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Control of Optical Properties of Polyimides by Introducing Electron-donating Alicyclic Amino Groups

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ABSTRACT:

[Introduction] Organic fluorescent materials are applicable in many fields such as light emitting devices (LEDs) and solar spectrum convertors. Recently, polyimides (PI), a thermally and chemically stable polymers, has been attracting much interests due to its potential applications as novel fluorescent materials. Previously, we proposed a molecular design concept for highly fluorescent PIs [1]. Moreover, we found that imide compounds having an electron-donating alicyclic amino group in the anhydride moieties exhibit stronger fluorescence compared with *N*-cyclohexylphthalimide (NHPI, without electron-donating group) [2]. In this study, we designed a dianhydride monomer having a piperazine moiety with high electron-donating ability. Furthermore, we synthesized PIs using piperazine-based dianhydride and alicyclic diamine, and their fluorescence properties were examined.

[Experimental] *Synthesis of ODPA-DCHM.* ODPA (4,4'-oxydiphthalic dianhydride) was dissolved in DMAc (*N*,*N*-Dimethylacetamide) with DCHM (4,4'-diamino-cyclohexylmethane). Poly(amic acid) solution thus obtained was spin-coated onto a silica substrate, and thermally imidized at 220 °C for 1.5 h under nitrogen to give ODPA-DCHM (homo-PI).
Synthesis of ODPA-NNIPz-DCHM. A dianhydride with piperazine moiety (NNIPz) was synthesized from 4-bromonaphthalic anhydride (2 eq) and piperazine (1 eq). NNIPz (8 mol%) was dissolved in DMAc with DCHM and ODPA (92 mol%) to afford a copoly(amic acid) solution. ODPA-NNIPz-DCHM (co-PI) film was obtained by the same procedure as ODPA/DCHM.
[Result and Discussion] The chemical structure and the excitation and fluorescence spectra of homo-PI and co-PI are shown in Fig. 1. The homo-PI exhibits blue fluorescence (λ_{em}=400 nm) by excitation at 340 nm, which is attributable to the local transition of ODPA moiety, whereas the co-PI shows green fluorescence (λ_{em}=525 nm) attributable to the local transitions of the NNIPz moiety, which is caused by the efficient Förster resonance energy transfer (FRET) from ODPA to NNIPz. Moreover, the co-PI exhibits significantly large fluorescence quantum yield (Φ = 46%), and the introduction of electron-donating alicyclic amino group into the dianhydride moiety is effective to enhance the fluorescence intensity of PIs. We also analyzed the energy transfer process in the co-PI by using a streak camera. The time-resolved fluorescence spectra of co-PI and the fluorescence decay profiles of homo-PI and co-PI are shown in Figs. 2 and 3, respectively. In Fig. 2, both of the blue fluorescence peak (λ_{em}=400 nm) and green fluorescence peak (λ_{em}=515 nm), which are attributable to the local transition of ODPA and NNIPz, respectively, are observed immediately after excitation. The fluorescence peak derived from ODPA was rapidly quenched, and then at a long time, the fluorescence derived from NNIPz becomes dominant and the spectrum coincides well with the steady-state fluorescence spectrum. These results indicate that effective energy transfer was induced from the ODPA to NNIPz. Furthermore, we evaluated the energy transfer efficiency (E=1−τ_{DA}/τ_D)), which represents the ratio of photons absorbed by the donor and transferred to the acceptor. Herein, τ_{DA} and τ_D denote the fluorescence lifetime (λ_{em}=410 nm) of co-PI and homo-PI, respectively. In Fig. 3, the values of τ_{DA} and τ_D are estimated as 0.86 ns and 7.94 ns, respectively, and E=89.2 %. This very high efficiency should be due to the significant overlap between the fluorescence spectrum of ODPA and the absorption spectrum of NNIPz. In summary, it was demonstrated that the absorption and fluorescence properties can be precisely controlled by copolymerization using two kinds of dianhydrides, which could contribute to the development of highly efficient LEDs and spectrum converters.

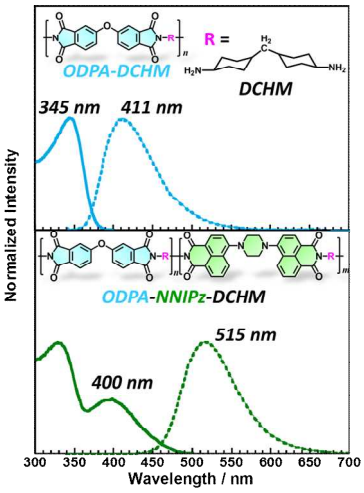

Fig. 1. Excitation and emission spectra of ODPA-DCHM (homo-PI) and ODPA-NNIPz-DCHM (co-PI).

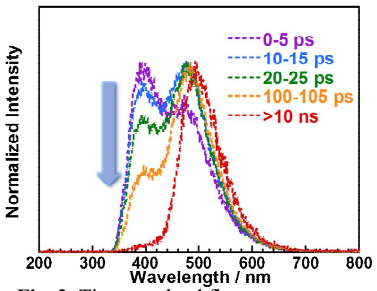

Fig. 2. Time-resolved fluorescence spectra of ODPA-NNIPz-DCHM (co-PI) measured by a streak camera.

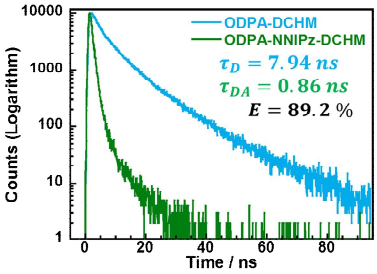

Fig. 3. Fluorescence decay profiles of ODPA-DCHM (homo-PI) and ODPA-NNIPz-DCHM (co-PI) from the spectra in Fig. 2.

[Reference] [1] J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, 19, 15212-15224 (2009). [2] R. Orita, K. Kanosue, R. Ishige, S. Ando, *Annual Meeting on Photochemistry, Japan 2016*, 2D02.
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