B02

An Imide Compound and Polyimides Forming Multiple Intramolecular Hydrogen Bonds and Exhibiting Large Stokes-shifted Yellow Fluorescence

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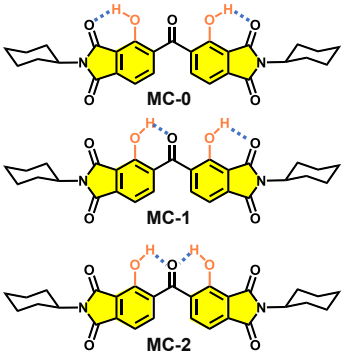
Introduction

Polyimides (PIs) exhibit excellent thermal, mechanical and environmental properties.[1] Our group has reported a highly fluorescent PI derived from 1-hydroxypyromellitic dianhydride (PHDA) and 4,4'-diamino-dicyclohexylmethane (DCHM), which emits a large Stokes-shifted photo-luminescence through excited-state intramolecular proton transfer (ESIPT). However, due to its highly planar structure, PHDA moieties are easily aggregated, and this aggregated form generates a competitive photophysical process with ESIPT.[2] To solve this problem, a novel 2,2'-dihydroxy-3,3',4,4'-benzophenonetetracarboxylic dianhydride (DHBA) was newly designed and synthesized, and the optical properties of its corresponding model compound (DH-MC, **Scheme 1**) and a polyimide derived from DHBA (DH-PI, **Scheme 2**) were investigated.



Scheme 1. Different H-bonding structures of DH-MC.

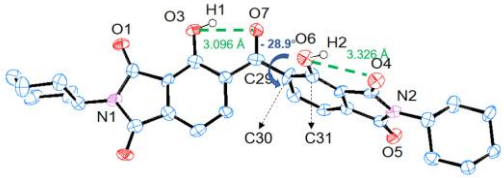


Fig. 1. Crystal structure of DH-MC.

Notably, DH-MC have multiple proton donor and acceptors. Thus, it can generate three different intramolecular H-bonding structures, namely MC-0, MC-1, and MC-2, as shown in **Scheme 1**. The most stable H-bonding structure can be predicted by the TD-DFT calculation, and it can be confirmed by the single-crystal XRD analysis. Besides, the optical properties of DH-MC and DH-PI were carefully measured and discussed in this study.

Experiment

DHBA dianhydride was synthesized according to reference [3]. All the PI films were prepared by the conventional two-steps thermal imidization method from poly(amic acid) silyl ester (PASE) solution: The prepared PASE solution was spin-coated onto fused silica and soda-lime glass substrates, dried at 70 °C for 1 h, followed by thermal curing at 220 °C for 1.5 h. All the heating procedures were conducted under nitrogen flow, and the heating rate was 3.0 °C /min.

Results and Discussion

As described above, DH-MC can form three different H-bonded structures. The energy of each conformation in both of the ground and excited states were estimated by TD-DFT calculations, which showed that MC-1 is the most stable H-bonding structure in both the ground enol state and the excited keto state. MC-1 could be the most stable H-bonding structure during ESIPT photocycle, which is consistent with the result from single-crystal XRD analysis as described below.

The crystalline structure of DH-MC is displayed in **Fig. 1**. Importantly, the distance between O3 and O7 (3.096 Å) is shorter than that between O6 and O4 (3.326 Å). Therefore, even though

O7 shows less electronegativity than O1, H-bonds is formed between O3 and O7. In addition, the torsional angle of O7-C29-C30-O6 was estimated as −28.9°.

In the solid state, DH-MC shows a large Stokes-shifted yellow fluorescence when excited at 340 nm by UV light. (**Fig. 2**) However, another absorption peak was observed at 470 nm which resulted in a yellowish coloration. These species can be attributed to an anionic form from its fluorescence wavelength. (**Fig. 3**) The optical properties of the DH-PI film are similar to those of DH-MC powder that shows an intense yellow coloration from the anionic form with yellow fluorescence from the ESIPT photocycle. In addition, a novel method for spectral converting performance was developed, where transmission spectra of PI films were detected at *300–800* nm by using Xeon light. The DH-PI film absorbs UV and blue lights and enhances yellow light by ESIPT fluorescence. Besides, the quantum yield of this film was relatively low (Φ = 0.04) due to the aggregation-induced quenching.

To obtain colorless PI films, a copolyimide, CoPI-0.03 was synthesized from DHBA and 4,4'-oxydiphthalic dianhydride (ODPA), in which the content of DHBA moieties was controlled as low as 3%, as shown in **Scheme 2**. The CoPI-0.03 films exhibit prominent ESIPT fluorescence owing to the efficient energy transfer from the ODPA to DHBA moieties. (**Fig. 4**) In addition, its wavelength converting spectrum shows that this film absorbs UV light and significantly enhances yellow light. It should be noted that is this CoPI-0.03 showed a significantly higher Φ of 0.14 than that of DH-PI owing to the suppression of aggregation induced quenching in the copolyimide.

References

[1] J. Wakita, S. Ando, et al. *J. Phys. Chem. B*, 2009, **113**, 15212-15224.

[2] K. Kanosue, S. Ando, et al. *Macromolecules*, 2016, **49**, 1848-1857.

[3] G. Shin, et al. *J. Polym. Sci. Pol. Chem*, 2007, **45**, 776-788.

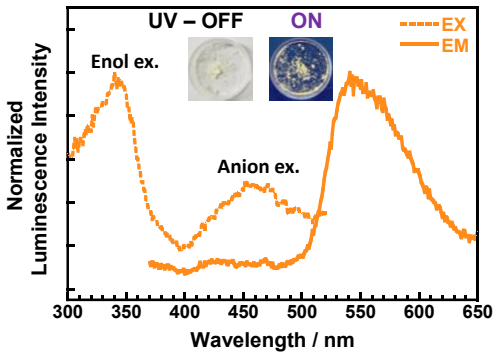


Fig. 2. Steady-state excitation/emission spectra of DH-MC powder (λ_{ex} = 340 nm, λ_{em} = 540 nm).

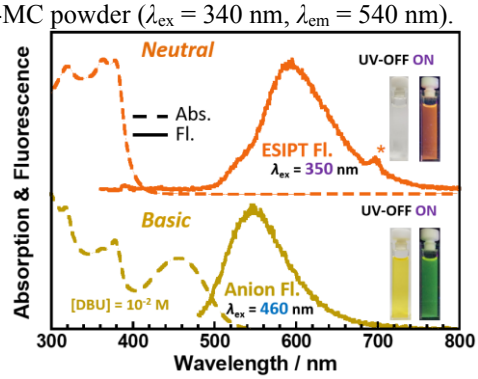
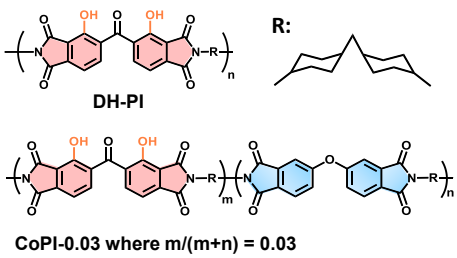


Fig. 3. Steady-state UV-vis absorption and fluorescence spectra of DH-MC dissolved in toluene and toluene/DBU ([DH-MC]: 10^{-5} M). Inserted graphs are the photos of MC solutions under sunlight and UV light (375 nm).



Scheme 2. Chemical structures of DH-PI and CoPI-0.03.

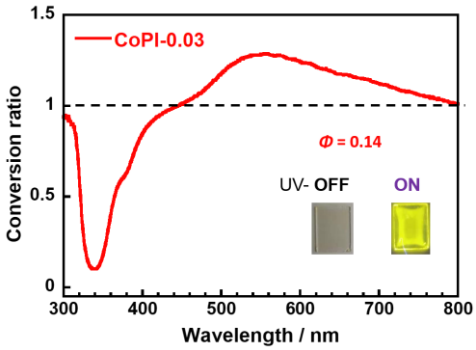


Fig. 4. Wavelength converting spectrum of CoPI-0.03. Inserted photos are CoPI-0.03 film under sunlight and 365 nm UV irradiation.