Room-Temperature Phosphorescent Polyimide for Wavelength Converting Applications

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Abstract

For development of highly photoluminescent polyimide (PI) optical materials based on room-temperature phosphorescence (RTP), a novel semi-aromatic PI was synthesized using a steric biphenyl tetracarboxylic dianhydride substituted by bromine (Br) atoms. A solid thin film of the PI is perfectly colorless because of suppression of the aggregation formation of the PI chains owing to the steric biphenyl structure. The PI film showed strong RTP emission at 510 nm with a very large Stokes shift ($\nu \approx 12{,}138$ cm^{-1}) when excited at 315 nm. In addition, the phosphorescence intensity of the PI film was significantly enhanced under both low temperature and vacuum conditions due to effective suppression of molecular motions and the triplet-triplet energy transfer to atmospheric oxygen. These results clearly indicate that the introduction of Br atoms into the steric biphenyl dianhydride moiety makes PI highly phosphorescent as well as sensitive to oxygen and temperature.

Introduction

Polyimides (PIs) are a class of super-engineering plastics due to the high thermal, mechanical and chemical stabilities originating from the rigid molecular structure and strong intermolecular interactions. Recently, fluorescence properties of PI solid films have been widely studied [1-3]. Fluorescent PI films are expected to be applied for spectral downshift converters in a wide range of applications including solar cells and crop cultivation. However, the small energy difference between absorption and fluorescence wavelength, so-called Stokes shift, of fluorescent PIs are insufficient for practical wavelength conversion (**Figure 1**). Most recently, organic carbonyl compounds substituted bromine (Br) atoms have been reported to exhibit very large Stokes shifted room-temperature phosphorescence (RTP) thanks to the enhanced spin-orbital coupling based on the heavy Br atom, resulting in the efficient intersystem crossing to generate triplet (**Figure 2**) [4]. In our previous study, we successfully developed a Br-containing PI which exhibited large Stokes shifted RTP in the solid thin film. However, this PI film has a deep-yellow coloration because of the visible absorption of the aggregated PI chains in the solid state. In the present study, for development of highly colorless RTP PI films, a novel semi-aromatic PI (DBr-PI) was synthesized using a steric biphenyl tetracarboxylic dianhydride substituted by Br atoms, which is expected to suppress the aggregation formation, and the photoluminescence properties were extensively examined in the solid film state.

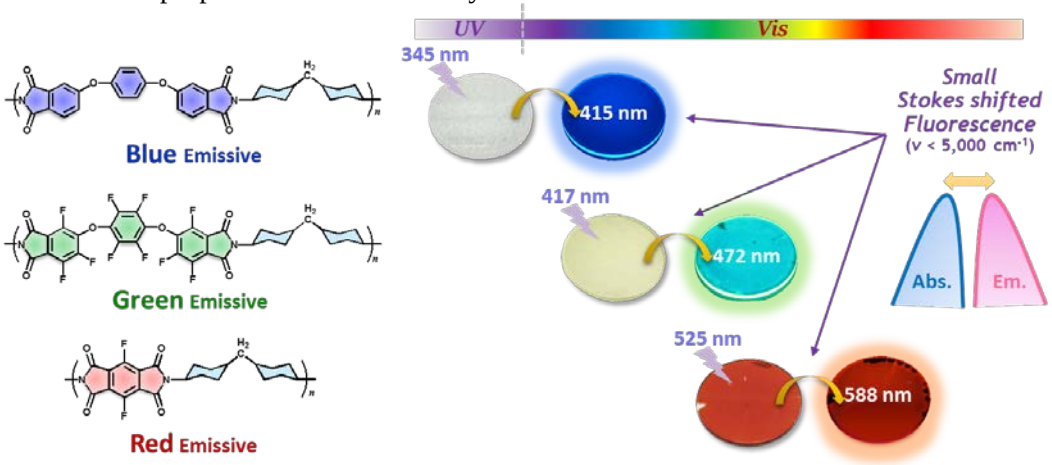

Figure 1. Conventional Fluorescent PIs and Their Small Stokes Shifts.

Experimental

Diaminocyclohexylmethane was reacted with dibromo-biphenyl tetracarboxylic dianhydride in DMAc under nitrogen atmosphere for 24 h. The reaction solution was spin-coated onto a fused silica substrate, followed by soft-baking at 70 C for 1 h and subsequent thermal imidization at 220 C for 1.5 h under nitrogen flow. The film thickness was estimated to be ca. 5.0 μm.

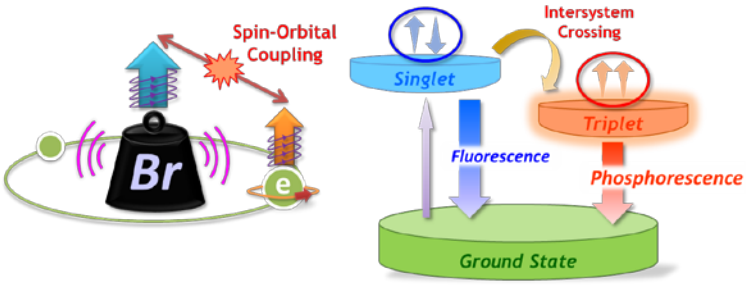

Figure 2. Room-Temperature Phosphorescence Based on Heavy Atom Effect of Bromine.

Results and Discussion

In the UV-vis absorption spectrum of the DBr-PI film (**Figure 3a**), an intense absorption band attributable to the local electronic transition at the dianhydride moiety of the PI repeating unit. No absorption derived from the aggregated PI chains was observed owing to the steric Br-substituted dianhydride, which effectively suppresses the aggregation formation, resulting in the perfectly colorless film. In the excitation/emission spectra of the DBr-PI film (**Figure 3b**), a very large Stokes shifted RTP ($\nu \approx 12{,}138$ cm^{-1}) was observed at 510 nm when excited at 315 nm. In addition, the phosphorescence intensity was significantly enhanced under vacuum and low temperature condition because of effective suppression of molecular motions and the triplet-triplet energy transfer to atmospheric oxygen (**Figure 4**). These results indicate that the introduction of Br atoms into the steric biphenyl dianhydride makes PI highly colorless and phosphorescent at room temperature with the very large Stokes shift applicable to wavelength conversion as well as oxygen and temperature sensors.

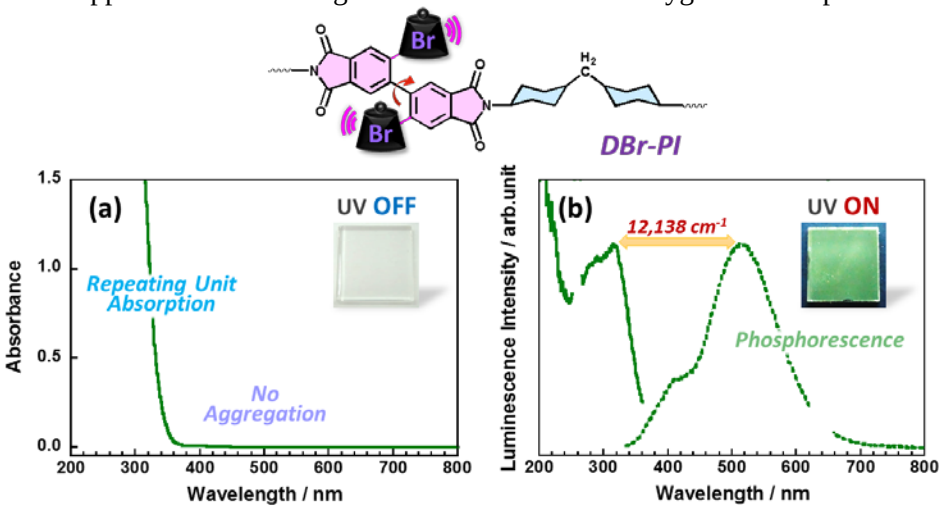

Figure 3. (a) UV-vis absorption and (b) excitation/emission spectra of DBr-PI film (λ_{ex} = 315 nm).

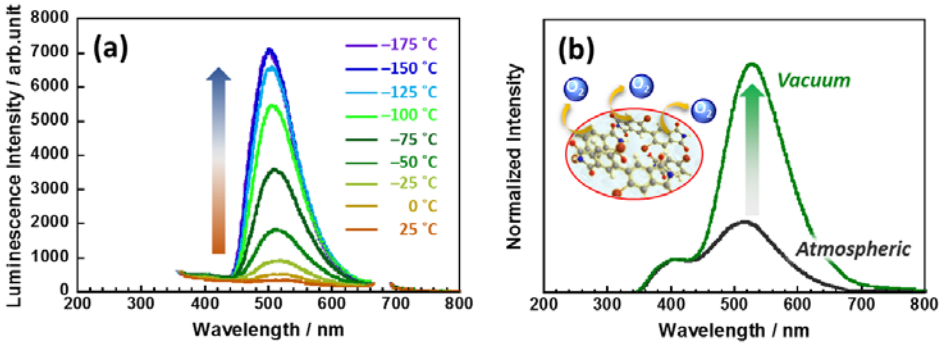

Figure 4. Emission spectra of DBr-PI film under (a) variable temperatures, and (b) vacuum conditions.

References

1. J. Wakita, S. Inoue, N. Kawanishi, S. Ando, *Macromolecules* **2010**, *43*, 3594.
2. K. Kanosue, T. Shimosaka, J. Wakita, S. Ando, *Macromolecules* **2015**, *48*, 1777.
3. K. Kanosue, V. Gulbinas, S. Ando, et al., *Macromolecules* **2016**, *49*, 1848.
4. K. Kanosue, S. Ando, et al., *ACS Macro Letters* **2016**, *Submitted*.