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Analysis of Prolonged Irradiation-induced Delayed Luminescence of Imide Compounds Dispersed in Polymer Matrices

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[Introduction] Long-lived luminescent materials exhibit persisting luminescence for several seconds to days after ceasing external photo-irradiation and are applied to bioimaging and emergency signs [1,2]. Most of them in practical use are inorganic materials requiring rare metals and high temperature processes [3]. Recently, pure organic long-lived luminescent materials have attracted significant attention owing to their good processability and non-toxicity. Phosphorescence (PH) has been studied to develop long-lived luminescence based on organic materials [4]. However, in general, PH is rarely observed at room temperature in air because it is easily deactivated by molecular motion and energy transfer to oxygen. We found that fluorescent imide compounds (ICs) exhibit long-lived prolonged UV irradiation-induced delayed luminescence (PIDL) and clarified the physical mechanism.

[Experimental] The ICs having naphthalic (NT-IC [5]), biphenyl (*s*BP-IC), and oxydiphthalic cores (OD-IC) (**Fig. 1**) were synthesized and dispersed in poly(methyl methacrylate) (PMMA) at 0.2 wt%. Absorption and emission spectra during UV irradiation were measured.

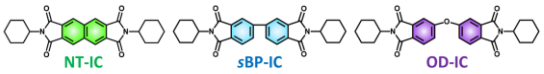

Fig. 1 Chemical structures of ICs.

[Results & Discussion] Fig. 2 shows the emission spectra and variations in the peak area of fluorescence (FL) and PIDL during UV irradiation of *s*BP-IC, in which only FL is observed at 400 nm during UV irradiation for a few minutes (*i.e.* induction time, τ_{ID}), but PIDL peak newly emerged at 510 nm after τ_{ID} and increased with time. This PIDL is attributable to long-lived PH from the excited triplet state (T_1) because the peak position of PIDL was the same as that of PH (510 nm) at 77 K. NT-IC and OD-IC exhibited similar PIDLs to *s*BP-IC. **Fig. 3 (a)** shows the oxygen concentration dependence of τ_{ID} for each film. The τ_{ID}s of ICs linearly increased with increase of oxygen concentration, suggesting that oxygen quenching (OQ) should be closely related to the PIDL [6]. The photophysical processes are explainable as follows (**Fig. 4**): During UV irradiation, (i) a part of the excited singlet ^{1}IC is converted to the triplet ^{3}IC via intersystem crossing, (ii) the energy of ^{3}IC is transferred to triplet $^3O_2$ (ground state) around the IC, and then $^3O_2$ is excited to the singlet $^1O_2$ accompanied with the deactivation of ^{3}IC, (iii) thus, the decrease in $^3O_2$ around ICs lowers the probability of OQ, and ^{3}ICs start to exhibit PIDL after a certain time of τ_{ID}. The characteristic absorbance of $^1O_2$ detector (DPBF) around 418 nm (A_{DP}) decreases when it is decomposed by UV light or $^1O_2$. The A_{DP} of a film containing DPBF+*s*BP-IC significantly decreased under UV irradiation compared with the one containing only DPBF, and the photo-degradation of DPBF was suppressed by addition of $^1O_2$ quencher (β-carotene) (**Fig. 3(b)**). These facts clearly indicate that $^1O_2$ is generated by UV-irradiation of ICs, and the PH of ICs, competing with OQ, causes long-lived PIDL after the duration of certain τ_{ID}s.

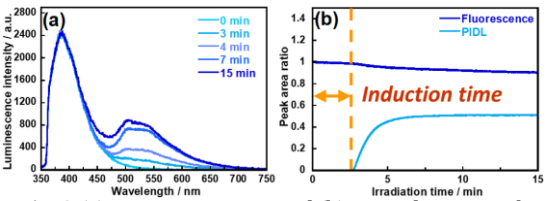

Fig. 2 (a) Emission spectra and (b) FL and PIDL peak areas change during UV irradiation of *s*BP-IC.

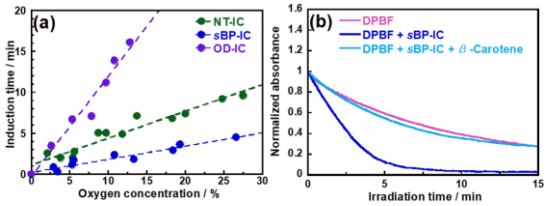

Fig. 3 (a) Induction time depending on oxygen concentration of ICs and (b) time evolution of absorbance of DPBF during UV irradiation.

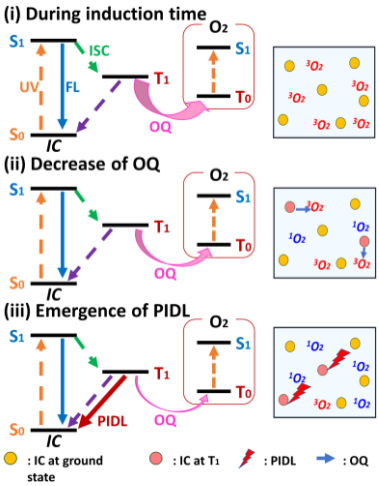

Fig. 4 Scheme of PIDL mechanism.

Reference: [1] J. Mei, et al., *ACS Appl. Mater. Interfaces*, **10**, 12217–12261 (2018). [2] Y. Li, et al., *Chem. Soc. Rev.*, **45**, 2090–2136 (2016). [3] J. Botterman, et al., *Opt. Express*, **23**, A868–A881 (2015). [4] K. Kanosue, et al., *ACS Macro Lett.*, **5**, 1301 (2016). [5] M. Doi, et al., *J. Photopolym. Sci. and Tech.*, **34**, 423 (2021). [6] M. Louis, et al., *Adv. Mater.*, **31**, 1807887 (2019).