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

***Marina DOI,* Ryohei ISHIGE, Shinji ANDO**

Department of Chemical Science and Engineering, Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo, 152-8552, Japan
doi.m.aj@m.titech.ac.jp

Introduction

Long-lived luminescent (LL) materials exhibit persisting luminescence for several seconds to days after ceasing 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 easy 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 polymer matrices exhibit long-lived prolonged UV irradiation-induced delayed luminescence (PIDL) [6]. In this study, the photophysical mechanism of the PIDL was clarified based on the emission spectra of the ICs observed during UV irradiation.

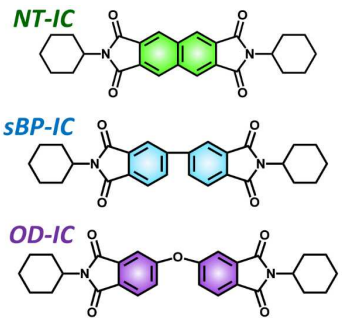

Fig. 1 Chemical structures of ICs.

Experimental

The ICs having naphthalic (NT-IC [7]), biphenyl (*s*BP-IC), and oxydiphthalic (OD-IC) cores (**Fig. 1**) were synthesized. The ICs were dispersed in poly(methyl methacrylate) (PMMA) films, and the weight fractions of NT-IC and OD-IC were set to 0.2 wt%, and those of *s*BP-IC were 0.2, 0.5, 1.0, 2.5, and 4.0 wt%. The emission spectra of these films during UV irradiation were measured. The excitation wavelength of NT-IC was 365 nm, and those of *s*BP-IC and OD-IC were 340 nm.

Results & Discussion

*s*BP-IC dispersed in PMMA at 0.2 wt% exhibited only fluorescence (FL) at 384 nm after UV irradiation for a few seconds (**Fig. 2(a)**). Meanwhile, it exhibited a new emission peak at 510 nm in addition to the FL after several minutes of continuous UV irradiation. This emission, called PIDL, is attributable to PH because its spectral features (wavelength range and shape) are very close to the PH observed under

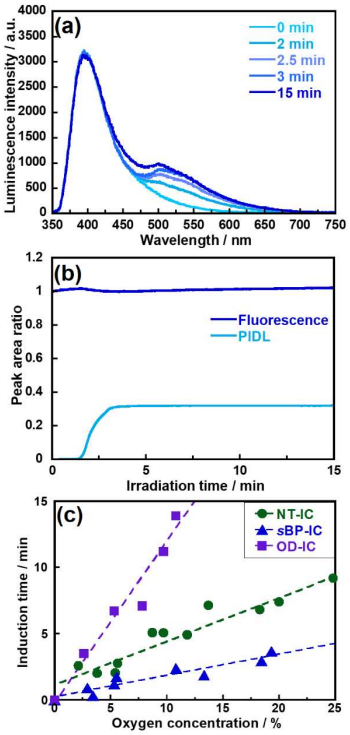

Fig. 2 (a) Time evolution of emission spectra, and (b) peak area ratio of the peaks during UV irradiation of *s*BP-IC. (c) t_{ID} with various oxygen concentration of ICs.

vacuum. The variations in peak areas of FL and PIDL during UV irradiation of *s*BP-IC indicate that there is an induction time (t_{ID}) for 1.60 min, in which only FL is observed, before the appearance of PIDL (**Fig. 2(b)**). NT-IC and OD-IC also exhibited similar PIDL properties. When the oxygen concentration ($[O_2]$) around the sample films was varied from 0 to 27 %, t_{ID} of NT-IC, *s*BP-IC, and OD-IC increased linearly with the increase in $[O_2]$ (**Fig. 2(c)**), which suggests that the PIDL is sensitive to $[O_2]$.

Fig. 3 shows a proposed photophysical mechanism of PIDL. (a) During t_{ID}, the PH of IC is suppressed by energy transfer, *i.e.* oxygen quenching (OQ), from the excited triplet state (T_1) of IC to the ground state triplet molecular oxygen ($^3O_2$). Simultaneously, $^3O_2$ is excited to singlet oxygen ($^1O_2$). Then, although $^1O_2$ 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.

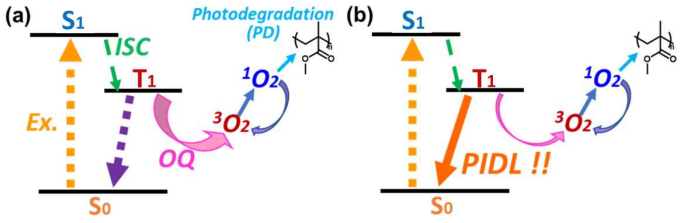

Fig. 3 Photophysical processes of the emissions via T_1 with (a) short-time and (b) long-time UV irradiation.

Fig. 4(a,b) shows the schemes inside the film with different concentrations of *s*BP-IC ([IC] = 0.2–4.0 wt%). It can be hypothesized that when all $^3O_2$ within the sphere centered on IC of radius *X*, *i.e.* excitation range (R_E), is excited to $^1O_2$ by ICs in the T_1 state, OQ should be sufficiently suppressed, and then the ICs can exhibit PIDL. Thereby, (a) if ICs are dispersed in PMMA at a low [IC], the ICs would exhibit PIDL after all $^3O_2$ within R_E is excited to $^1O_2$. (b) If ICs are dispersed at a high [IC], the distances between the ICs can be shorter than *X*, and most of the R_Es are overlapped. Thus, $^3O_2$ is excited faster than in (a), and t_{ID} should be shortened. **Fig. 4(c)** shows the experimental result of t_{ID} with various [IC] of *s*BP-IC, in which the t_{ID} decreased with an increase in [IC]. This clearly indicates that within the [IC] range of 0.2–4.0 wt%, the R_Es of ICs are overlapped, and the ICs exhibited PIDL after all $^3O_2$ in the film was excited to $^1O_2$.

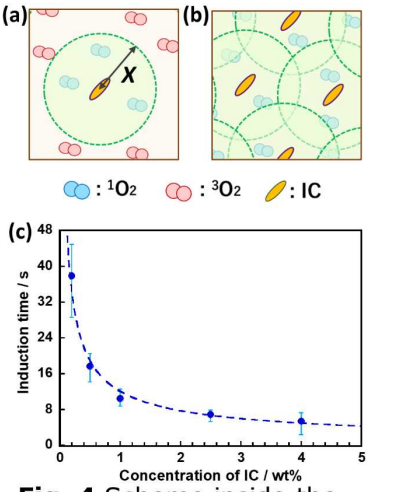

Fig. 4 Scheme inside the films at (a) low and (b) high [IC]. (c) t_{ID} with various [IC].

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