Dual Excited-State Intramolecular Proton Transfer Reaction in 3-Hydroxy-2-(pyridin-2-yl)-4H-chromen-4-one

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The synthesis, characterization and fundamental of the dual excited-state proton-transfer properties of 3-hydroxy-2-(pyridin-2-yl)-4H-chromen-4-one (1a) are reported. In the electronic ground state, there exist two competitive hydrogen bonding (HB) isomers for 1a. Conformer 1a(O) reveals a five-membered ring HB structure between O–H and carbonyl oxygen, while conformer 1a(N) possesses a six-membered ring HB formation between O–H and pyridyl nitrogen. In a single crystal, the X-ray crystallography unveils an exclusive formation of conformer 1a(N). In solution such as CH2Cl2, 1a(O) and 1a(N) are in equilibrium, and their respective absorption chromophores are significantly different due to different degrees of hydrogen-bond induced π electron delocalization. Upon excitation, both conformers 1a(O) and 1a(N) undergo excited-state intramolecular proton transfer (ESIPT) reaction. Following ESIPT, 1a(O) gives rise to a tautomer emission maximized at 534 nm in CH2Cl2. Conversely, due to dominant radiationless quenching processes the tautomer emission for 1a(N) cannot be obtained with a steady-state manner but can be resolved from time-resolved fluorescence. Time resolved fluorescence estimates an equilibrium constant of 27 ± 5 in favor of 1a(N) in CH2Cl2. Ultrafast ESIPT also takes place for the unique 1a(N) form in the crystal. Due to the prohibition of quenching processes in the solid state, bright tautomer emission maximized at 540 nm is resolved for 1a(N) (Φ ∼ 0.3). The interplay between two HB conformers with on(1a(O))/off(1a(N)) character in tautomer emission may find future applications such as the recognition of organic Lewis acid/base in organic solvents.

1. Introduction

Proton transfer has been ubiquitously found in chemical and biological reactions.1 Among various types of proton transfer patterns, the category relevant to excited-state intramolecular proton transfer (ESIPT) has received much attention owing to the simplicity of its reaction pattern. Numerous ESIPT molecules have been strategically designed and synthesized in an aim to shed light on the fundamental in proton-transfer mechanism2 and/or to explore their potential applications (we cite only a small selection of representative reports).3

In terms of hydrogen bonding (HB) structure, most ESIPT molecules possess either five- or six-membered ring hydrogen bonds between O–H (or N–H) and C=O (or pyridinic nitrogen). Recently, we have explored a new class of ESIPT molecules bearing a seven-membered ring HB structure akin to the core chromophore of the green fluorescence protein.4 Among those ESIPT molecules possessing five-membered ring hydrogen bond, 3-hydroxyflavone (3HF, see Scheme 1) has been considered a paradigm ever since its ESIPT property was discovered by Kasha and co-workers.5 In nonpolar solvent such as cyclohexane, 3HF exhibits the S0 → S1 (ππ*) transition maximized at 340 and 354 nm, while the fluorescence of 3HF shows an anomalously large Stokes shifted band maximized at ∼526 nm (Φ = 0.36, τf = 3 ns).6 Upon methylation 3HF to form 3-methoxyflavone, 3-methoxyflavone shows normal Stokes shifted fluorescence maximized at ∼360 nm in cyclohexane.6a It is thus concluded that ESIPT takes place from the hydroxyl proton to the carbonyl oxygen, giving rise to the proton-transfer tautomer emission. Due to its relatively weak, five-membered ring hydrogen bond (c.f. six-membered ring hydrogen bond), 3HF was once adopted as a model compound to demonstrate appreciable barrier during ESIPT. Subsequently, it was found that the retardation of ESIPT at low temperature is mainly due to the external HB interaction caused by traces of protic solvent impurity (e.g., water, alcohols) present in the nonpolar solvents.6a In the dry, extensively purified nonpolar solvent such as cyclohexane, the time-resolved measurement rendered an ultrafast time of ESIPT for 3HF (τpt < 240 fs),6b,c,d and ESIPT is essentially barrierless, which is perhaps induced by the low frequency, skeletal motions associated with the hydrogen bond.7

In yet another approach, study of ESIPT coupled excited-state intramolecular charge transfer (ESICT) by strategically functionalizing 3HF with electron donating substituents has been an intriguing fundamental topic. Using 4′-N,N-diethylamino-3-hydroxyflavone (see Scheme 2) as an example,8 upon excitation, adiabatic, ultrafast charge transfer takes place from the diethylamino moiety to the carbonyl oxygen, resulting in a charge transfer state (CT*, * denotes the electronically excited state, see Scheme 2). After solvent relaxation, the equilibrated CT*, CTeq*, then undergoes CTeq* → PTeq* (PT denotes the proton transfer tautomer) proton transfer. Due to the great difference in equilibrium polarization between CTeq* and PTeq* (see Scheme 2), a solvent polarity induced barrier is introduced,
SCHEME 1: Molecular Structures of 3HF, 1a (Isomer Included), 1b, and Their Respective ESIPT Processes

which then channels into the proton transfer coordinate. Such a nuclear (hydrogen atom) motion coupled solvent polarization effect has been rationalized by a mechanism similar to the weak-coupling electron transfer described by the Marcus theory. Due to the relatively slow, solvent induced barrier coupled ESIPT rate, the associated dual emission and its ratiometric effect has been rationalized by a mechanism similar to the weak-coupling electron transfer described by the Marcus theory.8c,9

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General Procedure for the Synthesis of Chalcones. KOH (2.9 equiv) was added to a suspension of relevant aldehyde (1.0 equiv, see Scheme 3) and the appropriate acetoephone (1.05 equiv) in EtOH (6 mL/mmol acetoephone). The mixture was stirred at 50 °C for 3 h, then cooled down to room temperature and left overnight. The reaction mixture was poured into water and acidified with aqueous HCl (1 M) to yield 380 mg (82%) of 3-Hydroxy-2-(pyridin-3-yl)-3-(pyridin-4-yl)prop-2-en-1-one (a).

(E)-1-(2-Hydroxyphenyl)-3-(pyridin-2-yl)prop-2-en-1-one (b). Using isonicotinaldehyde (1.5 mL, 15 mmol) gave 2.2 g (65%) of b, which was further recrystallized from EtOH. 1H NMR: δ 12.7 (s, 1H), 8.6 (d, J = 4.0 Hz, 1H), 8.2 (d, J = 15.2 Hz, 1H), 7.0–7.8 (m, 1H), 7.7 (d, J = 1.6 Hz, 1H), 7.84–7.48 (m, 1H), 7.47–7.44 (m, 1H), 7.30–7.28 (m, 1H), 7.27–6.98 (m, 1H), 6.94–6.90 (m, 1H). 13C NMR: δ 193.8, 163.3, 152.5, 150.0, 143.0, 136.8, 136.5, 130.1, 125.7, 123.9, 119.9, 118.8, 118.3.

(E)-1-(2-Hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one (b). Using isonicotinaldehyde (1.5 mL, 15 mmol) gave 2.2 g (65%) of b, which was further recrystallized from EtOH. 1H NMR: δ 7.92–7.88 (m, 2H), 7.56–7.52 (m, 1H), 7.48–7.43 (m, 2H), 7.30–7.26 (m, 1H), 7.23–7.20 (m, 1H), 6.97 (d, J = 19, 1H), 6.91–6.87 (m, 1H). 13C NMR: δ 161.8, 147.0, 135.8, 133.1, 130.6, 125.7, 123.3, 123.0, 122.9, 119.0, 117.4, 112.3.

General Procedure for the Synthesis of 3-Hydroxy-2-(pyridinyl)-4H-chromen-4-one. Aqueous 30% H2O2 (8–11 equiv) was added to a solution of the appropriate chalcone (a or b, see Scheme 3) (1.0 equiv) and aqueous 4 M NaOH (5.0 equiv) in a 1:1 mixture of MeOH and THF (20 mL/mmol chalcone) at 0 °C. The reaction was stirred at room temperature overnight. The mixture was then acidified with aqueous HCl (1 M) and the product filtered off. Spectroscopic and analytical data for a and b are shown below.

3-Hydroxy-2-(pyridin-2-yl)-4H-chromen-4-one (1a). The crude product (440 mg, 1.3 mmol) was recrystallized from EtOH to yield 380 mg (82%) of 1a. 1H NMR: δ 8.5 (m, 1H), 8.28 (m, 1H), 8.11 (d, J = 8 Hz, 1H), 7.96 (m, 1H), 7.64 (d, J = 1 Hz, 1H), 7.50 (d, J = 0.5 Hz, 1H), 7.48–7.41 (m, 1H), 7.39–7.33 (m, 1H). 13C NMR: δ 173.6, 154.3, 152.5, 146.6, 141.0, 139.9, 135.8, 134.7, 133.1, 125.7, 123.9, 122.9, 121.4, 119.0, 117.4, 112.3.

2. Experimental Section

Scheme 3 depicts synthetic routes of 1a and 1b. All reactions were performed under nitrogen. Solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck precoated glass plates (0.20 mm with fluorescent indicator UV254) and were visualized with UV light irradiation at 254/366 nm. Flash column chromatography was carried out with the use of silica gel from Merck (230–400 mesh). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. The 1H and 13C NMR spectra were obtained on Bruker (76%) of 1a (Isomer Included), 1b, and Their Respective ESIPT Processes.
3-Hydroxy-2-(pyridin-4-yl)-4H-chromen-4-one (1b). The crude product (500 mg, 1.3 mmol) was recrystallized from EtOH to yield 400 mg (84%) of 1a. 1H NMR: δ 7.91–7.88 (m, 1H), 7.51–7.46 (m, 1H), 7.00–6.98 (m, 1H), 6.93–6.91 (m, 1H), 6.89–6.83 (m, 2H), 6.79–6.75 (m, 2H). 13C NMR: δ 173.7, 161.5, 143.3, 136.6, 130.7, 121.1, 119.5, 117.5, 115.5, 111.3, 107.94. FAB-MS: m/z 239.0 (M+ + 1).

Crystallographic Data Collection and Refinement. Data collection of compound 1a(N) was carried out on a NONIUS KappaCCD diffractometer with Mo radiation (λ = 0.71073 Å) at 150(1) K. A preliminary orientation matrix and unit cell parameters were determined from 15 frames, each frame corresponds to the 1 degree ω scan in 20 s, followed by spot integration and least-squares refinement. Data were measured using ω scans, 0.50 degree per frame, 100 s per degree. Cell parameters were retrieved and refined using DENZO-SMN software on all observed reflections. Data reduction was performed with the DENZO-SMN software. An empirical absorption was based on the symmetry-equivalent reflections and applied the data using the SORTAV program. The structure analysis was made by using SHELXL program on PC computer. The structure was solved using the SHELXS-97 program and refined using SHELXL-97 program by full-matrix least-squares on F2 values. All hydrogen atoms were generated geometrically (C–H = 0.95) and refined using a riding mode with the exception of the hydrogen atom (H(2)) of hydroxyl group, which is located in the difference Fourier map with the corresponding positions. The final full-matrix, least-squares refinement on F2 was applied for all observed reflections |I| > 2σ(I). All calculations were performed using the SHELXTL software package. Crystallographic data and details of data collections and structure refinements of 1a(N) are listed in the Supporting Information.

Measurements. Steady-state absorption and emission spectra were recorded with a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively. The various solvents were of spectragrade quality (Merck Inc.) and were used upon receipt. Benzene and acetonitrile showed traces of fluorescence impurities and were fractionally distilled prior to use. Nanosecond lifetime studies were performed with an Edinburgh FL 900 photon-counting system with a hydrogen-filled or a nitrogen lamp as the excitation source. The emission decays were analyzed by the sum of exponential functions, which allows partial removal of the instrument time broadening and thus renders a temporal resolution of ~200 ps. The setup for picosecond dynamical measurements consisted of a femtosecond Ti-Sapphire oscillator (82 MHz, Spectra Physics). The fundamental train of pulses was pulse-selected (Neos, model N17389) to reduce the repetition rate to typically 0.8–8 MHz, and then used to produce second harmonics (375–425 nm) as

SCHEME 2: Relaxation Processes for Excited-State Charge Transfer Coupled Proton Transfer Demonstrated by N,N-Diethylamino-3-hydroxyflavones

SCHEME 3: Synthetic Routes of 1a and 1b
an excitation light source. A polarizer was placed in the emission path to ensure that the polarization of the fluorescence was set at the magic angle (54.7°) with respect to that of the pump laser to eliminate fluorescence anisotropy. An Edinburgh OB 900-L time-correlated single photon counting system was used as a detecting system, rendering a temporal resolution of \(\sim 15\) ps.

Fluorescence upconversion measurements were performed with a femtosecond optically gated system (FOG-100, CDP). The fundamental of a Ti:sapphire laser (Spectra Physics) at 750–850 nm with an average power of 0.5 W and a repetition rate of 82 MHz was used to produce second harmonics (SH) at 375–425 nm by focusing onto a 0.5 mm thick BBO type-I crystal. The SH were then separated from the fundamental pulses with a dichroic mirror and used as the pump pulses. The pump pulses were then focused onto a rotating cell, and the optical path length was 1.0 mm. The resulting fluorescence was collected by an achromatic lens and then focused on another BBO type-I crystal (0.5 mm). The optically delayed remaining fundamental pulses were also focused on the BBO crystal and used as gate pulses for the sum-frequency generation. A Berek’s variable waveplate was placed in the pump beam path to ensure that the polarization of the pump laser was set at the magic angle (54.7°) with respect to that of the probe laser to eliminate

Figure 1. Normalized absorption and emission spectra of \(1a\) (red -○-) and \(1b\) (black -(*) in \(\text{CH}_2\text{Cl}_2\) (\(\sim 2 \times 10^{-3}\) M, \(\lambda_{ex} \sim 350\) nm) and the single crystal emission of \(1a\) (blue -○-) (\(\lambda_{ex} = 360\) nm).

Figure 2. Absorption spectrum (black -○-) and the excitation spectrum (red -*, monitored at 534 nm) of \(1a\) in \(\text{CH}_2\text{Cl}_2\) (\(\sim 2 \times 10^{-5}\) M).

Figure 3. Absorption and emission spectra of \(1a\) prior to the addition of \(\text{HCl}_g\) (black -○-). The absorption and emission of \(1a\) (\(\sim 2 \times 10^{-5}\) M) in \(\text{CH}_2\text{Cl}_2\) purged with \(\text{HCl}_g\) to reach the saturation (red -*, see text for detail). The excitation spectra of \(1a\) in \(\text{CH}_2\text{Cl}_2\) purged with \(\text{HCl}_g\) to reach the saturation by monitoring at 430 nm (blue -○-) and 560 nm (green -△-), respectively.

Figure 4. (a) The molecular structure of \(1a\) with thermal ellipsoids set at 50% probability level. (b) The molecular packing of \(1a(N)\) viewed along the \(c\)-axis. (c) The 1D chain-like architecture of \(1a(N)\) in an ABAB pattern (dashed line) through the \(\pi-\pi\) intermolecular interaction among \(1a(N)\) molecules.
in CH$_2$Cl$_2$. Such a titration procedure is supposed to protonate the pyridinic nitrogen and hence to block the formation of O$-$H---N HB. Figure 3 reveals the emission spectrum of 1a in CH$_2$Cl$_2$ purged with HCl$_{g}$ to reach full protonation (until changes in the emission spectra cease). In comparison to neutral 1a, the tautomer emission (560 nm) was increased by $\sim$25 folds, accompanied by a rather small portion of the normal (430 nm) emission. It is worthy to point out here that the excitation spectrum monitored at both normal (430 nm) and tautomer emission (560 nm) of the protonated 1a is exactly the same, which is also identical with respect to the absorption spectrum (see Figure 3), indicating that both 430 and 560 nm bands originate from the same ground-state species. Details of the associated relaxation dynamics for neutral versus protonated 1a will be further discussed.

In light of the above observations, we thus conclude the existence of equilibrium between 1a(N) and 1a(O) HB conformers in CH$_2$Cl$_2$, in which the protonation blocks the 1a(N) HB conformer, leading to the formation of 1a(O)H$^+$ HB conformer. Note that such 1a(O) $\rightleftharpoons$ 1a(N) equilibrium in ground-state must be fast in terms of kinetics because $^1$H NMR could not resolve any O$-$H peak. This viewpoint of equilibrium is also supported by the absorption and emission spectra of 1b, in which only 1b(O) HB conformer exists due to the lack of an O$-$H---N(pyrindine) hydrogen bond. As a result, 1b exhibits a unique tautomer emission maximized at 547 nm (see Figure 1), and the excitation spectrum (not shown here), which is independent of the monitored emission wavelength, is identical to the absorption profile. In brief, the results of steady-state UV absorption and fluorescence measurements imply an equilibrium between 1a(O) and 1a(N) in solution. The absorption profile for 1a(N) is red-shifted with respect to that of 1a(O), plausibly due to different degrees of hydrogen bond induced $\pi$ electron delocalization (vide infra). Upon excitation, 1a(O) undergoes fast ESIP$^T$, giving rise to a unique 534 nm tautomer emission. In sharp contrast, no steady-state emission could be resolved for 1a(N) in CH$_2$Cl$_2$ as well as in other polar, aprotic solvents such as toluene and acetonitrile. Further insight into the relaxation dynamics of 1a(N) will be elaborated in the section of fluorescence up-conversion measurement.

Single crystals of 1a were also successfully grown. As shown in Figure 4a, the X-ray structural determination reveals a dominant 1a(N) population in a single crystal form, which exhibits an intramolecular O(2)---N(1) hydrogen bond with N---O distance of 2.589(2) Å. The small dihedral angle (4.36°) of N(1)C(10)C(9)C(8) reveals that the 2-pyrindyl moiety is nearly coplanar with respect to the parent chromone moiety. This result can be rational by the O(2)---N(1) hydrogen bond formation together with partial $\pi$ bond character of C(9)--C(10) with bond distance of 1.462(2) Å. It is important to note that adjacent 1a(N) molecules are parallel and superimposed in an ABAB pattern (Figure 4b) to form a 1D chain-like architecture (Figure 4c) through the $\pi$--$\pi$ intermolecular interactions between the pyridyl--pyridyl moieties and between chromone--chromone.
TABLE 1: Photophysical Properties of 1a, 1a(O)H⁺ in CH₂Cl₂, and 1a in Single Crystal

<table>
<thead>
<tr>
<th></th>
<th>λ_ex/nm</th>
<th>λ_em/nm</th>
<th>relaxation dynamics/ps</th>
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<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>351</td>
<td>N: —</td>
<td>450 nm [ τ₁ = 0.13 (0.98), τ₂ = 28.9 (0.02) ]</td>
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<tr>
<td></td>
<td></td>
<td>T: 534</td>
<td>540 nm [ τ₁ = 0.35 (0.37), τ₂ = 22.8 (0.63) ]</td>
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<td></td>
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<td>580 nm [ τ₁ = 0.24 (0.18), τ₂ = 22.6 (0.82) ]</td>
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<td></td>
<td></td>
<td></td>
<td>620 nm [ τ₁ = 0.42 (0.03), τ₂ = 22.6 (0.97) ]</td>
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<td></td>
<td></td>
<td></td>
<td>660 nm [ r = 22.4 ]</td>
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<td></td>
<td></td>
<td></td>
<td>660 nm [ τ₁ = 24(0.96), τ₂ = 1400 (0.04) ]</td>
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<tr>
<td>single crystal</td>
<td></td>
<td>N: —</td>
<td>430 nm [ r = 4900 ]</td>
</tr>
<tr>
<td>77 K CH₂Cl₂</td>
<td></td>
<td>T: 540</td>
<td>540 nm [ r = 3500 ]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T: 528</td>
<td>530 nm [ r = 4900 ]</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>361</td>
<td>N: 430</td>
<td>430 nm [ r = 15.7 ]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T: 560</td>
<td>580 nm [ τ₁ = 14.8 (~0.48), τ₂ = 647 (0.52) ]</td>
</tr>
</tbody>
</table>

* The experimental error for the fitted time constant is less than ~10%. b Data in parentheses are the fitted pre-exponential factor. c The relaxation dynamics were measured by time-correlated single photon counting.

3.2. ESIPT Dynamics. More insight into the mechanism of ESIPT for 1a may be resolved by the associated relaxation dynamics. Figures 5a-e show the time-resolved up-converted fluorescence signal of 1a (1 × 10⁻³ M in CH₂Cl₂) at various emission wavelengths (λ_em ~ 380 nm). Pertinent spectroscopic and dynamic data are listed in Table 1. Upon monitoring at 450 nm, which is supposed to be in the normal emission region but could not be resolved from a steady state manner due to fast ESIPT (vide supra), the time-resolved 450 nm emission is composed of response limited rise and decay (<150 fs) components (see Figure 5a). On the other hand, when monitoring exclusively at the tautomer emission region of e.g. 660 nm, as shown in Figure 5e, multieponential decay curves were observed. The best deconvoluted fitting of the relaxation dynamics renders a response limit risetime (<150 fs), a fast but resolvable decay, and a nearly constant value (within the acquisition time of 100 ps) with a small pre-exponential factor contribution (<4%) compared with the fast decay (~96%) components. The system response limited decay for the normal emission as well as rise for the tautomer emission unambiguously indicates an ultrafast rate of ESIPT. The fast and resolvable decay time constant was measured to be 22.6 ± 0.3 ps. The very long decay constant indeed is attributed to a long population decay, which was further resolved to be 1.4 ns by the time-correlated single photon counting measurement.

We then took the fitted pre-exponential value of the 22.6 ps decay component at various monitored wavelengths and plotted the emission intensity versus wavelength, shown in Figure 6. Obviously, the up-converted emission of the fast decay (22.6 ps) component was maximized at ~577 nm, which is significantly red-shifted with respect to the 534 nm peak obtained with the steady state measurement. On the other hand, upon integrating the long-decay (1.4 ns) component, the plot for the emission intensity versus emission wavelength reveals a maximum at ~530 nm (see Figure 6), which is consistent with that obtained from the steady state measurement. Thus, the relaxation dynamics, in combination with the steady state results, show that both conformers 1a(O) and 1a(N) undergo ESIPT reaction in solution (e.g., CH₂Cl₂). Following ESIPT, 1a(O) gives rise to a tautomer emission maximized at 534 nm with an observed lifetime of 1.4 ns in CH₂Cl₂, while the tautomer emission for 1a(N) undergoes a fast decay constant of 22.6 ps and its intensity is too weak to be resolved in a steady state manner. Note that the normal emission of 1a(N), although it could not be resolved with a steady state means, is expected to be red-shifted compared to that of 1a(O). This viewpoint is supported by the time-resolved fluorescence monitored at shorter wavelengths such as 540 nm (see Figure 5b), in which in addition to the 22.6 ps decay component, the time-resolved profile also exhibits an ultrafast, unresolved decay component (<150 fs). Finally, ultrafast ESIPT also takes place for 1a(N) in the crystal, as...
supported by the large Stokes shifted fluorescence with a system response risetime (<150 fs), while the prohibition of the nonradiative decay process (vide infra) in the single crystal leads to a bright 540-nm tautomer emission ($\Phi_f \sim 0.3$) with a lifetime as long as 3.5 ns.

One intriguing feature lies in the relaxation dynamics of the protonated form, i.e., 1a(O)H$^+$ in CH$_2$Cl$_2$. Dual emission ascribed to normal (430 nm) and tautomer (560 nm) species was resolved for 1a(O)H$^+$ in CH$_2$Cl$_2$ (see Figure 3, vide supra). Upon monitoring at the normal emission of 430 nm, the time-resolved signal is composed of a response-limited rise (<150 fs) and a single exponential decay of 15.7 ps (see Figure 7). On the other hand, the relaxation dynamics monitored at the tautomer emission of 560 nm are established by a resolvable rise (14.8 ps) and a rather long decay component (647 ps). Note that the latter data are acquired by the time-correlated single photon counting technique. Within experimental and fitting uncertainty, the decay of the normal emission is matched with respect to the rise of tautomer emission, consistent with a precursor–successor type of ESPT relationship. Although the dynamics are clearly resolved, in comparison to the > (150 fs)$^{-1}$ rate of ESPT in 1a(O) (or 1a(N)) in neutral form, the much slower ESPT time scale (~15 ps) in 1a(O)H$^+$ is intriguing. On one hand, it may imply the rise of an intrinsic, appreciable barrier during ESPT for 1a(O)H$^+$. However, since the driving force of the forming oxy-anion dual hydrogen bonds (see Figure 8) is greater than that of the single hydrogen bond in 1a(O), this hypothesis, in our view, may be groundless. Alternatively, it is more plausible that the cationic form 1a(O)H$^+$ and its proton transfer tautomer possess drastically different dipole moments in the excited state, such that the solvent polarity induced barrier is appreciable, which then channels into the ESPT reaction. Nevertheless, this viewpoint requires more rigorous examination, including solvent polarity dependent studies with both steady-state and dynamics approaches, which is not the main focus of this study. Details will be addressed in future work.

We have also made attempts to extract the associated thermodynamic parameters of the HB equilibrium via a temperature-dependent absorption study. Unfortunately, owing to the relatively high freezing point (223 K) of CH$_2$Cl$_2$ and great similarities in spectral profiles between 1a(O) and 1a(N), we failed to obtain the thermodynamics via the steady state approach. Alternatively, we realize that the ratios of the preexponential factors for 22.6 ps versus 1.4 ns component are within 22 to 32 in the monitored emission range of 540–580 nm. Assuming that 1a(O) and 1a(N) exhibit very similar radiative lifetime, i.e., the same transition dipole due to the similarities in spectral features (in terms of spectral profile and absorptivity), we qualitatively estimate the ground-state equilibrium constant for 1a(O)$\rightleftharpoons$1a (N) in 298 K CH$_2$Cl$_2$ to be within 27 ± 5 M$^{-1}$. The thermally favorable 1a(N) population can be rationalized by the greater basicity of pyridinic nitrogen.

**Scheme 4: Calculated Energy Potential Diagram of 1a with Dual ESPT Pathways after Applying Solvation in CH$_2$Cl$_2$**

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**Figure 8.** Proposed ESPT mechanism of 1a(O)H$^+$. Note that a large change of the dipole moment is expected during the ESPT process (see text for detailed discussion).
(c.f. carbonyl oxygen), together with the associated six-membered ring HB geometry (c.f. five-membered-ring HB structure in 1a(O)).

3.3. Theoretical Approach. Supplementary support of the ground-state thermodynamics is provided by the computational approach (see Experimental Section). The full geometry optimization based on the B3LYP/6-31G(d) theoretical level reveals that 1a(N) is more stable than 1a(O) by 3.79 kcal/mol in gas phase. It is worthy to note that if considering the polarization function on hydrogen such as 6-31G(d,p), the optimized geometry of the tautomeric form of 1a(O) is converged to 1a(O).

The result implies that the tautomer form of 1a(O) in the ground-state is very unstable with respect to the normal forms, such that the 1a(O) proton transfer tautomer → 1a(O) reverse proton transfer may be rather small or even barrierless. After applying solvation in CH2Cl2 based on Onsager theory, the difference in energy is reduced to 3.59 kcal/mol, still in favor of 1a(N), qualitatively in agreement with that estimated experimentally.

Further calculations show that the corresponding proton-transfer tautomer is higher in energy than the respective 1a(O) and 1a(N) by 15.10 and 7.47 kcal/mol in the ground state. To each ground-state we then simply add absorption and emission peak frequency (see Figures 1) to mark the energy level of the corresponding S1 state. As a result, the overall energetics is depicted in Scheme 4. The results clearly indicate that ESIPT for both 1a(O) and 1a(N) is thermodynamically favorable, consistent with the experimental results.

Another interesting feature lies in the frontier orbital analysis. On the basis of time dependent DFT (TD-DFT), the S0 → S1 ππ* transition was calculated to be 3.49 eV (355 nm) and 3.43 eV (361 nm) for 1a(O) and 1a(N), respectively, the results of which are well-correlated with the peak (343 nm) of excitation spectrum for 1a(O) and an expected red-shifted absorption of 1a(N). The frontier orbital analyses reveal that the π-electron density of the proton-transfer tautomer form of 1a(O) in the excited-state is mainly delocalized at the chromone moiety, while that of the tautomer form of 1a(N), in sharp contrast, is largely spread around the pyridine moiety and extended to the carbonyl oxygen. As expected, the former is similar to the electronic configuration of 1b tautomer (see Table 2). The results manifest two different electronic configurations of tautomers resulting from ESIPT of two respective isomers. Due to the

| TABLE 2: Theoretical Results on Energy and Frontier Orbitals of Various Electronic States of 1a(O), 1a(N), and 1b |
|---|---|---|---|---|---|---|
| 1a(O) (normal form) | Excitation | E_{ex}(eV) | λ_{ex}(nm) | (f) | 1a(O) (tautomeric form) |
| S1 | HOMO→LUMO+1(83%) | 3.74 | 331.8 | 0.2587 | HOMO→LUMO+2(72%) |
| S2 | HOMO-2→LUMO+1(51%), HOMO-3→LUMO+30%, HOMO-1→LUMO+10% | 4.03 | 308.8 | 0.0027 | HOMO-1→LUMO+1(94%) |
| 1a(N) (normal form) | Excitation | E_{ex}(eV) | λ_{ex}(nm) | (f) | 1a(N) (tautomeric form) |
| S1 | HOMO→LUMO+1(81%) | 3.63 | 341.7 | 0.2379 | HOMO→LUMO+1(60%), HOMO→LUMO+1(23%) |
| S2 | HOMO-1→LUMO+1(92%) | 4.05 | 306.4 | 0.0163 | HOMO-1→LUMO+1(68%), HOMO-1→LUMO+1(16%) |
| 1b (normal form) | Excitation | E_{ex}(eV) | λ_{ex}(nm) | (f) | 1b (tautomeric form) |
| S1 | HOMO→LUMO+1(82%) | 3.79 | 327.1 | 0.2538 | HOMO→LUMO+1(73%) |
| S2 | HOMO-1→LUMO+1(73%), HOMO-4→LUMO+1(17%) | 3.98 | 311.7 | 0.0011 | HOMO-1→LUMO+1(85%), HOMO-3→LUMO+1(12%) |
| HOMO | LUMO | HOMO | LUMO |
drastically different lifetimes measured in this study (vide supra),
the interconversion between these two proton-transfer tautomers in
the excited-state is not likely to occur. This can be rationalized by
the necessity of breaking the strong hydrogen bond for
interconversion, the time scale of which seems to be incompa-
rable with the respective relaxation dynamics. Likewise, the
conversion between excited 1a(O) and 1a(N) species is also
prohibited due to the ultrafast rate of ES1PT for each isomer in
the excited state (see Scheme 4).

3.4. Relaxation after ES1PT.
Last but not least, after ES1PT, the dominant radiationless deactivation process for 1a(N)
tautomer in solution is also of fundamental interest. As supported
by the above X-ray analysis, the associated photophysics of 1a
in a single crystal clearly originate from the 1a(N) conformer.
As depicted in Figure 1, independent of the excitation wave-
lengh, the 1a(N) conformer in solid exhibit a unique, bright
emission maximized at 540 nm. In comparison to the onset of
the absorption spectrum of ~400 nm, the large Stokes shifted
emission warrants the occurrence of ES1PT in 1a(N) solid
crystal, resulting in the 540 nm tautomer emission. This is in
sharp contrast to the lack of steady-state emission for 1a(N)
in CH2Cl2 and other solvents. The results are reminiscent of many
ES1PT molecules exhibiting extremely weak tautomer emission
in solution due to cis-trans isomerization, which induces a
dominant deactivation channel for the emission quenching in
the excited state.25 For example, in the case of 2-[(2-hydroxy-
phenyl)benzothiazole, it has been well-known that following
EC1PT molecules exhibiting extremely weak tautomer emission
in solution due to cis-trans isomerization, which induces a

4. Conclusion
In conclusion 1a has been synthesized and characterized and its
dual ES1PT channels explored. In the solid state, 1a exists
exclusively in 1a(N) HB conformer, which, upon excitation,


