

## Multi-colored fluorescence properties of thiol-containing imide compounds via excited state intramolecular proton transfer

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### Introduction

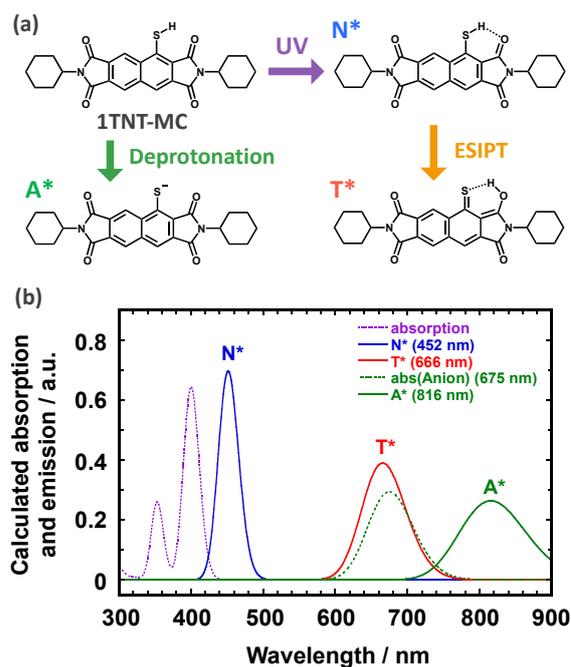
Fluorescent organic and polymeric materials have advantages in terms of cost, weight, and non-toxicity. We have been reporting a series of highly fluorescent polyimides applicable to solar-spectrum converters, owing to their excellent thermal stability, mechanical strength, and chemical resistance [1]. However, achieving long wavelength fluorescence (FL) under UV irradiation with high transparency in the visible region is challenging due to the limited Stokes shift (*SS*) of FL. 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 FL with a large *SS*. We have reported a series of novel ESIPT imide compounds with phenolic hydroxyl (OH-type) and substituted amino (NH-type) groups exhibiting multi-color FL [2–5]. Recently, Chou *et al.* reported a derivative of 3-thioflavone containing a thiol group (SH-type) exhibits a bright-red FL *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.

### Experiment

1TNT-MC was synthesized using 2,4,6,7-naphthalenetetracarboxylic dianhydride (JFE Chemical Corp.), cyclohexylamine, and a brominating reagent (tribromocyanuric acid). The optical measurements of 1TNT-MC were taken at room temperature at a concentration of  $2.5 \times 10^{-4}$  mol/L.

### Results and Discussion

**Fig. 1** shows the chemical structures and the calculated absorbance and FL 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)), which predicts that 1TNT-MC would exhibit FL peaks corresponding to  $N^*$ ,  $T^*$ , and  $A^*$  forms at 452, 666, and 816 nm in cyclohexane (Cycchex), respectively. This indicates that a large Stokes-shifted reddish FL *via* ESIPT would be observed in solution state, and similar experimental results were obtained in dimethyl sulfoxide (DMSO), acetonitrile (MeCN), and chloroform ( $\text{CHCl}_3$ ). The experimental excitation and emission spectra of 1TNT-MC in DMSO, MeCN, and  $\text{CHCl}_3$ , and Cycchex are shown in **Fig. 2(a)**. Intense  $N^*$  FL with vibrational structures were observed around



**Fig. 1** (a) Structural change in  $N^*$ ,  $T^*$ , and  $A^*$  forms, and (b) calculated absorption (dotted line) and emission (solid line) spectra of 1TNT-MC in Cycchex.

400 nm as well as small and broad peaks at 500–600 nm in MeCN, CHCl<sub>3</sub>, and Cyhex. The latter peaks with large SS are attributable to T\* FL. In contrast, only a broad and intense T\* FL 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. 2(b)). This long wavelength emission is attributable to A\* FL because the corresponding excitation peaks were shifted from the UV to the visible region. A\* is generated by the strong basicity of DBU deprotonating the –SH hydrogen in the ground state. Accordingly, 1TNT-MC exhibits N\* (blue area), T\* (red area), and A\*(green area) FL in different solutions, and its FL colors can be controlled by adjusting the proton-accepting ability of the solvent. Also, Fig. 2 and Table 1 showed that emission wavelengths of T\* and A\* were shifted to longer wavelengths, FL lifetimes became longer, and quantum yields decreased with increasing solvent polarity. This may be due to the stabilization of excited molecules by solvation in highly polar solvents. Interestingly, the T\* and A\* emission of 1TNT-MC exhibits a much wider range of solvatochromism than those of the previously reported OH-type and NH-type ESIPT compounds. This may be attributed to the small electronegativity of the sulfur atom, which weakens the strength of intramolecular –S–H···O= hydrogen bonding, resulting in a significant change in the stable structure and electronic state in solution.

## References

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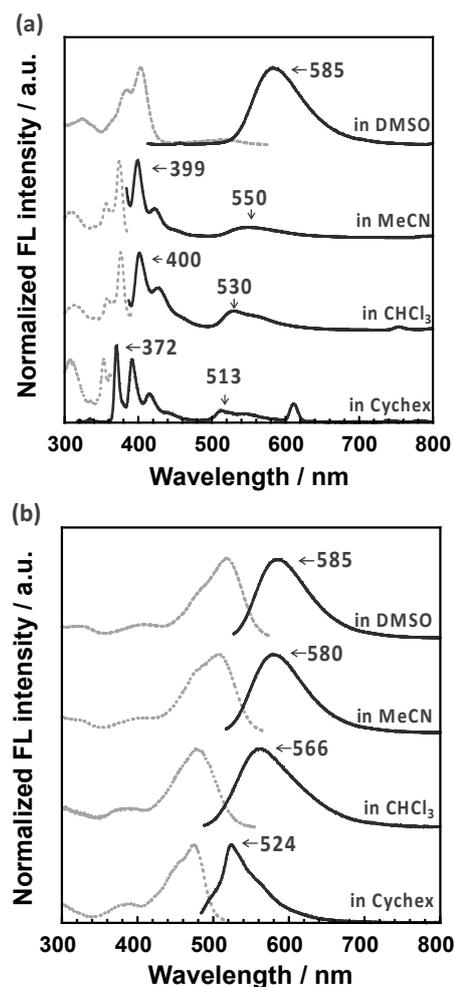


Fig. 2 Excitation (dotted line) / emission (solid line) spectra of 1TNT-MC (a) in various solvents and (b) those after adding DBU (basic condition).

Table 1 FL lifetimes and quantum yields of 1TNT-MC measured in various solvents.

| Solvent           | Lifetime /ns |     |     | Quantum yield |      |      |
|-------------------|--------------|-----|-----|---------------|------|------|
|                   | N*           | A*  | T*  | N*            | A*   | T*   |
| DMSO              | -            | 6.7 | 7.6 | -             | 0.16 | 0.08 |
| MeCN              | 5.8          | 6.7 | 7.4 | 0.14          | 0.11 | 0.06 |
| CHCl <sub>3</sub> | 1.6          | 5.4 | 4.9 | 0.24          | 0.64 | 0.12 |
| Cyhex             | 1.3          | 3.5 | 2.1 | 0.49          | 0.41 | 0.18 |