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

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INTRODUCTION:

Polyimide (PI) is a kind of polymer with excellent thermal, mechanical, and environmental properties. Recently, fluorescent PIs have attracted much attention due to their special application as wavelength converters.[1,2] Especially PIs with large Stokes shifted fluorescence have been obtained utilizing excited-state intramolecular proton transfer (ESIPT).[3] For example, our group has reported PHDA/DCHM PI derived from 1-hydroxypyromellitic dianhydride (PHDA) and 4,4'-diaminodicyclohexylmethane (DCHM), exhibited a large Stokes shifted orange photoluminescence via ESIPT.[4] However, due to the highly planar structure, PHDA moieties are easily aggregated. This aggregated form generated a competitive photophysical process with ESIPT. To solve this problem, 2,2'-dihydroxy-3,3',4,4'-benzophenonetetracarboxylic dianhydride (DHBA) was newly designed and synthesized, and the optical properties of a model compound based on the DHBA (DH-MC, **Scheme 1**) and a polyimide derived from DHBA (DH-PI, **Scheme 2**) were investigated.

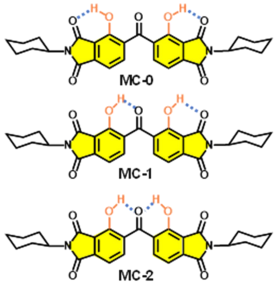
EXPERIMENTAL:

DHBA dianhydride was synthesized according to reference [5]. 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. The completion of imidization reaction was confirmed by FT-IR spectra.

RESULTS AND DISCUSSION:

DH-MC has multiple proton donors and proton 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 energy of each conformation in both the ground and excited states were predicted 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 X-ray diffraction (XRD) analysis as described below.

The conformation of DH-MC in the crystalline lattice revealed by the XRD is displayed in **Fig. 1**. Comparing the distances between O atoms having hydrogen accepting ability, the distance between O3 and O7 was 3.096 Å, which is shorter than that between O6 and O4 (3.326 Å). Therefore, even though O7 shows less electron negativity than O1, a H-bond is preferably formed between O3 and O7. In addition, the torsional angle of O7-C29-C30-O6 is



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

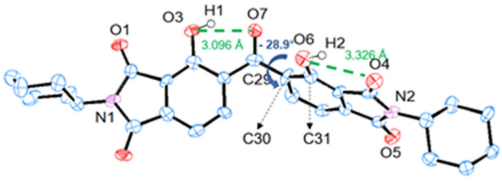


Fig. 1. Conformation of DH-MC in the crystalline lattice.

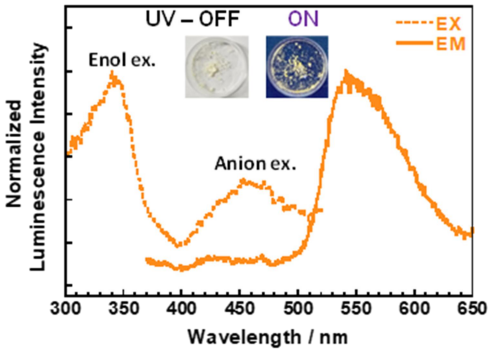


Fig. 2. Steady-state excitation/emission spectra of DH-MC powder (λ_{ex} = 340 nm, λ_{em} = 540 nm).

−28.9°.

In the solid-state, DH-MC shows a large Stokes-shifted (v = 11,230 cm^{-1}) yellow fluorescence at 550 nm when excited at 340 nm by UV light, as displayed in **Fig. 2**. This large Stokes shifted fluorescence originates from the ESIPT process. However, another absorption peak was observed at 470 nm, resulting in a yellowish coloration. This absorption is attributable to an anionic form based on its absorption and fluorescent wavelengths. **Fig. 3** displays the absorption and fluorescence spectra of DH-MC in solutions. In the toluene solution, it only shows a large Stokes shifted (v = 11,622 cm^{-1}) orange fluorescence at 590 nm when excited at 350 nm. However, by adding 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, an organic base) to change the solution in basic state, the anionic form can be generated. This anionic form absorbs blue light at 460 nm and gives fluorescence at 540 nm. As a result, this solution shows yellowish coloration and green fluorescence.

The optical properties of the DH-PI film were similar to that of DH-MC powder, which has intense yellowish coloration due to the anionic formation. Moreover, due to the strong aggregation, the DH-PI shows a relatively low quantum yield (Φ) of 0.03 attributable to the aggregation-induced quenching (AIQ). To obtain a colorless film with a sufficient high Φ value, a copolyimide namely CoPI-0.03 was synthesized from DHBA and 4,4'-oxydiphthalic dianhydride (ODPA), in which the molar content of DHBA moieties was controlled as low as 0.03 as shown in **Scheme 2**. Even the content of DHBA was low, a prominent ESIPT fluorescence from the DHBA moieties was observed owing to the efficient energy transfer from the ODPA to PHDA moieties. Furthermore, due to the reduced anion concentration and the suppressed aggregation, the CoPI-0.03 film was colorless and exhibited bright yellow fluorescence with a high Φ of 0.14.

Finally, we developed a novel wavelength converting measurement system, in which the transmittance of the Xenon light can be measured between 300–800 nm. In the wavelength converting spectra, the DH-PI film absorbs UV and blue lights and enhances yellow light by large Storks-shifted fluorescence. However, the CoPI-0.03 film mainly absorbs UV light and enhances yellow light by fluorescence, as shown in **Fig. 4**. This CoPI-0.03 film shows the excellent colorlessness, high quantum yield, and excellent wavelength converting properties has great potential for wavelength conversion applications.

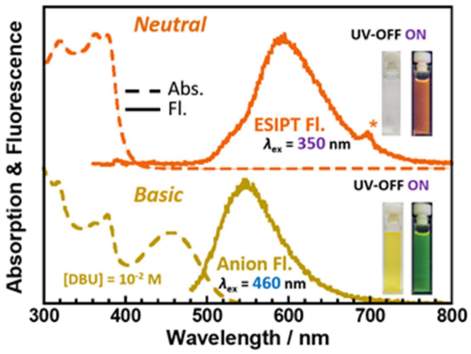
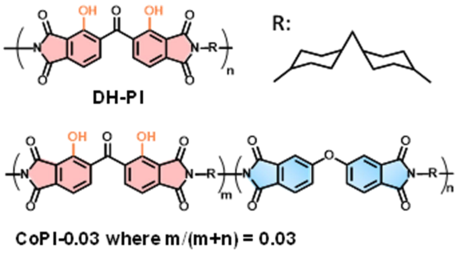


Fig. 3. Steady-state UV-vis absorption and fluorescence spectra of DH-MC dissolved in toluene and toluene/DBU ([DH-MC]: 10^{-5} M). Photographs of MC solutions under sunlight and UV light (375 nm) are inset.



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

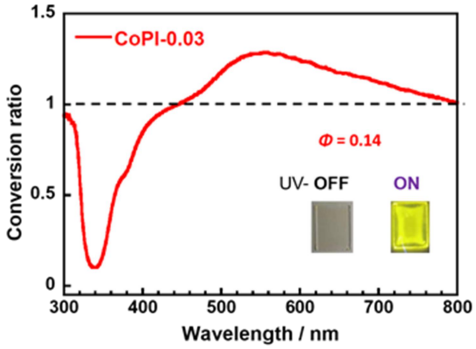


Fig. 4. Wavelength converting spectrum of CoPI-0.03. Inserted photographs are CoPI-0.03 film under sunlight and 365 nm UV irradiation.

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