Analysis of Luminescence Properties of Phosphorescent Imide Compounds having Naphthalene Structure

Marina Doi, Koichiro Muto, Naiquiang Liang, Eisuke Fujiwara, Ryohei Ishige, Shinji Ando

(Dept Chem. Sci. Eng., Tokyo Institute of Technology)

Introduction: Luminescent polyimides (PIs) are attracting many interests due to the potential applications as novel photoluminescence materials bearing excellent thermal and chemical stability. Photoluminescence properties of PIs strongly depend on not only the chemical structures but also the aggregation state. Applying "hydrostatic pressure" is used to control the aggregation state. Recently, we have reported that the luminescence intensities of fluorescent PIs are reduced under high pressure due to the enhancement of non-radiative deactivation caused by inter-molecular interactions [1,2]. In contrast, the luminescence intensities of phosphorescent PIs were increased at lower temperatures (77 K), which is attributable to suppressing local molecular motion [3]. Therefore, the phosphorescent PIs has a potential to increase the luminescence intensity under high pressure by suppressing local molecular motion. The phosphorescent imide compounds having 2,3,6,7-naphthalene structure were expected to exhibit strong phosphorescence under high pressure due to suppressing local molecular motion by π - π stacking. This study aimed to clarify the optical properties of the imide compounds.

Experimental and measurements: We prepared the NT-MC and DBrNT-MC (**Fig. 1**) dispersed in PMMA matrix. Emission spectra, emission lifetime, and quantum yields were measured for these films.

Results and discussions: The emission spectra of NT-MC and DBrNT-MC dispersed in PMMA matrix shows fluorescence peak (400 nm) and phosphorescence peak (520 nm) (**Fig. 2)**. NT-MC showed higher fluorescence intensity than phosphorescence intensity, whereas DBrNT-MC showed higher phosphorescence intensity than that of fluorescence. This result indicates that intersystem crossing was enhanced by introducing bromine atoms. In contrast, the quantum yield of DBrNT-MC was smaller than that of NT-MC (**Table 1**). It is attributed to weaker phosphorescence intensity at room temperature than fluorescence intensity. In addition, the result is also attributable to non-radiative deactivation enhanced by reduction in inter-molecular interactions caused by closing due to introducing heavy bromine atoms. The phosphorescent lifetime of NT-MC under vacuum was measured and it exhibited long phosphorescent lifetime for 1.5 s or more (**Fig. 3**). It is long emission lifetime compared to other phosphorescent imide compounds exhibiting for milliseconds and it is expected to apply for optical materials exhibiting long emission. In conclusion, intersystem crossing was facilitated by introducing bromine atoms but it induced decrease of phosphorescence intensity.

In the future, optical measurements of the films will be performed under high pressure. And we will synthesize PIs containing NT or DBrNT and measure the optical properties.

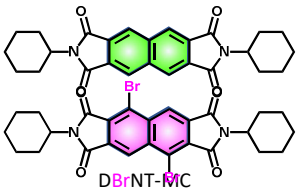

Fig. 1 Chemical structure of NT-MC and DBrNT-MC

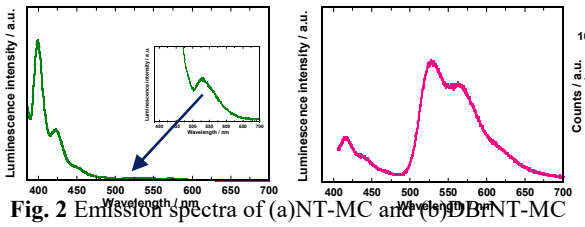

Fig. 2 Emission spectra of (a)NT-MC and (b)DBrNT-MC

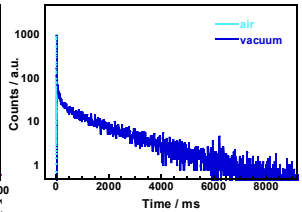

Fig. 3 Phosphorescent lifetime of NT-MC under vacuum

Table 1 Quantum yield

	Quantum yield [%]
NT-MC	24.4
DBrNT-MC	4.05

[1] K. Takizawa, J. Wakita, K. Sekiguchi, S. Ando, *Macromolecules*, 45, 4764-4771 (2012).
[2] E. Fujiwara, H. Fukudome, K. Takizawa, R. Ishige, S. Ando, *J. Phys. Chem. B*, 122, 8985-8997 (2018).
[3] K. Kanosue, S. Hirata, M. Vacha, R. Augulis, V. Gulbinas, R. Ishige, S. Ando, *Mater. Chem. Front.*, 3, 39-49 (2019).

Analysis of Luminescence Properties of Phosphorescent Imide Compounds having Naphthalene Structure.

Marina Doi, Koichiro Muto, Naiquiang Liang, Eisuke Fujiwara, Ryohei Ishige, Shinji Ando (*Department of Chemical Science and Engineering, Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo, 152-8552, Japan*)