Synthesis and Optical Properties of Fluorescent Compounds Toward End-capped Polyimides Exhibiting Red/White ESIPT Fluorescence

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Fluorescent polyimides (PIs) are expected to be applied to solar spectrum down-convertor due to their excellent properties such as thermal stability, mechanical strength, and chemical resistance. In particular, the compounds, which exhibit fluorescence via excited-state intramolecular proton transfer (ESIPT) mechanism in which the protons at the acidic groups (enol) is transferred to the basic groups (keto), have much interests because they have extremely large Stokes shifts. Previously, we have reported two imide model compounds (3SAPI, 3TfAPI) (**Fig. 1**) with intramolecular hydrogen bonds which exhibit fluorescence with large Stokes shifts via ESIPT in solution and solid states [1,2].

In this study, we investigated the optical properties of 3SAPI and 3TfAPI dispersed in PMMA matrix, and tried to synthesize ESIPT anhydrides for developing novel end-capped fluorescent PI films. In the measurements, the films in which $CHCl_3$ was used as a solvent and 3SAPI was dispersed in PMMA at 0.3, 1.0 wt% and 3TfAPI at 1.0 wt% were used.

Both 3SAPI and 3TfAPI dispersed in PMMA were colorless and transparent films, and emitted red or yellow fluorescence under UV irradiation, respectively, as seen in Fig. 2 insets. Excitation / emission spectra of 3SAPI and 3TfAPI films are shown in **Fig. 2**. Both films exhibited fluorescence with very large Stokes shifts which are assignable to fluorescence from keto form via ESIPT process. While 3TfAPI showed weak fluorescence from enol form at 376 nm, 3SAPI exhibited strong emission at 432 nm. This peak can be attributed to fluorescence derived from aggregation structure because the emission intensity is reduced in film at 0.3 wt% and has different excitation wavelength from keto fluorescence. For 3SAPI dispersed in PMMA, pink emission was realized thanks to the aggregation.

The synthetic procedure of ESIPT anhydride is shown in **Fig. 3**. In both Step 1 and Step 2, it was difficult to remove impurities. In the future, we will try to synthesize ESIPT anhydrides by another route in order to get the pure compounds and will go on to develop end-capped fluorescent PIs.

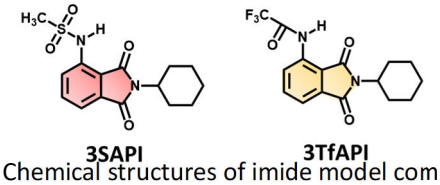

Fig. 1 Chemical structures of imide model compounds.

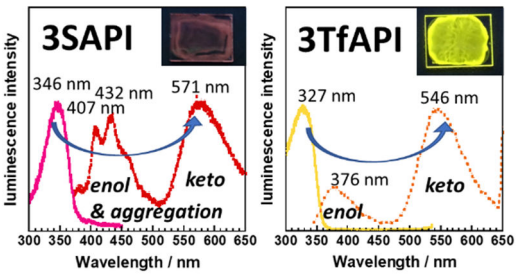

Fig. 2 Excitation / emission spectra of 3SAPI and 3TfAPI dispersed in PMMA with 1.0 wt%.

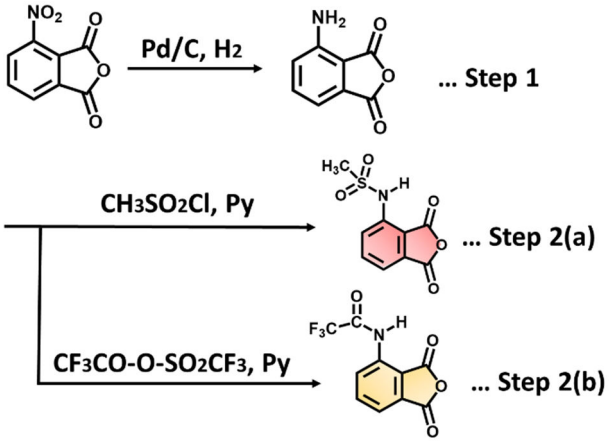

Fig. 3 Synthetic procedure.

[1] T. Kambara, K. Kanosue, S. Ando, *Abstract of Annual Meeting on Photochemistry 2014*, 1P109.

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