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ARTICLES

Imidazole-Based Excited-State Intramolecular Proton-Transfer (ESIPT) Materials: Observation of Thermally Activated Delayed Fluorescence (TDF)

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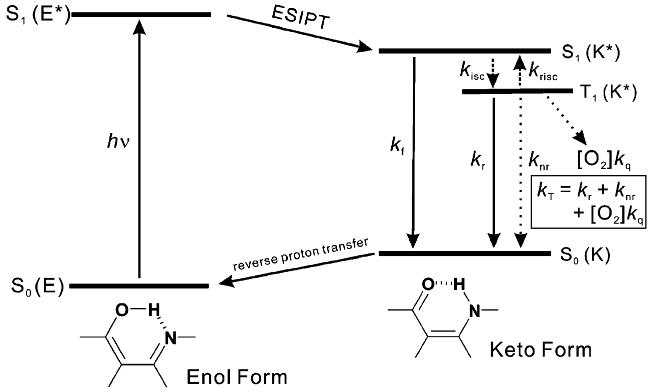
We report the first observation of thermally activated delayed fluorescence (TDF) from an excited-state intramolecular proton-transfer (ESIPT) molecule, a hydroxyl-substituted tetraphenyl imidazole derivative (HPI−Ac), in degassed solutions as well as in low-temperature organic matrixes. In the absence of oxygen, the blue emission of an identical spectral feature was observed in the nanosecond (∼4.4 ns) and microsecond (∼25 μs) time domains, and the fluorescence intensity increased with temperature. From the temperature dependence of the time-resolved spectra of HPI−Ac, the energy gap between the first-excited singlet state and the lowest triplet state was determined to be 7.6 ± 0.3 kJ/mol (630 ± 25 cm^{-1}), and the limiting rate constant of intrinsic reverse intersystem crossing was estimated to be 1.3 (±0.5) × 10^{7} s^{-1}.

Introduction

The excited-state intramolecular proton-transfer (ESIPT) reaction, a fast enol-to-keto (E-to-K) prototropy occurring in the excited states of intramolecularly hydrogen-bonded molecules, has been extensively investigated because of its fundamental interest and potential applications.[1−5] Because ESIPT molecules are normally more stable in the E form in the ground state but in the K* form in the excited state, photoexcitation of such molecules is immediately followed by four-level cyclic proton-transfer reactions (E → E* → K* → K → E) mediated by intramolecular hydrogen bonds (see Scheme 1). It is characteristically observed, therefore, that the absorption from E and emission from K* result in an anomalously large Stokes shift without self-absorption, finally providing ideal motives for four-level lasing,[4,6] UV photostabilizers,[7] and solar energy concentrators.[8]

Recently, we reported a novel class of highly efficient blue-emitting imidazole-based ESIPT molecules, i.e., hydroxyl-substituted tetraphenylimidazole (HPI) and its acetate-containing derivative (HPI−Ac), which readily formed large single crystals exhibiting intense blue fluorescence at 460 nm and showing low-threshold amplified spontaneous emission (see Chart 1).[9] The four sterically crowded phenyl groups substituted into the imidazole ring provide positive steric effects toward a strong photoluminescence in a dense crystal state. A high photoluminescence quantum efficiency (Φ_{PL}) of 0.52 was achieved by limiting the excessive tight stacking responsible for intermolecular vibrational coupling and relevant nonradiative relaxation in the HPI−Ac crystal. From ongoing studies on the fluorescence kinetics in the solution and solid states in this work, another interesting phenomenon of HPI−Ac was observed. When the solutions were degassed by argon gas purging, there arose a simultaneous increase in the intensity and lifetime of the luminescence compared to those of the "prompt" fluorescence of air-equilibrated samples. The spectral features of the prompt fluorescence in the nanosecond time domain and the "delayed" luminescence attenuated to the microsecond time domain were found to be the same. This unusual delay phenomenon has been called the delayed fluorescence (DF), resulting from more complicated routes through the triplet manifolds.[10−12]

SCHEME 1. Modified Jablonski Diagram for the Photophysical Processes in HPI−Ac



Generally, DF can arise from either thermal activation of triplet states or triplet−triplet annihilation to regenerate fluoresc-

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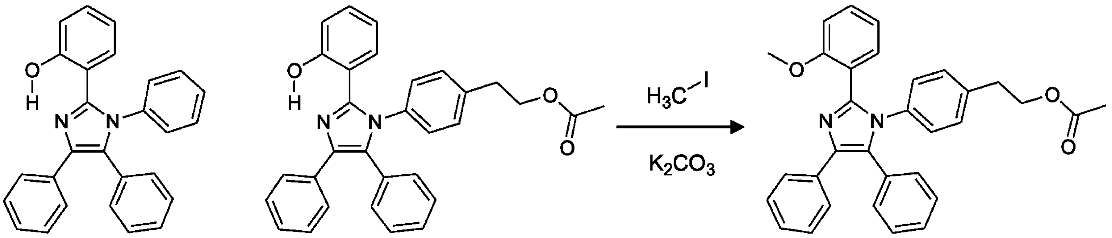
CHART 1. Structures of Hydroxyl-Substituted Tetraphenyl Imidazole (HPI), the Acetate-Containing Derivative (HPI−Ac), and Methyl-Blocked HPI−Ac (MeOPI−Ac)



HPI HPI-Ac MeOPI-Ac

ing singlet states. The former type of DF has been called thermally activated DF (TDF). Although the mechanisms of DF has been explored for many years,[10−17] the phenomena of TDF has been reported rather rarely. TDF has been observed in some dyes including aromatic ketones,[15,18] thiones,[19] hydrocarbons,[20] and other phosphorescent molecules.[21−23] In this work, we report the first observation of TDF in a class of ESIPT molecules by a temperature-dependent time-resolved study of the luminescence and determine values of the singlet−triplet energy gap (ΔE_{ST}) as well as the intrinsic rate constant of the reverse intersystem crossing.

Experimental Section

Materials. The synthesis and structural identification of the ESIPT compounds (structures shown in Chart 1) were described in our previous work.[9] Briefly, the HPI−Ac molecules were prepared according to the classical method of lophine synthesis.[24] In this case, 5.0 g of benzil (23.8 mmol) and 2.55 mL of salicylaldehyde (23.8 mmol) were dissolved in 120 mL of glacial acetic acid at room temperature. Then, 4.89 g of 2-(4-aminophenyl)ethanol (35.7 mmol) and 9.17 g of ammonium acetate (119 mmol) were added. The mixture was heated at 110 °C for 12 h. After termination of the reaction, the dark solution was poured into copious amounts of water. Recrystallization from ethyl acetate solution afforded 7.9 g of white HPI−Ac powder in 70% overall yield.

Measurements. Chemical structures were fully identified by ^{1}H NMR spectroscopy (JEOL, JNM-LA300), ^{13}C NMR spectroscopy (Bruker, Avance DPX-300), GC-mass spectrometry (JEOL, JMS-AX505WA), and elemental analysis (CE Instruments, EA1110). Static absorption and emission spectra were obtained using a UV/vis spectrometer (Scinco, S-3100) and a homemade fluorimeter consisting of a 75-W Xe lamp (Acton Research, XS432), two monochromators (Acton Research, Spectrapro-150 and -300), and a photomultiplier tube (Acton Research, PD438), respectively. Photoluminescence quantum yield (Φ_{PL}) values for solution samples were obtained using 9,10-diphenylanthracene as a reference.[25] Pulse-excited emission spectra were measured using an actively/passively mode-locked Nd:YAG laser (Quantel, YG701) and an intensified CCD (Princeton Instruments, ICCD576G) attached to a spectrometer (Acton Research, Spectrapro-500) as the excitation source and detector, respectively. Samples were excited at the front face by pulses of 315 nm, generated through a Raman shifter filled with methane at 10 atm and pumped by the fourth-harmonic pulses (266 nm) of the Nd:YAG laser. Sample temperature was controlled by a closed-cycle He cryostat (Janis, CCS-100).

Results and Discussion

Figure 1 shows the evolution of the absorption and emission spectra of HPI−Ac in air-equilibrated $CHCl_3$ as a function of Ar gas purging. Upon absorption of a photon, the solution shows a strong and large Stokes-shifted fluorescence at 465 nm with a very weak shoulder at around 390 nm. Previously, we showed that the E form of HPI−Ac undergoes ESIPT to tautomerize into the K* form within 5 ps after photoexcitation.[9] The fluorescence lifetime of K* was measured to be 4.4 ns. In comparison, MeOPI−Ac, a non-proton-transfer reference compound without a hydroxyl proton, shows only a normal Stokes-shifted fluorescence with a maximum at 389 nm. Thus, the origins of fluorescence emission at around 390 and 465 nm for the HPI−Ac solution are clearly assigned to E* and K* emissions, respectively. With gradual elimination of oxygen molecules dissolved in the solution by purging with argon gas, the K* fluorescence becomes more intense. After prolonged degassing of the air-equilibrated solution for 60 s, the Φ_{PL} value increased from 0.18 to 0.22. The enhancement of the K* fluorescence upon removal of the oxygen molecules from the solution implies that the triplet state of K, the population of which is usually quenched by collision with molecular oxygen, plays a role in the enhancement of fluorescence.[10] The inset of Figure 1 shows that the time-resolved emission spectrum collected 25 μs after photoexcitation exactly matches the prompt fluorescence spectrum measured at the moment of photoexcitation. This is very unusual recalling that the lifetime of prompt fluorescence is on the time scale of 4.4 ns. The clear coincidence of these two spectra indicates that the 25-μs-delayed luminescence is related to the DF. Here, it is noteworthy that MeOPI−Ac, a non-ESIPT analogue of HPI−Ac, does not show DF (see the Supporting Information, Figure S-4). DF can arise from either TDF by thermal activation of triplet states or triplet−triplet annihilation for the regeneration of fluorescing singlet states. The most distinguishing feature of TDF is that the lifetime of DF is the same as that of phosphorescence and is independent of the concentration of triplet states.[20] On the other hand, the lifetime of DF induced by triplet−triplet annihilation is usually one-half that of phosphorescence and strongly depends on the population of triplet states because it is essentially a bimolecular process between triplet states.[21]

Figure 2 shows the time-resolved luminescence spectra of HPI−Ac in organic matrixes of $CHCl_3$ obtained in the time domain of microseconds at several low temperatures. At a temperature of 50 K, a single emission band with a peak at 510 nm is observed. This band is unambiguously assigned to the phosphorescence of triplet K species, because the E form is known to transform immediately into the K* form within 5 ps after photoexcitation. With increasing temperature, the photoexcitation yields a new emission band growing around 460 nm at the expense of the K* phosphorescence around 510 nm. This blue band is attributed to the DF of K* because of the spectral similarity to the prompt fluorescence of K*. As briefly described above, TDF comes from the thermal activation of the triplet

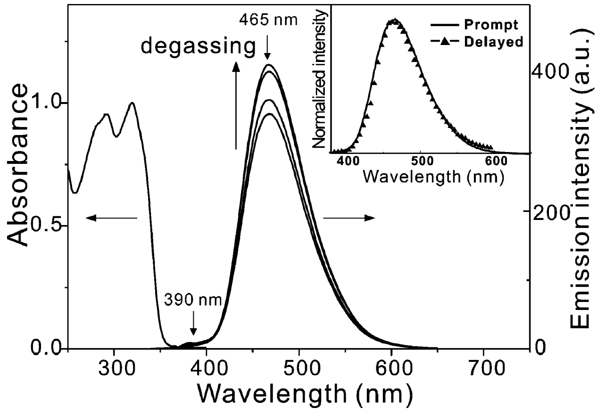


Figure 1. Absorption and emission, excited at 318 nm, spectra of HPI−Ac in $CHCl_3$ (1.0×10^{-5} M) at room temperature. The gradual elimination of oxygen from the solution by Ar gas purging gave rise to the increase of the emission intensity. Inset: Identical spectra of the prompt (measured at the moment of excitation with a gate time of 2.5 ns) and delayed (collected 25 μs after the photoexcitation with a gate time of 2.5 μs) fluorescence, excited at 315 nm.

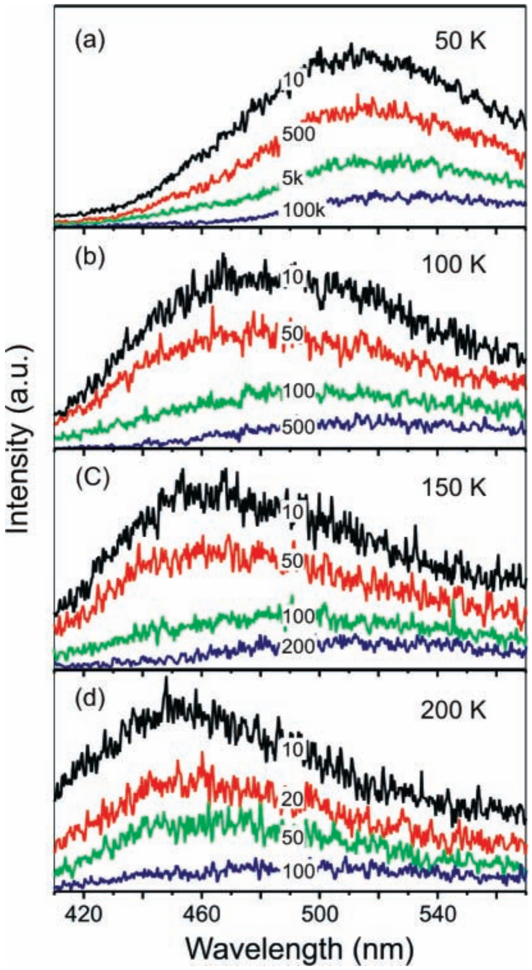


Figure 2. Time-resolved emission spectra of HPI−Ac, excited at 315 nm, in $CHCl_3$ at (a) 50, (b) 150, (c) 180, and (d) 200 K. Time delays (in microseconds) between excitation and collection are given near the spectra.

state, which is then driven to the singlet state by reverse intersystem crossing. The rate constant for reverse intersystem crossing (k_{risc}) is related to temperature according to[12,13,20]

$$k_{risc} = k^{\circ}_{risc} \exp(-\Delta E_{ST}/RT) \tag{1}$$

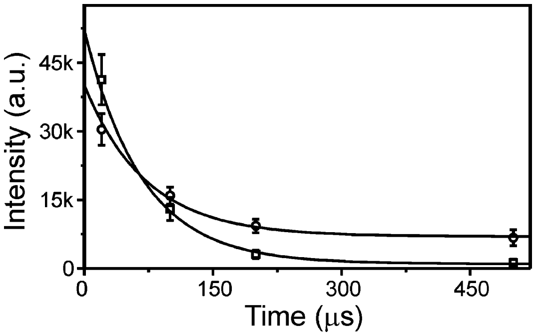


Figure 3. Decay profiles of phosphorescence, monitored at 530 nm (circles), and DF, monitored at 440 nm (squares), of HPI−Ac, excited at 315 nm, in matrixes of $CHCl_3$ at 180 K. The DF at 440 nm decays in 67 (±3) μs (98%), whereas the phosphorescence at 530 nm shows a decay profile composed of a 72 (±4) μs component (83%) and a millisecond component (17%).

where ΔE_{ST} represents the value of the $S_1 - T_1$ energy gap. Therefore, the intensity of TDF shows a characteristic dependence on temperature. In principle, without triplet−triplet annihilation, the observed triplet decay rate (k_{obs}) can be expressed as

$$k_{obs} = k_T + k_{df} \tag{2}$$

where k_T is the sum of rate constants related to the relaxation of the triplet state other than k_{risc} and k_{df} is given by

$$k_{df} = \phi_f k^{\circ}_{risc} \exp(-\Delta E_{ST}/RT) \tag{3}$$

if the lifetime of the singlet state is far shorter than $1/k_{risc}$; ϕ_f in eq 3 represents the fluorescence quantum yield. Equation 2 predicts that the contribution of TDF to the apparent relaxation of the triplet state increases with temperature because k_T is not as sensitive to temperature as k_{df}. One should note that the experimental conditions of low-temperature organic matrixes were carefully chosen to minimize the effects of temperature on k_T. As a consequence, the spectral evolution with temperature in Figure 2 shows agreement with eq 2. It is clearly shown that the apparent lifetime of DF decreases with increasing temperature.

Figure 3 shows typical decays of phosphorescence, collected at 530 nm, and DF, obtained at 440 nm, at 180 K. At a given temperature, the lifetime of DF seems virtually the same as that of phosphorescence within experimental error.[26] The observation of such identical lifetimes of DF and phosphorescence supports the conclusion that the DF arises from the TDF mechanism and not from the triplet−triplet annihilation mechanism. This is also consistent with the fact that HPI−Ac molecules of rather low concentration are immobilized in low-temperature organic matrixes in our sample.

By combining eqs 2 and 3 and taking the logarithm, we can derive an Arrhenius-type equation as[22]

$$\ln(k_{obs} - k_T) = \ln(k^{\circ}_{risc}\phi_f) - \Delta E_{ST}/RT \tag{4}$$

In eq 4, it is assumed that k_T is independent of temperature for our experimental conditions because k_T consists of the rate constants of radiative intersystem crossing (k_r), nonradiative intersystem crossing (k_{nr}), and quenching by impurities such as molecular oxygen ($[O_2]k_q$) (see Scheme 1). Generally, the triplet-state lifetimes of aromatic molecules are known to be independent of temperature if bimolecular quenching mechanisms or photoreactions are absent.[10] Note that all of the temperature-dependent experiments here were performed using low-tem-

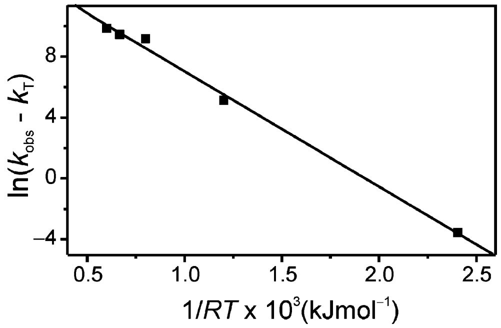


Figure 4. Arrhenius plot for the delayed fluorescence rate of HPI−Ac.

perature organic matrixes so as to suppress collisional quenching processes. Therefore, if we plot the linear least-squares fit according to eq 4, we can determine the values of k_T, $k^\circ_{risc}\phi_f$, and ΔE_{ST}.[22] In fact, the linear plot in Figure 4provides the values of k_T, $k^\circ_{risc}\phi_f$, and ΔE_{ST} for the HPI−Ac molecule (K form) to be 1.5 ($\pm$0.1) $\times$ 10^3 s^{-1}, 2.3 ($\pm$0.9) $\times$ 10^6 s^{-1}, and 7.6 $\pm$ 0.3 kJ/mol (630 $\pm$ 25 cm^{-1}), respectively. Note that the value of 7.6 kJ/mol can be regarded as an upper limit of ΔE_{ST}, because we assumed a negligible dependence of k_T on temperature. Given that the prompt fluorescence quantum yield of the air-equilibrated HPI−Ac solution is 0.18 as reported earlier,[9] we can estimate the limiting rate constant of k°_{risc} from the product $k^\circ_{risc}\phi_f$ to be 1.3 ($\pm$0.5) $\times$ 10^7 s^{-1}. Alternatively, the ΔE_{ST} value can be spectroscopically estimated from steady-state data such as the separation between the positions of the 0,0 electronic transition in fluorescence and in phosphorescence[27] or the intensity ratio of delayed fluorescence to prompt fluorescence with temperature (for a recent review, see ref 20d). Unfortunately, our current experimental conditions allow us neither to resolve those vibronic bands of the spectra nor to deconvolute spectra.

It is noteworthy, however, that the observed value of 630 cm^{-1} for ΔE_{ST} is much smaller than the reported values for other organic molecules, which commonly fall in the range of 1000−3000 cm^{-1}.[20,21,27] Thanks to the small value of ΔE_{ST}, the fluorescing singlet state of HPI−Ac can be easily repopulated from triplet manifolds by reverse intersystem crossing with a relatively small amount of heat applied to the molecule. We also observed similar TDF phenomena in a series of molecules having an HPI core (see Supporting Information), because the photoluminescence mainly occurs in the central HPI unit. In this respect, we believe that a derivative of HPI holds a strong potential in electroluminescence applications for high device efficiencies, because it can utilize both singlet and some triplet excitons as emissive sources.

In summary, the thermally activated delayed fluorescence of a hydroxy-substituted tetraphenylimidazole derivative (HPI−Ac) was observed in degassed solutions as well as in low-temperature organic matrixes. From the temperature dependence of the time-resolved spectra of HPI−Ac, the energy gap between the first-excited singlet state and the lowest triplet state was determined to be 7.6 kJ/mol. The limiting rate constant of reverse intersystem crossing from the triplet state to the excited single state was evaluated to be 1.3 $\times$ 10^7 s^{-1}. The photodynamics of HPI−Ac are summarized in Scheme 1.

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Supporting Information Available: Supplementary data on optical characteristics and material properties, including synthesis and experimental data, absorption and emission spectra, phosphorescence and DF spectra, and a photograph of HPI-Ac fluorescence. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The decay measured at the wavelength of K* phosphorescence has a minor additional long-lived component lasting to the millisecond time scale, speculated to come from a small contribution of impurities. We repeated the measurements and found that the contribution of this long-lived component varied depending on sample preparation. In addition, a MeOPI-Ac solution showed a phosphorescence band with a peak wavelength of 530 nm. Because our samples were kept in the metallic reservoir of the cryostat for temperature-dependent measurements, the samples seemed to undergo a side reaction to give impurities having a molecular structure similar to that of the E form of HPI-Ac during cooling processes.

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