Luminescence Properties of Phosphorescent Imide Compounds having Naphthalene Structure

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Introduction

Phosphorescent polyimide (PI) has been attracting much interests owing to its large Stokes shift which is applicable to solar wavelength down conversion systems [1,2]. The phosphorescence intensity of PIs can be enhanced at very low temperatures due to suppression of local molecular motion [2]. Hence, the phosphorescent PIs having rigid main chain structures are expected to show outstanding phosphorescence properties owing to their restricted local molecular motion. In this study, the optical properties of imide compounds containing naphthalene core with rigid planar structures and bromine atoms with the heavy atom effect were investigated to understand the optical properties of phosphorescent PI.

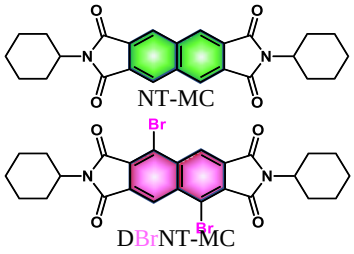

Fig. 1 Chemical structures of NT-MC and DBrNT-MC.

Experimental

Model compounds, NT-MC and DBrNT-MC having a 2,3,6,7-naphthalene structure (**Fig. 1**), were synthesized and dispersed in polymethyl methacrylate (PMMA) matrix. UV-vis absorption spectra, emission spectra, and emission lifetime measurement were conducted for these films formed on silica.

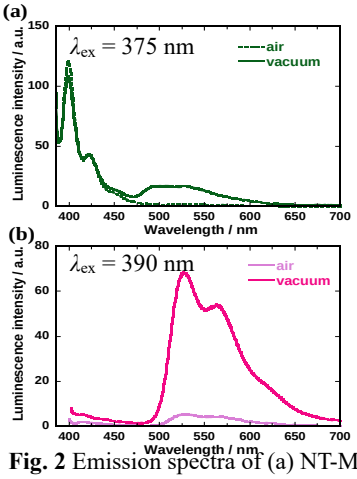

Fig. 2 Emission spectra of (a) NT-MC and (b) DBrNT-MC in PMMA matrix (λ_{ex}: excitation wavelength.)

Results and Discussion

The emission spectra of NT-MC and DBrNT-MC in PMMA under atmospheric pressure and vacuum showed two peaks (400 and 520 nm) (**Fig. 2**). Since only the latter emission increased its intensity under vacuum, these peaks were assignable to fluorescence (FL) and phosphorescence (PL), respectively. The FL intensity was higher than the PL intensity for NT-MC, whereas the FL was lower than PL for DBrNT-MC, which indicates that intersystem crossing pathway was accelerated by introducing Br atoms. Furthermore, the PL lifetime (τ_p) of each film was measured under vacuum (**Fig. 3**). The τ_p of NT-MC film (1.52 s) was significantly longer than that of DBrNT-MC film (4.98 ms), where τ_p is expressed as $\tau_p = 1 / (k_p + k_{nr})$ (k_p : radiation rate of PL, k_{nr} : non-radiative deactivation rate of PL). Hence, the relatively short τ_p of DBrNT-MC film is caused by Br atoms, enhancing the k_p [3,4]. Consequently, it was clarified that the heavy atom effect decreases τ_p with increasing PL intensity in the imide compounds, and this trade-off relationship is a key to design novel room temperature phosphorescent PIs.

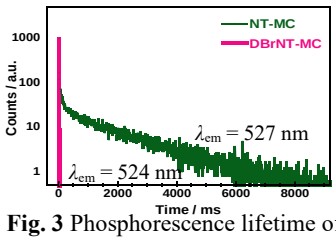

Fig. 3 Phosphorescence lifetime of the model compounds in PMMA matrix under vacuum monitored at 360 nm

References

1) K. Kanosue, S. Ando, *ACS Macro Lett.*, 5, 1301–1305 (2016).
2) K. Kanosue, V. Gulbinas, R. Ishige, S. Ando, *Mater. Chem. Front.*, 3, 39-49 (2019).