STEPI12
Polyimides & High Performance Polymers
June 6-9 2019
Montpellier, Sud de France

Photophysical Processes and Sensor Properties of Multicolor Fluorescent Polyimides Based on ESIPT and FRET

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Highly fluorescent polyimides (PI) [1–4] are expected to be applied to solar spectral convertors because of their excellent heat resistance and mechanical strength. For the practical use, further increase in Stokes shift (*SS*), the difference between absorption and fluorescence (FL) wavelengths, and enhancement of quantum yield are desired. We have recently synthesized a new imide compound with a bulky substituent, **3TsAPI** (**Fig. 1**a), exhibiting excited-state intramolecular proton transfer (ESIPT).[5] The ESIPT occurring at substituted amide groups is a phenomenon in which the transition state after photoexcitation shows long-wavelength FL due to structural stabilization by hydrogen atom transfer from the enamine (N*) to the imine (T*) form.[5,6]

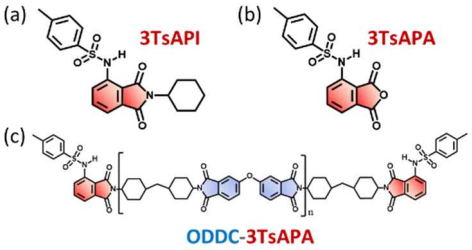

Fig. 1 Chemical structures of (a) imide compound (3TsAPI), (b) anhydride (3TsAPA), and (c) end-capped PI (ODDC-3TsAPA).

3TsAPI exhibited bright orange FL (λ_{em} = 580 nm, *SS* = 9786 cm^{-1}) in the solid state with a high quantum yield (Φ=0.22) and multi-color FL from purple to red in solution, depending on the polarity of solvents. Based on the TD-DFT calculations, these phenomena are caused by the competing effects between the FLs derived from the anionic (A*) form, in which the hydrogen of the amide group is dissociated, in addition to the N* and T* forms (**Fig. 2**) [2]. In this study, we synthesized a series of end-capped PIs (**ODDC-3TsAPA**, Fig. 1c), in which a photo-active **3TsAPA** (Fig. 1b) having the same core structure as 3TsAPI was introduced at the ends of a blue fluorescent PI (ODDC) with varying the end group molar fractions (*r* = 1.98, 3.96, 7.92, 14.8%) to develop a novel PI film that exhibits multi-color FL, and investigated its photo-physical properties.

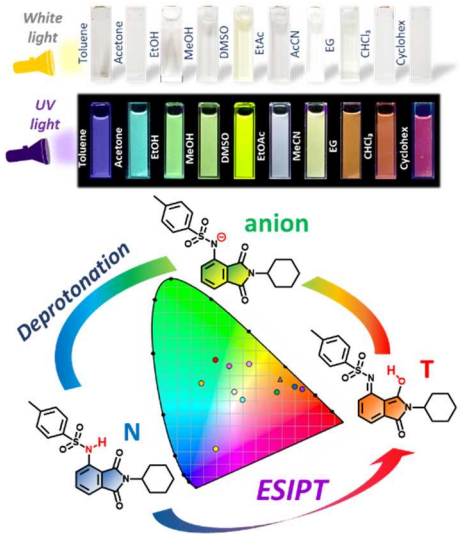

Fig. 2 Full-color fluorescent solvato-chromism of 3TsAPI in various organic solvents.

The UV-vis absorption/emission spectra of ODDC-TsA thin films, the *r*-dependence of the FL color under white light or UV light irradiation, and the chromaticity diagram of the emission color of each film are shown in **Fig. 3**. All of the PI films were colorless and transparent under white light, absorbed UV light, and exhibited purple to orange FL. In the emission spectrum, the intensity of the peak at 400 nm decreased with increasing *r*, which was attributed to the FL of ODDC in the main chain. On the other hand, the peak intensities at 450 nm and 585 nm increased with increasing *r*, and these FLs are attributed to those from the A* and T* forms of 3TsAPA moiety at the PI termini. In the thin film with the highest end group fraction (*r* = 14.8), the Förster resonance energy transfer (FRET) efficiency, E_{FRET}, reached 82%, and thus, even though 3TsAPA is present only at the chain ends, orange FL with a higher intensity than that of blue FL from the ODDC main chain was obtained.

The chromaticity diagrams of the emission colors converted from the emission spectra measured by changing the irradiation wavelengths by 10 nm in the range of 330-400 nm are shown in **Fig. 4**. Under short wavelength excitation, three types of FL are competing: a) ODDC FL (main chain), b) A* type FL via FRET from ODDC to the A* type of 3TsAPA, and c) T* type FL via FRET to the N* type and subsequent ESIPT, because they are close to the optimal excitation wavelength of ODDC. Since the medium excitation wavelength is close to the excitation wavelength of 3TsAPI, in addition to ODDC FL, d) the terminal 3TsAPA is directly excited and T* type FL is enhanced. Finally, the long wavelength irradiation excites neither ODDC nor T* types, and thus e) the A form is directly excited and shows A* type FL.

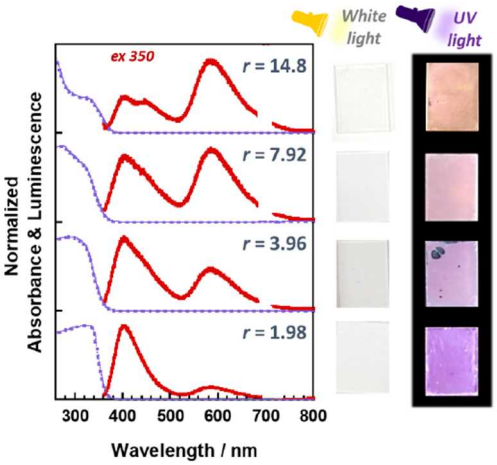

Fig. 3 UV−vis absorption and emission spectra of ODDC-3TsAPA (λ_{ex} = 350 nm) prepared with variable *r* values, and their photos under white (UV off) and UV (λ = 365 nm) irradiation (UV on).

Finally, when PI thin film with *r* = 14.8 was exposed to trifluoroacetic acid (TFA) vapor, the fluorescent color changed from orange to light blue (**Fig. 5**). This may be due to the formation of hydrogen bonds between TFA and 3TsAPA, which suppresses the T* FL. Succeedingly, when exposed to triethylamine vapor, the fluorescent color changed to green, which was attributed to the formation of A*. The 5% weight loss temperatures for all PI films were above 430 °C, indicating that the films have high thermal stability. In conclusion, we have succeeded in fabricating a novel fluorescent PI film whose emission color changes widely depending on the ambient atmosphere. Future applications are expected to include environmental sensor applications.

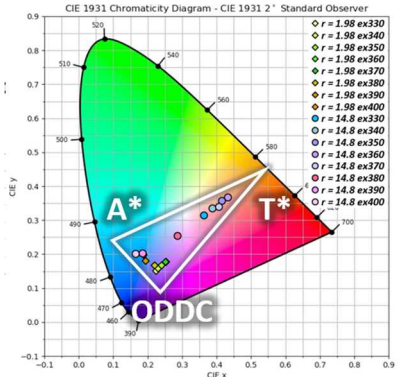

Fig. 4 CIE coordinates of the fluorescence colors of ODDC-3TsAPA with *r* = 1.98, 14.8 irradiated at different wavelengths.

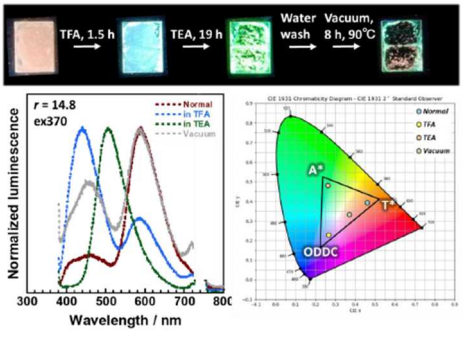

Fig. 5 Photographs of ODDC-3TsAPA PI films irradiated by UV light (λ = 365 nm) prepared with *r* = 14.8 (top left) → exposed to TFA → followed by exposure to TEA → finally washed with water, the normalized fluorescence spectra (bottom left), and the CIE coordinates (right).

References

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