Pressure-Induced Variations in Luminescence Properties of Polyimides with Fluorescent End-Group having Excited-state Intramolecular Proton Transfer (ESIPT) Ability

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Polyimides (PIs) are known as high-performance engineering plastics exhibiting high thermal and chemical stability, mechanical strength, and good flexibility. Semi-aliphatic PIs having 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. The optical properties of PIs significantly depend on not only the primary structures but also the aggregation structures. Recently, we have reported fluorescence properties of the PIs were sensitive to pressure because the inter-chain distances can be significantly reduced under high pressure. In this study, we have investigated the luminescence properties of PIs having end-groups with ESIPT fluorescent ability, 3HPA, under variable pressures.

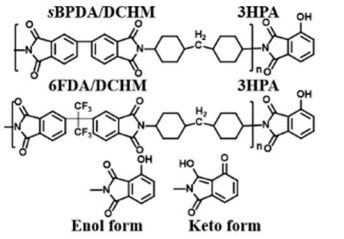

Fig. 1 Chemical structures of end-capped PIs.

The structure of end-capped semi-aliphatic PIs, *s*BPDA, /DCHM-3HPA (*s*BPDC-3HPA) and 6FDC/DCHM-3HPA (6FDC-3HPA) are shown in **Fig. 1**. Fluorescence spectra of these PI films up to 2 GPa were measured using a diamond anvil cell (DAC, Syntech Co. Ltd.) at each high pressure.

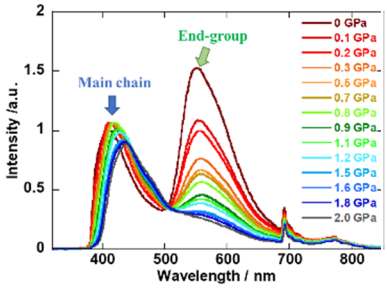

Fig. 2 Fluorescence spectra of *s*BPDA/DCHM-3HPA at each elevated pressure.

The intensity of ESIPT fluorescence derived from the keto form of the end-groups in *s*BPDC-3HPA (560 nm) was significantly decreased at elevated pressures up to 2 GPa (Fig. 2). This reduction is explainable by suppression of Förster resonance energy transfer (FRET) from the main chain to the end-groups. On the other hand, Fig. 3 shows an increase in the intensity of ESIPT fluorescence in 6FDC-3HPA at high pressures. In case of 6FDC-3HPA, the FRET process should not occur because the main chain exhibit LE ($n \rightarrow \pi^*$) transition ($S_0 \rightarrow S_1$) without fluorescence. Therefore, suppression of molecular motions under high pressure can be a reason for the increase in fluorescence intensity. In conclusion, we have revealed that the ESIPT fluorescence from the end-capped PIs can be enhanced under high pressure because of a suppression of the FRET process between the end-groups and main chain.

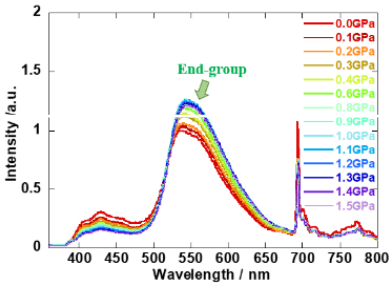

Fig. 3 Fluorescence spectra of 6FDA/DCHM-3HPA at elevated pressures.