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Oxygen-sensitive Luminescence of A Polyimide with Brominated end groups based on Room-temperature Phosphorescence

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[Introduction]

Polyimide (PI) has been attracting much interest owing to its potential applications as novel luminescent materials bearing high thermal and radiation stabilities. Previously, we have designed highly fluorescent (FL) [1] and room-temperature phosphorescent (RTP) PIs [2,3]. In particular, RTP PIs are potentially applicable to oxygen sensors because they exhibit highly oxygen-sensitive luminescence. However, most of RTP PI films exhibit low optical transparency and low luminescence quantum yield due to strong absorption in the visible region which mainly originates from their aggregation [2]. In this study, we designed and synthesized a novel end-capped PI which consists of a highly FL PI with end groups containing bromine atom as heavy halogen and tried to develop colorless and transparent RTP PI films.

[Experiment]

End-capped PI films (OD-4Br) were prepared by the conventional two-step procedure using ODPA (4,4'-oxydiphthalic dianhydride) as a dianhydride, DCHM (4,4'-diaminocyclohexylmethane) as a diamine, and 4BrNA (4-bromonaphthalic anhydride) as end groups as presented in Fig. 1 insets.

[Results and Discussion]

The absorption and emission spectra of OD-PI and OD-4Br are shown in Fig. 1. These films show absorption bands only in the UV regions, which supports the colorlessness and high transparency. In the emission spectra, OD-PI exhibited blue fluorescence (λ_{em} = 404 nm) by excitation at 340 nm. OD-4Br exhibited dual emission (λ_{em} = 404, 508 nm) by excitation at 350 nm, which are assignable to luminescence from the main chain and the end groups, respectively. In addition, OD-4Br exhibits significantly higher quantum yield (Φ = 21 %) than OD-PI (Φ = 11 %). These results suggest that efficient energy transfer occurred from the main chain to the end group. As shown in Fig. 2, luminescent peaks at 560 and 600 nm were dramatically enhanced under vacuum, which revealed the RTP property of the end groups. When the OD-4Br luminescent colors were displayed in the CIE coordinates, OD-4Br showed different colors (blue and yellow) under atmospheric and vacuum, respectively. This is because the quenching of RTP by oxygen is reduced under vacuum. In summary, these results demonstrated that a FL PI having brominated end groups exhibited colorlessness, high transparency, and high quantum yield, as well as high RTP properties, which is promising for oxygen sensor applications.

[References]

- [1] J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **19**, 15212-15224 (2009). [2] K. Kanosue, S. Ando, *ACS. Macro. Lett*, **5**, 1301-1305, (2016). [3] K. Kanosue, S. Hirata, M. Vacha, R. Augulis, V. Gulbinas, R. Ishige, S. Ando, *Mater. Chem. Front.*, **3**, 39-49 (2019).

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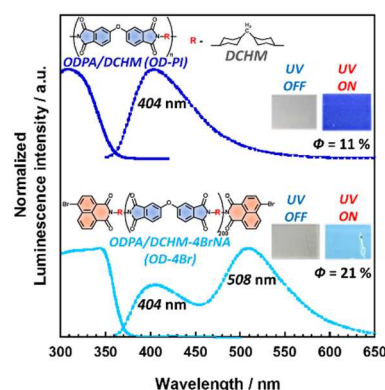


Fig. 1. Absorption / emission spectra of OD-PI and OD-4Br.

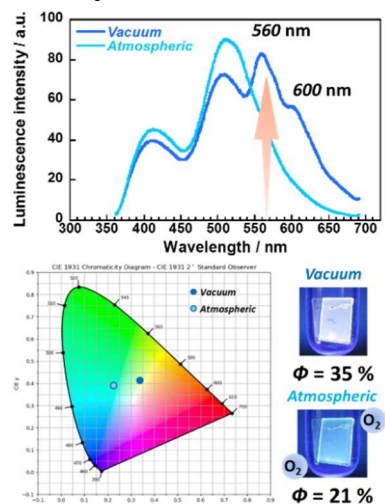


Fig. 2. Luminescence spectra and CIE coordinates of OD-4Br under atmospheric and vacuum condition.