STEPI 10
Polyimides & High Performance Polymers
6-8 June 2016
Montpellier, France

Design and Synthesis of Multi-Colour Luminescent Polyimides with Very Large Stokes Shifts and Their Performance for Solar Spectral Conversion

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Polymeric optical materials exhibiting high quantum-yield luminescence (fluorescence and phosphorescence) are expected to be used for wavelength down-conversion in a wide range of applications such as flat panel displays, photovoltaic devices, and crop cultivators. However, conventional fluorescent polymers consisting of π-conjugated sequences do not have high thermal, environmental, and light stabilities, and polymers containing phosphorescent dyes generally include heavy noble metals such as Ir, Pt, Re, & Ru.

We have proposed and confirmed a novel molecular design concept for "highly fluorescent PIs" (HFPIs) based on the TD-DFT calculations and optical measurements of imide model compounds.[1] The principles for designing highly HFPIs can be described as follows: (1) use of alicyclic diamines, and (2) use of aromatic dianhydrides that have flexible linkages with extended π-conjugation. In addition, a novel key concept for "highly phosphorescent PIs" (HPPIs) is a use of heavy halogens such as bromine (Br) and iodine (I).

According to these concept, we have successfully synthesized a fluorescent PI with strong blue emission from HQDEA and DCHM (Fig.1), of which the quantum yield (Φ) was 0.11. We have reported a series of HFPIs derived from perfluorinated aromatic dianhydrides, such as 10FEDA and P2FDA, which exhibited strong bluish green and red fluorescence (Fig.1). Although their fluorescence intensity was significantly enhanced, these HFPIs are not fully suitable to wavelength converters because the energy gaps between the absorption and fluorescence peaks, called 'Stokes shifts', were not large enough. For enhancing the Stokes shifts of HFPIs, the third principle for designing HFPIs was required.

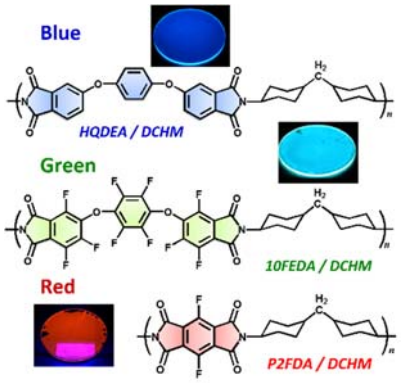


Fig. 1 Multi-color fluorescent PIs.

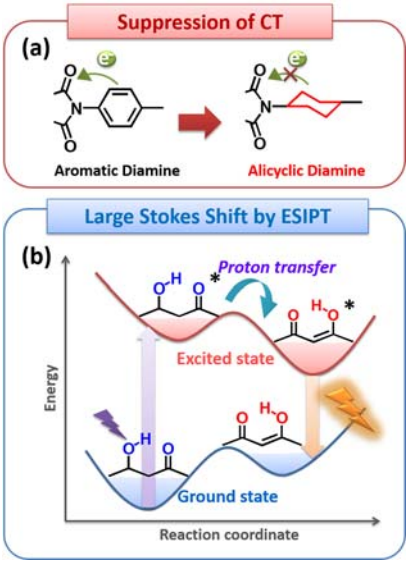
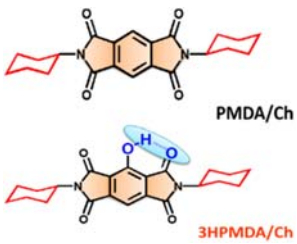


Fig. 2 Strategy for designing of (a) highly fluorescent PIs (b) with large Stokes shift based on ESIPT

We have recently reported that a series of imide compounds containing -OH groups and forming ideal intramolecular hydrogen bonding (intra-HB) between -OH and C=O groups, exhibits strong green to orange fluorescence with very large Stokes shifts (v=7655~ 11394 cm^{-1}) via excited-state intramolecular proton transfer (ESIPT) [2-4] (Figs. 2 and 3). Direct excitation of an 'enol form' by UV radiation readily generates the Franck-Condon excited state, which rapidly undergoes ESIPT process to generate an 'excited-state keto'



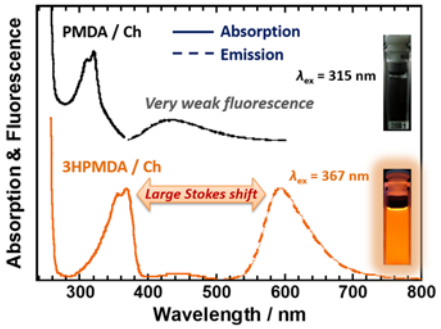


Fig. 3 Structures and spectra of imide compounds (a) with very weak emission and (b) intense red-emission via ESIPT.

tautomer. Due to the large energy difference between the enol and keto tautomers, the excited-keto exhibits an unusual and strong emission with a large Stokes shift. Moreover, the corresponding deprotonated mono-anion and di-anion species were formed in basic conditions with an organic base (DBU), which was characterized by highly visible halochromism (pH dependence) in their absorption and emission spectra (Fig. 4).[4]

Photo images of P2HDA-DCHM films under white light and UV light exposure are shown in Fig. 5.[4] The film is pale yellow in colour and has an absorption peak with a maxima at 407 nm. The fluorescence is observed at 642 nm as a prominent red emission band, indicating that ESIPT is a dominant process even in the solid state and causes a large Stokes shift (8994 cm^{-1}). The Φ value of around 0.05 was not high enough due to the high concentration of dianhydride moiety, though this Φ is much higher than the conventional PIs.

The transmission light-conversion spectrum in the UV/visible region of an HFPI copolymer derived from HQDEA (99.7 %) and P2HDA (0.3 %) as the dianhydride components is shown in Fig. 6. As mentioned above, HQDEA and P2HDA afford blue- and red-emitting HFPIs, and efficient energy transfer occurs from the HQDEA to P2HDA moieties in the excited state. The film thus obtained looks pale pink in colour and has a strong absorption peak with a maxima at 350 nm. In turn, the light intensities in the blue (~450 nm) and orange (~600 nm) regions are obviously enhanced by 10~16 % due to its fluorescent emission. The Φ value was as high as 0.13. This spectrum demonstrates that judiciously designed HFPI films are promising for tough/flexible wavelength converters, in which the UV and violet components of solar and LED light are efficiently converted to visible (blue to red) light without consuming external energy.

Most recently, we have developed novel highly phosphorescent PIs based on heavy atom effects of bromine (Br) atoms. (Fig. 7). The details of the interesting propeties will be presented and discussed at the conference. [7]

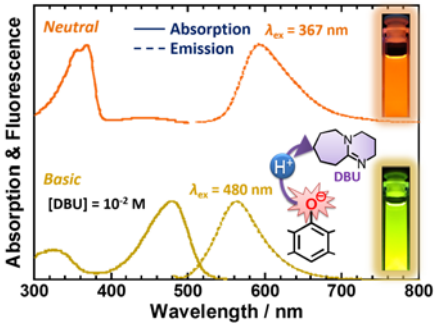


Fig. 4 Spectral change by base.

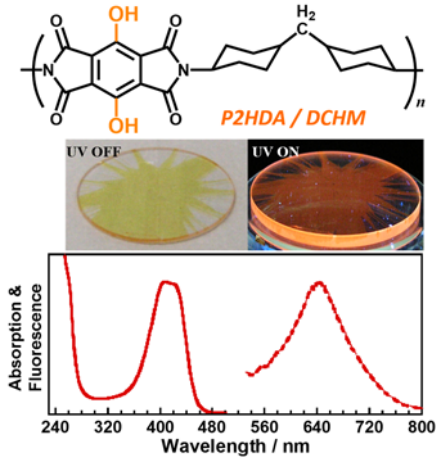


Fig. 5 Red-emitting PI film via ESIPT (Stokes shift : 8994 cm^{-1}).

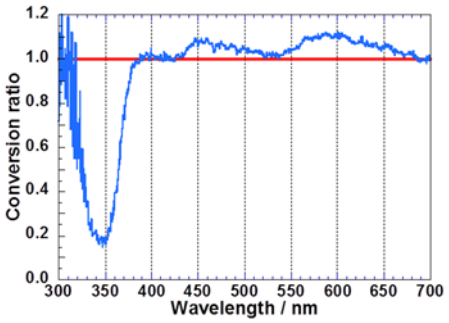


Fig. 6 Spectral conversion ratio of a blue & red fluorescent co-PI film.

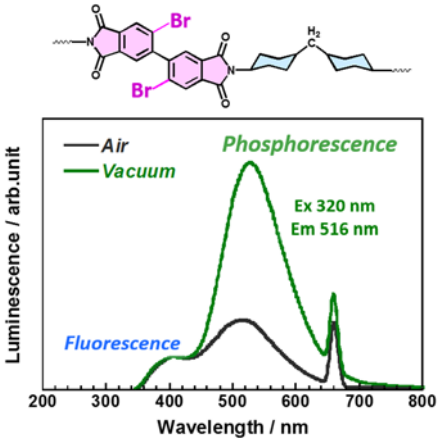


Fig. 7 Phosphorescent PI based on heavy atom effects of Br atoms.

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[7] Kanosue, K; Ishige, R.; Ando, S, *submitted.*