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Photoluminescence Properties of Novel Fluorescent Polyimide based on Excited State Intramolecular Proton Transfer at the End Groups

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Introduction:

Polyimides (PIs) have attracted broad attention because of the excellent comprehensive performance. Among them, highly fluorescent PIs have been reported [1], which had a bright future to be used as wavelength down converters for solar cell and agriculture. However the Stokes shifts of traditional fluorescent PIs are still not large enough, we introduced 'excited-state intramolecular proton transfer (ESIPT)' structures into PIs [2-4]. Highly fluorescent PIs based on ODPA/DCHM/3HPA have been reported [2], in which 3HPA is ESIPT end-group which exhibits strong green fluorescence emission. In general, introduction of bulky side chains can improve fluorescent properties because of the suppression of aggregation induced quenching and intermolecular interactions. In this report, 6FDA was adopted, instead of ODPA, to prepare 6FDA/DCHM/3HPA ESIPT PIs (**Fig. 1**). Comparing with ODPA, 6FDA has two bulky trifluoromethyl groups which can contribute to the enhancement of fluorescence.

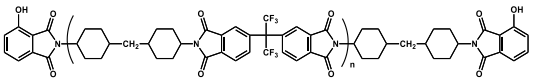

Fig. 1. Structure of 6FDA-based PIs.

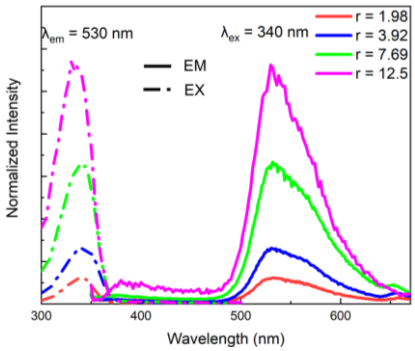

Fig. 2. Excitation/emission spectra of 6FDA-based PIs. *r* corresponds to the end group fraction.

Experiment:

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

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

Results and Discussion:

All the 6FDA-based PIs showed intense ESIPT fluorescence at 530 nm by excitation at 340 nm, which originates from the end groups (**Fig. 2**). In addition, the 6FDA-based PIs exhibited relatively high quantum yields (*Φ*s) (**Table 1**) without the main chain fluorescence as compared with the ODPA-based PIs of which the *Φ*s were smaller than 0.1.[2] This is attributable to the non-fluorescent nature of the 6FDA-based PIs and the looser aggregation structures owing to the bulky and less-polarizable $-CF_3$ groups. Accordingly, the introduction of bulky $-CF_3$ groups into the main chain of PIs is an effective way to enhance the fluorescence at the longer wavelength, and 6FDA is a good candidate to prepare colorless and highly fluorescent copolyimides.

Keywords: Polyimide, Fluorescence, ESIPT

References:

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