Photophysical Mechanism of Prolonged Irradiation-induced Delayed Luminescence Observed for Luminescent Polyimides

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[Introduction] Long-lived luminescent (LL) materials exhibit persistent luminescence for several seconds to days after ceasing excitation, and they have been applied to bioimaging[1] and emergency signs[2]. In particular, pure organic LL materials have attracted significant attention due to their environmental friendliness, low cost, and facile synthesis. Phosphorescence (PH) has been studied as a candidate for LL due to its longer lifetime than fluorescence (FL)[3]. However, it is difficult to observe PH in air at room temperature because an excited triplet state (T_1) showing PH is easily quenched due to its long lifetime. Recently, we have reported that photoluminescent imide compounds (ICs) dispersed in polymethyl methacrylate (PMMA) film exhibit a curious LL under continuous UV irradiation, which is called prolonged irradiation-induced delayed luminescence (PIDL)[4]. During the first few minutes of induction time, ICs exhibit only FL without PH due to oxygen quenching (OQ) by the ground state oxygen ($^3O_2$). Simultaneously, $^3O_2$ is continuously excited to a singlet state ($^1O_2$), resulting in a gradual decrease in $^3O_2$. After the induction time, the PH process becomes dominant over the OQ process, and ICs start to exhibit PIDL with a long emission lifetime. However, ICs dispersed in PMMA film may have issues with long-term stability in terms of phase separation and dispersibility. Thus, the development of single-component polymers that exhibit PIDL is desired[5]. In this study, we focus on polyimides (PIs) with sequential imide groups in the main chain, and the mechanism of PIDL generation was investigated using PIs by controlling their compositions and surrounding environments.

[Experimental] Two types of PIs (S6-PI and SP-PI, **Fig. 1**) were prepared by copolymerization with three different dianhydrides (DBSA, 6FDA, and PMDA) and a diamine (DCHM). DBSA was used as an emitter, and 6FDA and PMDA were used to dilute the DBSA concentration to suppress non-radiative deactivation via excitation energy transfer. Poly(amic acid)s (PAAs), precursors of PIs, were synthesized in *N,N*-dimethylacetamide solution, in which the weight fraction of DBSA was set to 0.2 wt%. The PAAs spin-coated on silica substrates were thermally imidized at 220 °C to obtain PI films. The emission spectra, emission lifetime, and quantum yield of these films were measured.

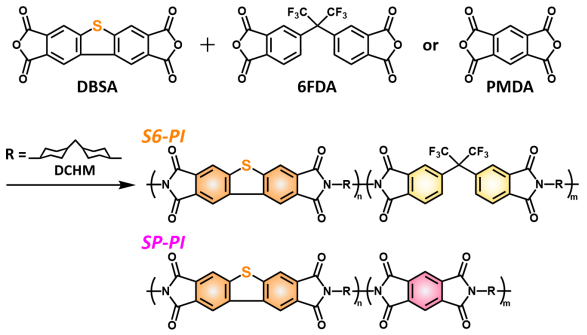

Fig. 1 Synthesis route of S6-PI and SP-PI.

[Results and Discussion] **Fig. 2** shows the emission spectra of S6-PI and SP-PI in air and under vacuum. In air, both PIs exhibited only FL without PH, suggesting that non-radiative deactivation from the T_1 state was significant. In contrast, under vacuum, S6-PI exhibited strong PH in addition to FL, whereas SP-PI showed weak PH. To clarify this difference, the rate constants of the following photophysical processes were evaluated from the luminescence quantum yield and the lifetime: OQ (= k_Q), non-radiative deactivation from T_1 state except for OQ (local molecular motion and excitation energy

transfer) (= k_{TS}), and intersystem crossing (ISC) (= k_{ISC}). The resulting respective rate constants for S6-PI were k_Q = 86900 s^{-1}, k_{TS} = 16.9 s^{-1}, k_{ISC} = 59.6 s^{-1}, and for SP-PI were k_Q = 107000 s^{-1}, k_{TS} = 29.0 s^{-1}, k_{ISC} = 13.9 s^{-1}. Since S6-PI has a similar order of k_Q to the IC dispersed in PMMA[4], it is suggested that the PH of S6-PI was quenched via active OQ in air but significantly increased by removing O_2 under vacuum. On the other hand, SP-PI showed only a weak PH under vacuum despite having a sufficiently large k_Q and small k_{TS} to exhibit PH. This is attributed to the fact that the k_{ISC} of SP-PI is much smaller than that of S6-PI. It has been reported that ISC is enhanced by intramolecular torsion[6]. In the case of SP-PI, copolymerization with rigid and planar PMDA promoted dense packing between dianhydrides, suppressing the torsion of DBSA and weaken the ISC. As a result, the triplet excitons were decreased, leading to the weak PH.

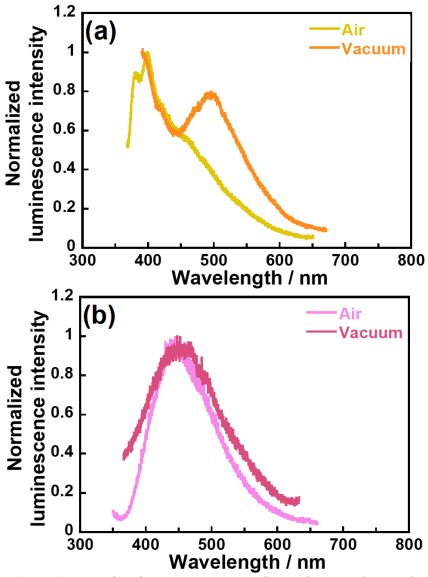

Fig. 2 Emission spectra in air and under vacuum for (a) S6-PI and (b) SP-PI. The excitation wavelength was 360 nm for S6-PI and 340 nm for SP-PI.

PIDL is a phenomenon in which a phosphor exhibits PH after a decrease in $^3O_2$, *i.e.*, under pseudo-vacuum condition. Since S6-PI showed strong PH under vacuum, it has the potential to exhibit PIDL. The time variation of emission spectra of S6-PI was measured during continuous UV irradiation in air. Each spectrum was decomposed into FL and PIDL spectra, and the time evolution of the area ratio of PIDL was plotted against time (**Fig. 3(a, b)**). S6-PI did not show PIDL, suggesting a high O_2 permeability. Therefore, the top surface of S6-PI film was covered with poly(vinyl alcohol) as O_2 barrier to prevent the permeation of O_2. Consequently, S6-PI exhibited PIDL after 13.2 min of induction time (**Fig. 3(b)**), which is the first time observation of the PIDL in PIs. This indicate that the permeation of O_2 is to be suppressed for generation of PIDL in PIs.

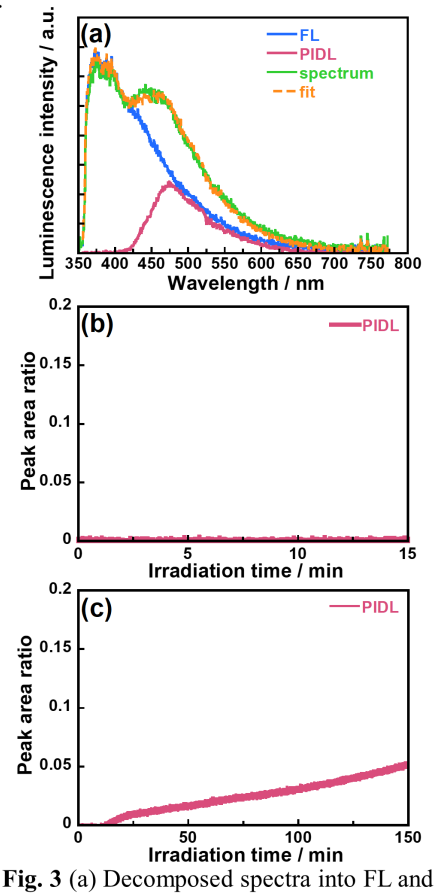

Fig. 3 (a) Decomposed spectra into FL and PIDL components. Time evolution of area ratio of PIDL for S6-PI (b) without and (c) with O_2 barrier film.

These results suggest that, in order to develop PIs that exhibit PIDL, it is important to have a large rate constant of intersystem crossing to produce a large number of triplet excitons and a low O_2 permeability in the thin film.

[1] Y. Qin, *et al.*, *Chem. Eng. J.* **2024**, *487*, 150424. [2] P. Li, *et al.*, *Laser Photonics Rev.* **2024**, *18*, 2300751. [3] T.-F. Yi, *et al.*, *Coord. Chem. Rev.* **2024**, *516*, 215987. [4] M. Doi, R. Ishige, S. Ando, *ChemPhotoChem*. **2023**, *7*, e202200310. [5] W. Huang, *et al.*, *J. Am. Chem. Soc.* **2023**, *145*, 7343. [6] H. Fu, *et al.*, *J. Phys. Chem. Lett.* **2010**, *1*, 2499.