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Photoluminescence Properties of Polyimides Having Fluorescent End-Groups Based on Excited State Intramolecular Proton Transfer

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Introduction

Excited-state energy transfer (ESIPT) is a physical process which exhibits: 1) Large Stokes shifts, 2) Easy population inversion, 3) Extremely fast kinetics ($K_{ESIPT} > 10^{12}$ S^{-1}) and can proceed even at low temperatures [1]. We have reported novel polyimides (PIs) having end-groups with ESIPT ability, in which efficient energy transfer occur from fluorescent main chain to ESIPT-active end groups [2]. On the other hand, bulky side group can reduce interchain interactions and self-quenching, which enhances photoluminescent ability [3]. In this work, a series of end-capped ESIPT PIs derived from 6FDA having bulky trifluoromethyl ($-CF_3$) groups were synthesized (**Fig. 1**), and their photoluminescent behaviors were investigated.

Experimental

All PI films were prepared by spin coating of the poly(amic acid) solution (15 wt% in DMAc) subsequent to thermal imidization at 210 ℃ under nitrogen. UV/vis absorption spectra, fluorescent excitation / emission spectra and relative photo-luminescent quantum yields of PI films were measured by a Hitachi U-3500 spectrophotometer, Hitachi F-4500 fluorescence spectrometer, and calibrated integrating sphere (HAMAMATSU C9920), respectively.

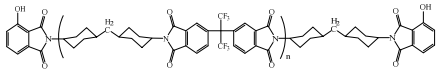

Fig. 1. Structure of 6FDA based PIs

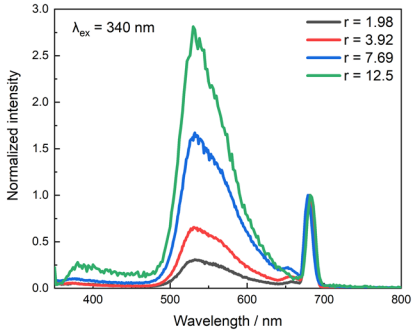

Fig. 2. Emission spectra of 6FDA based PIs. *r* corresponds to the end group fraction.

Results and Discussion

All the 6FDA based PIs (**Fig. 1**) showed ESIPT fluorescence at 530 nm by excitation at 340 nm, which originate from ESIPT end groups. Besides, the 6FDA based PIs exhibited relatively high quantum yields (Φs) as listed in Table 1 compared with ODPA based PIs whose Φs were less than 0.1, which is attributable to the looser aggregation structures owing to the bulky $-CF_3$ groups. Accordingly, introduction of bulky $-CF_3$ groups into the main chain of PI is an effective way to enhance the fluorescent properties, and 6FDA is a good candidate to prepare highly fluorescent copolyimides.

Table 1. End group fraction *r*, degree of polymerization *n*, and fluorescent quantum yield Φ of 6FDA based PIs.

r	*n*	Φ
1.98	100	0.14
3.92	50	0.25
7.69	25	0.22
12.5	15	0.21

References

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