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 molecular aggregated state. Recently, we reported that the intensity of main-chain fluorescence in PIs decreased at higher pressures due to enhanced nonradiative deactivations facilitated by intermolecular energy transfer[2]. In this study, correlation between the aggregated state and the fluorescent properties in PIs having end-groups displaying ESIPT fluorescence was examined based on emission spectra under high pressure.

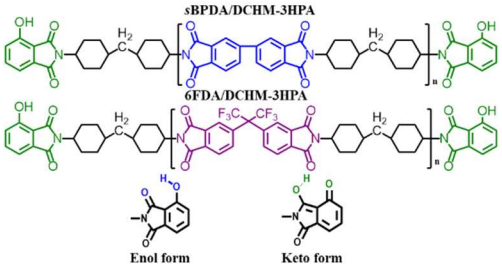

Fig. 1 Chemical structures of end-capped PIs.

Experimental & methods: The chemical structures of the target end-capped PIs, *s*BPDA/DCHM-3HPA (*s*BPDC-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 (λ_{ex} = 365 nm, Hamamatsu Photonics) was used as an excitation light source.

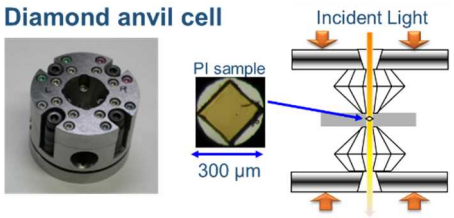

Fig. 2 Photo image of DAC and schematic illustration of the cross-section

Results and discussions: The intensity of the fluorescent peak observed at 550 nm, assignable to the keto form of the end-groups of *s*BPDC-3HPA, significantly decreased with increasing the pressure. This is explainable by the enhancement of intermolecular energy transfer accompanied by a decrease in the main-chain / end-groups distance. (**Fig.3(a)**). On the other hand, the intensity of end-group fluorescence of 6FDC-3HPA at 550 nm obviously increased at elevated pressures (**Fig.3(b)**). In this case, energy transfer between the main-chain and end-groups was suppressed because of the lower optical absorbance of 6FDC units. Thereby, the increase in fluorescence is attributable to the suppression of local molecular motion by pressure. These results clearly indicate that the restraint of intermolecular energy transfer in PIs having fluorescent end-groups is a key factor to develop novel luminescent materials which show outstanding fluorescence properties even in densely aggregated states.

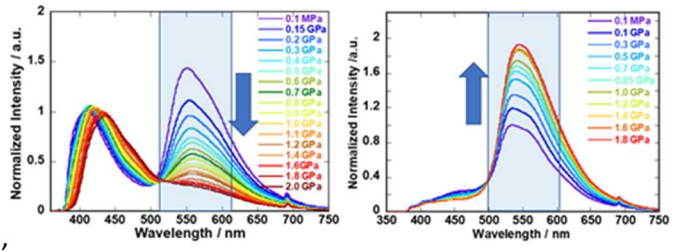

Fig. 3 Variations in emission spectra of (a) *s*BPDC-3HPA and (b) 6FDC-3HPA by applying pressure up to 2.0 GPa

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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