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Novel phthalimide compound having proton-transfer ability and exhibiting full colored fluorescence in the visible region under UV irradiation

Atsuko Tabuchi, Teruaki Hayakawa, Shigeki Kuwata, Ryohei Ishige, and Shinji Ando*
(Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1-E4-5 Ookayama, Meguro-ku, Tokyo 152-8552, Japan)
Tel: +81-3-5734-2889, Fax: +81-3-5734-2889, E-mail: tabuchi.a.aa@m.titech.ac.jp

INTRODUCTION:

Highly fluorescent polyimides (FL-PIs) are promising candidates for solar spectrum down-convertors owing to their excellent properties such as thermal stability, mechanical strength, and chemical resistance. However, long wavelength fluorescence is difficult to achieve for the colorless FL-PIs due to the small Stokes shifts (*SS*) [1]. We have reported that a series of imide compounds forming intramolecular hydrogen bond emit green to reddish fluorescence with very large *SS* values (*SS* > 10,000 cm^{-1}) *via* excited-state intramolecular proton transfer (ESIPT) [1−3]. In the ESIPT process, excited energy is relaxed with structural relaxation (tautomerization) from *Normal* form (N*) to *Tautomer* (T*) through proton transfer in the excited states, resulting in a longer wavelength fluorescence. In this study, we designed and synthesized a new fluorophore of *N*-cyclohexylphthalimide substituted with a *p*-toluenesulfonyl (tosyl) group (3TsAPI, **Figure 1a**), which exhibits large *SS* fluorescence based on ESIPT. The 3TsAPI exhibited full-color solvatochromic fluorescence in organic solvents having different polarities. The mechanism of full-color FL was clarified by several spectroscopic measurements and the time-dependent density functional theory (TD-DFT).

EXPERIMENTAL:

The synthesis route of 3TsAPI was reported elsewhere [4]. The concentration of 3TsAPI in the solvents was set to 2.5 × 10^{-4} mol/L, and the UV-vis absorption and photoluminescence spectra were recorded at room temperature.

RESULTS AND DISCUSSION:

TD-DFT calculations predicted that 3TsAPI in toluene absorbs only UV radiation and exhibit reddish fluorescence *via* ESIPT (**Figure 1b**). The synthesized 3TsAPI exhibits orange fluorescence with a

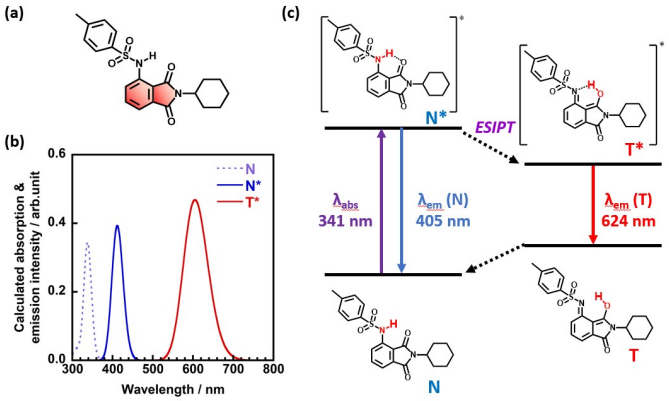

Figure 1. (a) Chemical structure of 3TsAPI. (b) Calculated UV-vis absorption (dashed line) and emission (solid lines) spectra of 3TsAPI in *Normal* form (N*, blue) and *Tautomer* form (T*, red) in toluene. (c) Photophysical process relating to this form.

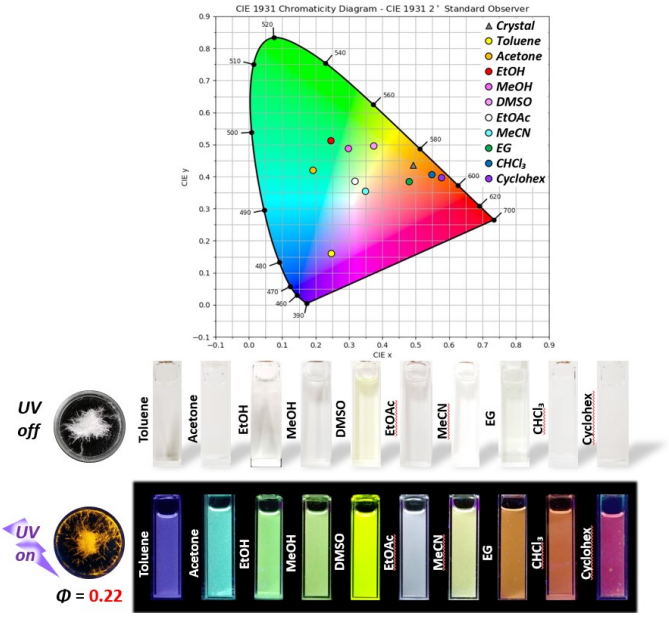

Figure 2. International Commission on Illumination (CIE) coordinates for the fluorescence colors of 3TsAPI in the crystalline state and in various organic solvents, and photographs of crystal and these solutions under white light (UV off) and UV (*λ*= 365 nm) irradiation (UV on).

very large *SS* (9784 cm^{-1}) at a high quantum yield (Φ = 0.22) in the crystalline state because the bulky tosyl and cyclohexyl substituents suppress aggregation caused quenching (ACQ) (**Figure 2**). Interestingly, 3TsAPI exhibits fluorescence in the full-color range from purple to red when dissolved in 10 kinds of organic solvents (**Figure 2**). We tried to clarify its mechanism using UV-vis absorption (λ_{abs}), excitation (λ_{ex}), and emission (λ_{em}) spectroscopy; lifetime (τ) measurements; and TD-DFT calculations. The acquired values of λ_{abs}, λ_{ex}, λ_{em}, *SS* and τ are summarized in **Table 1**. The fluorescence spectra exhibited three different bands at around 400, 500, and 600 nm, named F_{400}, F_{500}, and F_{600}, respectively. First, F_{600} is attributable to T* fluorescence due to the very short lifetime (τ < 1.0 ns) and very large *SS* (11277 cm^{-1} < *SS*) in accord with the calculated T* fluorescence (λ_{em} = 624 nm). Second, F_{400} is attributable to N* fluorescence due to its short lifetime (1.0 < τ < 5.0 ns) in accord with the calculated N* fluorescence (λ_{em} = 405 nm). Since the electron-withdrawing tosyl group possibly induces dissociation of the hydrogen atom in the amide group, the λ_{abs} and λ_{em} were calculated for the anionic form (A*) in DMSO as λ_{abs} = 429 nm, λ_{em} = 513 nm (**Figure 3a**). The observed λ_{ex} and λ_{em} of F_{500} are close to those calculated for A*. In addition, F_{500} can be effectively suppressed by addition of a small amount of trifluoroacetic acid into the solution as shown in **Figure 3b**. Therefore, F_{500} is attributable to A* fluorescence. In summary, the significant changes in fluorescent colors of 3TsAPI depending on the polarity of solvents is achieved based on a subtle balance among the N*, T*, and A* forms, arising from the interactions between 3TsAPI and the various solvents.[4] These properties have a great potential for spectral converting and chemical sensing applications.

Table 1. Photoluminescence properties, absorption wavelengths (λ_{abs}), excitation and emission wavelengths (λ_{ex}, λ_{em}), Stokes shifts (ν), fluorescence lifetimes (τ), and quantum yields (Φ) of 3TsAPI dissolved in organic solvents with different polarities. Data row of fluorescence emitted from N*, A*, and T* states are colored with light blue, green, and orange, respectively.

Solvent	λ_{abs} /nm	λ_{ex} /nm	λ_{em} /nm	ν /cm^{-1}	τ /ns	Φ
Toluene	342	346	602	12288	0.4	0.06
		361	409	3263	4.8	0.07
Acetone	337	351	599	11796	0.2	0.01
		351	420	4681	1.6	
		400	496	4822	11.2	0.19
EtOH	339	395	507	5585	7.1	0.15
MeOH	337, 400	392	508	5825	9.7	0.09
DMSO	339, 419	419	528	4927	5.6	0.21
EtOAc	338	350	600	11905	0.1	0.02
		400	490	4592	12.6	0.31
MeCN	337	345	597	12235	0.1	0.02
		395	493	5049	7.7	0.14
EG	337	355	592	11277	0.9	0.02
		355	427	4750	0.4	
$CHCl_3$	341	350	601	11927	0.3	0.04
Cyclohex	341	346	598	12168	0.3	0.03

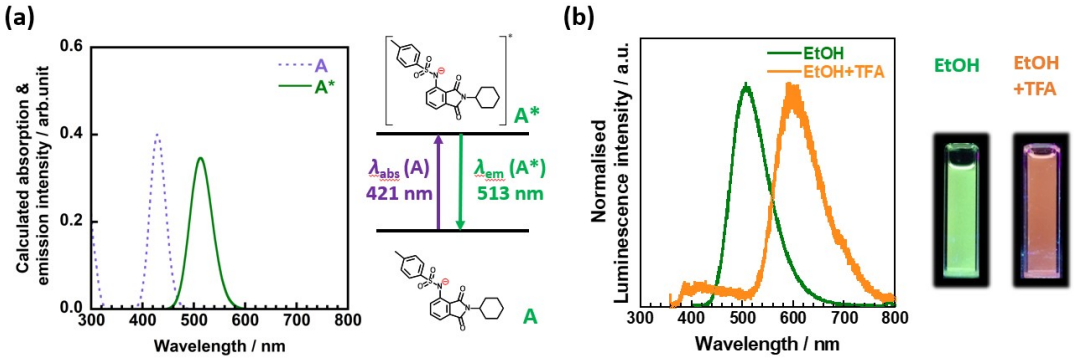

Figure 3. (a) Calculated UV-vis absorption (dashed line) and emission (solid lines) spectra of 3TsAPI in anionic form (A and A*) in DMSO, and the photophysical process of anionic form. (b) Emission spectra of 3TsAPI dissolved in EtOH (λ_{ex} = 395 nm, green) and a mixed solvent of EtOH/TFA (λ_{ex} = 347 nm, orange). The concentration of TFA was 2.0 × 10^{-4} mol/L.

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