Diffusion Behavior of Gas Molecules Monitored by the Phosphorescence Processes of Imide Compound Dispersed in Polymer Matrix at Lower Temperatures

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[Introduction] Phosphorescent (PH) materials have been expected to be applied to bioimaging, spectrum converter, and so on due to their longer emission wavelength and lifetime than fluorescence (FL) [1]. However, PH is rarely observed in air at room temperature due to non-radiative deactivation (NR) processes from the excited triplet state (T_1), such as local molecular motion, and quenching by oxygen (OQ). OQ is an energy transfer from the T_1 of phosphor to the surrounding oxygen [2,3]. Therefore, a detailed study of the NR process is essential to improve the PH properties. In this study, the NR processes of imide compound (IC) dispersed in a polymer matrix were investigated under various atmospheric gases at lower temperatures to probe the diffusion behavior of gas molecules in poly(methyl methacrylate) (PMMA).
[Experimental] An IC containing biphenyl core (*s*BP-IC, **Fig. 1(a)**) was dispersed in PMMA film, in which the weight fraction was set to 0.2 wt%. The emission spectra were measured under O_2, Ar, N_2. CO_2, and He atmospheres at 100–298 K, and the excitation wavelength was set to 340 nm. The rate constant of NR, relating to the molecular motion (k_{TS}) of *s*BP-IC, was estimated using the emission lifetimes and quantum yields.
[Results and discussion] **Fig. 1(a)** shows the temperature evolution of emission spectra of *s*BP-IC under O_2 at 100–220 K, and **Fig. 1(b)** shows the temperature dependence of spectrum areas of PH (A_{PH}). A_{PH} kept constant between 100–150 K, and then gradually decreased, suggesting that PH was quenched above 150 K due to vigorous O_2 diffusion. The γ-relaxation of PMMA associated with $-CH_3$ rotation started at 100–120 K [4]. Thus, it was suggested that γ-relaxation was activated at 150 K, inducing diffusion of O_2. The k_{TS} relating to the molecular motion of *s*BP-IC also increased above 150 K under Ar, N_2, CO_2, and He, while it remained low under vacuum (**Fig. 1(c)**). Thus, the following mechanism can be proposed. The diffusion of Ar, N_2, CO_2, and He was activated by γ-relaxation of PMMA above 150 K. These gases have a plasticization effect on PMMA, resulting in an enhancement of the γ-relaxation. Accordingly, the molecular motion of *s*BP-IC was enhanced and, the k_{TS} became larger than under vacuum.

[1] K. Kanosue, S. Ando, *ACS Macro Lett.* 5, 1301 (2016). [2] S. Reineke, *et al.*, *Sci. Adv.* 5, eaau7310 (2019). [3] M. Doi, R. Ishige, S. Ando, *ChemPhotoChem*, 7, e202200310 (2023). [4] J. Williams, *et. al.*, *Macromolecules* 11, 700 (1978).

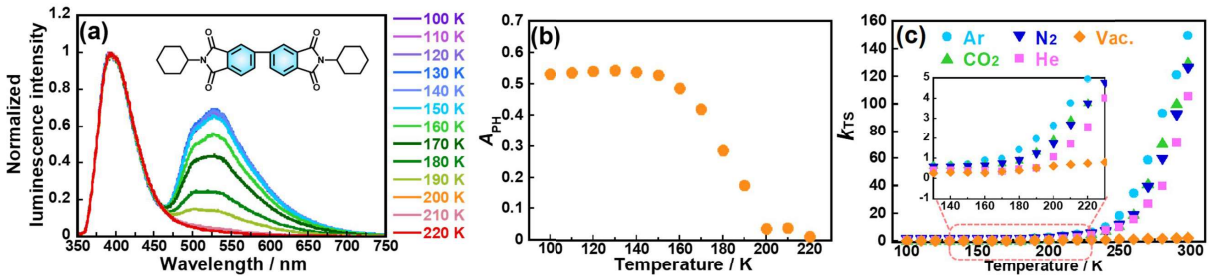

Figure 1. (a) Temperature variations in the emission spectra and (b) temperature dependence of A_{PH} under O_2 between 100 and 220 K of sBP-IC dispersed in PMMA. (c) Temperature dependence of k_{TS} between 100 and 298 K under vacuum, Ar, N_2, CO_2, and He atmospheres.