Optical Properties of Fluorescent and Phosphorescent Imide Compounds and Polyimides having Naphthalene Skeletal Structure

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[Introduction] Polyimide (PI) is one of the super engineering plastics composed of dianhydride and diamine monomers. PIs attract many interests due to the excellent thermal and chemical stabilities, and mechanical strength. Moreover, appropriate combinations of dianhydride and diamine give luminescent properties to the PIs. Recently, we have developed room-temperature phosphorescent PIs for solar spectral converters[1–3]. For practical applications, further improvements in optical properties such as quantum yields and transparency of films are necessary. The phosphorescence intensity of PIs can be enhanced at very low temperatures where local molecular motions are suppressed[1]. Hence, the phosphorescent PIs having rigid main chain structures are expected to show outstanding phosphorescence properties. It was also reported that the introduction of bromine atoms into the dianhydride moiety of PIs enhances intersystem crossing due to the heavy atom effect and improves the intensity of phosphorescence[1]. In this study, we synthesized novel imide model compounds (MCs) and PIs containing a rigid naphthalene core, and those substituted with bromine atoms (**Fig 1**). The effects of the rigid naphthalene structure and the heavy atom effect on the luminescent properties of the PIs were investigated by absorption and emission spectra combined with lifetime measurements.

[Experimental] We synthesized model compounds (NT-MC and Br-MC) and PIs (N6-PI and Br6-PI) having a 2,3,6,7-naphthalene structure (NT) and bromine-substituted NT (DBrNT) (**Fig. 1**). Films of MCs dispersed in poly(methyl methacrylate) were prepared to evaluate their optical properties in the isolated state. In addition, because the homo-polyamide acids derived from NT and DBrNT have poor solubility and difficult to form solid films, copolyimide (coPI) films were prepared by using 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA). 6FDA has excellent solubility without influence on the emission process of the naphthalene core. Excitation and emission spectra, quantum yields, and emission lifetime measurements were conducted for these films formed on fused silica substrates.

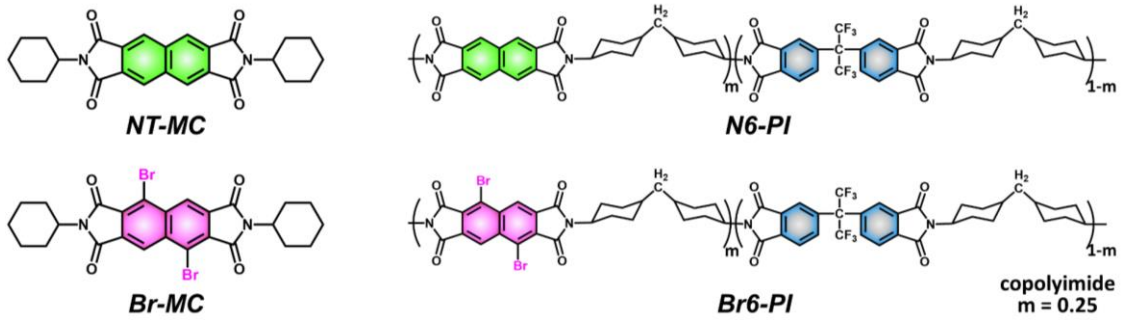

Figure 1 Chemical structures of MCs and PIs

[Results and Discussion] The emission spectra of the MCs at ambient conditions showed two peaks at 400 and 530 nm) (**Fig. 2a,b**). Since only the latter emission peak increased its intensity under vacuum condition, these peaks were assignable to the fluorescence (Fl.) and phosphorescence (Ph.), respectively. NT-MC exhibited a strong Fl. and a weak Ph. peaks, whereas Br-MC exhibited a weak Fl. and a strong Ph. peaks. Comparing the quantum yields of Fl. (Φ_f) and Ph. (Φ_p) estimated from the area ratio of each emission peak, Ph. was significantly enhanced owing to the promotion of intersystem crossing by introducing bromine atoms (**Table 1**). The emission lifetime of NT-MC at 77 K is shown in **Fig. 2c**. In general, typical Ph. lifetime (τ_p) of organic compounds are in the order of μs–ms, and τ_p>100 ms is called 'long-lived Ph. lifetime'[4][5]. NT-MC exhibited $\tau_p = 3.63$ s at 77 K, and it is readily categorized as a very long-lived Phos. This remarkable property is attributed to the suppression of local molecular motion by the rigid naphthalene core. The emission spectra of N6-PI and Br6-PI films are shown in **Fig. 2a,b** as compared with the MCs. N6-PI exhibits a strong Fl. and a weak Ph., while Br6-PI exhibits a weak Fl. and a strong Ph.. Further, NT and DBrNT copolymerized with 6FDA exhibit similar optical properties with their corresponding MCs. Moreover, the long τ_p of N6-PI is maintained as $\tau_p = 1.77$ s at 77 K (**Fig. 2c**). Consequently, it was clarified that the coPI with rigid naphthalene core can maintain the inherent properties of NT and DBrNT, and NT-MC and N6-PI showed long-lived room temperature Ph. Furthermore, the introduction of heavy bromines to the naphthalene core effectively enhances the luminescence efficiency and the lifetime of the PIs.

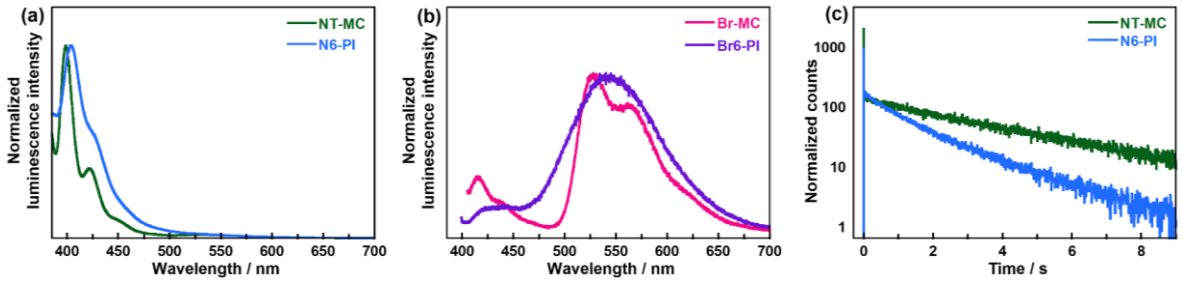

Figure 2 (a) Emission spectra of NT-MC and N6-MC ($\lambda_{ex} = 375$ nm). (b) emission spectra of Br-MC and Br6-PI ($\lambda_{ex} = 390$ nm). (c) Phosphorescence lifetime of NT-MC measured at 77 K ($\lambda_{ex} = 360$ nm, $\lambda_{em} = 508$ nm).

Table 1 Quantum yield of each luminescence of MCs ($\boldsymbol{\Phi}$: quantum yield, $\boldsymbol{\Phi_f}$: fluorescence quantum yield, $\boldsymbol{\Phi_p}$: phosphorescence quantum yield)

	$\boldsymbol{\Phi}$	$\boldsymbol{\Phi_f}$	$\boldsymbol{\Phi_p}$
NT-MC	0.33	0.32	0.01
Br-MC	0.10	0.01	0.09

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