

## Development of Colorless and Transparent Polyimide Copolymer Films Displaying Large Stokes Shifted Orange-Color Photoluminescence

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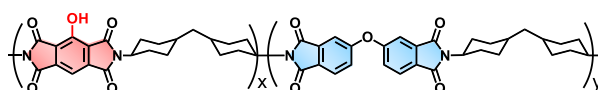
### 【Abstract】

A series of polyimide copolymers (CoPIs) derived from 4,4'-oxydiphthalic anhydride (ODPA), 1-hydroxy pyromellitic dianhydride (PHDA), and 4,4'-diamino-dicyclohexylmethane (DCHM) were developed for solar spectral conversion (solar concentrator) applications. On fused silica substrates, a film of CoPI-0.03 (molar ratio of PHDA unit is 0.03) is colorless and exhibits large Stokes shifted orange fluorescence. This fluorescence originates from the excited-state intramolecular proton transfer (ESIPT) at the PHDA moiety. However, this film shows an intense yellowish color under white light and yellow fluorescence by UV irradiation on soda-lime glass substrate. Based on the analysis of optical properties of a model compound derived from PHDA and cyclohexylamine, it was conformed that the yellowish color and yellow fluorescence originate from anionic form of PHDA moiety. Meanwhile, sulfuric acid was doped into CoPI films to inhibit the anion formation, and then highly transparent CoPI films with excellent colorlessness and large Stokes shifted photoluminescence were successfully obtained on soda glass substrates. These CoPI films are highly promising and have great potential for solar converting applications.

### 【Introduction】

Our group has reported a series of polyimide copolymers (CoPIs, **Scheme 1**) synthesized from 4,4'-oxydiphthalic anhydride (ODPA), 1-hydroxy pyromellitic dianhydride (PHDA), and 4,4'-diamino-dicyclohexylmethane (DCHM). In these CoPIs, the ODPA moiety shows blue fluorescence at 410 nm when excited at 340 nm, while the PHDA moiety shows orange fluorescence at 595 nm when excited at 370 nm. This orange fluorescence originates from the excited-state intramolecular proton transfer (ESIPT) phenomenon. The molar ratio of ODPA moieties (95~99%) is much larger than that of PHDA moieties (1~5%). However, the prominent ESIPT fluorescence was observed for all CoPI films due to the efficient energy transfer from the ODPA moiety to the PHDA moiety. Among these CoPIs, the CoPI-0.03 (the molar ratio of PHDA was 0.03) demonstrated the best performance due to the excellent colorlessness and prominent ESIPT fluorescence.

Fused silica substrates composed of amorphous SiO<sub>2</sub> have excellent transparency in the UV and visible regions. Therefore, film samples are commonly prepared on silica substrates for optical



**Scheme 1.** Chemical structure of CoPI.

measurements. However, soda-lime glass substrates are common in large-scale applications due to their low price and good transparency. Interestingly, the CoPI-0.03 film shows different optical

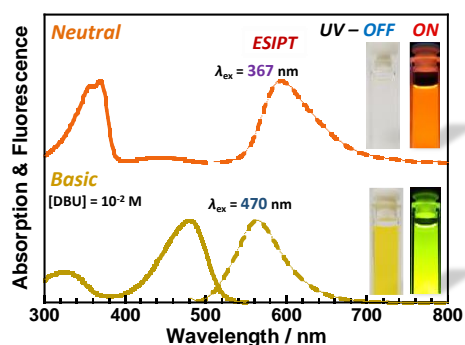
properties depending on the substrate material: on a silica substrate, the film is colorless and exhibits orange fluorescence. However, on a soda glass substrate, the film shows an intense yellowish color and yellow fluorescence, which is obviously undesirable for solar converting applications. This study aims to clarify and solve the problem and then develops highly transparent CoPI films with large Stokes shifted orange fluorescence on soda glass substrates.

### 【Experimental】

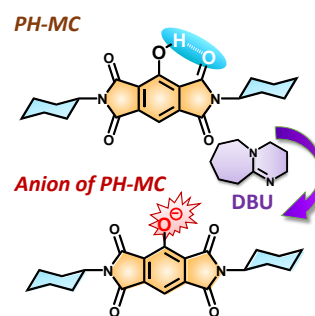
The synthesis of PHDA has been reported elsewhere [1]. All the PI films were prepared by the conventional two steps thermal imidization method from poly(amic acid) silyl ester (PASE) solutions: the PASE solution was spin-coated on a fused silica or a glass substrate, followed by drying at 70 °C for 1 h and subsequent thermal curing at 220 °C for 1.5 h. All the heating procedures were conducted under nitrogen flow, and the heating rate was set at 3.0 °C/min. For the sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) doped CoPI films, an appropriate amount of H<sub>2</sub>SO<sub>4</sub> was added to a PASE solution and stirred for 30 mins before spin-coating and thermal imidization.

### 【Results and Discussion】

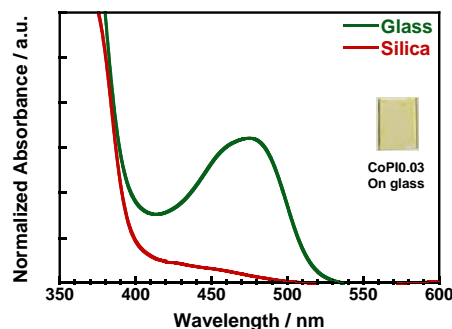
It is well known that ESIPT molecules are sensitive to environmental acidity. Kanosue et al. reported that the anionic form of ESIPT imide compounds exhibited different optical properties depending on the ionic state of solvents. [2] Thus, to investigate the anion formation of PHDA unit and its fluorescence, a model compound (PH-MC) having good solubility in organic solvents was synthesized. **Fig. 1** shows the absorption/fluorescence spectra of PH-MC dissolved in chloroform (CHCl<sub>3</sub>) and CHCl<sub>3</sub>/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) solutions. DBU is a kind of organic base. The CHCl<sub>3</sub> solution looks transparent with a yellowish color and emits bright orange fluorescence. An intense UV absorption peak and a weak blue absorption peak are observed at 367 nm and 440 nm, respectively. We have reported that the weak absorption in the visible region originates from the aggregated form of PHDA units. [1] Besides,



**Fig. 1** Steady-state UV-vis absorption and fluorescence spectra of PH-MC dissolved in CHCl<sub>3</sub> and CHCl<sub>3</sub>/DBU (concentration: 10<sup>-5</sup> M). Inserted graphs are the photos of MC solutions under sunlight and UV light (375 nm).



**Scheme 2** Schematic representation of anion formation of PH-MC.

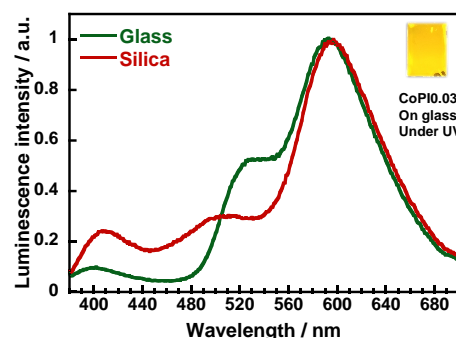


**Fig. 2** Steady-state UV-vis absorption spectra of CoPI-0.03 formed on glass and silica substrates. The inserted graph is the photo of CoPI-0.03 on the glass substrate.

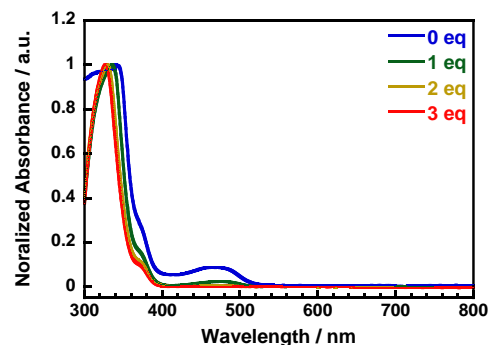
the prominent fluorescence peak at 590 nm with a very large Stokes shift ( $10299\text{ cm}^{-1}$ ) is readily attributed to the ESIPT keto emission of the PHDA moiety. However, in the  $\text{CHCl}_3/\text{DBU}$  solution, the absorption/emission spectra and fluorescence color are entirely different. The absorption peak is red-shifted to 480 nm, while the fluorescence peak is blue-shifted to 560 nm. Since DBU is a strong organic base, the PHDA unit generated anionic form in  $\text{CHCl}_3/\text{DBU}$ , as indicated in **Scheme 2**. Thereby, the 480 nm absorption and 560 nm emission are attributed to the anionic form of PHDA unit. Finally, this  $\text{CHCl}_3/\text{DBU}$  solution shows a yellowish color, and it exhibits a bright greenish-yellow fluorescence with a small Stokes shift ( $3419\text{ cm}^{-1}$ ) under UV light (370 nm).

Intriguingly, the CoPI-0.03 film exhibited different absorption/fluorescence depending on the substrate material. **Fig. 2** compares the steady-state UV-vis absorption spectra of CoPI-0.03 formed on silica and soda-glass substrates. The CoPI-0.03 film on the silica shows no apparent absorption band over 400 nm. However, the CoPI-0.03 film on the glass substrate shows a prominent absorption peak around 470 nm, resulting in the yellow color of the PI film. Besides, **Fig. 3** shows that the CoPI-0.03 film on the glass has a more prominent emission peak at 520 nm than the CoPI-0.03 on the silica substrate. This enhanced 470 nm absorption and 520 nm emission agree well with those of the anionic form of PHDA unit, which indicates that the anion formation in CoPI-0.03 films is significantly enhanced on the glass than the silica. These different optical properties of CoPI-0.03 originates from the different basicity at the surface of the substrates: silica is made of pure amorphous  $\text{SiO}_2$ , while soda-glass contains several metallic and ionic species like silicates and carbonates (like  $\text{Na}_2\text{SiO}_3$ ,  $\text{CaSiO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CaO}$ , and  $\text{Na}_2\text{O}$ ). Therefore, anionic form of PHDA unit is more easily generated on the alkaline-containing glass substrates compared with the neutral silica substrates.

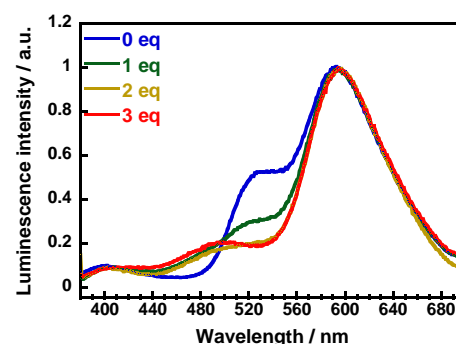
The absorption of blue light and the emission of yellow fluorescence of the CoPI-0.03 film are undesirable for solar converting application. The complete colorlessness, high transparency in the



**Fig. 3** State-state emission spectra of CoPI-0.03 on glass and silica substrates. ( $\lambda_{ex} = 370\text{ nm}$ ) The inserted graph is the photo of CoPI-0.03 on the glass substrate under UV light (375 nm).



**Fig. 4** Steady-state UV-vis absorption spectra of CoPI-0.03 doped with different concentrations of  $\text{H}_2\text{SO}_4$  formed on glass substrates.



**Fig. 5** Steady-state emission spectra of CoPI-0.03 doped with different concentrations of  $\text{H}_2\text{SO}_4$  formed on glass substrates. ( $\lambda_{ex} = 370\text{ nm}$ )

visible region, and bright long-wavelength fluorescence are demanded. To suppress the anion formation of PHDA moieties, a small amount of  $\text{H}_2\text{SO}_4$  was doped into the CoPI films. Here, we choose  $\text{H}_2\text{SO}_4$  because of its high boiling temperature and strong acidity. **Fig. 4** shows the steady-state UV-vis absorption spectra of these films. In this study, 'eq' means an equivalent of  $[\text{H}^+]$  ions to PHDA units. The PI film without acid (0 eq) shows a significant anion absorption at 470 nm. With an increase of  $\text{H}_2\text{SO}_4$  concentration, this peak gradually was decreased and disappeared by 2eq. This result proves that 2eq  $\text{H}_2\text{SO}_4$  is sufficient to inhibit the anion formation on the glass substrate completely. **Fig. 5** displays the steady-state emission spectra of these CoPI-0.03 films ( $\lambda_{ex} = 370$  nm). The anion fluorescence at 520 nm is significantly suppressed by doping of  $\text{H}_2\text{SO}_4$ . Meanwhile, another fluorescence peak slightly appeared at 490 nm (its excitation wavelength is the same as that of the enol form of PHDA unit), and its intensity is positively proportional to the  $\text{H}_2\text{SO}_4$  concentration. It could be attributable to a partly protonated form of CoPIs due to the excess of acid. Finally, we prepared a large sized (6-inch  $\phi$ ) film with excellent colorlessness/optical transparency with a large Stokes shifted orange photoluminescence on the soda glass substrate, as shown in **Fig. 6**. This film is highly promising and has a great potential for solar converting applications.



**Fig. 6** Photographs of a large size film of CoPI-0.03 doped with 2eq  $\text{H}_2\text{SO}_4$  formed on the soda glass substrate. Left: under sunlight. Right: under 375 nm UV light.

### 【Conclusion】

A model compound of PH-MC exhibits a large Stokes shifted orange fluorescence at 595 nm by absorbing 370 nm UV light in  $\text{CHCl}_3$ . This fluorescence originates from the excited keto form of the PHDA moiety via ESIPPT photophysical process. Meanwhile, the anionic form of PH-MC exhibits an absorption peak at 470 nm with an emission peak at 560 nm. Additionally, CoPI-0.03 film with a molar content of PHDA is 3 % formed on a fused silica substrate, showed excellent colorlessness and bright orange fluorescence via ESIPPT. However, CoPI-0.03 film on a soda-glass substrate shows a yellowish color and yellow fluorescence, which are undesirable for solar converting applications. This phenomenon originates from the significant anion formation on more basic (alkali) glass substrates compared with neutral silica substrates.

To achieve colorless CoPI films on soda-glass substrate, a small amount of  $\text{H}_2\text{SO}_4$  was doped into CoPI films. The doping of  $\text{H}_2\text{SO}_4$  effectively inhibit the anion formation and improve the colorlessness of the CoPI film on the soda-glass substrate. These results indicate that a doping of 2eq of  $\text{H}_2\text{SO}_4$  is sufficient to suppress the anion formation on the glass. Finally, a large sized (6-inch  $\phi$ ) film with excellent colorlessness and large Stokes shifted orange photoluminescence was successfully prepared on a soda-glass substrate. This acid-doped CoPI film is highly promising and has a great potential for solar converting applications.

### 【References】

- [1] K. Kanosue, R. Augulis, D. Peckus, R. Karpicz, T. Tamulevičius, S. Tamulevičius, V. Gulbinas, S. Ando, *Macromolecules*, 2016, **49**, 1848.
- [2] K. Kanosue, T. Shimosaka, J. Wakita, S. Ando, *Macromolecules*, 2015, **48**, 1777.