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Excited-State Intramolecular Proton Transfer and Stimulated Emission from Phototautomerizable Polyquinoline Film

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Introduction

Semirigid or rigid polyquinolines are processable heteroaromatic polymers with distinct electronic, photoconductive, nonlinear optical, and electroluminescent properties.[1−5] It is well-known that polyquinolines form an acid−base complex and thus show processability in acidic solvents because the nitrogen atom in the quinoline ring is protonated.[6] This proton acceptability can be employed for excited-state intramolecular proton transfer (ESIPT) when combined with an intramolecular hydrogen (H) bond.[7,8] ESIPT is a phototautomerization driven by proton transfer from acidic proton donor to basic acceptor in the excited state within the framework of an intramolecular H bond. Phototautomerizable molecules in the ground state exist mainly in enol form (E), while upon photoexcitation (E*) they transform rapidly and subsequently to the energetically more stable excited keto form (K*) by ESIPT and decay radiatively to the ground-state keto form (K). It has generally been observed that absorption from E and emission from K* give rise to an abnormally large Stokes' shift without self-reabsorption. Moreover, the intrinsic four-level process (E → E* → K* → K) provides an ideal scheme for stimulated emission by easy population inversion of the proton transferred keto form because K does not initially exist. A critical limitation of ESIPT to actual applications is low efficiency and prominent concentration quenching of keto emission. Accordingly, most of ESIPT phenomena have been investigated in a highly diluted system.[9−12]

Chart 1 shows phototautomerizable semirigid polyquinolines capable of ESIPT with high chromophore content. The flexible ether linkage reduces the backbone rigidity to improve solution processability and also plays an important role of confining conjugation that is a crucial requirement for ESIPT.[13] Photophysical and photochemical processes related to the ESIPT unit of PQH and PQDH, 2-[4-(4-methoxyphenyl)-quinolin-2-yl]phenol, are depicted in Chart 2. The fluorescence kinetics and electroluminescence of PQH, which retains ESIPT units in every second repeating unit, have already been reported in our previous work.[14] PQDH is a novel and extremely concentrated ESIPT polymer, all the repeating units of which are ESIPT chromophores. Herein are reported synthesis, optical properties, and stimulated emission of PQDH.

Chart 1. Phototautomerizable Semirigid Polyquinolines

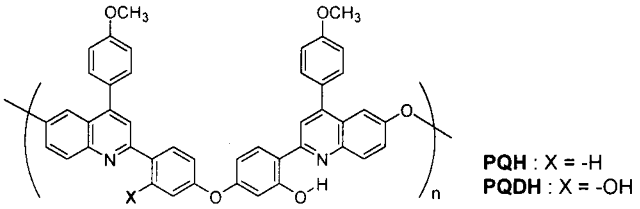
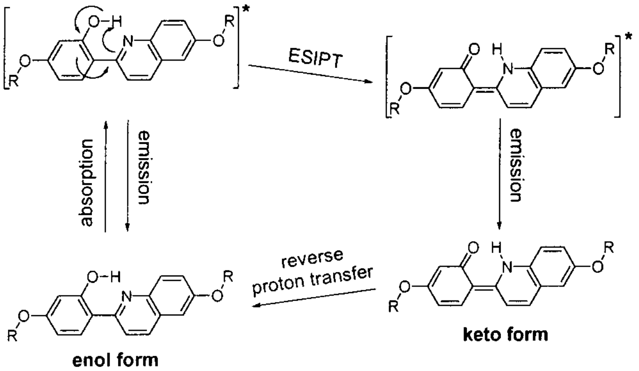


Chart 2. Photophysical and Photochemical Processes of Phototautomerizable Quinoline Unit



Experimental Section

Synthesis. Bis(aminoketone) monomer (**2**) was prepared according to the literature method.[15] Synthetic routes of bis(ketomethylene) monomer (**1**) and PQDH are depicted in Scheme 1. PQDH was prepared by the Friedländer reaction between bis(ketomethylene) (**1**) and bis(aminoketone) (**2**) monomers following the reported procedures.[16] Chemical structures were identified by ^{1}H NMR (JEOL JNM-LA300, 300 MHz) and IR (Midac FT-IR spectrophotometer) spectroscopies.

Bis(ketomethylene) Monomer (1). 3 g of 2′,4′-dihydroxyacetophenone and 3.04 g of 4′-fluoro-2′-hydroxyacetophenone were dissolved in 10 mL of DMSO containing 3.3 g of K_2CO_3 and a catalytic amount of 18-crown-6. The reaction mixture was heated to 100 °C and stirred overnight. After cooling, the mixture was poured into excess water. The filtered precipitate was purified by column chromatography eluting with ethyl acetate and *n*-hexane (volume ratio increasing from 1:4 to 1:2) with the yield of 11%. FT-IR (KBr window, cm^{-1}): 3059, 2983, 2925, 2863, 2723, 2602, 1635, 1491, 1425, 1362, 1325, 1252, 1227, 1174, 1149, 1136, 1065, 1022, 991, 957, 868, 802. ^{1}H NMR ($CDCl_3$, ppm): 2.06 (s, 6H), 6.58 (d, $J = 2.4$ Hz, 2H), 6.60 (dd, $J = 2.4$, 8.2 Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 2H), 12.58 (s, 2H). Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93; O, 27.94. Found: C, 67.1; H, 4.6.

PQDH was purified by Soxhlet apparatus using hot methanol (60% yield). FT-IR (KBr window, cm^{-1}): 3410, 3066, 3045, 2956, 2933, 2839, 1597, 1502, 1415, 1250, 1178, 1126, 1026, 989, 837. ^{1}H NMR (formic acid-d_2, ppm): 7.12 (s, 3H), 10.29 (d, 1H), 10.34 (s, 1H), 10.41 (d, 2H), 10.92 (d, 2H), 11.19 (s, 1H), 11.30 (d, 1H), 11.50 (d, 1H), 11.61 (s, 1H), 11.70 (d, 1H). Anal. Calcd for $(C_{22}H_{15}NO_3)_n$: C, 77.41; H, 4.43; N, 4.10; O, 14.06. Found: C, 72.9; H, 4.3; N, 3.8.

Measurements. Inherent viscosity was measured using an Ubbelohde viscometer at a concentration of 0.5 g/dL in formic

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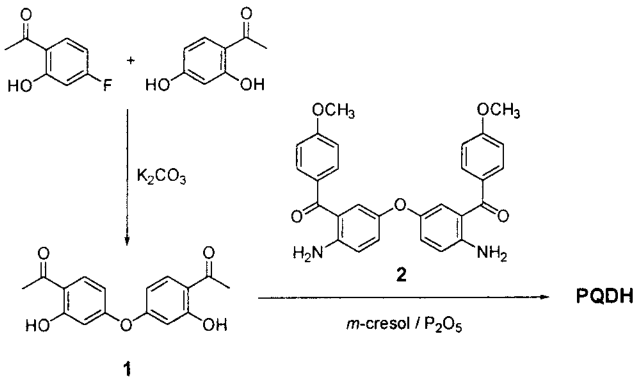
Scheme 1. Synthesis of Bis(ketomethylene) (1) and PQDH



acid at 30 °C. Thermal analysis was performed on Perkin-Elmer DSC7 at a rate of 20 °C/min. PQDH film was prepared onto glass substrate by spin-casting from the formic acid solution (3 wt %).

Absorption spectra were recorded on a HP 8452A diode array spectrophotometer. Emission spectra were obtained on a fluorescence spectrophotometer (Shimadzu, RF-5301PC). The transient transmission spectra were recorded by using a femtosecond Ti:sapphire laser system, the detailed procedure of which has been described in the literature.[17]

Results and Discussion

PQDH is hardly soluble in common organic solvents including chlorinated hydrocarbons and aprotic polar solvents such as tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide. Compared with the fair solubility of PQH in tetrachloroethane,[14] the poor solubility of PQDH is ascribable to the increased rigidity of polymer backbone caused by the double intramolecular hydrogen bonds in every repeating unit. In contrast to the insolubility in organic solvents, PQDH is highly soluble in acidic solvents like *m*-cresol containing a small amount of LiCl or formic acid, which is certainly assisted by acid–base complexation or protonation of quinoline moiety.[6]

The structural identification of PQDH was carried out by FT-IR, ^{1}H NMR, elementary analysis, and differential scanning calorimetry. The complete disappearance of carbonyl and primary amine bands in the FT-IR spectrum of PQDH confirmed the complete cyclization of quinoline ring, suggesting the formation of high molecular weight polymer. It was specifically noted that the hydroxyl group in PQDH which are responsible for ESIPT activity appeared as a very broad band extending from 2300 to 3700 cm^{-1} as a intramolecular hydrogen bond. In the ^{1}H NMR spectrum of PQDH in formic acid-d_2 solution, chemical shifts of all protons were significantly shifted to downfield, owing to the electron-deficient nature of quinoline ring by protonation. Quinoline ring in polymer was also identified by the ratio of integration and the splitting feature of NMR spectrum. In the elementary analysis, a lower value of carbon content by ca. 4% was observed, which is often observed for thermally stable aromatic polymers with high carbon content.[6] PQDH powder has a very high glass transition temperature of 280 °C, indicative of the backbone rigidity and thermal stability. PQDH solution in formic acid showed excellent film formability, and the inherent viscosity was measured to be 0.44 dL/g at 0.5 g/dL concentration.

Figure 1 shows the absorption and photoluminescence (PL) spectra of PQDH solution and spun film. PQDH is soluble in tetrachloroethane (TCE) in the 10^{-6} M range and gave solution absorption spectrum identical to that of PQH having the same chromophore unit.[14] The solution PL of PQDH in TCE is too weak to detect because of the limited concentration in TCE. It should be reminded, however, that the rather concentrated PQH solution in TCE gave dual emission from both enol and keto forms (400 and 590 nm, respectively).[14] As can be seen in Figure 1, PQDH film spun from formic acid solution exhibited characteristic ESIPT behavior, i.e., UV absorption (376 nm) and orange keto emission (590 nm) with large Stokes' shift. Despite the extremely high concentration of ESIPT chromophore, the keto emission of PQDH film is so strong as to be seen bright by the naked eye under room light. Similar to the case of PQH film, the complete absence of enol emission in the blue region suggests that the excited enol form (E*) in PQDH film decays mainly to the excited keto form (K*) by effective ESIPT rather than to the ground enol form (E) with normal emission. This happens probably because the torsional motion is virtually frozen in the film state so that the intramolecular hydrogen bond is energetically more favored than in solution.

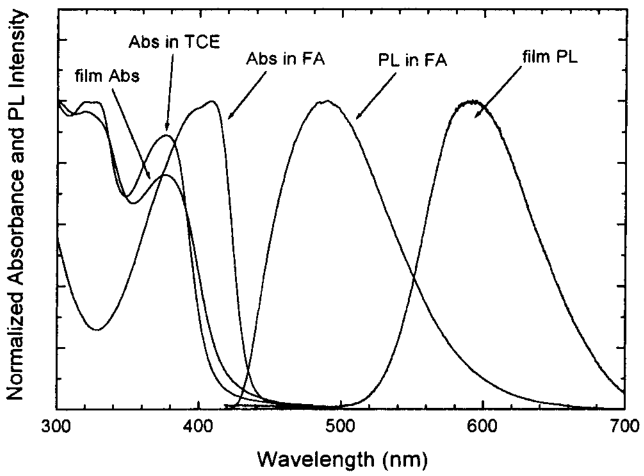


Figure 1. Absorption (Abs) and photoluminescence (PL) spectra of PQDH film and solution in tetrachloroethane (TCE) and formic acid (FA).

In the formic acid solution of PQDH, the absorption band was red-shifted by 32 nm relative to that in TCE, while PL was blue-shifted by 100 nm relative to the keto emission of the film (see Figure 1). The bathochromic shift of the absorption can be understood as the change of electronic properties by protonation, i.e., the increased electron acceptability of the quinoline ring. Compared with the enol emission of PQH solution at 400 nm, it can be concluded that the single band emission from the formic acid solution at 490 nm is the red-shifted one from the protonated enol form of PQDH. Importantly, the absence of keto emission means that ESIPT is inhibited in formic acid because the proton accepting site for ESIPT, i.e., quinoline nitrogen, is preblocked in the ground state by protonation. This fact is another clear evidence that the orange emission from the PQDH film is the keto emission by ESIPT. Interestingly, the protonated emission at 490 nm disappeared completely in the film spun from the formic acid solution. Easy removal of formic acid by fast evaporation during spin-casting indicates that the acid–base interaction between formic acid and quinoline would be of partial protonated or hydrogen-bonded character.

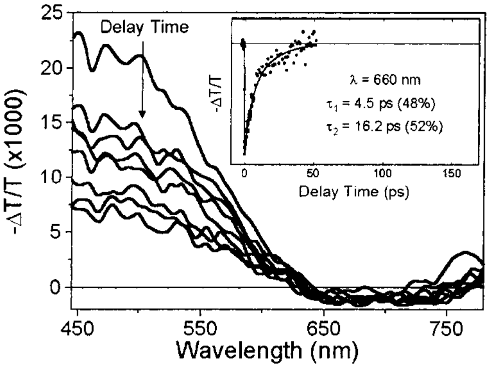


Figure 2. Photomodulation (PM) spectra of PQDH film after various delay times. The inset shows a temporal profile of 660 nm band in PM spectra.

Another important optical property of PQDH is optical gain in the transient photomodulation (PM) spectrum ($-\Delta T/T$) obtained by pump−probe measurement, where T is the probe transmission and ΔT is its transient modulation. PM spectra of the PQDH film after various delay times shown in Figure 2 have a negative band between 640 and 760 nm. This negative band can be assigned as optical gain by stimulated emission (SE), where the delayed probe beam stimulates the proton transferred K* into SE.[10,18−20] The temporal profile of the optical gain at 660 nm showed exponential decay with a fast time constant lower than 20 ps. Compared with the fluorescence lifetime of the keto emission from PQH film (∼300 ps),[14] the fast decay of the optical gain indicates the rapid depletion of the excited-state population by stimulated emission.[19,20] This finding strongly confirms that population inversion is easily achievable in the PQDH film due to the four-level nature of ESIPT.

Conclusions

A phototautomerizable semirigid polyquinoline (PQDH) with extremely high ESIPT chromophore content was synthesized and identified. Optical gain due to stimulated emission was observed by the femtosecond pump−probe measurement.

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