

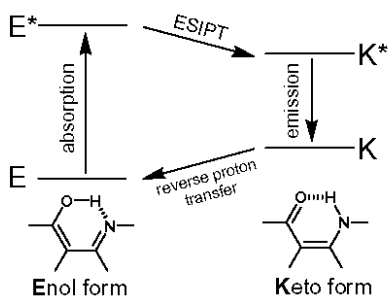
Excited-State Intramolecular Proton Transfer (ESIPT) Fluorescence in a Polymeric System

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Introduction

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. Fluorescence emission with suppressed self-absorption and the efficient stimulated emission are, therefore, inherent to the fluorescent ESIPT molecules, which render them useful as the luminescence probes, laser dyes, polymer photostabilizers, scintillators, and solar collectors (see Scheme 1).



Scheme 1. Schematic Representation of ESIPT Photocycle

To realize the practical devices made of ESIPT molecules, however, several issues like the prevalent concentration quenching and lower quantum efficiency of fluorescence emission have to be solved by the survey of novel and efficient ESIPT molecules. Recently, we have been working along this line to develop several new structures and ideas of fluorescent ESIPT molecules, polymers, and dendrimers, which will be summarized in this presentation [1-10]

Results and discussion

First, the quinoline-based novel ESIPT chromophore (MQ) was designed by using the semi-empirical molecular orbital (MO) calculation to diagnose the effective process in this particular class of molecules (Figure 1). [1]

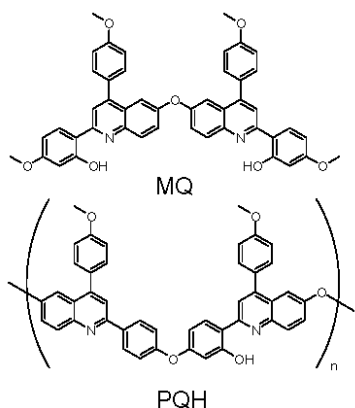


Figure 1. Structure of photo-tautomerizable quinoline dye (MQ) and semi-rigid polyquinoline (PQH) exhibiting ESIPT. [1]

MQ was successfully synthesized and characterized to show ESIPT fluorescence as well as the electroluminescence. The molecule was prepared by Friedländer reaction between bis-(aminoketone) and 2-hydroxy-4-methoxyacetophenone in the presence of *m*-cresol and P₂O₅ with high yields, which forms an extremely clear film by vacuum deposition.

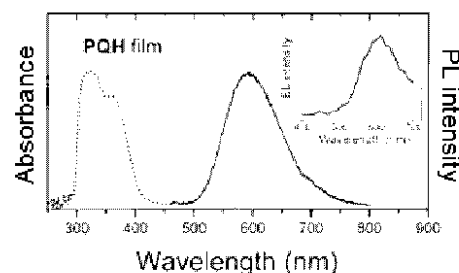


Figure 2. Absorption (dotted) and fluorescence (solid) spectra, excited at 310 nm, of PQH film. Inset: EL spectrum of a PQH single-layer device. [2]

Subsequently, polymers (PQH series) which incorporate quinoline based ESIPT chromophores as a structural element have been synthesized. [2,3] PQH's underwent ESIPT via a preexisting intramolecular hydrogen bond at ambient temperature and exhibited large Stokes-shifted (~250 nm) tautomeric fluorescence. The typical EL devices were fabricated to show the electroluminescence from PQH thin film (see the inset of Figure 2).

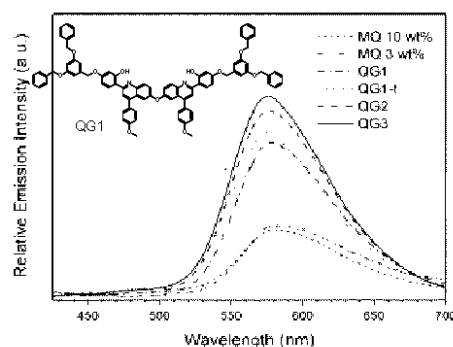


Figure 3. Structure of QG1 and relative emission intensities of QG_n films and MQ-polystyrene blend films (3, 10 wt %), each spectrum obtained by excitation at 370 nm. [4]

Poly(aryl ether) dendrimers of three different generations ($n=1,2,3$) cored with photo-tautomerizable quinoline (QG_n) were also synthesized and characterized to investigate the effect of dendritic architecture on the ESIPT activity [4]. It was found that the dendritic shells are able to decouple the core planarity from the molecular surroundings and to enhance ESIPT emission by the spatial isolation of ESIPT cores (Figure 3). It was specifically demonstrated that the ESIPT dendrimers are a new class of solid ESIPT medium with large content of active chromophores and efficient ESIPT emission.

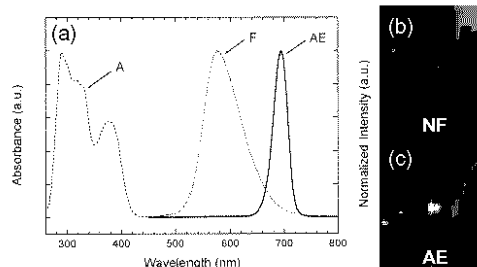


Figure 4. (a) Absorption (A), ordinary orange fluorescence (F), and amplified red emission (AE) spectra of QG2 spun film. [5]

Figure 4 shows the amplified spontaneous emission from the quinoline-based dendrimer film.[5] Nonresonant emission amplification from the film of a poly(aryl ether) dendrimer (QG2) was investigated by pico- and femtosecond spectroscopy. QG2 film was found to have optical net gain in the spectral region of proton-transfer emission due to easy population inversion by the four-level nature of ESIPT and ignorable absorption loss. It has been concluded that the emission amplification from the QG2 film is proton-transfer ASE by stimulated emission within gain medium.

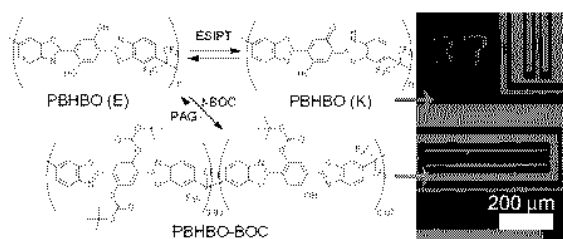


Figure 5. Schematic diagram of the excited-state intramolecular proton transfer (ESIPT) in PBHBO and *t*-BOC blocking/deblocking conversions. The photograph shows fluorescence micro-patterned films exhibiting excited-state intramolecular proton transfer (ESIPT)-fluorescence. The dark orange areas are the irradiated parts through the photomask. [8]

Stable fluorescence image recording using the H-bond-induced gated protonation of ES IPT molecules and polymers were investigated. [6,8] We have reported a novel method of fabrication and fluorescence patterning of high performance polybenzoxazole (PBHBO, Figure 5) films exhibiting excited-state intramolecular proton transfer (ESIPT)-fluorescence. Remarkable increase of solubility and accompanied fluorescence change was obtained by the *t*-BOC blocking of hydroxyl groups in PBHBO. In contrast to the insoluble rigid PBHBO, the *t*-BOC blocked polymer (PBHBO-BOC) was highly soluble in most organic solvents, enabling solution-state measurements and high-quality polymer film fabrication. Moreover, deblocking of *t*-BOC group from PBHBO-BOC and accompanied fluorescence modulation could be effected either by the acidic condition or by the heat treatment. Particularly, the chemical amplification resist (CAR) method was successfully employed for the dual color fluorescence photopatterning of PBHBO film. [8]

A simple and novel strategy for generating white luminescence from polymer thin film was demonstrated, which operates on the principle of limited energy transfer between different ES IPT dyes (see Figure 6). Due to this limited energy transfer, emissions from orange and bluish-green ES IPT dyes as well as from PVK (each representing red-green-blue) could be combined to generate white-light-electroluminescence. [10]

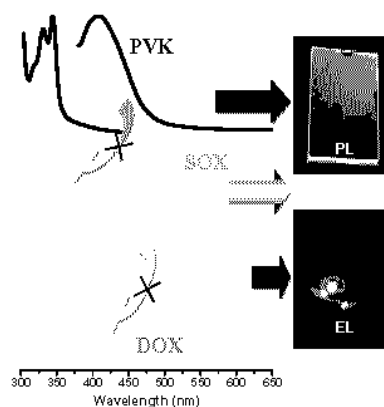


Figure 6. Absorption and emission spectra of PVK and green and orange emitting ES IPT molecules, and photograph showing the photoluminescence and electroluminescence from the dye-doped polymer film. [10]

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