Fluorescence and phosphorescence properties of copolyimides containing naphthalene core in the main chain

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Introduction

We have been developing a variety of fluorescent and room temperature phosphorescent (RTP) polyimides (PIs) for application to solar spectral converters [1]. For practical applications, further improvements in optical properties, such as quantum yields and emission lifetime, are demanded. The phosphorescence intensity of bromine-substituted PIs can be enhanced at lower temperatures because local molecular motions including vibrations are suppressed [2,3]. Thus, the phosphorescent PIs consisting of larger π−conjugated moiety are expected to show outstanding phosphorescence properties due to the suppression of molecular motions by strong π−π stacking interactions. In this study, we synthesized novel PIs consisting of dianhydride having a rigid naphthalene core (**Fig. 1**) and diaminodicyclo hexylmethane (DCHM), and the effects of the rigid naphthalene structure on the phosphorescent properties were investigated by emission spectra of imide compounds and the PIs. In addition, to convert a wide wavelength range of UV light to visible light, copolymers (CoPIs) were synthesized with other dianhydrides which absorb UV light at different wavelengths from the naphthalene core and investigated the energy transfer process in the excited state between the dianhydrides by comparing the emission spectra of the PIs.

Experimental

We synthesized imide compounds (NT-MC and Br-MC) and CoPIs (N6-PI, Br6-PI, NO-PI, and BrO-PI) having a 2,3,6,7-naphthalene structure (NT) and bromine-substituted NT (DBrNT) (**Fig. 1**). Poly(methyl methacrylate) (PMMA) films, in which the MCs were homogeneously dispersed, were prepared to evaluate the optical properties of the naphthalene core in the isolated state. Because the homo poly(amic acid)s, a precursor of PI, derived from NT and DBrNT have poor solubility in polar solvents and difficult to form smooth films, CoPI films were prepared by using 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA) which has excellent solubility without influence on the emission process of the naphthalene core. In addition, CoPI films derived from naphthalene dianhydride and 4,4'-oxydiphtalic dianhydride (ODPA)

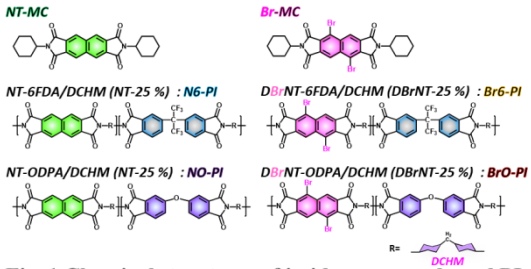

Fig. 1 Chemical structures of imide compounds and PIs

absorb UV-light with different wavelength. Emission spectra were measured for these films formed on fused silica substrates.

Results and Discussion

The emission spectra of N6-PI and Br6-PI films are shown in **Fig. 2(a, b)** as compared with those of the MCs. NT and DBrNT copolymerized with 6FDA exhibited similar emission spectra with their corresponding MCs. In particular, Br-MC exhibited RTP due to the rigidity of naphthalene core as well as the heavy atom effect of bromines, and Br6-PI also exhibited strong RTP (**Fig. 2(b)**). Consequently, it was clarified that the CoPIs with bulky 6FDA can maintain the inherent properties of NT and DBrNT. **Fig. 3** shows the emission spectra of ODPA-PI and BrO-PI irradiated at different wavelengths; the optimum excitation wavelengths for DBrNT and ODPA are 390 nm and 340 nm respectively. This means that each dianhydride can be selectively excited by adjusting the wavelength of irradiated UV light. ODPA-PI exhibited a fluorescence at 400 nm, whereas BrO-PI did not display any emission peak around 400 nm after irradiation at 340 nm (**Fig. 3**). This clearly indicates that efficient energy transfer occurred from the excited ODPA to DBrNT moieties, and thus the ODPA moiety showed little emission in BrO-PI. These results indicate that copolymerization with different dianhydrides is a facile and versatile way to manipulate the energy transfer mechanisms in the excited state, which enables to absorb a wide wavelength range of UV light and convert to useful visible light at longer wavelengths with desirable efficiency.

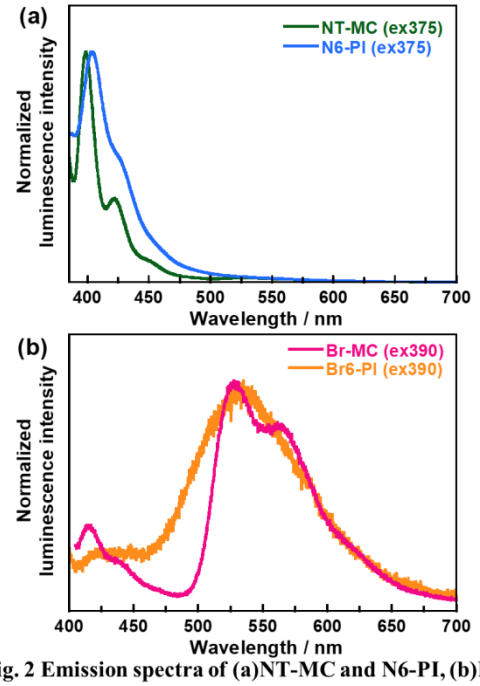

Fig. 2 Emission spectra of (a)NT-MC and N6-PI, (b)Br-MC and Br6-PI

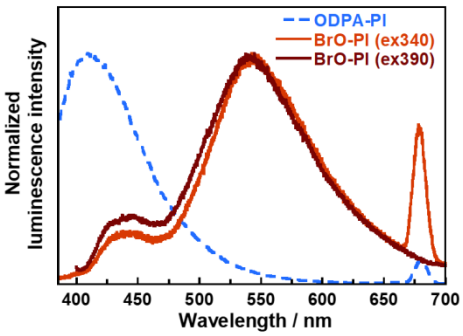

Fig. 3 Emission spectrum of ODPA-PI and BrO-PI irradiated at 340 and 390 nm

References

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