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Pressure-Induced Variations in Luminescence Properties of Polyimides with Fluorescent End-Group Displaying Excited-state Intramolecular Proton Transfer

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Introduction

Semi-aliphatic PIs having terminal groups exhibiting excited-state intramolecular proton transfer (ESIPT) have been attracted interests owing to their prominent fluorescence with large Stokes shifts[1]. The optical properties of polyimides (PIs) are significantly affected not only by the primary structures but also the aggregation structures. Recently, we have reported the pressure-induced variations of fluorescence property caused by reducing the inter-chain distances under high pressure[2]. In this study, the luminescence properties of PIs having terminal groups with ESIPT fluorescent ability were investigated under variable pressures.

Experimental

The structure of the end-capped semi-aliphatic PI, sBPDA/DCHM-3HPA, is shown in **Fig. 1**. Fluorescence and excitation spectra were measured with a spectrophotometer (HITACHI, F-7100) at atmospheric pressure. High pressures up to 2 GPa was applied to the PI films using a diamond anvil cell (DAC, Syntech Co. Ltd.).

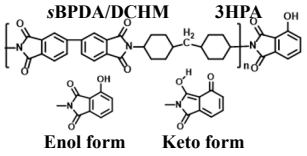

Fig. 1 Chemical structure of end-capped PI.

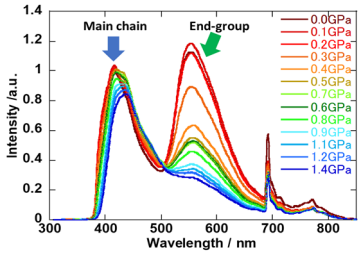

Fig. 2 Fluorescence spectra of *s*BPDA/DCHM-3HPA at elevated pressures.

Results and Discussion

Pressure-induced variations in the fluorescence spectra of *s*BPDA/DCHM-3HPA film by excitation at 365 nm are shown in **Fig. 2**. Fluorescence attributable to the main chain and the keto form of end-group are observed at 410 and 560 nm, respectively. The intensity of fluorescence emitted from the end-groups was significantly weakened than that from the main chain by applying pressures. As shown in **Fig. 3**, the excitation spectrum of *s*BPDA/DCHM is overlapped with the fluorescence peak of the enol form end-group, which suggests that Förster resonance energy transfer (FRET) occurred from the excited enol form to the main chain. In other words, the bathochromic shift of the excitation peak of the main chain enhanced the main chain fluorescence via FRET process at elevated pressure[2]. This result is beneficial to understand the photophysical process of end-capped PIs displaying ESIPT fluorescence.

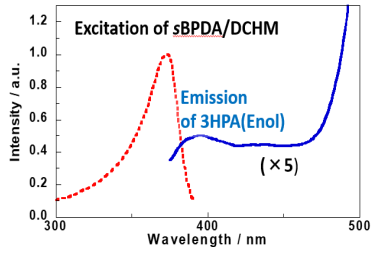

Fig. 3 Normalized excitation spectra of *s*BPDA/DCHM and emission spectra of 3HPA.

References

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[2] K. Takizawa, S. Ando et. al, *Macromolecules*, **44**, 49 (2011). *ibid*. **47**, 3951 (2014).