Development of a white-color fluorescent polyimide end-capped with a luminophore undergoing excited state intramolecular proton transfer

Atsuko Tabuchi, Mayuko Nara, Teruaki Hayakawa, Ryohei Ishige, Shinji Ando
Tokyo Institute of Technology
e-mail: tabuchi.a.aa@m.titech.ac.jp

Introduction

White-light emitting organic molecules and polymers have been receiving a great deal of attention because they are applicable to simple and low-cost white organic light-emitting diodes (WOLEDs) which is expected to contribute to the miniaturization of various ICT devices. Moreover, OLEDs based on a single luminophore possess high stability and excellent productivity. To achieve a white light emission, luminescence spectra covering the whole visible wavelength region is required. Although we have successfully prepared highly fluorescent polyimides (PIs) exhibiting high thermal and environmental stability, long wavelength fluorescence was difficult to achieve due to the small Stokes shifts (*SS*) [1]. To overcome this problem, we have developed a novel fluorescent imide compound forming intramolecular hydrogen bond (*3TfAPI*, **Fig. 1a**). This compound emits long-wavelength fluorescence with very large *SS* values (8947-12317 cm^{-1}) through excited-state intramolecular proton transfer (ESIPT) in $CHCl_3$ solution and in the crystalline state (**Fig. 1b**) [2]. ESIPT is the process in which the energy is relaxed by the structural relaxation (tautomerization) from Normal form (N*) to Tautomer (T*) through proton transfer in the excited states, resulting in a long-wavelength fluorescence. In this study, we designed and synthesized an ESIPT anhydride (*3TfAPA*, **Fig. 1c**), and attempted to develop a novel white-color luminescent PI film by introducing *3TfAPA* anhydride as an end-capping agent to a blue-fluorescent PI (*ODDC* or *ODtDA*) with different molar ratios. (**Fig. 1d**)

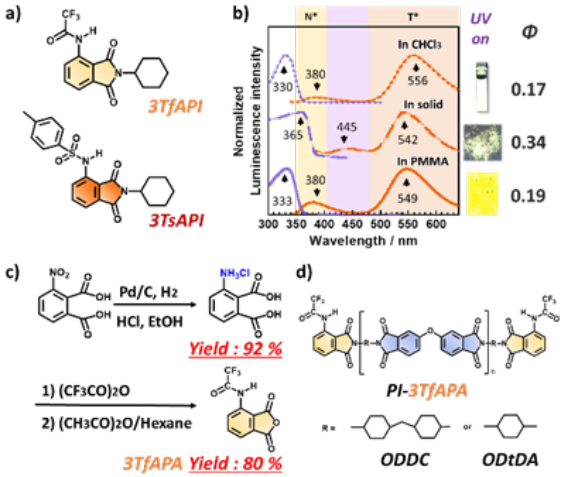

Fig. 1 (a) Chemical structures of imide compounds (*3TfAPI*, *3TsAPI*). (b) Excitation/ emission spectra of *3TfAPI* in solution, in crystalline state, and in PMMA matrix. (c) Synthetic scheme of a new ESIPT anhydride (*3TfAPA*). (d) Chemical structures of end-capped PIs (*ODDC-3TfAPA, ODtDA-3TfAPA*).

Experimental

4,4′-Oxydiphthalic anhydride (*ODPA*) and 4,4′-diaminodicyclohexylmethane (*DCHM*) or 1,4-*t*-Diaminocyclohexan (*tDACH*) were reacted in *N,N*-dimethylacetamide (DMAc) for 1 day

to give poly(amic acid) (PAA) precursors. Meanwhile, *3TfAPA* was added to the PAA solutions with predetermined molar ratios (*r*/50) and stirred for 2 days to give PAAs of *ODDC-3TfAPA* or *ODtDA-3TfAPA* (*r* = 1.98, 3.96, 7.92, 14.8). Viscous PAA solutions were spin-coated onto fused silica substrates, soft-baked at 70°C for 50 min, and subsequently imidized by thermal curing from 70°C to 220°C at a heating rate of 3°C/min under a N_2 flow. The PI film was kept at 220°C for 1.5 h to obtain end-capped PI films.

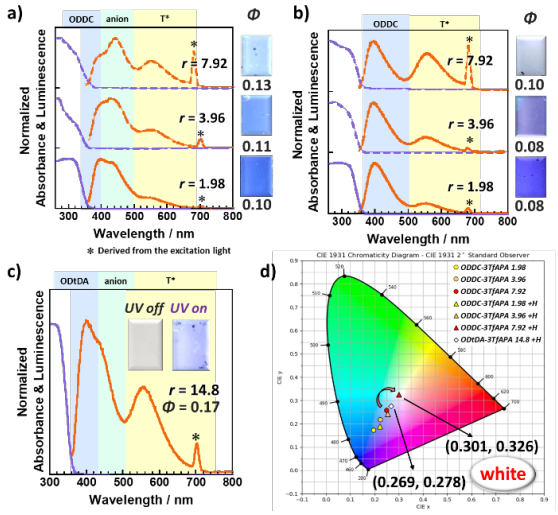

Fig. 2 UV-vis absorption and luminescence spectra of (a) *ODDC-3TfAPA*, (b) *ODDC-3TfAPA* with 0.5–1eq.H_2SO_4, (c) *ODtDA-3TfAPA* with 0.5eq. H_2SO_4. (d) CIE(1931) chromaticity coordinates of the end-capped PIs.

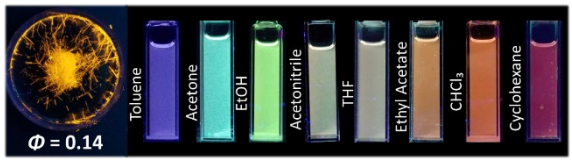

Fig. 3 Fluorescent solvatochromism of *3TsAPI* in various solvents (excited at 360 nm).

Results and Discussion

ODDC-3TfAPA films exhibited colorlessness, high optical transparency, and bright blue to light-blue fluorescent emissions under UV irradiation (**Figs. 2a** and **2d**). Comparison of emission spectra showed that the peak at 400 nm is readily attributed to the fluorescence from the *ODDC* (main chain) and those at 440 and 550 nm are originated from the *3TfAPA* termini. The large *SS* fluorescence at 550 nm (*SS*=10088 cm^{-1}) is attributable to the T* fluorescence, while the fluorescence at 440 nm was attributed to the anionic form of *3TfAPA* because this peak was effectively suppressed by adding a small amount of H_2SO_4 (0.5–1 equimolar of *3TfAPA*) to the PAA solution before imidization (**Fig. 2b**). The pure 'white-color fluorescence' was successfully obtained at *r* = 7.92 owing to the suppression of anionic fluorescence.

Moreover, by introducing a rigid and linear *ODtDA* main chain, local molecular motion was effectively suppressed, resulting in a higher quantum yield (Φ =0.17) than *ODDC* by 1.7 times (**Fig. 2c**). In summary, pure white fluorescence with the high quantum yield was successfully obtained at room temperature from a blue-fluorescent PI end-capped with a yellow-fluorescent ESIPT anhydride. Just recently, we have found that solutions of a new type of model compound (*3TsAPI*, **Fig. 1a**) having *p*-toluenesulfonyl group show 'rainbow colored' solvatochromism. Utilizing this result, we will try to develop multi-colored fluorescent PIs for various ranges of optical applications.

References

1) J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **19**, 15212-15224 (2009).
2) T. Kambara, K. Kanosue, S. Ando, *Abst. Annual Meet. Photochem.* 1P109 (2014).
3) K. Kanosue, T. Shimosaka, J. Wakita, S. Ando, *Macromolecules*, **48**, 1777-1785 (2015).