

Prolonged Irradiation-induced Delayed Luminescence of Imide Compounds Dispersed in Polymer Matrix and its Relation to Oxygen Quenching

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[Introduction] Long-lived luminescent (LL) materials exhibit persistent luminescence for several seconds to days after ceasing the external stimuli such as stress or photo-irradiation, and they have been applied to bioimaging and emergency signs [1,2]. Most of them used in commercial applications are inorganic crystals containing rare metals and produced by high-temperature processes [3]. Thus, pure organic LL materials have attracted significant attention owing to their green processes, low cost, and facile film formation. Phosphorescence (PH) has been studied to develop organic LL materials due to its long luminescence lifetime of 10^{-6} –10 s [4]. However, in general, PH is rarely observed at room temperature in air because it is easily deactivated by local motions, *i.e.* molecular vibration, and triplet energy transfer to atmospheric oxygen [5]. Recently, we have reported that imide compounds (ICs) dispersed in a polymer matrix exhibit long-lived prolonged UV irradiation-induced delayed luminescence (PIDL) [6]. In this study, the photophysical mechanism of the PIDL is clarified based on the time-dependent emission spectra of the ICs observed during UV irradiation.

[Experimental] The ICs having naphthalic (NT-IC [7]), biphenyl (*s*BP-IC), and oxydiphthalic (OD-IC) cores (**Fig. 1**) were synthesized. These ICs were dispersed in poly(methyl methacrylate) (PMMA), in which the weight fractions were set to 0.2 wt%. The emission spectra of these films were measured during UV irradiation. The excitation wavelength of NT-IC was set to 365 nm, and those of *s*BP-IC and OD-IC were 340 nm.

[Results and Discussion] *s*BP-IC-dispersed PMMA film exhibited only fluorescence (FL) at 384 nm after UV irradiation for a few seconds (**Fig. 2(a)**). However, it exhibited a new emission peak at 510 nm after a continuous UV irradiation for several minutes, and its intensity gradually increased with the irradiation time. This new emission is called PIDL and attributable to PH because its spectral features (wavelength range and shape) are very close to the PH observed under vacuum. To investigate the increasing process of PIDL, the emission spectra were decomposed into FL and PIDL spectra, and the variations in peak areas of them were plotted against the irradiation time (**Fig. 2(b)**). Interestingly, an induction time (t_{ID}) of 1.60 min was observed, during which only FL is observed prior to the appearance of PIDL. NT-IC and OD-IC also exhibited similar PIDL behavior.

Since the excited triplet states (T_1) exhibiting PIDL are sensitive to atmospheric oxygen, the t_{ID} s of NT-IC, *s*BP-IC, and OD-IC were

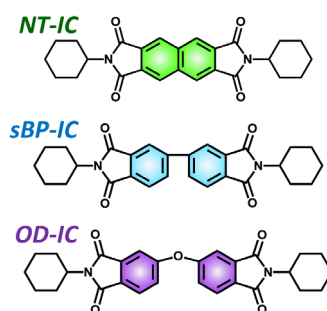


Fig. 1 Chemical structures of ICs.

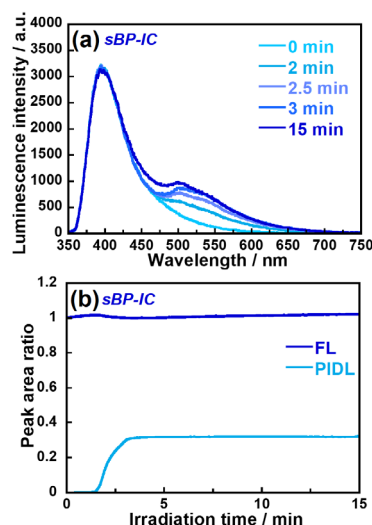


Fig. 2 (a) Various emission spectra and (b) time evolution of emission peak areas during UV irradiation in air for *s*BP-IC.

measured at various oxygen concentrations ($[O_2]$) around the films (**Fig. 3**). The t_{ID} s linearly increase with the increase in $[O_2]$, which strongly suggests that t_{ID} reflects the existence of oxygen.

Based on these results, the following photophysical mechanism of PIDL generation was proposed. (a) During t_{ID} , the PH of IC is quenched by energy transfer, *i.e.* oxygen quenching (OQ), from the T_1 state of IC to the ground state triplet molecular oxygen (3O_2). Simultaneously, 3O_2 is excited to singlet oxygen (1O_2). Then, although some 1O_2 is deactivated to 3O_2 , 1O_2 slowly accumulates in the excited state or is consumed *via* photodegradation of PMMA, resulting in a decrease in 3O_2 . (b) After t_{ID} , the PH process becomes dominant over the OQ process, and then ICs exhibit PIDL.

A PMMA-dispersed *s*BP-IC film was set in a fused silica test tube and purged with oxygen. Its emission spectra were measured during UV irradiation at 100 and 200 K (**Fig. 5**). At 100 K, *s*BP-IC exhibited PH immediately after the start of irradiation, and its intensity increased within several seconds. This is because the diffusion of oxygen in PMMA is suppressed and the collisions between oxygen and ICs rarely occur, resulting in the suppression of OQ. In contrast, only FL was observed at 200 K without any PH, indicating that OQ process is more dominant than PH. Moreover, no PIDL was observed even after 15 min of UV irradiation, in which sufficient 3O_2 was continuously supplied from outside of the film *via* diffusion in PMMA because the test tube was filled with oxygen. Even though a part of 3O_2 was excited by triplet ICs, OQ process is still dominant over the appearance of PH. These results suggest that oxygen diffusion is closely related to the local molecular motion of PMMA whose β' relaxation was reported to start at ~ 205 K [8].

[References]

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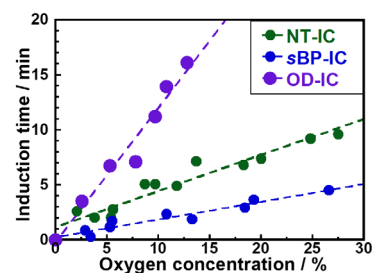


Fig. 3 Oxygen concentration dependences of induction time of NT-IC, *s*BP-IC, and OD-IC.

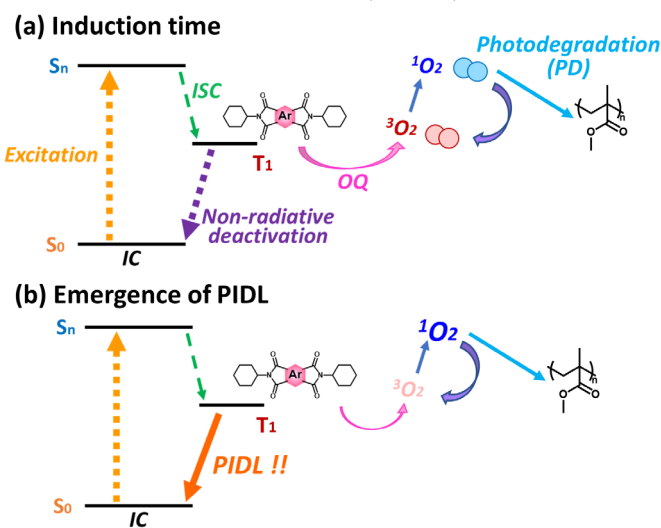


Fig. 4 Proposed photophysical mechanism of PIDL.

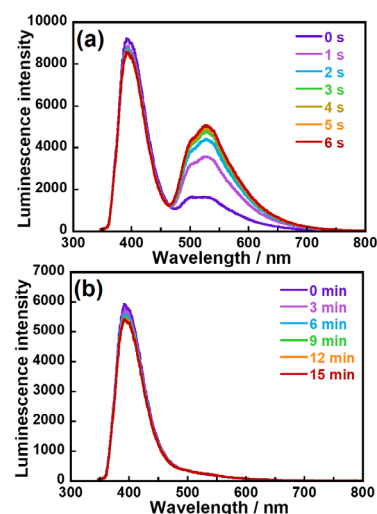


Fig. 5 Emission spectra for *s*BP-IC in an oxygen atmosphere during UV irradiation at (a) 100 and (b) 200 K.