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Excited-State Intramolecular Proton Transfer via a Preexisting Hydrogen Bond in Semirigid Polyquinoline

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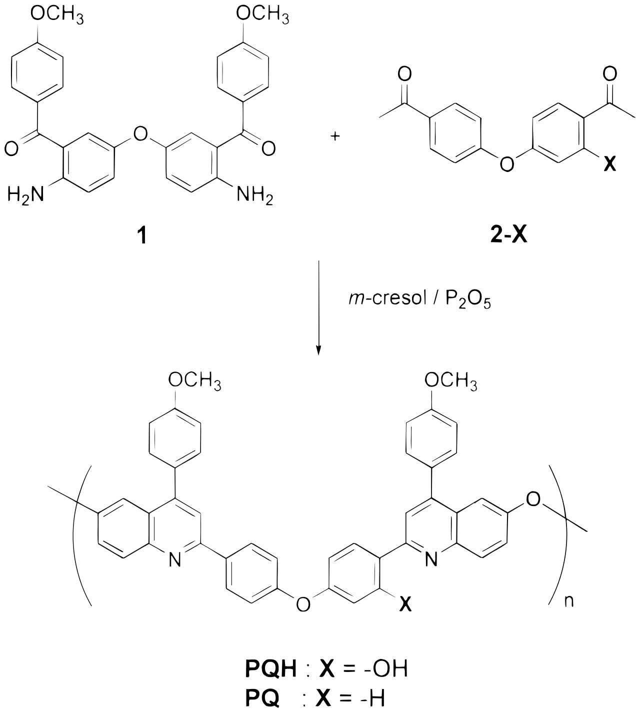
Excited-state intramolecular proton transfer (ESIPT) is a phototautomerization occurring in the excited states of the molecules possessing a cyclic intramolecular or solvent-bridged hydrogen bond.[1] Since this process is fast enough to accompany the short-lived first excited singlet state, the electronic excitation of a normal form (N) in the ground state yields a proton-transferred excited-state tautomer (T*) of the much lower energy. This T* relaxes radiatively or nonradiatively to the metastable ground state T, which reverts to N via reverse proton transfer. Therefore, the different absorbing and emitting species result in a large Stokes shift. Since the first report,[2] ESIPT has led to a wide range of potential applications such as luminescence probes,[3] laser dyes,[4] polymer photostabilizers,[5] scintillators,[6] and solar collectors.[7] To date, ESIPT has been studied mainly in the solution systems for small organic molecules such as benzazole[8−12] and pyridine derivatives,[13,14] etc. In most cases, however, phototautomeric fluorescence is rather weak for practical applications at ambient temperature due to more effective internal conversion or broken hydrogen (H) bond by torsional motion.[14] So it has been used essentially as only a probe for ESIPT phenomenon. To address these limitations, we have considered polymeric ESIPT system and designed semirigid prototype polyquinoline (PQH), which comprises intramolecular H bond between the enol and imine groups[15] (Scheme 1).

Scheme 1. Synthetic Scheme of PQH and PQ



We examined the possibility of ESIPT in PQH theoretically with semiempirical molecular orbital calculation of the simplified model structure[16] of PQH shown in Figure 1, following a reported method.[17] On the basis of the reaction path (Figure 1) depicted from the calculated energies and bond lengths of N, T, and transition state (TS) in the ground and first excited singlet states, ESIPT was considered very possible in PQH.

PQH was prepared from bis(aminoketone) (**1**) and OH-substituted bis(ketomethylene) (**2-OH**) monomers by Friedländer reaction following reported procedures[15,18] (Scheme 1). As PQH has two possible emitting sites, i.e., protic (i.e., OH-substituted) and aprotic units, we also prepared fully aprotic polyquinoline (PQ) for comparison, using aprotic bis(ketomethylene) (**2-H**) monomer. PQH shows excellent thermal stability with the glass transition and initial decomposition temperatures of 230 and 450 °C, respectively, and good solubility in *m*-cresol, formic acid, and tetrachloroethane (TCE), enough to cast an optically clear film. The weight-average molecular weight of PQH was estimated as 8000 (PDI = 1.4) from gel permeation chromatography (GPC).

Figure 2 shows the static absorption and fluorescence spectra of PQH and PQ. Aprotic PQ in TCE gives ordinary absorption and photoluminescence (PL) bands that are partially overlapping each other (Figure 2a). The absorption spectrum of PQH is structured similar to that of PQ and matches well with the calculated one as indicated by vertical bars[19] in Figure 2b in terms of the excitation energies and oscillator strengths at different vibrationally coupled transitions. Except for the slight red shift of absorption edge, no remarkable difference was observed between the absorption of PQH and PQ, implying that the electronic effect of OH substitution is not significant. With respect to PL, however, the enol group exerts a noticeable influence, so that PQH solution shows an additional red PL band besides the normal blue one (Figure 2b). This suggests a probable occurrence of the ESIPT process. The blue band, when compared with the spectrum of aprotic PQ, may originate both from the aprotic unit and from N* of the protic one, while the red band is attributable to T*. The excitation spectra for each band, though not shown here, are almost superimposable on one another, implying that the precursors of both bands originate from the same species in the ground states. Thus, PQH exists predominantly as the N form in the ground state, and its Franck−Condon-excited state is the precursor of T*.[20] In the PQH film spin-coated from TCE solution, the absorption spectrum is the same as that of solution, while the blue PL is totally quenched, giving only the red band (Figure 2c). This suggests that ESIPT becomes much more efficient in film than in solution. In film, the torsional motion is virtually frozen far below the

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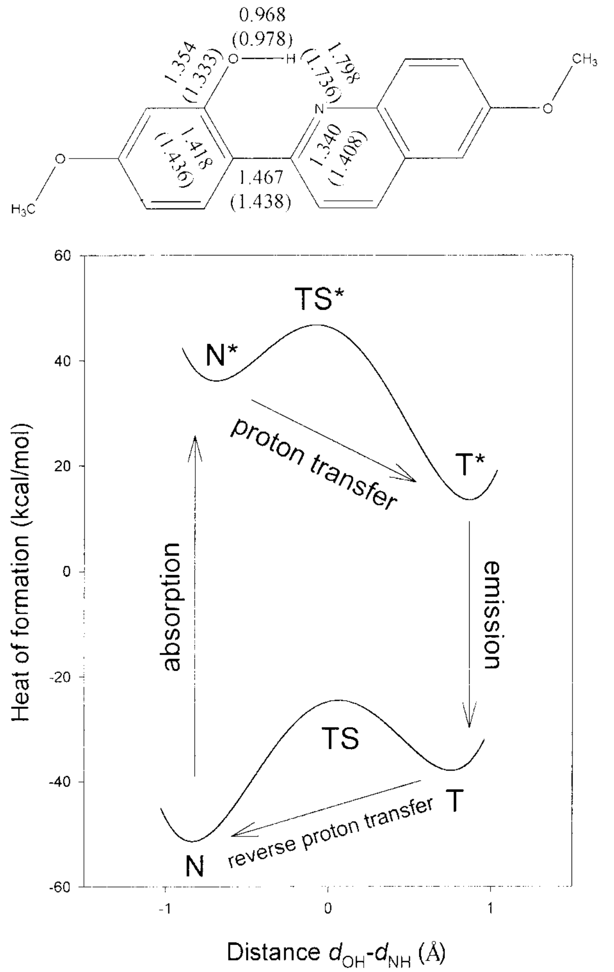

Figure 1. Calculated bond lengths in the ground and first excited singlet states of the simplified model structure and the schematic diagram of proton-transfer reaction path. Excited-state values are given in the parentheses. N, T, and TS indicate normal form, tautomer, and transition state, respectively.

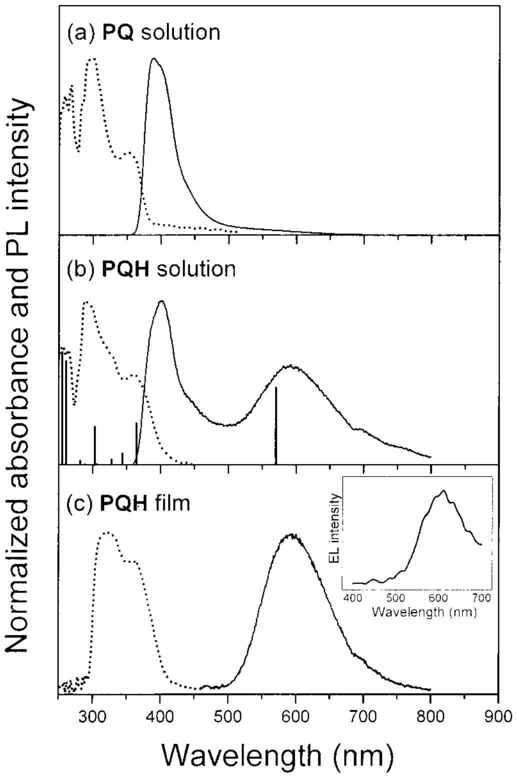

Figure 2. Absorption (dotted) and fluorescence (solid) spectra, excited at 310 nm, of PQ in TCE solution (a), PQH in TCE solution (b), and PQH film (c). Vertical bars in the absorption spectrum of (b) indicate the calculated transition energies and oscillator strengths for the model structure in Figure 1. Vertical bar in the red fluorescence band in (b) indicates the T* → T adiabatic transition line calculated from Figure 1. The inset of (c) is the EL spectrum of a PQH single-layer device.

glass transition temperature so that the H-bonded conformer is preferred energetically. Furthermore, no blue emission also indicates that the energy of the excited aprotic unit transfers completely to the protic unit of a lower energy in advance of ESIPT. To our interest, the tautomeric PL from PQH film is so strong as to be seen brilliant by the naked eye under room light.

Picosecond emission kinetic profiles[21] in Figure 3 show direct evidence that the red emission of PQH in both solution and film is the fluorescence from T* following ESIPT, rather than phosphorescence from N*. As expected from static spectra, the excitation of the aprotic PQ decays with the time of 450 ps, much more slowly than the blue emission decay of PQH, to the vertically lower energy states (Figure 3a). As for PQH solution, conformers without a H bond may also exist though H-bonded one is favorable energetically. In Figure 3b, the fast decay time of 19 ps (91%) for the blue emission of the TCE solution is ascribed to proton transfer in the H-bonded conformer, while the slow one of 140 ps to the internal rotation of non-H-bonded PQH around the C (phenol)−C (quinoline) bond in order to obtain a geometry suitable for proton transfer.[8,22] Furthermore, the delayed rise at 600 nm is a clear evidence that T* arises from the ESIPT of Franck−Condon excited N.[8,20] It should be noted that the incorporation of red-tailed N* emission makes the observed rise of the red band mistakenly faster than the fast decay of the blue one. For this reason, we assign 19 ps, instead of 7 ps, to the ESIPT time. The biphasic decay of the red emission suggests that besides ESIPT an additional photochemical process takes place from S_1. T* resulting from ESIPT is the excited zwitterionic form (Z*), and we assign 30 ps to the electronic rearrangement time of Z* to convert into the excited keto form (K*). Electronic rearrangement is known to follow fast proton transfer to form relatively more stable species in the S_1 states of quinoline derivatives.[23,24] The slower decay time of 400 ps is attributable to the decay time of K*.

In film, the ESIPT and rearrangement take place in the shorter times of 8 and 20 ps and occur more efficiently, showing no long-lived blue emission. The slow decay time of 300 ps is considered as the relaxation time of K*. The shorter times for all the observed processes in film are owing to the effect of better-organized geometry where the torsional motion is frozen and only the energetically favored H-bonded conformer is present.

The intense large Stokes-shifted (~250 nm) luminescence has led us to consider the applicability of ESIPT process in PQH film. The electroluminescence (EL) spectrum from the single-layer device assembly of Al/PQH (55 nm)/ITO at 20 V shows only the red band from T* about the same as the PL spectrum (the inset of Figure 2c). To our best knowledge, this is the first report

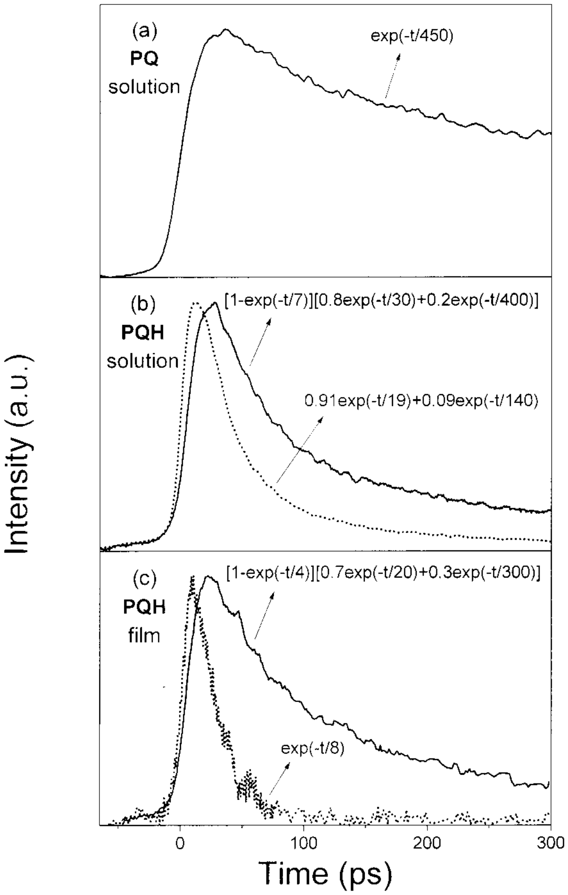

Figure 3. Fluorescence kinetic profiles at 450 nm (dotted) and 600 nm (solid) of PQ in TCE solution (a), PQH in TCE solution (b), and PQH film (c). The kinetic functions shown above were deconvoluted from the instrument response functions.

on ESIPT-involved EL and can be understood by the simple explanation: the exciton produced in the predominantly existing N* by the recombination of hole and electron decays with the radiation of K* following fast proton transfer. The large Stokes shift in PQH leads to the EL without any self-absorption.

In summary, we have synthesized semirigid PQH with alternating building blocks, one of which has an intramolecular H bond, and examined the ESIPT of the polymer. A TCE solution of PQH shows dual blue and red fluorescence bands while a PQ solution shows the blue one only. As semiempirical molecular orbital calculation supports the ESIPT phenomenon in PQH, the blue band is emitted from N* following ESIPT while the red one is emitted from T*. In solution, intramolecularly H-bonded N* undergoes ESIPT in 19 ps to produce Z*, which subsequently undergoes electronic rearrangement in 30 ps to yield K*. On the other hand, N* without the H bond needs to wait for 140 ps until hindered internal rotation creates a proper geometry for ESIPT. The PQH film shows only the red band in both PL and EL measurements and experiences ESIPT and electronic rearrangement in the shorter times of 8 and 20 ps, respectively. PQH, especially in film, may be promising in a variety of applications including novel EL devices.

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(16) The calculation was performed with the Mopac 97 program (Fujitsu). In the geometry of the protic repeating unit of PQH optimized by using PM3 parameters, the quinoline and phenolic group, which form a cyclic intramolecular H bond, are found to be almost in-plane. The pendant phenyl ring is twisted at about 67° with respect to the quinoline plane, and thus its effect on the electronic property of quinoline moiety is found to be very small from the comparison of the calculated HOMO and LUMO levels of the structures with and without lateral phenyl substituent (ca. 1% error with respect to the band gap). On the basis of this, the model structure without a lateral phenyl group was adopted to calculate the tautomerization path simply.
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(21) Fluorescence kinetic profiles were measured by using a streak camera (Hamamatsu, C2830) of 10 ps temporal resolution, which was attached with a CCD detector (Princeton Instruments, RTE128H) and an actively/passively mode-locked Nd:YAG laser (Quantel, YG501) with the pulse duration of 25 ps. Samples were excited with 290 nm pulses generated from a Raman shifter, filled with methane gas of 15 atm, and pumped with 266 nm pulses from the laser.
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