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

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Introduction

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 [1]. In particular, the compounds which exhibit fluorescence via excited-state intramolecular proton transfer (ESIPT) mechanism have attracted much interests because they exhibit extremely large Stokes shifts. Previously, we have reported two imide model compounds (3SAPI, 3TfAPI) (**Fig. 1**) which form intramolecular hydrogen bonds and exhibit fluorescence with large Stokes shifts via ESIPT in solution and the solid states [2]. In this study, we investigated the optical properties of 3SAPI and 3TfAPI dispersed in PMMA matrix and tried to synthesize novel anhydrides with ESIPT property for developing novel end-capped fluorescent PIs.

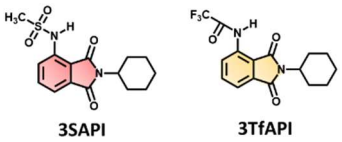

Fig. 1 Chemical structures of imide model compounds.

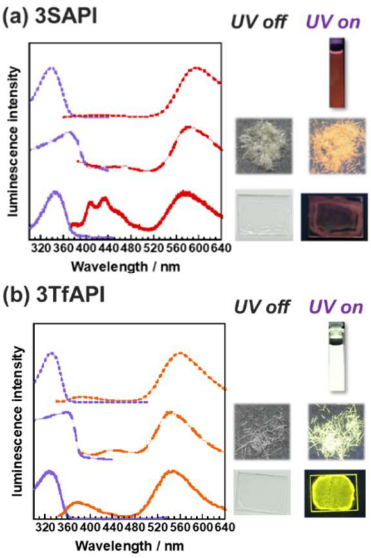

Fig. 2 Excitation / emission spectra of (a) 3SAPI and (b) 3TfAPI in $CHCl_3$ solution (top), solid state, and PMMA matrix (bottom), respectively.

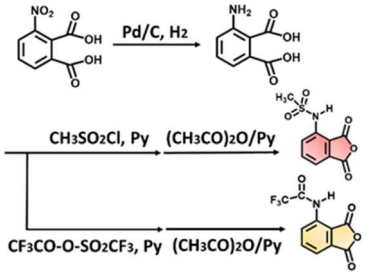

Fig. 3 Synthetic schemes for new ESIPT anhydrides.

Results and Discussion

3SAPI and 3TfAPI were dispersed in PMMA matrix at 1.0 wt%. These films were colorless, transparent, and emitted pink or yellow fluorescence under UV irradiation, respectively. Excitation / emission spectra of 3SAPI and 3TfAPI in $CHCl_3$ solution, in powdery solid state, and in PMMA films are shown in **Fig. 2**. Both films exhibited fluorescence with very large Stokes shifts which are assignable to fluorescence from the keto form via ESIPT. While 3TfAPI showed weak fluorescence from enol form at 376 nm, 3SAPI exhibited strong emission at 432 nm, which was not observed in solution and solid state. It is attributable to the fluorescence derived from aggregation structures because the emission intensity reduced with decreasing 3SAPI concentration, and the excitation wavelength (377 nm) was different from the keto fluorescence (346 nm). For 3SAPI dispersed in PMMA, pink colored emission was observed owing to the aggregation structures. These findings were useful for analyzing the optical properties of PI films end-capped by ESIPT compounds. Now, we are developing new ESIPT anhydrides applicable to end-capped PIs with the synthetic procedures shown in **Fig. 3**. These end-cap groups would be good candidates for large Storks-shifted PIs.

References

1) J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **19**, 15212-15224 (2009).
2) T. Kambara, K. Kanosue, S. Ando, *Abst. Annual Meeting on Photochemistry* 2014, 1P109.