Synthesis and photophysical processes of a tosyl-substituted ESIPT phthalimide that emits full-color fluorescence in solution

A. Tabuchi, T. Hayakawa, S. Kuwata, R. Ishige and S. Ando*
Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan
e-mail: tabuchi.a.aa@m.titech.ac.jp

I. Introduction

Highly fluorescent polyimides (FL-PIs) are promising candidates for solar spectrum down-convertors owing to their excellent properties such as thermal and photothermal stability and chemical resistance. We have reported that a series of imide compounds that form intramolecular hydrogen bond emit green to reddish fluorescence with very large *SS* values (> 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 novel ESIPT phthalimide compound (3TsAPI, **Fig. 1a**) that exhibits large *SS* fluorescence based on ESIPT. 3TsAPI exhibited full-color solvatochromic fluorescence in various solutions. The mechanism of full-color FL was clarified by several photophysical measurements and the time-dependent density functional theory (TD-DFT).

II. Results and Discussion

TD-DFT calculations predicted that 3TsAPI absorbs only UV light and exhibit reddish fluorescence *via* ESIPT (**Fig. 1b**). The synthesized 3TsAPI exhibits orange fluorescence with a very large *SS* (9784 cm^{-1}) at a high quantum yield in the crystalline state because the bulky tosyl substituent suppresses aggregation caused quenching (ACQ) (**Fig. 1c**). Interestingly, 3TsAPI exhibits fluorescence in the full-color range from purple to red when dissolved in ten kinds of organic solvents (**Fig. 1c**). The experimental parameters of the full-color FL obtained by UV-vis absorption (λ_{abs}), excitation (λ_{ex}) and emission (λ_{em}) spectroscopy, lifetime (τ) measurements, and TD-DFT calculations are summarized in **Table 1**. The FL spectra can be decomposed into three peaks at around 400, 500, and 600 nm, named F_{400}, F_{500}, and F_{600}, respectively. First, F_{600} is attributed to T* fluorescence due to the very short lifetime (τ < 1.0 ns) and very large *SS* (11277 cm^{-1} < *SS*) in accordance with the calculated T* fluorescence (λ_{em} = 624 nm). Second, F_{400} is attributed to N* fluorescence due to its short lifetime (1.0 < τ < 5.0 ns) in accordance 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. The experimental 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. Therefore, F_{500} is attributed to A* fluorescence. In summary, the significant changes in fluorescent colors of 3TsAPI depending on the polarity of solvents is caused by the subtle equilibrium of 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.

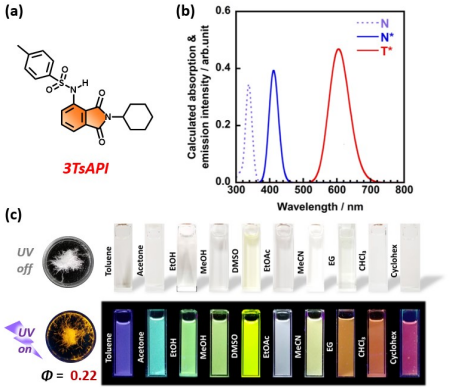

Fig.1 (a) Chemical structure of 3TsAPI (b) Calculated UV-vis absorption (dashed line) and emission (solid lines) spectra of 3TsAPI in Normal form (N*, blue) and Tautomer form (T*, red). (c) Photographs of 3TsAPI in the crystalline state and in organic solvents under white light (UV off) and UV irradiation (UV on).

Table 1. Photophysical parameters of 3TsAPI in solutions.

Solvent	λ_{abs} /nm	λ_{ex} /nm	λ_{em} /nm	*SS* /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	
CHCl3	341	350	601	11927	0.3	0.04
Cyclohex	341	346	598	12168	0.3	0.03

References

[1] J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **19**, 15212-15224 (2009).
[2] J. Wakita, S. Inoue, N. Kawanishi, S. Ando, *Macromolecules*, **43**, 3594-3605 (2010).
[3] T. Kambara, K. Kanosue, S. Ando, *Abst. Annual Meet. Photochem.* 1P109 (2014).
[4] A. Tabuchi, T. Hayakawa, S. Kuwata, R. Ishige, S. Ando, *Mater. Adv.(RSC),* DOI: 10.1039/d1ma00308a (2021).