

Pressure-Induced Variations in Luminescence Properties of Polyimides having Fluorescent End-groups Exhibiting Excited-State Intramolecular Proton Transfer

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Introduction: Polyimides (PIs) are known as high-performance engineering plastics exhibiting high thermal and chemical stability, mechanical strength, and good flexibility. PIs having fluorescent end-groups exhibiting excited-state intramolecular proton transfer (ESIPT) ability have been attracted lots of interests owing to their prominent fluorescence with large Stokes shifts^[1]. On the other hands, the fluorescent properties of PIs significantly depend on not only the primary structures but also the aggregated state. Recently, we have reported that the intensity of main-chain fluorescence in PIs is decreased at high pressures due to the promotion of nonradiative deactivation caused by enhancement of intermolecular energy transfer^[2]. In this study, the correlation between the aggregated state and the fluorescent properties in PIs with end-groups exhibiting ESIPT fluorescence was examined on the base of photoluminescence spectroscopy under high pressure.

Experimental and methods: The chemical structures of end-capped PIs, sBPDA/DCHM-3HPA (sBPDC-3HPA) and 6FDC/ DCHM-3HPA (6FDC-3HPA), are shown in **Fig. 1**. To generate high pressure, PI films were loaded into a sample chamber of diamond anvil cell (DAC, Syntech Co. Ltd.) (**Fig. 2**). The ruby fluorescence technique was used to measure the pressure inside sample chamber. The photoluminescence spectra of the PI films at high pressures (from 0.1 MPa to 2.0 GPa) were measured by a multichannel CCD spectrometer (Hamamatsu Photonics), and a LED light ($\lambda_{\text{ex}} = 365 \text{ nm}$, Hamamatsu Photonics) was used as an excitation light source.

Results and discussions:

The intensity of the fluorescent peak observed at 550 nm, assignable to the end-groups of sBPDC-3HPA, significantly decreased with increasing the pressure. This is explainable by the enhancement of intermolecular energy transfer caused by decrease in the distance between the main-chain and end-groups (Fig.3(a)). On the other hand, the intensity of end-group fluorescence of 6FDC-3HPA observed at 550 nm obviously increased at elevated pressures (**Fig.3(b)**). In case of 6FDC-3HPA, the energy transfer between the main-chain and end-groups was suppressed because of the small optical absorbance of 6FDC. Therefore, the increase in fluorescence is attributable to the suppression of local molecular motion by the hydrostatic pressure. These results clearly indicate that the restraint of intermolecular energy transfer in PIs having fluorescent end-groups is a key factor for novel luminescent materials showing outstanding fluorescence properties even in densely aggregated states.

Reference:[1] K. Kanosue, S. Ando, et al., *Macromolecules*, 48, 1777 (2015). *ibid.* 49, 1848 (2016).

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

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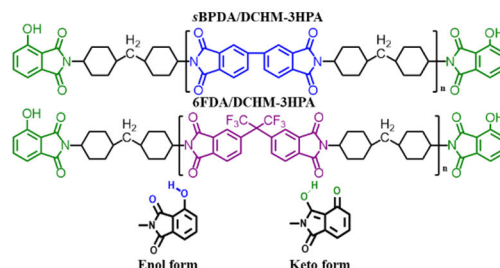


Fig. 1 Chemical structure of end-capped PIs.

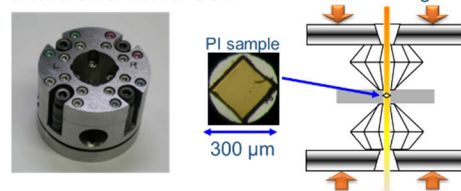


Fig. 2 Schematic illustration of DAC and its cross-section

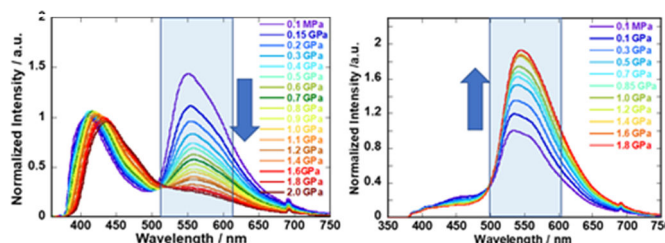


Fig. 3 Variations in emission spectra of (a) sBPDC-3HPA and (b) 6FDC-3HPA by applying pressure up to 2 GPa