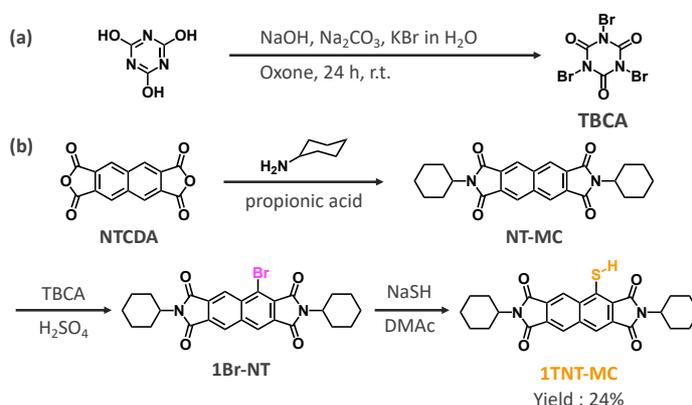


## Luminescence Behavior of Thiol-Containing Imide Compounds via Excited State Intramolecular Proton Transfer

(Tokyo Tech.) ANDO, Yuka; DOI, Marina; TABUCHI, Atsuko; LIU, Haonan; ANDO, Shinji

**[Introduction]** Fluorescent organic and polymeric materials have advantages in terms of cost, weight, and non-toxicity. We have been reporting a series of highly fluorescent polyimides applicable to solar-spectrum converters, owing to their excellent thermal stability, mechanical strength, and chemical resistance [1]. However, achieving long wavelength fluorescence under UV irradiation with high transparency in the visible region is challenging due to the limited Stokes shift (SS) of fluorescence. Therefore, we have focused on the excited-state intramolecular proton transfer (ESIPT) phenomenon which undergoes in imide compounds. Upon excitation, the hydrogen in an inter-molecularly hydrogen-bond structure transfers to the carbonyl oxygen in the imide group in the excited state. Simultaneously, the molecular structure changes from the normal form (N\*) to the tautomer form (T\*) accompanying an energy dissipation. Therefore, ESIPT generally provides a long-wavelength fluorescence with a large SS. We have reported a series of ESIPT imide compounds with phenolic hydroxyl (OH-type) and substituted amino (NH-type) groups as novel ESIPT compounds exhibiting multi-color fluorescence [2–5]. Recently, Chou et al. reported a derivative of 3-thiolflavone containing a thiol group (SH-type) exhibits a bright-red fluorescence *via* ESIPT [6]. In this study, a novel thiol-containing imide compound (1TNT-MC) was designed and synthesized, which undergoes ESIPT, and its photophysical process was analyzed based on their excitation and emission spectra.

**[Experimental]** 1TNT-MC newly designed by TD-DFT was synthesized using NTCDA dianhydride (JFE Chemical Corp.), cyclohexylamine, and a brominating reagent (TBCA) (**Fig. 1**). The luminescence spectra of 1TNT-MC in various organic solvents were measured with F-7100 fluorescence spectrophotometer (Hitachi High-Tech) at room temperature at a concentration of  $2.5 \times 10^{-4}$  mol/L.



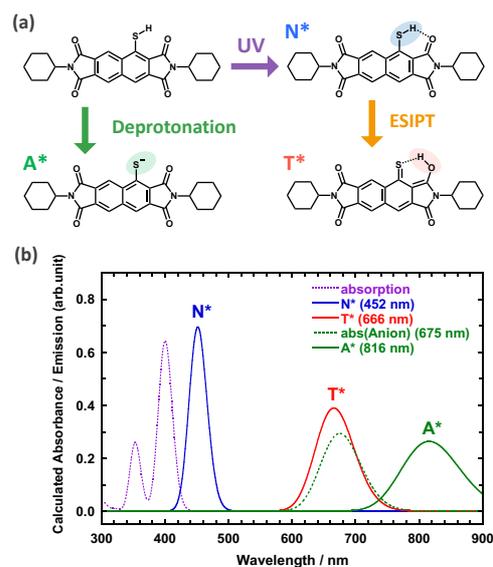
**Fig. 1** Synthetic schemes of (a) TBCA and (b) 1TNT-MC.

**[Results and Discussion]** **Fig. 2(a)** and **2(b)** show the structures and the calculated absorbance and fluorescence spectra of the N\*, T\*, and the anionic (A\*) forms of 1TNT-MC based on the TD-DFT (CAM-B3LYP/6-311+G(2d,p)//B3LYP/6-311+G(2d,p)), respectively, which predicts that 1TNT-MC would exhibit fluorescence peaks corresponding to N\*, T\*, and A\* forms at 452, 666, and 816 nm in cyclohexane (Cychex), respectively. This indicates that a large Stokes-shifted reddish fluorescence *via* ESIPT would be observed in solution state, and similar experimental results were obtained in dimethyl

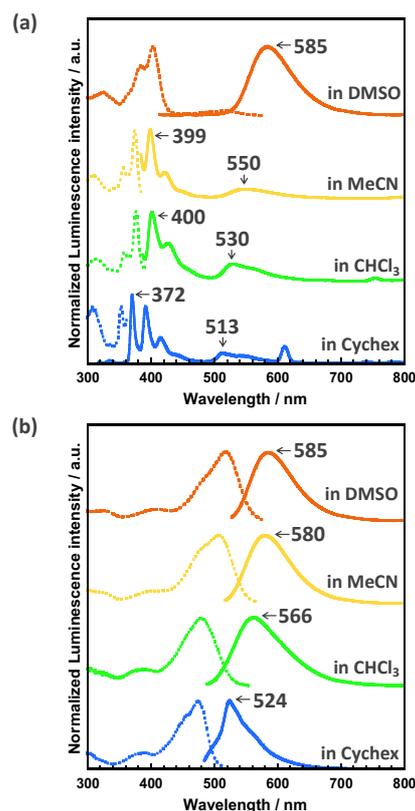
sulfoxide (DMSO), acetonitrile (MeCN), and chloroform (CHCl<sub>3</sub>). The experimental excitation and emission spectra of 1TNT-MC in DMSO, MeCN, CHCl<sub>3</sub>, and Cycchex are shown in **Fig. 3(a)**. Intense N\* fluorescence with vibrational structures were observed around 400 nm as well as small and broad peaks at 500–600 nm in MeCN, CHCl<sub>3</sub>, and Cycchex. The latter peaks with large SS are attributable to T\* fluorescence. In contrast, only a broad and intense T\* fluorescence was observed at 585 nm in DMSO. When a small amount of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) [10<sup>-2</sup> M] was added as an organic base, strong emission peaks were observed at 500–700 nm in all solutions (**Fig. 3(b)**). This long wavelength emission is attributable to A\* fluorescence because the corresponding excitation peaks were shifted from the UV to the visible region. This is because the strong basicity of DBU deprotonates the –SH hydrogen in the ground state. Accordingly, 1TNT-MC exhibits N\* (blue), T\* (reddish orange), and A\* (green) fluorescence in different solutions, and its fluorescence colors can be controlled by adjusting the proton-accepting ability of the solvent. Interestingly, the T\* and A\* fluorescence of 1TNT-MC exhibits a much wider range of solvatochromism than those of the previously reported OH-type and NH-type ESIPT compounds, which could be originated from the environmentally sensitive –S–H···O= hydrogen bonding.

### [References]

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**Fig. 2** (a) Structural change in N\*, T\*, and A\* forms, and (b) calculated absorption and emission spectra of 1TNT-MC in Cycchex.



**Fig. 3** Excitation (dotted line) / emission (solid line) spectra of 1TNT-MC (a) in various solvents and (b) after adding DBU (basic condition).