Preparation and optical properties of white-color fluorescent end-capped polyimide undergoing excited state intramolecular proton transfer

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[Introduction] White-light emitting organic molecules and polymers have been receiving a great deal of attention because they enable to fabricate 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 have high stability and excellent productivity. To achieve a white light emission, the luminescence spectrum should cover the whole visible region. When we firstly designed 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 novel fluorescent imide compounds that form intramolecular hydrogen bonds (*3HNHPI* and *3TfAPI*, **Fig.1a**). These compounds emit long-wavelength fluorescence with large SS values (> 10,000 cm^{-1}) through excited-state intramolecular proton transfer (ESIPT) in $CHCl_3$ solution and in the crystalline state [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, on the basis of the optical properties of *3TfAPI* dispersed in PMMA matrix (1.0 wt%), we attempted to develop a novel white-color luminescent PI film by a blue-fluorescent PI (*ODDC*) end-capped with *3TfAPA* dianhydride, that undergoes ESIPT, at different molar ratios. (*ODDC-3TfAPA*, **Fig.1b**)

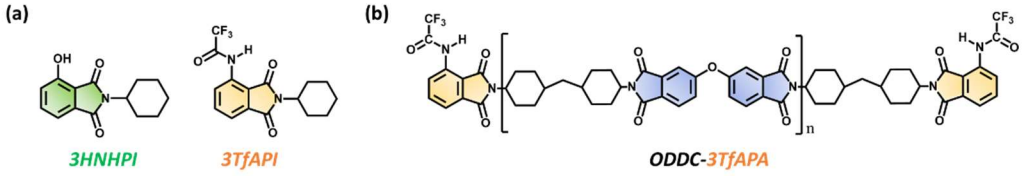

Fig.1 Chemical structures of (a) the imide model compounds (*3HNHPI* and *3TfAPI*) and (b) the end-capped PI (*ODDC-3TfAPA*).

[Experimental] A toluene solution containing *3TfAPI* and PMMA was drop-casted onto a fused silica substrate and dried at 60°C under a N_2 flow to prepare a PMMA film containing 1.0 wt% of *3TfAPI*. 4,4′-Oxydiphthalic anhydride (*ODPA*) and 4,4′-diaminodicyclohexylmethane (*DCHM*) were reacted in *N,N*-dimethylacetamide (DMAc) for 1 day to give a poly(amic acid) (PAA) precursor of *ODDC*. Meanwhile, *3TfAPA* was added to PAA solutions of *ODDC* with predetermined molar ratio (*r*/50) and stirred for 2 days to give PAAs of *ODDC-3TfAPA* (*r* = 1.98, 3.96, 7.92). For comparison, a PAA solution added with two-equimolar acid (H_2SO_4) to the end group (*r* = 7.92) was also prepared (*ODDC-3TfAPA*+2eq.H_2SO_4). 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.

[Results and Discussion] The optical properties of *3TfAPI* in $CHCl_3$, in the crystalline state, and in dispersed in PMMA matrix are summarized in **Fig.2a**. The long-wavelength fluorescence was observed at 542−556 nm in all the states. These peaks are attributable to the fluorescence from T* through ESIPT because of their very large SS values (8947-12317 cm^{-1}). They emitted yellowish fluorescence under UV irradiation as shown in **Fig.2a**. The luminescence quantum yields (Φs) in the crystalline state and in PMMA were higher than that in $CHCl_3$ due to the suppression of non-radiative deactivation caused by local molecular motion. Furthermore, we have developed a facile synthetic route of *TfAPA* via amine hydrochloride (*3APA-HCl*) as shown in **Fig.2b**, in which side reactions are effectively suppressed. The optical properties of *ODDC-3TfAPA* with different *r* values are shown in **Fig.2c**. The end-capped PI films exhibited high optical transparency and bright blue to light-blue fluorescent emission under UV irradiation (**Fig.2e**). In the emission spectrum, the peak at 400 nm is readily attributable to the fluorescence from the *ODDC* main chain, and those at 440 and 550 nm are originated from the *3TfAPA* terminal. The peak at 550 nm is attributable to the T* fluorescence based on the emission peak of *TfAPI*, while the peak at 440 nm was assumed to be from an anionic form of *3TfAPA*. When a small amount of H_2SO_4 (2 equimolar of *3TfAPA*) was added to the PAA (*ODDC-3TfAPA*+2 eq.H_2SO_4), this peak was effectively suppressed, and the T* fluorescence was significantly enhanced as shown in **Fig.2d**, resulted in a bright white-color emission at room temperature (**Fig.2e**). In summary, a white-color fluorescent PI film was successfully prepared from a blue-fluorescent PI by end-capping with an yellow-fluorescent ESIPT anhydride. This is a new design strategy for preparing thermally stable white-light emitting PI materials that are applicable to WOLEDs and the related ICT devices.

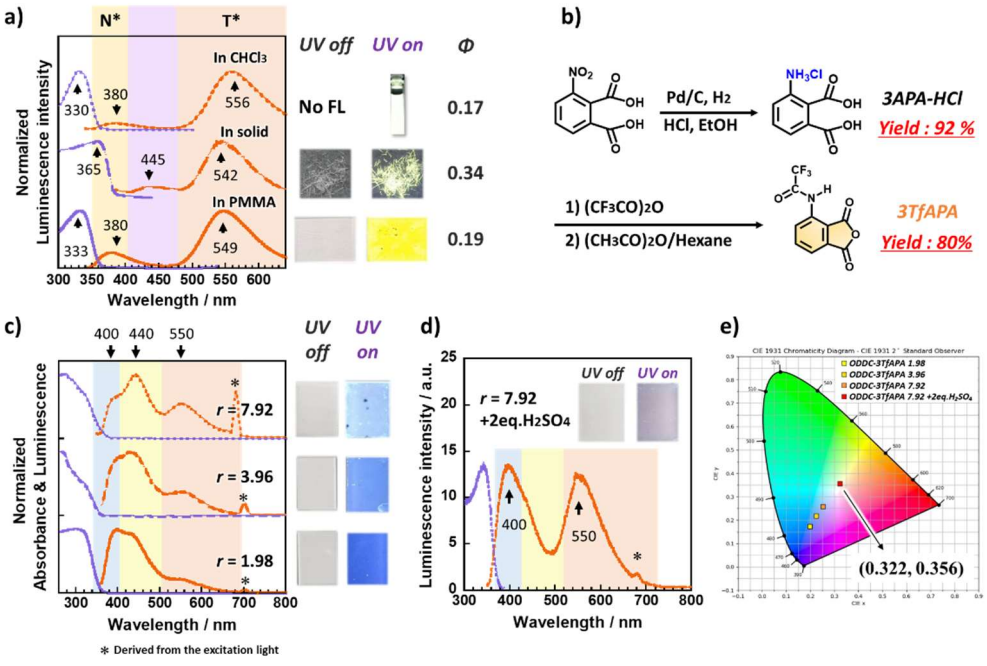

Fig.2 (a) Excitation / emission spectra of *3TfAPI* in solution (top), in crystalline state, and in PMMA matrix (bottom). (b) Synthetic scheme of the new ESIPT anhydride (*3TfAPA*). (c) UV/vis absorption and luminescence spectra of *ODDC-3TfAPA* (*r* = 1.98, 3.96, 7.92). (d) Excitation / emission spectra *ODDC-3TfAPA* +2eq.H2SO4 (*r* = 7.92). (e) CIE (1931) chromaticity coordinates of end-capped PIs.

[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).