9.Red-Shifted Fluorescence of Thiol-containing Imide Compound via Excited-State Intramolecular Proton Transfer

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Abstract: Highly fluorescent polyimides[1,2] are expected to be applied to solar wavelength converter due to their controllable optical properties with multi-color emissions, excellent heat resistance, and mechanical strength. For practical applications, further enhancement of Stokes shift (SS), which is the difference between the excitation and fluorescence (FL) wavelengths, and an increase in quantum yield are demanded.

Excited-state intramolecular proton transfer (ESIPT) is a phenomenon in which proton transfer occurs within a molecule upon exposure to excitation light, undergoing tautomerization from the enol form (E*) to the keto form (K*), resulting in long-wavelength FL. This mechanism is effective for expanding SS by shifting the FL to a longer wavelength (**Fig. 1**).

In this study, a novel imide compound (2SPM, **Fig. 2a**) possessing two thiol groups (−SH) was designed and synthesized with the aim of achieving reddish FL exhibiting an exceptionally large SS. The optical properties of 2SPM and its monothiol counterpart (1SPM, **Fig. 2b**), used as a control, were evaluated in various organic solvents. Their emission behaviors were systematically classified and discussed based on two indices: the solvent polarity parameter ($E_T(30)$) and hydrogen-bond accepting ability (β). The results revealed that 2SPM exhibits distinct emission characteristics depending on the surrounding microenvironment. Notably, excited-state double proton transfer (ESDPT) occurred in the solvents with low polarity, resulting in red FL. Furthermore, 'Solvent-assisted ESDPT' was induced in the solvents with high polarity and high β. These findings represent the first example of ESDPT in SH-type imide compounds, which demonstrates that the surrounding environment, *i.e.*, polarity and hydrogen-bond accepting ability, is the dominant factor for the photophysical processes of excited-state proton transfer. The insights thus obtained provide essential molecular design guidelines for predicting FL behaviors in various solution and extrapolating these properties to solid-state polymer environments, such as polyimide wavelength conversion films, for practical applications.

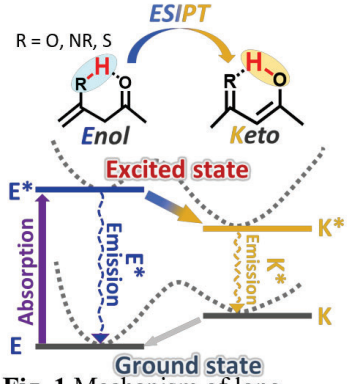

Fig. 1 Mechanism of long Stokes-shifted fluorescence via ESIPT.

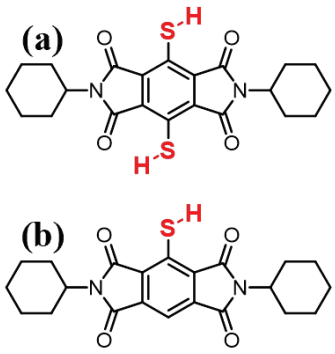

Fig. 2 Chemical structures of **(a)** 2SPM and **(b)** 1SPM.

Key words: Polyimide, ESIPT, Thiol group, ESDPT

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