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MULTI-COLOR FLUORESCENT POLYIMIDES WITH VERY LARGE STOKES SHIFTS AND THEIR PERFORMANCE FOR SOLAR SPECTRAL CONVERSION

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Polymeric materials exhibiting fluorescent emission are expected to be applied 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 sufficient thermal, environmental, and light stabilities.

Polyimides (PIs) are a class of super engineering plastics well known for their high thermal and chemical stability, optical and radiation resistance, and good mechanical properties originating from their rigid molecular structure and strong intermolecular interactions. Recently, 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 summarized as follows: (1) use of alicyclic diamines, and (2) use of aromatic dianhydrides that have flexible linkages with extended π-conjugation.

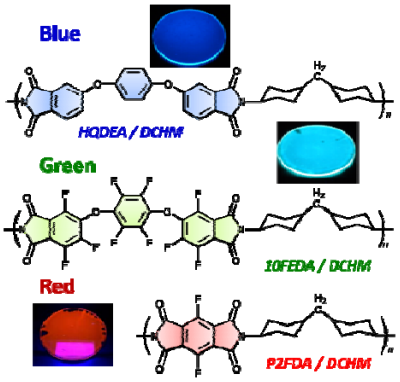

Fig. 1 Multi-color fluorescent PIs.

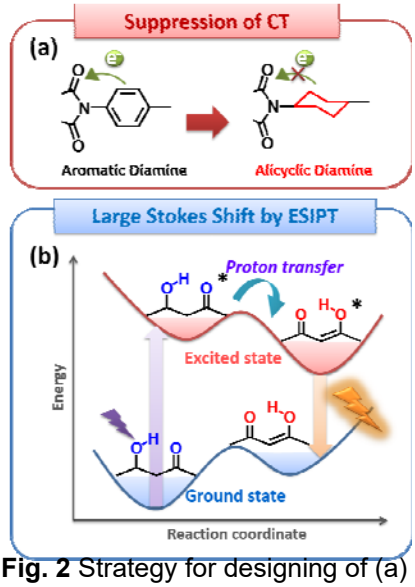

Fig. 2 Strategy for designing of (a) highly fluorescent PIs (b) with large Stokes shift based on ESIPT.

According to the concept, we have successfully synthesized a strongly blue fluorescent PI derived from HQDEA and DCHM (Fig.1), which has a quantum yield (Φ) of 0.11.[1] We have also reported a series of HFPIs synthesized 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 gap between the absorption and fluorescence, which corresponds to the difference between the excitation and emission wavelengths, called a Stokes shift, was not large enough. For enhancing the Stokes shifts of HFPIs, the third principle for designing new HFPIs is required.

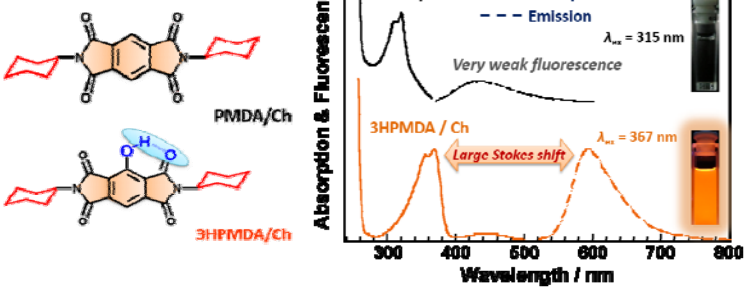

Fig. 3 Structures and spectra of imide compounds (a) with very weak emission and (b) intense red-emission via ESIPT.

We have recently reported that a series of imide compounds containing an -OH group and forming an ideal intramolecular hydrogen bonding (intra-HB) between the -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). Excitation of an 'enol form' by UV radiation readily generates the Franck-Condon excited state, which rapidly undergoes the ESIPT process to generate an 'excited-state keto' tautomer. During the subsequent relaxation to the ground state by radiative or non-radiative processes, a reverse proton transfer occurs to yield the original ground-state enol. Due to the large energy difference between the enol and keto tautomers, the excited-state keto exhibits an unusual emission at longer wavelengths 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 in their absorption and emission spectra (Fig. 4).[4]

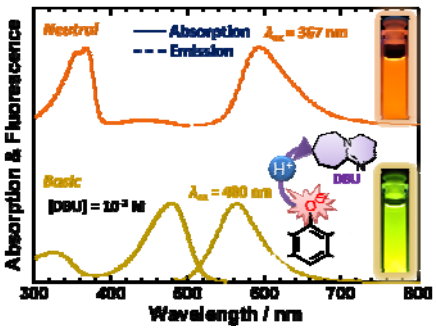

Fig. 4 Spectral changes of 3HPMDA/Ch caused by base.

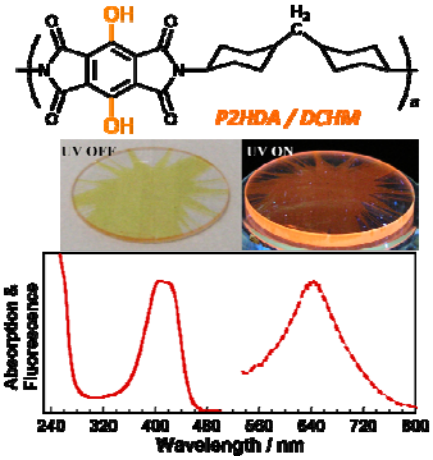

Fig. 5 Red-emitting PI film via ESIPT (Stokes shift : 8994 cm^{-1}).

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 color 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 0.01 was not high enough due to the high concentration of dianhydride moiety, though this Φ is significantly higher than conventional PIs.

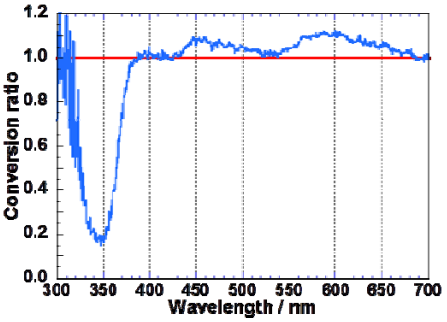

Fig. 6 Spectral conversion ratio of a blue & red fluorescent co-PI film.

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 component is shown in Fig. 6. As mentioned above, HQDEA and P2HDA afford blue- and red-emitting HFPIs, and efficient energy transfer occurs in the excited state from the HQDEA to P2HDA moieties. The film thus obtained is pale pink in color 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 10~14 % due to the fluorescent emission. The Φ value is as high as 0.127. This spectrum demonstrates that judiciously designed HFPI films are promising for tough/flexible wavelength converters, in which the UV component of solar and LED light is efficiently converted to visible (blue to red) light without consuming external energy.

References:

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