed conformational changes. This claim is supported by a correlation between the relative populations of Ex observed by steady-state emission spectra and the lifetimes of the excited singlet-states of the ArS in 1,4-dioxane. In summary, the photoacidity of the seven ArS appears kinetically restricted and is governed by the rate-determining proton-transfer step.

6.3 Short-Term Reversibility of the PCCT Reaction

Whether the PCCT mechanism included the formation of an exciplex or an ion pair, the termination of this process results in a repulsive ground-state between the neutral amine and the aromatic group. An unanswered question then becomes, “To what extent is the PCCT reversible?” The ground-state \( pK_{a} \)s of the ammonium salts indicate a strong preference for the protonated amine over the charged, protonated solvent molecule. However, another question related to the first becomes, “Is it possible for a protonated solvent molecule to diffuse sufficiently far from the excited ArA during its excited-state lifetime to avoid immediate recombination after deactivation?” The maximum distance (\( L_{D} \)) a solvent molecule can move from an ArS within the timescale of the PCCT can be approximated by eq 6.2
in which \( D \) is the rate of self-diffusion for a solvent molecule and \( \tau_{PA} \) is the time required for the decay of the photoacid excited-state (i.e., the exciplex or ion pair).

\[
L_D = \sqrt{\tau_{PA} D}
\]  

Eq 6.2 can be solved for the ArS using the diffusion coefficients at 298 K of 1,4-dioxane \((1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})\), THF \((7.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})\), and acetonitrile \((1.1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1})\), and the Debye equation. \( L_D \) must be compared to the distance at which the protonated solvent molecule escapes the electrostatic influence of ArS (N. B., the lone pair of electrons on the nitrogen atom and the negative charge of the chloride ion). The interaction energies can be estimated from the Bjerrum length \((\lambda_B, \text{eq } 6.3)\), which measures the distance at which thermal fluctuations can overcome electrostatic interactions between two point charges.

\[
\lambda_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_R k_B T}
\]

**Table 6.2 Predicted Maximum Diffusion Lengths \((L_D)\) and Bjerrum Lengths \((\lambda_B)\) for ArS in 1,4-Dioxane, Tetrahydrofuran, and Acetonitrile at 298 K.**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \lambda_B ) (nm)</th>
<th>( L_D ) PyCl (nm)</th>
<th>( L_D ) AnCl (nm)</th>
<th>( L_D ) NapCl (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Dioxane</td>
<td>28.1</td>
<td>6.3</td>
<td>2.9</td>
<td>9.0</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>8.0</td>
<td>10.1</td>
<td>-</td>
<td>22.6</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.5</td>
<td>11.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Although the values from eqs 6.2 and 6.3 provide only a rough approximation of the importance of the competing non-adiabatic processes, they are still useful. In the low polarity solvent, 1,4-dioxane, the $\lambda_B$ value, 28.1 nm, is significantly smaller than the $L_D$ values for PyCl, AnCl, and NapCl (Table 6.2). The low dielectric field of this solvent provides little counterbalance to the attractive interaction between the proton and the ground-state conjugate base (ArA). On this basis, we expect that the ArA will be reprotonated very rapidly in 1,4-dioxane. Consistent with this prediction, no photodegradation of the ArS solutions was observed even after prolonged spectroscopic measurements. However, a more exhaustive analysis after very long periods of irradiation with a more intense light source would be required to rule out definitively irreversible proton-transfer from the ArS* to a species other than the ArA. The fates of the ArS in more polar solvents is less obvious. In THF, both PyCl and NapCl have calculated $L_D$ values that slightly exceed the Bjerrum lengths. In acetonitrile, the maximum diffusion length of the protonated solvent molecule far exceeds the Bjerrum lengths. Regardless, the Bjerrum length is likely underestimated in all of these solvents because there is no specific attraction between the chloride counterions and the ArA after the loss of the proton. Thus, the anions may diffuse from the vicinity of the ArA and lead to initial association with ‘migrant’ protons.

6.4 Conclusions Concerning ArS Photoacidity

The excited-state intermolecular proton-transfers exhibited by the seven ArS can be classified as a unique kinetically restricted photoacidity. A Förster treatment of the steady-state spectra predict $pK_a*$s ranging from -3.4 - 1.3 in THF. As was discussed in previous chapters, the extent of electron-transfer is largely determined by the solvent environment. Thus, solutions of ArS provide a wide range of thermodynamic conditions with which to measure the photoacidity. Despite these thermodynamic differences, $k_{PT}$ ranges from only $2.4 \times 10^8$ – $5.5 \times 10^8$ s$^{-1}$ for PyCl, AnCl, and NapCl in THF. A more robust comparison of the relationship between thermodynamics and kinetics can be made for solutions of PyCl.
of varying polarity. The proton-transfer can be inferred from the formation of transient charge-transfer states in solutions of varying polarity (i.e., 1,4-dioxane, THF, and acetonitrile). Under these conditions, the thermodynamic driving force for ion pair formation ($\Delta G_{rip}^c$) ranges from exothermic in acetonitrile ($\Delta G_{rip}^c = -0.03 \text{ eV}$) to strongly endothermic in 1,4-dioxane ($\Delta G_{rip}^c = 1.05 \text{ eV}$). The proton-transfer rate is only marginally affected and appears independent of these reaction conditions with calculated $k_{PT}$'s of $5.0 \times 10^8 \text{ s}^{-1}$, $5.6 \times 10^8 \text{ s}^{-1}$, and $3.8 \times 10^8 \text{ s}^{-1}$ for solutions of PyCl in 1,4-dioxane, THF, and acetonitrile respectively. Thus, the available thermodynamic and kinetic data for irradiated solutions of ArS indicate that photoacidity is limited by the formation of a highly ordered proton-transfer-complex. A moderate activation barrier is expected and was measured through temperature-dependent experiments presented in the previous chapter. The activation barrier reflects the transition-state entropy of the proton-transfer-complex and the enthalpy associated with cleavage of a covalent N-H bond. As a result of these kinetic constraints, exciplex (and ion pair) formation is limited, especially in the case of short-lived NapCl and AnCl. Finally, first-order approximations of proton-diffusion and recombination indicate short-term PCCT reversibility as a likely outcome. This is particularly true in 1,4-dioxane where the electrostatic attraction between the protonated solvent molecule and the excited-state conjugate base (an exciplex or ion pair) is the dominant interaction.
7 Photophysics of N,N-Dimethyl-3-(1-indolyl)propan-1-ammonium Chloride

7.1 Introduction

The PCCT mechanism and photoacidity exhibited by the ArS are unique in many respects. To the best of our knowledge, this is the first example of exciplex mediated photoacidity. The structure of the salts, particularly in the case of the closed conformation, resembles some secondary structures of photoactive proteins.\textsuperscript{77,78} Specifically, the ammonium-π bond is a common structural motif in proteins.\textsuperscript{79,80} In principle, this opens the door to biochemical PCCT reactions within the active-sites of photoactive proteins. In order to investigate this possibility, the photophysical properties of a model compound, \textit{N,N}-dimethyl-3-(1-indolyl)propan-1-ammonium chloride (InCl), were investigated. The indole group is a key feature of the most photoactive amino acid, tryptophan. The photophysics of tryptophan are complicated by multitude of competing excited-state dynamics,\textsuperscript{81-86} the confluence of which is still not completely understood.

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures and Abbreviations of Studied Indole Derivatives. Ring positions are labeled for tryptophan.}
\end{figure}
Tryptophan is used extensively in biochemical investigations of protein structure and function, and, as such, it becomes important to comprehend fully the photophysics of structurally related indoles. Even in the case of dilute solutions of indole, multi-exponential fluorescence decays and large solvatochromic effects have been observed in solutions of different polarity. The complicated photophysical properties are due primarily to overlapping absorptions of $^1L_a$ and $^1L_b$ excited-states. In low polarity solvents or in the gas-phase, $^1L_a$ is the lowest energy excited-state. As the polarity of the environment increases, $^3L_b$ is stabilized to a greater extent than $^1L_a$ and it becomes the lowest energy excited-state. High-level ab initio calculations suggest that level inversion of $^1L_a$ and $^1L_b$ is highly probable in polar environments. In addition, calculations and photoelectron spectroscopy experiments indicate the presence of a conical intersection between the $^1L_a$ and $^1L_b$ states and $S_0$ (the ground state) as well as between $^3L_b$ and a πσ* state (Figure 7.2). Thus, excitation to either the $^1L_a$ or $^1L_b$ locally-excited state leads to the population of multiple electronic configurations which can relax non-radiatively via cleavage of the N-H bond or through ring-distortions in the $^1L_b$ state. The hypothesized potential energy surfaces are depicted below (Scheme 7.1). In addition to the overlapping excited-states of indole, a comparison of fluorescence lifetimes of indole derivatives in cyclohexane and in the gas-phase suggest substantial intramolecular charge-transfer from the pyrrole ring to the phenyl side of the indole system. It was hypothesized that the more polar $^1L_b$ state can be quenched through charge-transfer interactions. In the absence of solvent stabilization (i.e., in the gas-phase), charge-transfer is energetically very difficult, and the fluorescence decays become monoexponential.
The photophysics of indole and tryptophan derivatives are further complicated by the presence of proximal functional groups along the amino acid backbone or affixed to the indole ring. In natural systems, protein folding in the tertiary structure and alignment within the secondary structure can bring varied functional groups within proximity to the excited-state indole lumophores. Charge-transfer from the excited-state indole to the carbonyl of the amino acid backbone is thought to be a major deactivation pathway for the excited-state. Through-space charge-transfer interactions of this nature are highly sensitive to both distance and orientation, and a distribution of them between donors and acceptors results in varied fluorescence lifetimes for tryptophan residues within one protein. Furthermore, NH$_3^+$ functional groups, commonly found in zwitterionic amino acids, have been observed to quench the fluorescence of excited-state indole through an excited-state proton-transfer reaction. The excited-state proton transfer is pH dependent and results in transfer of a proton from the ammonium group to the C$_5$ position along the phenyl ring. This is likely facilitated in part by intramolecular charge-transfer across the ring, which selectively increases the basicity of C$_5$ upon excitation of the $^1L_a$ state. Thus far, the excited-state proton-transfer was observed to occur intramolecularly in solutions of tryptophan,
tryptamine hydrochloride, and tryptophanylglycine.\textsuperscript{86,92,93} The excited-state proton-transfer has also been observed intermolecularly between indole and glycine in solution.\textsuperscript{91} Key features of the mechanism include large kinetic isotope effects, a strong pH dependency, and the formation of an (as of yet) unknown indole photoproduct (InP).\textsuperscript{86,93} Importantly, in the case of tryptamine hydrochloride, the intramolecular excited-state proton-transfer was strongly inhibited by addition of 18-C-6 crown ether which complexes with the proton-donor (the ammonium).

Transient absorption experiments have been performed by Bent and Hayon for solutions of tryptophan derivatives in order to investigate the excited-state intramolecular proton-transfer reaction.\textsuperscript{86} Transient absorptions, observed at 340, 445, and 560 nm, were ascribed to two distinct triplet-triplet absorptions; however, only one of the species was verified to be a triplet state through quenching with O\textsubscript{2} and disulfide compounds, and through sensitization experiments. The transient signal observed at 445 nm decayed with a time constant of \(~ 25\) ns in water at 298 K and was not quenched by either O\textsubscript{2} or disulfide compounds. This ‘triplet’ was observed only for tryptophan derivatives which contained a proximal NH\textsubscript{3}\,+ group and it is most likely the indole photoproduct (InP) that is assumed to be formed via an excited-state proton-transfer reaction. Recently, these experiments were validated by Leonard et al.\textsuperscript{93} who investigated the excited-state proton-transfer for tryptophan in water with femtosecond pump-probe experiments. The same authors also observed the temporal signatures at 340 nm and 445 nm: they formed with a time constant of 0.46 ns and decayed with a lifetime of 25 ns. The authors could not ascertain from the experimental data the exact nature of InP, only that it formed exclusively from an excited-state proton-transfer reaction. However, high-level ab initio calculations of protonated indole moieties confirm that protonation at the C\textsubscript{4}, C\textsubscript{5}, or C\textsubscript{6} site would result in a transient absorption signal in the range of 420 – 450 nm. It is therefore reasonable to ascribe the absorption at 445 nm (InP) to a transient protonated indole moiety. This mechanism is consistent with the large kinetic isotope effects observed by Yu et al. for tryptamine hydrochloride.\textsuperscript{91}
In summary, excitation of indole populates near-degenerate $^1L_a$ and $^1L_b$ states which interconvert through a conical intersection between the excited-state potential energy surfaces. In polar solvents, the $^1L_b$ state is quenched through internal charge-transfer across the ring. In the presence of an ammonium group, these charge-transfer interactions can facilitate an excited-state proton-transfer from the ammonium to the phenyl ring. The excited-state proton-transfer quenches the fluorescence of indole, resulting in the formation of a transient photoproduct (InP) which decays with a lifetime of ~ 25 ns and exhibits transient absorption at 445 nm. The confluence of these interactions is illustrated below (Scheme 7.1).

**Scheme 7.1 Hypothesized Excited-State Potential Energy Surfaces Involved in the Excited-State Proton-Transfer Exhibited by Indole and Tryptophan Derivatives in the Presence of a Proximal Ammonium Group.**
7.2 Photophysics of InCl

The excited-state dynamics of the indole derivatives discussed above provide an important context for which to discuss the photophysics of InCl. There is one key structural difference between InCl and many of the indole derivatives discussed above: the tethered ammonium group is affixed to the indole nitrogen instead of the C₃ position, as with tryptamine and tryptophan. As mentioned above for indole, the ¹Lₖ excited-state shares a conical intersection with a πσ* configuration on the nitrogen.¹ For indole, this can lead to a dissociation of the N-H bond upon excitation. However, the σ orbitals of the N-C bond are stabilized to a larger extent than are the σ orbitals of an N-H bond. This results in a much larger σ-σ* gap, and, thus, it is unlikely that dissociation of the σ bond can occur upon excitation. In addition, the alkyl substituent attached to this nitrogen is slightly electron donating and has been demonstrated to increase moderately charge-transfer from the ¹Lₖ state.³⁰ In order to isolate the effect of the tethered ammonium group, photophysical data from InCl were compared to those of 1-methylindole (MeI), a compound which (in theory) should exhibit the same photophysical behavior as that of InCl were it not for the tethered ammonium group. The photophysics of InCl are also compared with those of N,N,N-trimethyl-3-(1-indolyl)propan-1-ammonium chloride (MeInCl) to assess the role of the absence of an ammonium proton on the locally excited state. As discussed in Chapter 3, it is possible that InCl participates in a similar ground-state conformational equilibrium to those experienced by solutions of the ArS. A key difference in the closed conformation of InCl is the presence of a more electronegative heteroatom, nitrogen, which can affect the orientation and distance of the N—H bond to a greater degree than the π-cloud of naphthyl, anthryl, or pyrenyl; the increased electron density at the nitrogen atom of indole makes possible stronger hydrogen-π bonds. Such a strengthening is indicated by the larger energy difference calculated by DFT between the open and closed conformations (ΔEₒ𝑐 = -0.64 eV). In any case, the presumed hydrogen-π bond does not appear to affect the absorption spectrum of InCl; it is nearly identical in MeI and MeInCl.
The normalized excitation and emission spectra of MeI and InCl are also nearly identical, but both from MeInCl are red-shifted (Figure 7.4).

**Figure 7.3 UV-Vis Absorption Spectra of $10^{-5}$ M InCl (Black), MeI (Red), and MeInCl (Blue) in Acetonitrile under Air.**

**Figure 7.4 Normalized Excitation ($\lambda_{\text{emission}} = 330$ nm) and Emission ($\lambda_{\text{excitation}} = 295$ nm) Spectra of $10^{-4}$ M MeI (Black) and InCl (Red) and MeInCl (Blue) in Acetonitrile (Degassed).**
The similarities among the electronic spectra in acetonitrile belie the complicated photophysics of InCl, MeI, and MeInCl that are indicated by the excitation-wavelength dependence of the shape and position of the emission spectra for MeI, InCl and MeInCl (Figure 7.5).

Figure 7.5 Steady-State Excitation and Emission Spectra of 10^{-4} M MeI (Left), InCl (Middle), and MeInCl (Right) in Acetonitrile (Degassed).

Excitation from 275 – 295 nm results in an unstructured emission band centered at ~ 330 nm for both MeI and InCl. However, excitation at 305 nm causes a red-shift of the emission maximum by ~ 10 nm although, the excitation spectrum does not shift as a function of emission wavelength. In contrast, the emission of MeInCl is comprised of an unstructured band centered at 340 nm which does not depend on the excitation wavelength. The steady-state spectrum of InCl does not appear to contain an exciplex emission attributable to a PCCT mechanism (like those found upon excitation of PyCl, AnCl, and NapCl). However, as described above, indole is known to participate in an excited-state proton-transfer mechanism when an ammonium proton is in proximity to the LE state. An excited-state proton-transfer mechanism would necessarily quench the fluorescence efficiency of the LE state. Thus, fluorescence quantum yields (\(\Phi_f\)) were calculated for MeI, InCl, and MeInCl in acetonitrile using 2-methylnaphthalene as the standard (Table 7.1).^{60} Although the shape of the fluorescence band of InCl appears identical to that of MeI, its quantum yield is decreased by nearly 50%! Thus, the excited state(s) of InCl is being quenched in a manner not available to MeI.
As mentioned, MeInCl mimics the structure of InCl yet lacks the ammonium proton necessary for an excited-state proton-transfer. Therefore, if the quenched fluorescence of InCl is due exclusively to a proton-transfer mechanism, the quantum efficiency of fluorescence from MeInCl should be like that of Mel. However, within the limits of experimental error, it is the same as that of InCl. The quantum yields of Mel, InCl, and MeInCl indicate that while the ammonium group may lead to fluorescence quenching of the LE state, that mechanism does not include excited-state proton-transfer as an integral component of the deactivation.

Table 7.1 Fluorescence Quantum Yields for 10^{-5} M Mel, InCl, and MeInCl in Degassed Acetonitrile at Room Temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi_f$ (degassed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mel</td>
<td>0.30</td>
</tr>
<tr>
<td>InCl</td>
<td>0.16</td>
</tr>
<tr>
<td>MeInCl</td>
<td>0.16</td>
</tr>
</tbody>
</table>

SPC measurements provide additional insights into the excited-state dynamics of Mel, InCl and MeInCl. The fluorescence decays were fit best by three components ($\tau_1$, $\tau_2$, and $\tau_3$). The value of the longest-lived component ($\tau_3$) closely resembles the measured phosphorescence lifetime of 1-methylindole in water (33.3 ns);\textsuperscript{66} under aerated conditions, it is quenched and the fluorescence decays are fit best to a biexponential decay function. This indirect evidence suggests that $\tau_3$ may be measuring the decay of a triplet state. Assignment of the shorter decay constants is much less obvious. Mel is reported to decay monoexponentially in cyclohexane with a lifetime of 6.5 ns.\textsuperscript{90} The decay of Mel in 1-butanol has also been examined previously. It was found to decay monoexponentially at 300 K ($\tau = 5.1$ ns) and biexponentially at 243 K with decay constants of 1.8 and 4.7 ns.\textsuperscript{94} However, the decays in 1-butanol were attributed to solvent reorientational dynamics which have been demonstrated more recently to
occur on a much faster timescale. In all likelihood, the fast decay components (τ_1 and τ_2) can be attributed to emissions from the \(^1\)L_a and \(^1\)L_b states, which differ significantly in their polarity and electronic distribution. Based on similarities of τ_2 to decays from solutions of Mel in cyclohexane, it seems more likely to be associated with loss of the \(^1\)L_a state. The \(^1\)L_a state is less polar than the \(^1\)L_b state and unlike the \(^1\)L_b state, it does not overlap significantly with the charge-transfer states. The additional quenching of \(^1\)L_b through internal charge-transfer decreases the decay time and allows deconvolution of the two electronic configurations. In addition, the pre-exponential factors indicate a dramatic shift in the populations of the \(^1\)L_a and \(^1\)L_b states when the fluorescence decays of Mel and InCl are compared. The closed conformation of InCl places a charged ammonium cation in proximity to the excited-state indole and dramatically changes its local environment. The increased charge around the excited-state is expected to stabilize the more polar \(^1\)L_b state, and this is evidenced by an increase in the pre-exponential factor of τ_3 for InCl with respect to Mel.

While the current data indicate the long-lived emissive state may result from phosphorescence, they do not explain the increase of this component when the ammonium proton of InCl is substituted with a methyl group. The fluorescence of MelInCl is also fit best by a triexponential decay, but the majority of the emission comes from the longest-lived component (τ_3). It is important to note that the quaternary ammonium group of MelInCl cannot participate in a hydrogen-π bond and should, therefore, have a much different distribution of ground-state conformations than does InCl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>τ_1</th>
<th>τ_2</th>
<th>τ_3</th>
<th>χ^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mel</td>
<td>2.8 (0.10)</td>
<td>6.4 (0.88)</td>
<td>25.5 (0.02)</td>
<td>1.0</td>
</tr>
<tr>
<td>InCl</td>
<td>4.5 (0.81)</td>
<td>7.8 (0.18)</td>
<td>28.9 (0.01)</td>
<td>1.2</td>
</tr>
<tr>
<td>MelInCl</td>
<td>2.5 (0.25)</td>
<td>7.0 (0.20)</td>
<td>29.5 (0.55)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 7.2 Decay Constants (ns) and Normalized Pre-Exponential Factors (in Parentheses) from Emissions of Degassed 10^{-4} M Mel, InCl, and MelInCl at 330 nm (λ_{ex} = 295 nm) in Acetonitrile at 293 K.
Further insights into the dynamics of the fluorescence of these indole derivatives are gained through time-resolved emission spectroscopy (TRES) experiments. The SPC measurements clearly indicate that the steady-state spectrum of InCl is comprised of emissions from more than one species. TRES allows τ₃ to be deconvoluted from τ₁ and τ₂ because of the large difference in the decay constants. The total emission spectrum collected through TRES experiments decays to the baseline over the time-window of the experiment, 175 ns. However, intensity normalization of the spectra collected at different times after excitation show clearly the presence of a broader and red-shifted (~20 nm) emission at longer times. It is similar in structure to the steady-state emission spectrum of MeInCl, which has a larger contribution from τ₃. Weak, red-shifted emission, sensitivity to dissolved oxygen, and a decay constant of ~ 30 ns are characteristics of emission from a triplet state. However, further experimentation is needed to assign definitively the electronic state responsible for this emission.

Figure 7.6 TRES of 10⁻⁴ M InCl (λₘₑ = 295 nm): (Left) in 1,4-Dioxane, Collected from 0 – 175 ns at 292 K over 1024 Channels at a Peak Threshold of 6000 Counts and Intensity Normalized to the Steady-State Emission Spectrum; (Right) in Acetonitrile Intensity Normalized Time-Slices of TRES Spectra.
In addition to the dynamic measurements presented above, transient-absorption spectra were collected for InCl in 3 solvents using an excitation pulse centered at 310 nm (Figure 7.7). If the expected excited-state proton-transfer were occurring for InCl, transient absorption from the photoproduct InP would be expected at 340 and 445 nm. The reason for the absence of this signal is probably due to the low degree of overlap between the wavelengths of the excitation pulses at 320 nm (Chapter 2.1) and the absorption spectrum. Even when the concentration was increased to $10^{-3}$ M, no transient absorption could be detected.

![Transient Absorption Spectra of 10^{-4} M InCl in 1,4-Dioxane (Black), Tetrahydrofurin (Red), and Acetonitrile (Blue) Collected 1.4 ns after Excitation at 310 nm.](image)

**Figure 7.7** Transient Absorption Spectra of $10^{-4}$ M InCl in 1,4-Dioxane (Black), Tetrahydrofuran (Red), and Acetonitrile (Blue) Collected 1.4 ns after Excitation at 310 nm.

### 7.3 Conclusions Concerning the Photophysics of InCl

An analysis of the total steady-state and dynamic photophysics indicates the presence of a distinctly different (additional) deactivation pathway for InCl from those operating in MeI. However, comparisons of the quantum yields for emission of MeInCl demonstrate that its excited states are also
deactivated intramolecularly, although no excited-state proton transfer from the ammonium group is possible. Although it is possible that distinct and fortuitously balanced mechanisms are responsible for the quantum yields from InCl and MeInCl being virtually identical, the available experimental evidence indicates only that a tethered ammonium cation can quench the fluorescence of the indole LE state. In addition, dynamic measurements indicate intersystem crossing and triplet formation may be a viable pathway for the deactivation of the excited-singlet states of Mel, InCl, and MeInCl. Unexpectedly, the emission spectrum of MeInCl is dominated by emission from the longest-lived excited-state. Indeed, the steady-state spectrum of MeInCl is similar to the time-resolved emission spectra collected for InCl at long decay times (> 20 ns). The sensitivity of the longest-lived decay component to the concentration of oxygen is consistent with the behavior of an excited triplet state. Alternatively, intramolecular charge-transfer across the indole rings is a well characterized phenomenon. It is possible that additional charge density in proximity to the LE state, as is the case for InCl and MeInCl, facilitates greater charge-transfer, and as a consequence, increased intersystem crossing to the triplet state. However, conclusions drawn purely from the steady-state fluorescence and SPC experiments are speculative at best and must be corroborated by alternative investigative methods.
APPENDIX A  $^1$H NMR, UV-Vis Absorption, and Fluorescence Spectra of the ArS

Figure A.1  $^1$H NMR Spectrum of PyCl. $\delta$H (CDCl$_3$, 400 MHz): 2.46 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 2.89 (6H, s, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.00 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.50 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 7.81 (1H, m, ArH), 8.01 (3H, m, ArH), 8.06 (5H, m, ArH), 12.73 (1H, s, NH).

Figure A.2  $^1$H NMR Spectrum of PyBr. $\delta$H (CDCl$_3$, 400 MHz), 2.50 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 2.71 (6H, s, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.05 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.51 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 7.85 (1H, m, ArH), 8.01 (3H, m, ArH), 8.18 (5H, m, ArH), 11.72 (1H, s, NH).
Figure A.3 $^1H$ NMR Spectrum of PyTFA. $\delta$H (CDCl$_3$, 400 MHz), 2.33 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 2.70 (6H, s, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.05 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.45 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 7.81 (1H, m, ArH), 8.04 (3H, m, ArH), 8.17 (5H, m, ArH), 13.51 (1H, s, NH).

Figure A.4 $^1H$ NMR Spectrum of PyNO$_3$. $\delta$H (CDCl$_3$, 400 MHz), 2.37 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 2.79 (6H, s, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.10 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.48 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 7.84 (1H, m, ArH), 8.04 (3H, m, ArH), 8.17 (5H, m, ArH), 12.01 (1H, s, NH).
Figure A.5 $^1$H NMR Spectrum of PyTSA. $\delta$H (CDCl$_3$, 400 MHz), 2.32 (3H, s, CH$_3$(C$_6$H$_4$)SO$_3$), 2.37 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 2.70 (6H, s, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.05 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 3.45 (2H, m, CH$_2$CH$_2$CH$_2$NH(CH$_3$)$_2$), 7.13 (2H, d, CH$_3$(C$_6$H$_4$)SO$_3$), 7.80 (3H, m, ArH), 8.05 (6H, m, ArH), 8.19 (2H, d, CH$_3$(C$_6$H$_4$)SO$_3$), 11.22 (1H, s, NH).

Figure A.6 $^1$H NMR Spectrum of AnCl. $\delta$H (CDCl$_3$, 400 MHz), 2.36 (2H, m, CH$_2$-CH$_2$-CH$_2$-NH(CH$_3$)$_2$), 2.63 (6H, s, N(CH$_3$)$_2$), 3.03 (2H, m, CH$_2$-CH$_2$-CH$_2$-NH(CH$_3$)$_2$), 3.71 (2H, m, CH$_2$-CH$_2$-CH$_2$-NH(CH$_3$)$_2$), 7.43 (4H, m, ArH), 7.96 (2H, d, ArH), 8.14 (2H, d, ArH), 8.32 (1H, s, ArH), 12.49 (1H, s, NH).
Figure A.7 $^1$H NMR Spectrum of NapCl. $\delta$H (CDCl$_3$, 400 MHz), 2.28 (2H, m, CH$_2$-CH$_2$-CH$_2$-NH(CH$_3$)$_2$), 2.73 (6H, d, N(CH$_3$)$_2$), 2.90 (4H, m, CH$_2$-CH$_2$-CH$_2$-N(CH$_3$)$_2$), 7.29 (2H, m, ArH), 7.45 (2H, m, ArH), 7.61 (1H, m, ArH), 7.77 (2H, m, ArH), 12.67 (1H, s, NH(CH$_3$)$_2$).

Figure A.8 $^1$H NMR Spectrum of InCl. $\delta$H (CDCl$_3$, 400 MHz), 2.45 (2H, m, CH$_2$-CH$_2$-CH$_2$-NH(CH$_3$)$_2$), 2.68 (6H, d, N(CH$_3$)$_2$), 2.81 (2H, m, CH$_2$-CH$_2$-CH$_2$-N(CH$_3$)$_2$), 4.36 (2H, m, CH$_2$-CH$_2$-CH$_2$-N(CH$_3$)$_2$), 6.52 (1H, m, ArH), 7.13 (1H, m, ArH), 7.20 (2H, m, ArH), 7.32 (1H, m, ArH), 7.62 (1H, m, ArH), 12.80 (1H, s, NH(CH$_3$)$_2$).
Figure A.9 $^1$H NMR Spectrum of MelnCl. $\delta$H (CDCl$_3$, 400 MHz), 2.38 (2H, m, CH$_2$-CH$_2$-CH$_2$-N(CH$_3$)$_3$), 3.30 (9H, d, N(CH$_3$)$_3$), 3.71 (2H, m, CH$_2$-CH$_2$-CH$_2$-N(CH$_3$)$_2$), 4.39 (2H, m, CH$_2$-CH$_2$-CH$_2$-N(CH$_3$)$_2$), 6.52 (1H, m, ArH), 7.15 (3H, m, ArH), 7.37 (1H, m, ArH), 7.63 (1H, m, ArH).

Figure A.10 Normalized UV-Vis Absorption (Black), Excitation (Red, $\lambda_{\text{emission}} = 377$ nm), and Emission (Blue, $\lambda_{\text{excitation}} = 344$ nm) Spectra of $10^{-5}$ M PyCl in THF at Room Temperature.
Figure A.11 Normalized UV-Vis Absorption (Black), Excitation (Red, $\lambda_{\text{emission}} = 415$ nm), and Emission (Blue, $\lambda_{\text{excitation}} = 369$ nm) Spectra of $10^{-5}$ M AnCl in THF at Room Temperature.

Figure A.12 Normalized UV-Vis Absorption (Black), Excitation (Red, $\lambda_{\text{emission}} = 350$ nm), and Emission (Blue, $\lambda_{\text{excitation}} = 305$ nm) Spectra of $10^{-5}$ M NapCl in THF at Room Temperature.
Figure A.13 Normalized UV-Vis Absorption (Black), Excitation (Red, $\lambda_{\text{emission}} = 350$ nm), and Emission (Blue, $\lambda_{\text{excitation}} = 295$ nm) Spectra of $10^{-5}$ M InCl in THF at Room Temperature.
Figure B.1 Fluorescence Decay Histograms of 377 nm Emission ($\lambda_{ex} = 325$ nm for THF and Dichloromethane Solutions and $\lambda_{ex} = 344$ nm for Acetonitrile and 1,4-Dioxane Solutions) for $10^{-5}$ M PyCl in Dichloromethane (Black), 1,4-Dioxane (Red), THF (Magenta), and Acetonitrile (Blue). Fluorescence decays were collected over 2066 channels for THF and dichloromethane solutions and 1024 channels for 1,4-dioxane and acetonitrile solutions with a 500 ns time window at 292 K.
Figure B.2 Fluorescence Decay Histograms of 393 nm Emission ($\lambda_{ex} = 369$ nm) for $10^{-5}$ M AnCl in Dichloromethane (Black), 1,4-Dioxane (Red), THF (Magenta), and Acetonitrile (Blue). Fluorescence decays were collected over 1024 channels with a 200 ns time window at 292 K.

Figure B.3 Fluorescence Decay Histograms of 350 nm Emission ($\lambda_{ex} = 305$ nm) for $10^{-5}$ M NapCl in Dichloromethane (Black), 1,4-Dioxane (Red), THF (Magenta), and Acetonitrile (Blue). Fluorescence decays were collected over 2066 channels with a 200 ns time window at 292 K.
Figure B.4 Fluorescence Decay Histograms of 515 nm Emission ($\lambda_{ex} = 325$ nm) for $10^{-5}$ M PyCl in THF from 193 – 313 K. Fluorescence decays were collected over 2066 channels with a 500 ns time window.

Figure B.5 Fluorescence Decay Histograms of 515 nm Emission ($\lambda_{ex} = 325$ nm) for $10^{-5}$ M PyBr in THF from 193 – 313 K. Fluorescence decays were collected over 2066 channels with a 500 ns time window.
Figure B.6 Fluorescence Decay Histograms of 377 nm Emission ($\lambda_{ex} = 325$ nm) for $10^{-5}$ M PyTFA in THF from 193 – 313 K. Fluorescence decays were collected over 2066 channels with a 500 ns time window. Scheme 7.1 Hypothesized Excited-State Potential Energy Surfaces Involved in the Excited-State Proton-Transfer Exhibited by Indole and Tryptophan Derivatives in the Presence of a Proximal Ammonium Group.

Figure B.7 Fluorescence Decay Histograms of 377 nm Emission ($\lambda_{ex} = 325$ nm) for $10^{-5}$ M PyNO3 in THF from 193 – 313 K. Fluorescence decays were collected over 2066 channels with a 500 ns time window.
Figure B.8 Fluorescence Decay Histograms of 377 nm Emission (λ_{ex} = 325 nm) for 10^{-5} M PyTSA in THF from 193 – 313 K. Fluorescence decays were collected over 2066 channels with a 500 ns time window.

Figure B.9 Fluorescence Decay Histograms of 377 nm Emission (λ_{ex} = 344 nm) for 10^{-5} M PyA in THF from 278 – 328 K. Fluorescence decays were collected over 1024 channels with a 500 ns time window.
Figure B.10 Fluorescence Decay Histograms of 500 nm Emission ($\lambda_{ex} = 344$ nm) and for $10^{-5}$ M PyA in THF from 278 – 328 K. Fluorescence decays were collected over 1024 channels with a 200 ns time window.

Figure B.11 Fluorescence Decay Histogram of 330 nm Emission ($\lambda_{ex} = 295$ nm) for $10^{-5}$ M InCl in Acetonitrile. The fluorescence decay was collected over 1024 channels with a 200 ns time window.
Figure B.12 Fluorescence Decay Histogram of 330 nm Emission ($\lambda_{\text{ex}} = 295$ nm) for $10^{-5}$ M Mel in Acetonitrile. The fluorescence decay was collected over 1024 channels with a 200 ns time window.
REFERENCES


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