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Design and Development of Room-Temperature Phosphorescent Polyimides Based on Heavy Atom Effects

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[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 and limited quantum yields of the fluorescent PIs are insufficient for practical wavelength convertors. In contrast, Stokes shift of phosphorescence is generally larger than that of fluorescence because phosphorescence is an emission from 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. In this study, for development of phosphorescent optical materials based on PIs with heavy atom effects, two semi-aromatic PIs (3B-PI, 3I-PI) and two model compounds (3B-Ch, 3I-Ch) were newly synthesized (**Fig. 1**) using pyromellitic dianhydrides substituted by heavy halogen (Br, I), and their photoluminescence properties were examined in solid states.

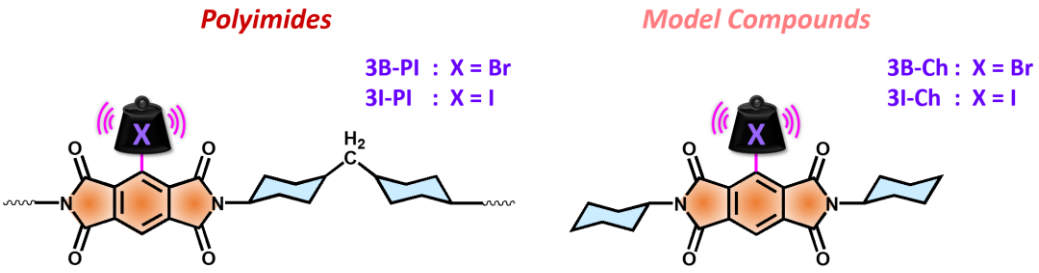

Figure 1. Chemical structures of halogen substituted PIs and model compounds.

[Experimental] *Preparation of PI films.* 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.

Synthesis of Model Compounds. Cyclohexylamine was reacted with 3-halogen substituted pyromellitic dianhydride in DMAc under nitrogen atmosphere for 12 h and refluxed at 150 °C under nitrogen flow. After cooling to room-temperature, a solid precipitated by excess of water was filtrated and dried. The compounds thus obtained were purified by recrystallization from *o*-xylene (3B-Ch) and pyridine (3I-Ch), respectively.

[Results and Discussion] The UV-vis absorption / emission spectra of 3B-PI and 3I-PI films (**Fig. 2a**,**c**) as well as the emission spectra of 3B-Ch and 3I-Ch powder (**Fig. 2b,d**) are shown in **Fig. 2**. 3B-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 3B-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 ($\nu \approx$ 10,000 cm^{-1}). These peaks were readily attributable to room-temperature phosphorescence. The quantum yield of 3B-PI (3 %) was slightly higher than that of 3I-PI (1 %), which could be due to the restricted molecular mobility of 3B-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.

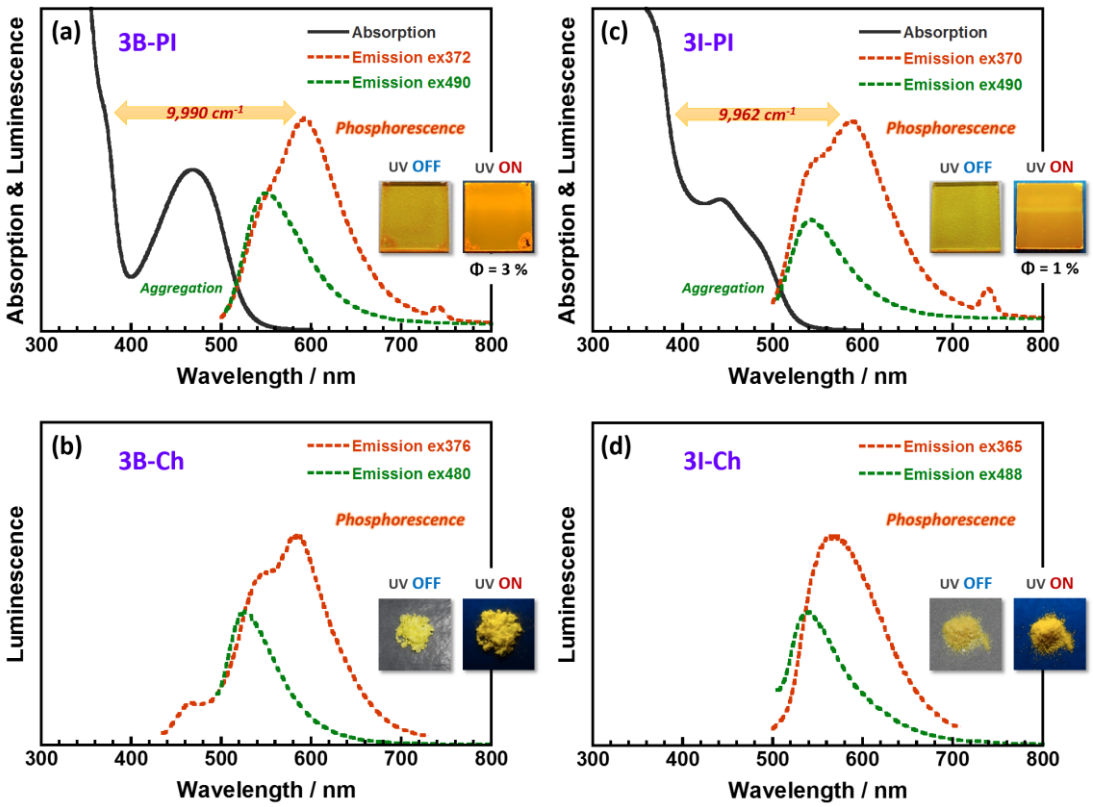

Figure 2. UV-vis absorption and photoluminescence spectra of PIs and model compounds.

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[3] J. Xu, A. Takai, Y. Kobayashi, M. Takeuchi, *Chem. Comm.* **2013**, *49*, 8447

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