# Highly Phosphorescent Polyimides for Wavelength Converting Applications

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## Abstract

For development of phosphorescent polyimide (PI) optical materials based on the heavy atom effects, two semi-aromatic PIs were newly synthesized using the pyromellitic dianhydrides substituted by heavy halogens (Br, I). The PI films formed on silica substrates showed strong phosphorescent emissions at around 590 nm when excited at around 370 nm at room temperature. Their Stokes shifts were as large as $\nu \approx 10{,}000\ \mathrm{cm}^{-1}$. In addition, absorption bands assignable to aggregated form were observed at around 450 nm. The phosphorescent intensities of these PIs were significantly enhanced under vacuum due to the effective suppression of triplet energy quenching by oxygen. These results clearly indicate that the introduction of heavy halogens (Br, I) into the dianhydride moiety of PIs makes them highly phosphorescent as well as sensitive to oxygen atmosphere.

## Introduction

Polyimides (PIs) are a class of super engineering plastics well-known due to their high thermal and mechanical stabilities originating from the rigid molecular structure and strong intermolecular interactions. Recently, fluorescent emission properties of PIs have been widely studied [1,2]. Fluorescent PIs are expected to be applied for spectrum down-convertor in a wide range of applications such as photovoltaic devices and crop cultivation. However, small Stokes shifts of the fluorescent PIs are insufficient for practical wavelength convertors (**Figure 1**). In contrast, Stokes shift of phosphorescence is generally larger than that of fluorescence because phosphorescence is an emission from energetically stable excited triplet state. Most recently, organic carbonyl compounds containing bromine (Br) were reported to exhibit phosphorescent emission at room temperature [3,4]. This is due to the spin-orbital coupling based on the heavy atom effect of Br, which accelerates intersystem crossing from the singlet to the triplet (**Figure 2**). In this study, for development of phosphorescent optical materials based on PIs with heavy atom effects, two semi-aromatic PIs (3Br-PI, 3I-PI) were newly synthesized using pyromellitic dianhydrides substituted by heavy halogen (Br, I), and their photoluminescence properties were examined in solid states.

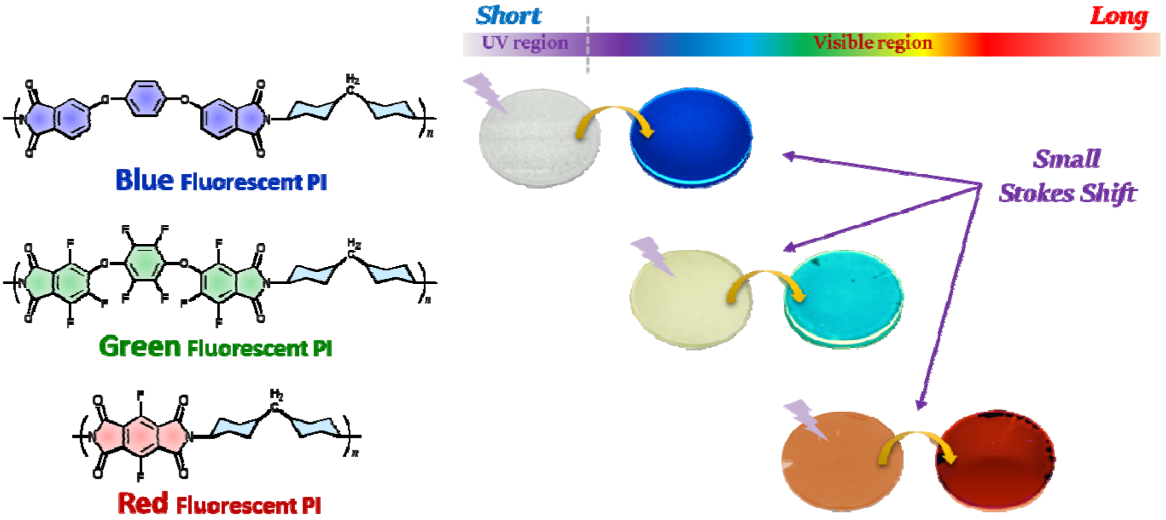

**Figure 1.** Conventional Fluorescent PIs and Their Stokes Shifts.

## Experimental

Diaminocyclohexylmethane was reacted with 3-halogen substituted pyromellitic dianhydride in DMAc under nitrogen atmosphere for 12 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.

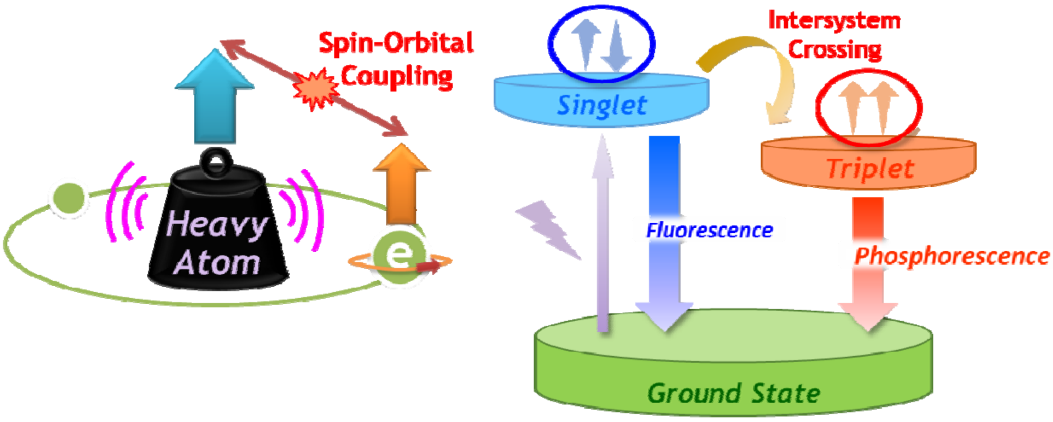

**Figure 2.** Room-Temperature Phosphorescence Based on Heavy Atom Effects.

## Results and Discussion

The UV-vis absorption / emission spectra of 3Br-PI and 3I-PI films are shown in **Figure. 3**. 3Br-PI and 3I-PI show intense absorption bands below 400 nm and around 450 nm which are attributable to the repeating unit of the PIs and the aggregated forms, respectively. The absorbance of the aggregated form of 3I-PI is slightly weaker than that of 3Br-PI due to steric hindrance of the larger atomic radius of iodine. All the samples obviously demonstrate orange-color luminescence peaks at around 590 nm with very large Stokes shifts ($v \approx 10{,}000$ cm$^{-1}$). These peaks were readily attributable to room-temperature phosphorescence. The quantum yield of 3Br-PI (3 %) was slightly higher than that of 3I-PI (1 %), which could be due to the restricted molecular mobility of 3Br-PI originating from its denser packing structure. Emission bands attributable to the aggregated forms with small Stokes shifts were also observed at around 550 nm in all the samples. In conclusion, introduction of heavy halogen atoms to the dianhydride moiety of PI readily provides room-temperature phosphorescence properties. Phosphorescent PIs are promising for opto-electronic and photonic applications as well as spectral down-converting materials.

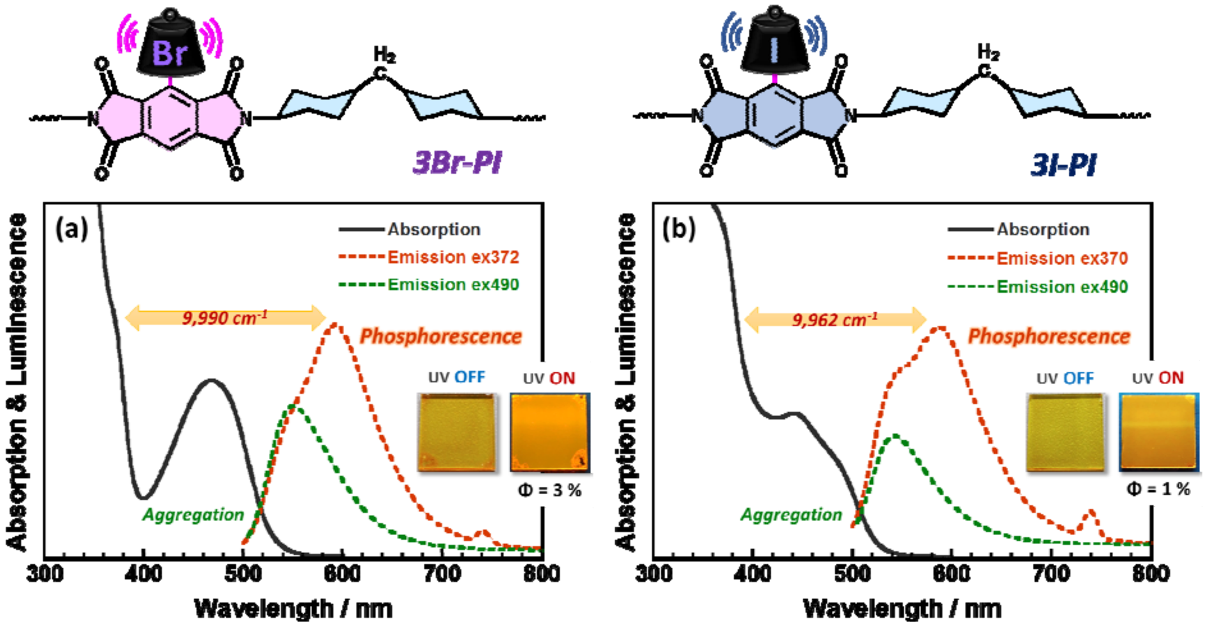

**Figure 3.** UV-vis Absorption and Photoluminescence Spectra of PIs.

## References

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