

# Excited-State Intramolecular Proton Transfer and Related Optical Properties in a Polymeric Material System

Sehoon Kim, Soo Young Park

School of Materials Science and Engineering, Seoul National University, ENG 445, San 56-1, Shillim-dong, Kwanak-ku, Seoul 151-744, Korea

## Abstract

Synthesis and properties of novel excited-state intramolecular proton transfer (ESIPT) materials recently developed in our group are described. Highly efficient ESIPT in polymeric system has been investigated theoretically and experimentally with a semi-rigid polyquinoline (PQH, PQDH) possessing an intramolecular tautomerizable hydrogen bond. Poly(aryl ether) dendrimers of three different generations that are cored with phototautomerizable quinoline (QG<sub>n</sub>, n=1,2,3) were also synthesized and characterized to investigate the effect of dendritic architecture on the ESIPT activity. Stimulated emission and amplified spontaneous emission in these organic materials system are discussed in terms of ESIPT activity.

## 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. ESIPT materials are promising for luminescence probes, laser dyes, polymer photostabilizers, scintillators, and solar collectors. In this presentation, polymers(PQH and PQDH)

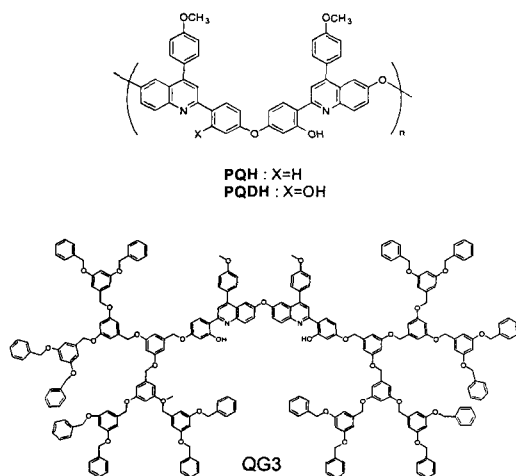
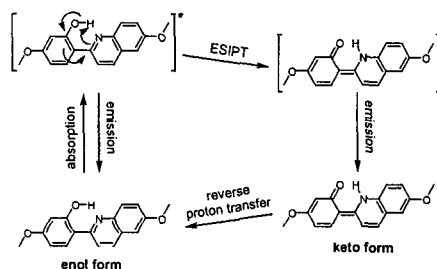


Chart 1. Cyclic four-level photophysical scheme of ESIPT chromophore



and dendrimers(QG<sub>n</sub>) that incorporate quinoline-based ESIPT chromophore as a structural element are described.

## Results

Chart 1 shows the four-level photophysical scheme of phototautomerizable quinoline chromophore. With a semi-rigid polyquinoline (PQH) possessing this chromophore, highly efficient ESIPT in polymeric system has been investigated theoretically and experimentally.<sup>1</sup>

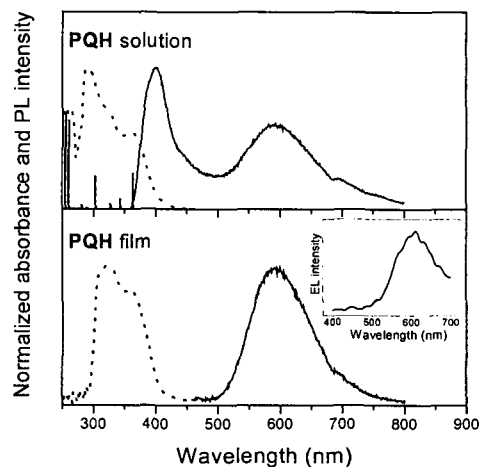


Figure 1. A bsorption (dotted) and fluorescence (solid) spectra, excited at 310 nm, of PQH in TCE solution (upper) and PQH film (lower). The inset is the EL spectrum of a PQH single layer device.

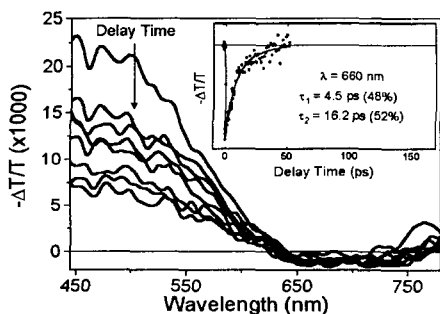


Figure 2. Photomodulation (PM) spectra of PQDH film after various delay times. The inset shows a temporal profile of 660 nm band in PM spectra.

PQH undergoes ESIPT via a preexisting intramolecular hydrogen bond at ambient temperature and exhibits large Stokes-shifted ( $\sim 250$  nm) tautomeric fluorescence (Figure 1).

Figure 2 shows optical gain (negative band) of PQDH film that was observed in the transient photomodulation (PM) spectrum ( $-\Delta T/T$ ) of PQDH film, obtained by pump-probe measurement using a femtosecond Ti:sapphire laser system, where  $T$  is the probe transmission and  $\Delta T$  is its transient modulation.<sup>2</sup> This finding clearly confirms that population inversion is easily achievable in the PQDH film due to the four-level nature of ESIPT.

Poly(aryl ether) dendrimers of three different generations ( $n=1,2,3$ ) that are cored with photo-tautomerizable quinoline (QGn) were also synthesized and characterized to investigate the effect of dendritic architecture on the ESIPT activity.<sup>3</sup> The second generation dendrimer (QG2) film showed nonresonant emission amplification, i.e., amplified spontaneous emission (ASE) by more effective stimulated emission.<sup>4</sup> Figure 3 shows typical ASE characteristics observed from the QG2 neat film.

### Conclusions

A novel quinoline-based ESIPT chromophore has been theoretically designed and incorporated into polymeric and dendritic systems. The neat films of the obtained ESIPT polymers and dendrimers were proven not to suffer from serious concentration quenching in spite of high concentration. From easily achievable stimulated emission and amplified spontaneous emission, it has been concluded that our ESIPT-active molecular materials are efficient gain media with high chromophore content, promising for proton transfer lasing application.

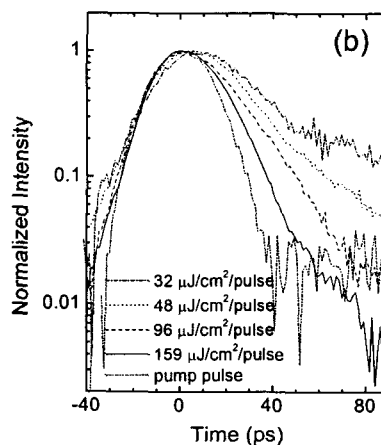
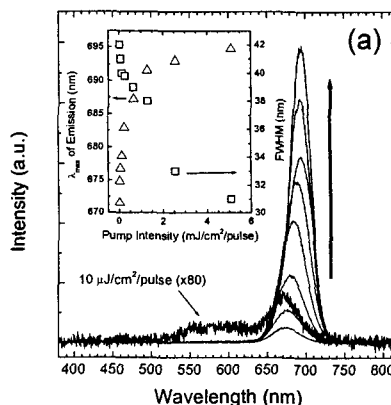


Figure 3. a) Emission spectra of QG2 spun film (480 nm thick). The excitation intensity increases from 10 to 5100  $\mu\text{J}/\text{cm}^2/\text{pulse}$  in the order indicated by the bold arrow. The inset shows the traces of  $\lambda_{\text{max}}$  and FWHM. b) Picosecond pump pulse and emission kinetics at various pump intensity.

### References

1. Dong Wook Chang, Sehoon Kim, Soo Young Park, Hyunung Yu, Du-Jeon Jang, *Macromolecules*, **33**, 7223, (2000).
2. Sehoon Kim, Dong Wook Chang, Soo Young Park, Sae Chae Jeung, Dongho Kim, *Macromolecules*, **35**, 6064, (2002).
3. Sehoon Kim, Dong Wook Chang, Soo Young Park, Hideki Kawai, Toshihiko Nagamura, *Macromolecules*, **35**, 2748, (2002).
4. Sehoon Kim, Soo Young Park, Iori Yoshida, Hideki Kawai, Toshihiko Nagamura, *J. Phys. Chem. Part B*, **106**, 9291, (2002).