

Comparison of optical properties of imide compounds containing sulfur and pentacyclic cores dispersed in PMMA under continuous UV irradiation.

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[Introduction] Phosphorescent (PH) materials have been expected to be used for bioimaging, luminous materials, and solar spectrum converters due to their longer emission wavelength and longer lifetime than fluorescence (FL) [1]. However, PH is rarely observed at room temperature in air because it is easily deactivated by local molecular motions, and oxygen quenching (OQ) which is an energy transfer from the excited triplet state (T_1) of phosphor to the ground state of triplet oxygen (3O_2) [2]. Recently, we have reported that imide compounds (ICs) dispersed in polymer matrix exhibit Prolonged Irradiation-induced Delayed Luminescence (PIDL) by continuous UV irradiation with the following mechanism [3]. At the start of irradiation, ICs do not exhibit PH due to OQ. During the first few minutes of irradiation, *i.e.* induction time (t_{ID}), the amount of 3O_2 gradually decreases *via* excitation and a decrease in OQ efficiency. After t_{ID} , ICs can exhibit PIDL because the PH process becomes dominant over the OQ. In this study, the PIDL properties of four types of ICs (**Fig. 1**) are compared to investigate the relationship between the chemical structure and OQ process.

[Experimental] Four types of ICs having ether (ODPA-IC), thioether (SDPA-IC), furan (DBOA-IC), and thiophene (DBSA-IC) cores were dispersed in PMMA at 0.2 wt%. The emission spectra were continuously measured during UV irradiation.

[Results and discussion] The IC-dispersed PMMA films exhibited only FL at around 400 nm at the start of irradiation (**Fig. 2**). Subsequently, they exhibited PIDL peaks at around 480 nm. Comparing ODPA-IC with SDPA-IC and DBOA-IC with DBSA-IC, the PIDL intensities increased due to the heavy atom effect of sulfur [3]. To investigate the t_{ID} , the emission spectra were decomposed into FL and PIDL spectra, and variations in the peak areas were plotted against the irradiation time (**Fig. 3**). The shortest t_{ID} of DBSA-IC is attributable to the largest rate of intersystem crossing which produces the largest number of ICs in the T_1 state, resulting in the enhancement of the excitation of 3O_2 *via* OQ. These results indicate that strong PIDL and short t_{ID} can be obtained by molecular design that increase the amount of T_1 generated.

References: [1] K. Kanosue, S. Ando, *ACS Macro Lett.*, **2016**, 5, 1301. [2] S. Hirata, *Adv. Opt. Mater.*, **2017**, 5, 1700116. [3] M. Doi, R. Ishige, S. Ando, *ChemPhotoChem*, **2023**, 7, e202200310. [4] K. Kanosue, S. Ando, *et. al.*, *Mater. Chem. Front.*, **2019**, 3, 39–49.

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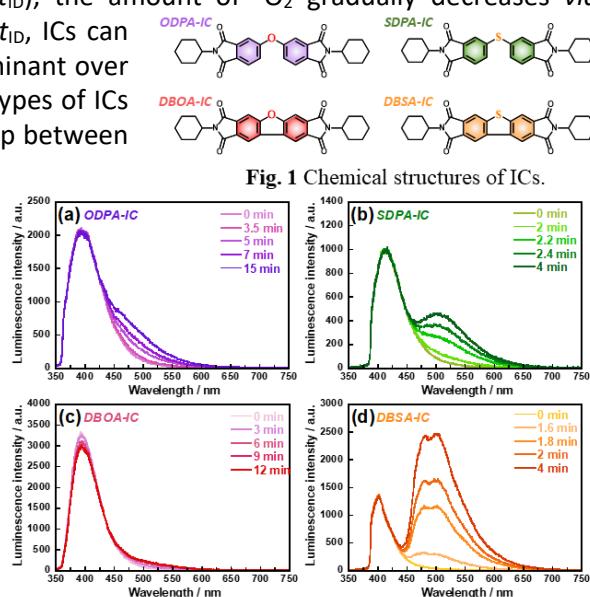


Fig. 1 Chemical structures of ICs.

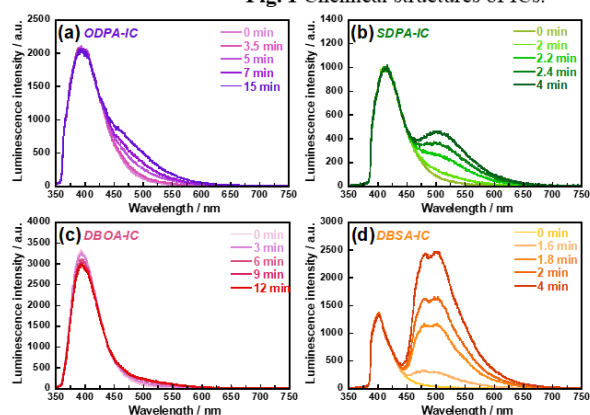


Fig. 2 Variation of emission spectra of ICs during UV irradiation. The excitation wavelengths were 340 nm for ODPA-IC and DBOA-IC and 365 nm for SDPA-IC and DBSA-IC.

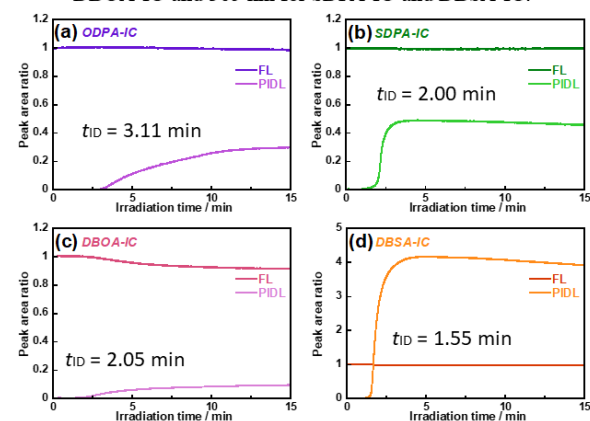


Fig. 3 Time evolution of peak area ratio of FL and PIDL spectra of ICs during UV irradiation.