Delayed Luminescence Properties of Imide Compounds having Naphthalene, Biphenyl and Oxydiphthalic Core Structures.

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I. Introduction

The long-lived luminescent (LL) materials have been applied to bioimaging and emergency signs, and most of them practically and currently used are inorganic materials [1]. Recently, metal-free organic LL materials synthesized facilely with low costs are demanded because the inorganic LL materials require the use of rare metals, high temperature processing, and high costs. Thermally activated delayed fluorescence (TADF) [2] and phosphorescence (Ph) [3] of organic LL have long life times because they are mediated by the excited triplet (T*) state but easily deactivated through local molecular motions and atmospheric oxygen. Hence, it is generally difficult to achieve LL of organic materials at room temperature and in air, even though there is high demand to apply organic LL in the atmospheric condition. Recently, we have found that imide compounds (MCs) containing naphthalene, biphenyl, and oxydiphthalic core structures exhibit long-lived delayed luminescence (DL) when they are dispersed in poly(methyl methacrylate) (PMMA) films. In this study, we investigated the DL properties of MCs to clarify the photophysical mechanism.

II. Experimental

We synthesized imide compounds (NT-MC, *s*BP-MC and OD-MC) having a 2,3,6,7-naphthalene structure (NT), 4,4′,5,5′-biphenyl structure (*s*BP), and 4,4′-oxydiphthlic structure (OD) (**Fig. 1**). The MCs were homogeneously dispersed in PMMA films at a concentration of 0.2 wt%.

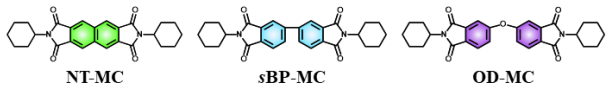

Fig. 1 Chemical structures of MCs.

III. Results and Discussion

Fig. 2 shows the emission spectrum and emission decay curve of *s*BP-MC as an example. The spectra of NT-MC, *s*BP-MC and OD-MC show only fluorescence peaks around 400 nm during UV irradiation for less than 1 min. After a few minutes of irradiation, new emission peaks appeared around 500, 510, and 480 nm, respectively, and the intensity of these peaks increased with the irradiation time. The new peaks are attributable to Ph emissions from T* state because the wavelengths of them are matched with their Ph observed at lower temperatures (77 K) of each sample. After UV irradiation for 15 min, it was turned off, and then the new emission peaks of MCs decayed exponentially with the DL lifetime (<τ>) of 1.16, 0.84, and 0.33 s, respectively. The decay curves were fitted by $I(t) = A\cdot\exp(-\tau/t)$ to estimate <τ>. **Fig. 3** shows a scheme of the luminescence mechanism of the DL of MCs. MCs exhibit weak Ph within a short period of UV irradiation, because of a) the low efficiency of intersystem crossing (ISC) due to the large energy gap between the excited singlet (S*) and T* states and b) the quenching processes by oxygen in air. When UV is irradiated for a long time, excitons diffuse to the T* state via ISC, and MCs exhibited long-lived DLs due to the weakening of quenching process in parallel with the consumption of dissolved oxygen. In conclusion, it was found that NT-, *s*BP-, and OD-MCs dispersed in PMMA exhibit long-lived DL based on Ph emission at room temperature in air, which can contribute to the development of practical LL organic materials.

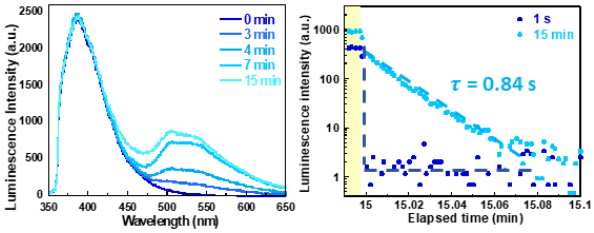

Fig. 2 Emission spectra with various elapsed times from start of UV irradiation (left) and emission decay curve (right) of *s*BP-MC (λ_{ex} = 340 nm) after 1 s and 15 min irradiation.

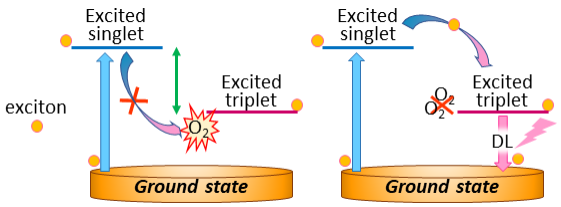

Fig. 3 Scheme of DL mechanism (left: short-time irradiation, right: long-time irradiation).

References

[1] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, *J. Electrochem. Soc.*, 143, 2670, 1996.
[2] W. Li, Z. Li, C. Si, M.Y. Wong, K. Jinnai, A.K. Gupta, R. Kabe, C. Adachi, W. Huang, E. Zysman-Colmn, I.D.W. Samuel, *Adv. Mater.*, 32, 2003911, 2020.
[3] K. Kanosue, S. Ando, *ACS Macro Lett*, 5, 1301, 2016.