Polyimides and Imide Compounds Exhibiting High Optical Transparency and Enhanced Phosphorescence Emission under Atmospheric and Very High Pressure

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Colorless, transparent, and environmentally stable polymer films with large luminescence Stokes shift are in demand for down-conversion of solar UV radiation. We have synthesized a highly fluorescent polyimides (HFPI) with strong blue emission using a conventional dianhydride and an alicyclic diamine (**BP-PI**, **Fig.1a**), of which the quantum yield (Φ) was 0.11. (**Fig. 2a**) [1] Moreover, we have reported a series of HFPIs derived from perfluorinated aromatic dianhydrides, such as 10FEDA and P2FDA, which exhibited strong bluish green and red fluorescence. Although their fluorescence intensity was significantly enhanced, these HFPIs are not fully suitable to solar wavelength converters because their energy gaps between the absorption and fluorescence peaks, called 'Stokes shifts', were not large enough. To develop such polymer films which exhibit enhanced phosphorescence at room temperature or low temperature with a large Stokes shift and excellent thermal stability, a semi-aromatic polyimide (**DBrBP-PI**, **Fig.1b**) was newly synthesized using a biphenyl-tetracarboxylic dianhydride substituted with two bromine (Br) atoms.[2] Thin films of DBrBP-PI were completely colorless because of the effective suppression of aggregation of the PI chains due to the steric effects of the Br-substituted dianhydride structure. The PI films exhibited bright green phosphorescence at 512 nm (Φ = 0.02) with a very large Stokes shift of 12215 cm^{-1} as well as prompt blue fluorescence at around 408 nm when excited at 315 nm at 298 K (**Fig. 2b**). The glass transition and the 5 wt% loss temperatures of DBrBP-PI were 325°C and 427°C, respectively. The phosphoresce intensity of the DBrBP-PI film was significantly enhanced under vacuum (Φ = 0.22) and at

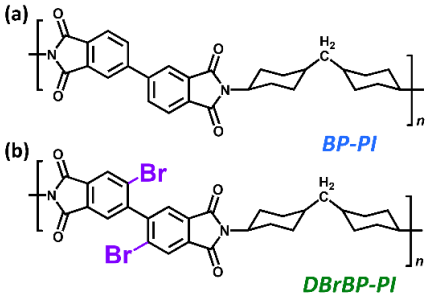

Fig.1. (a) BP-PI & (b) DBrBP-PI.

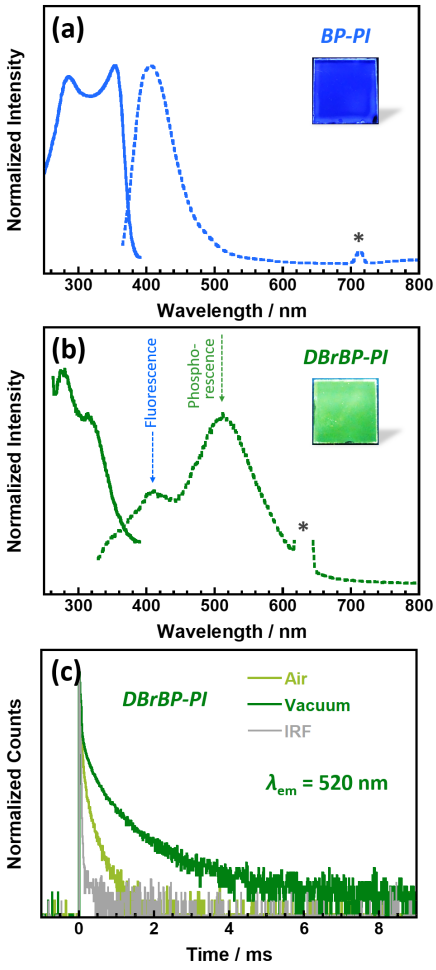

Fig.2. Excitation and emission spectra of (a) BP-PI and (b) DBrBP-PI, and (c) emission delay curves of DBrBP-PI.

a low temperature (Φ = 0.76 at 77 K, **Fig. 3**) owing to suppression of triplet state quenching by atmospheric oxygen and dumping of the molecular motions of PI chains in the solid film. The photo-luminescence decay curves with a very long relaxation time (~msec) under vacuum also support the inherent phosphorescence nature of DBrBP-PI (**Fig. 2c**).

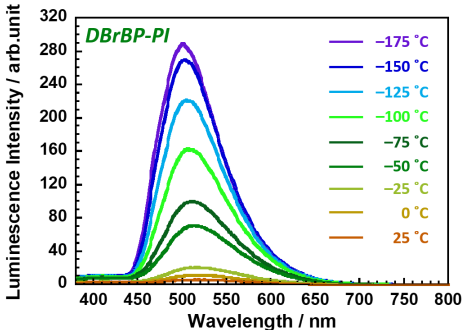

Fig.3. Photoluminescence emission spectra of DBrBP-PI films at low temperatures excited at 367 nm.

For clarifying relation between the luminescence properties and the aggregation state of the phosphorescent PI thin film, UV/vis absorption and photoluminescence spectra were measured under high pressures up to 10 GPa using a diamond anvil cell.[3] The PI thin film exhibited fluorescence and phosphorescence at room temperature and atmo-spheric pressure, and reduction of intermolecular distance under high pressure increases dipolar-dipolar interactions and non-radiative deactivation accompanied by intermolecular energy transfer. Although both the fluorescence and phosphorescence intensities significantly decreased at elevated pressures, note that the decaying behavior of the fluorescence was more significant than that of phosphorescence (**Fig. 4a**), which is explainable by the difference in energy transfer mechanism, i.e. Förster resonance energy transfer (FRET) for the fluorescence, and Dexter electron transfer (DET) for the phosphorescence.

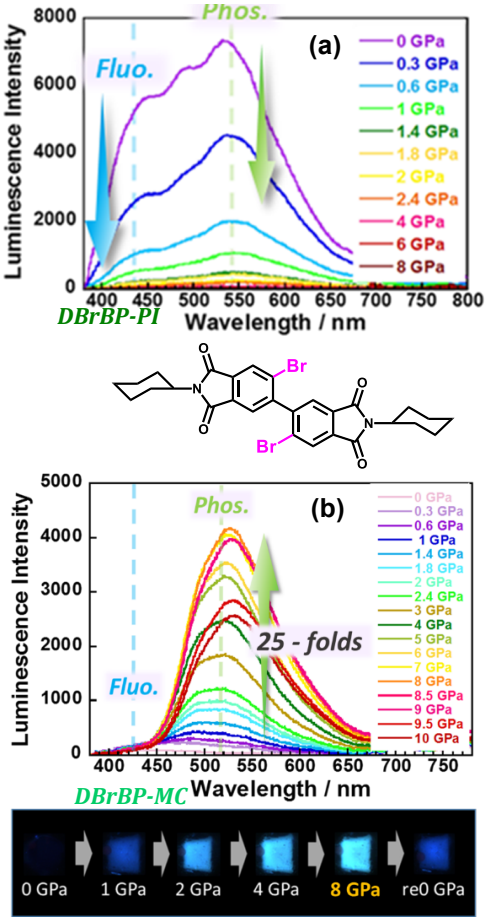

Fig.4. Pressure dependent photoluminescent spectra of (a) DBrBP-PI film and (b) DBrBP-MC imide compound dispersed in PMMA with photo images at each pressure.

Furthermore, to elucidate the influence of local molecular motion on the room temperature phosphorescence (RTF) of an imide compound (**DBrBP-MC**), DBrBP-MC was dispersed in polymethylmethacrylate (PMMA) at a low concentration, and emission spectra were measured under high pressures (**Fig. 4b**). Contrary to DBrBP-PI, the phosphorescence intensity significantly increased at elevated pressures; the emission intensity at 8 GPa was larger by ca. 25 times than the atmospheric pressure (0 GPa). This indicates that the nonradiative deactivation of excitation energy of the imide compound was greatly suppressed by the two factors; 1) Reduction in intermolecular energy transfer by homogeneous dispersion in PMMA matrix, and 2) Dumping of local molecular motion by pressurization. These results suggest new design concepts toward colorless and thermally stable solar down-converters with high efficiency using RTF PIs.

References

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