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Excited-State Double Proton Transfer on 3-Iodo-7-Azaindole Dimer in a Single Crystal

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Self-dimerization of 7AI has long been recognized for undergoing the excited-state double proton transfer (ESDPT) resulting in a large Stokes-shifted emission.[1−3] Much research has focused on the dynamics of ESDPT in the 7AI dimer in the solution phase. Early dynamic studies have revealed that the rate of proton transfer is within $(0.3-1.0) \times 10^{12}$ s^{-1} for the 7AI(N) dimer in nonpolar solvents.[4a,b] Recently, by the use of a femtosecond upconversion technique, Chachisvillis et al.[4c] have further resolved multiexponential tautomer rise times (0.2−0.6, 1, and 12 ps transient states) which are the basis of a nonconcerted double-proton transfer. However, Takeuchi and Tahara[4d] reassigned those 0.2−0.6 and 12 ps components to the rate of internal conversion and vibrational relaxation, respectively based on a concerted ESDPT model. Very recently, through a femtosecond transient absorption/upconversion study, Fiebig et al.[4e] concluded that on the global potential energy both trajectories of the symmetric and asymmetric vibrational motion coupled with the solvent dynamics must be considered for the ESDPT in solution phase. Only when the internal energy is low (e.g., low temperature) can one examine the process of tunneling and nonconcertedness.

Unfortunately, in solution phase, dynamics of temperature-dependent ESDPT on the 7AI dimer have been prohibited due to the formation of thermodynamically more favorable hydrogen-bonded oligomers at low temperature.[5,6] The oligomer formation also hampers the study of proton-transfer spectroscopy in the triplet-state manifold. In a 77 K methylcyclohexane glass containing concentrated 7AI a steady-state emission maximum at 480 nm is dominated by the phosphorescence of the non-proton-transfer oligomer form.[5,6] In another approach, the crystal phase may provide indisputable information on the intrinsic dynamics of the proton.[7] Unfortunately, the crystal structure of 7AI reveals an unusual hydrogen-bonding configuration. It consists of tetrameric units of approximate S_4 symmetry, in which the molecules are associated by means of four complementary N−H- - -N hydrogen bonds,[8] (Figure 2a). Thus, the study of intrinsic ESDPT dynamics in the 7AI crystal is not feasible due to the lack of dual hydrogen-bonded dimeric form.

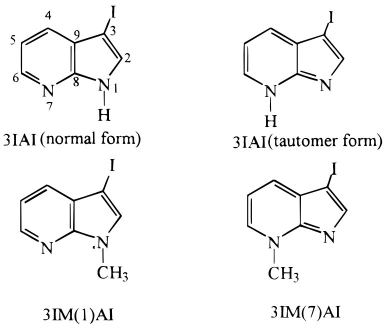

Figure 1. Structures of 3IAI and its corresponding proton-transfer isomer as well as methylated derivatives.

We have thus been focusing on the molecular modification aiming at (1) searching for 7AI analogues in which an intact dual hydrogen-bonded dimer may be formed in its perfect crystalline so that the intrinsic ESIPT can be explored, (2) the study of proton-transfer spectroscopy in the triplet-state manifold enhanced by the heavy-atom perturbation. Accordingly, 3-iodo-7-azaindole (3IAI) and its derivatives (see Figure 1) were synthesized.[9] The crystal structure of 3IAI is composed of two crystallographically independent molecules, forming a cyclic dimer via dual N−H···N hydrogen bonds (Figure 2b).[11] In contrast to the theoretically calculated equal dual hydrogen bonds of the 7AI dimer,[12] two 3IAI molecules interact with slightly different N−H···N dual hydrogen bonds (N(1)···N(7)′ = 2.930 Å, N(7)···N(1)′ = 2.935 Å) in which the N−H···N angles deviate from linearity by 11.2° and 14.6°, respectively. As shown in the packing diagram of 3IAI (Figure 2d), parallel cyclic dimers are stacked via the interaction between their ring π-systems to form alternating slabs. The orientation of the parallel molecules in one slab is nearly perpendicular to those in adjacent slabs. Figure 3 presents fluorescence spectra of a 3IAI single crystal taken at 298, 77, and 10 K.[13] In contrast to a weak normal fluorescence ($\lambda_{max} \approx$ 350 nm) observed in the 7AI single crystal, the 3IAI dimer in the single crystal exhibits a unique, large Stokes-shifted fluorescence ($\lambda_{max} \approx$ 500 nm) throughout 298−10 K. Room-temperature phosphorescence maximized at ∼600 nm was also observed in the 3IAI single crystal (see Figure 3). A detailed time-dependent spectral evolution indicates that both fluorescence and phosphorescence consist of a single emitting species with a decay rate of 1.7×10^9 s^{-1} ($\tau_f \approx$ 0.6 ns) and 2.0×10^5 s^{-1} ($\tau_p \approx$ 5.0 μs), respectively at 298 K. In a comparative study 3IM(1)AI (see Figure 1,[9]), a nonproton-transfer model of 3IAI, reveals a fluorescence and phosphorescence maximum at 370 and 510 nm, respectively at room temperature. Conversely, the model com-

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[9] 3IAI was synthesized according to a procedure reported previously.[10] NMR analyses: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.15 (m, 1H); 7.47 (s, 1H); 7.76 (d, J = 8.78 Hz, 1H); 8.32 (d, J = 4.78 Hz, 1H), 10.77 (brs, 1H). 3IM(1)AI was synthesized by adding sodium hydride (57%, 60 mg) to the THF solution containing 3IAI (0.15 g), followed by the addition of methyl iodide (30 mg). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 4.31 (s, 3H); 6.93 (t, J = 6.8 Hz, 1H); 7.65 (d, J = 6.0 Hz, 1H); 7.87 (s, 1H); 7.98 (d, J = 7.7 Hz, 1H). 3IM(7)AI was synthesized by the reaction of 3IAI (0.12 g) and CH$_3$I (0.58 g) in THF under N$_2$. NaOH (2.5 N, 3 mL) was then added, and the mixture was stirred for ∼20 min to obtain 3IM(7)AI (60 mg). ^{1}H NMR (CDCl$_3$, 400 MHz), δ 4.34 (s, 3H); 6.99 (t, J = 6.24 Hz, 1H); 7.69 (d, J = 6.0 Hz, 1H); 7.90 (s, 1H); 8.00 (d, J = 7.64 Hz, 1H).

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[11] A single crystal of 3IAI with dimensions of 0.45 × 0.40 × 0.40 mm was obtained by slow evaporation in a benzene solution. See Supporting Information for details of the crystallographic work.

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[13] An Nd:YAG-pumped optical parametric oscillator coupled with a second harmonic device serves as an excitation source. The resulting fluorescence was detected by an intensified charge-coupled detector (ICCD, Princeton Instrument, model 576G/1). To obtain the phosphorescence the gate was open at a delay time of >50 ns.

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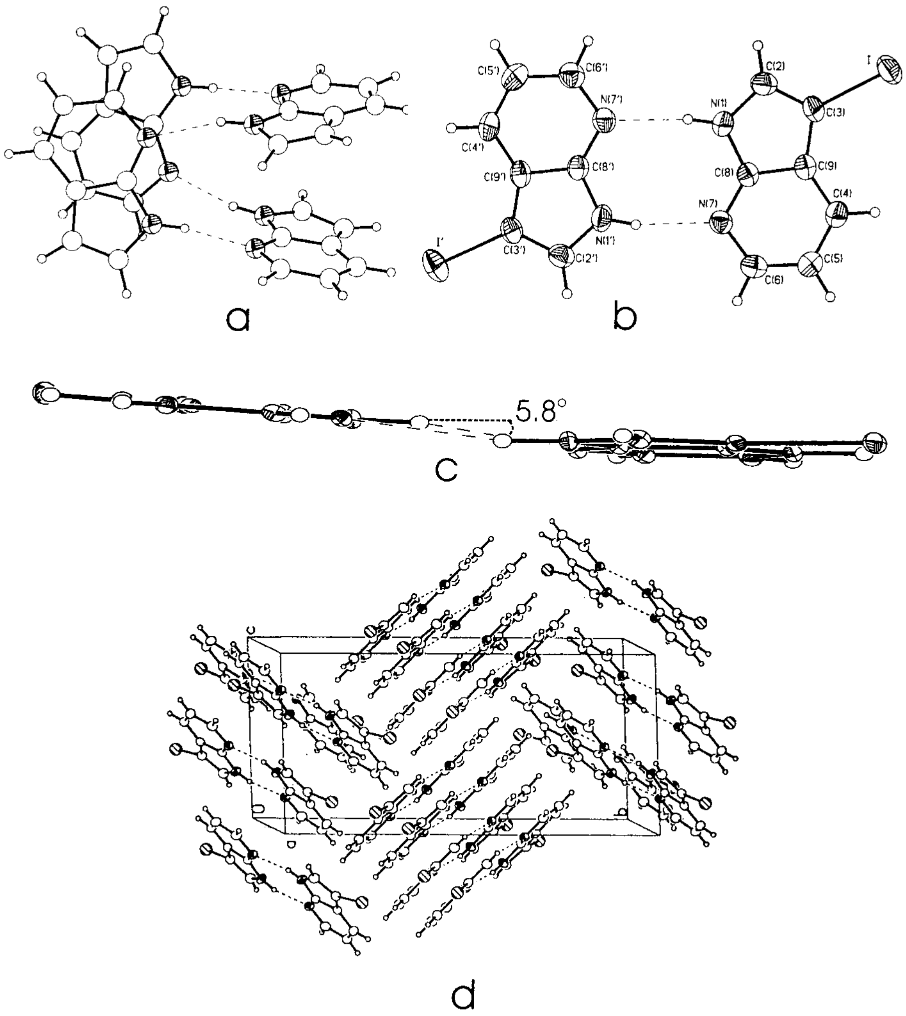

Figure 2. The tetramer formation of 7AI in the crystal (a). Three projections of 3IAI dimer in the crystal: perpendicular to the molecular plane (b), along the molecular plane (c), and in a unit cell (d).

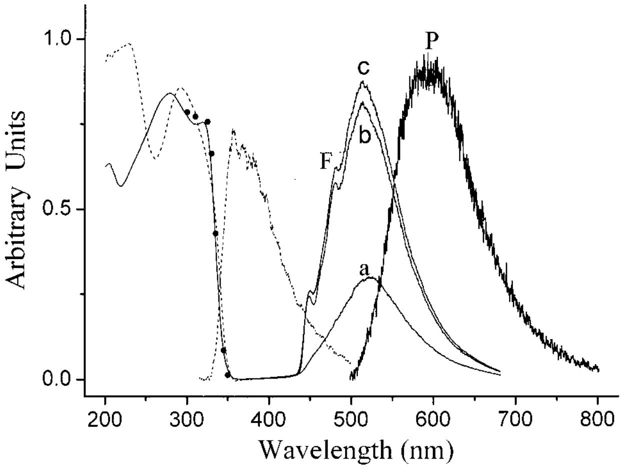

Figure 3. (- - -) The absorption and fluorescence spectra of the 7AI solid at room temperature. (—) The absorption, fluorescence (F) and phosphorescence (P, 298 K) of 3IAI in which the fluorescence was monitored as a function of temperature at (a) 298, (b) 77, and (c) 10 K. (• • •) The phosphorescence excitation spectrum of 3IAI (298 K). The crystal orientation was 45° with respect to the polarization of the exciting light. The band-pass used for measuring the phosphorescence was ~5.0 nm at 600 nm, which may cause the loss of the vibronic structure.

pound of the proton-transfer tautomer, 3IM(7)AI,[9] exhibits room-temperature fluorescence and phosphorescence maximized at 520 nm ($\tau_f \approx 0.4$ ns) and 605 nm ($\tau_p \approx 27.5$ μs), respectively in its single crystal form, of which the spectral features resemble those observed in the 3IAI single crystal. Accordingly, the results of 3IAI for the first time unambiguously demonstrate the occurrence of ESDPT in a single crystal of 7AI analogues and resolve as well the iodine-atom-enhanced phosphorescence originating from the proton-transfer tautomer. Since two molecular frames of 3IAI are in a small twisted angle of 5.8° in the crystal (see Figure 2c) one might expect the dynamics to be governed by the geometry adjustment of a planar configuration prior to the ESDPT, resulting in an appreciable energy barrier. However, a unique proton-transfer tautomer fluorescence along with a detection-limited rise time ($>5 \times 10^9$ s^{-1}) was still observed at 10 K when the excitation wavelength was tuned to the near onset of the S_0-S_1 transition (~350 nm). The result concludes the occurrence of ESDPT with a negligibly small energy barrier where proton tunneling may take place. In summary, the results provide a prototype to mimic the intrinsic ESDPT dynamics of the 7AI-like dual hydrogen-bonded dimer with complete structural information, which are believed to bring up a broad spectrum of interest in the field of proton-transfer studies.

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Supporting Information Available: X-ray data for 3IAI (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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