MULTI-COLOR FLUORESCENT / PHOSPHORESCENT IMIDE COMPOUNDS AND POLYIMIDES EXHIBITING VERY LARGE STOKES SHIFTS AND THEIR APPLICATION FOR SOLAR SPECTRAL CONVERSION

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Abstract

Polymers exhibiting fluorescent (FL) and phosphorescent (PH) emission are applicable to wavelength down-converters in a wide range of applications such as flat panel displays, flexible displays, photovoltaic devices, and crop cultivators. However, π-conjugated FL polymers do not have sufficient mechanical properties and thermal, environmental, and radiation stabilities. In 2009, we developed a series of semi-aromatic polyimides (PIs) exhibiting strong blue- to green-FL emission (**Fig. 1**).[1] The high quantum efficiency (> 0.11) of the PIs was attributable not only to the suppression of charge-transfer (CT) interactions but also to the enhancement of the locally excited π–π* transition and effective suppression of concentration quenching by steric effects. We have reported a series of imides and PIs containing electron-donating alicyclic amino groups or one or two –OH groups which form ideal intramolecular hydrogen bonds with C=O groups and exhibit strong and tunable multi-color (blue, green, yellow, to deep red) FL with very large Stokes shifts (7,655~11,394 cm^{-1}) via excited-state intramolecular proton transfer (ESIPT) (**Fig. 2**).[2] Colorless copolymer films derived from blue- and red-FL PIs exhibit strong red FL, and the transmission intensities in the visible blue and orange regions are enhanced by ~16 %. Furthermore, we have developed colorless and highly phosphorescent PIs by introducing heavy halogens (Br, I) in the skeletal structures of dianhydrides.[3] Recently, full-color solvatochromism was observed for a tosyl-amino substituted imide compound due to the combination of FL emissions from the three different excited states: locally excited (N*), intramolecular proton-transferred (T*), and anion states (A*) (**Fig. 3**).[4] Judicious design of highly FL and PH PIs provides promising materials for fabricating tough and flexible wavelength converters that efficiently absorb UV light from the sun or LEDs and emit tunable visible to near-infrared radiation without consuming any external energy.

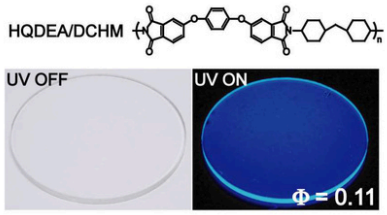

Fig.1 Colorless blue-fluorescent PI.

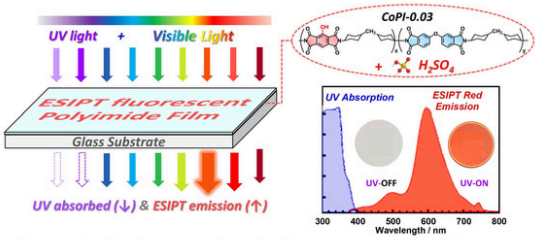

Fig.2 Colorless and red-fluorescent Co-PI applicable to solar spectral conversion.

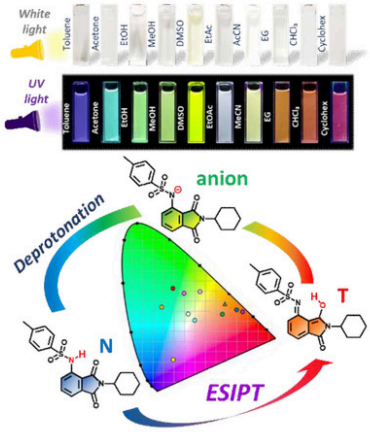

Fig.3 Full-color solvatochromic fluorescence based on NH-type ESIPT and anion formation.

[1] *J. Phys. Chem. B*, **2009**, *113*, 15212; *Macromolecules*, **2012**, *45*, 4764; *Macromolecules*, **2019**, *52*, 3813; *Phys. Chem. Chem. Phys.*, **2024**, *26*, 15461

[2] *Macromolecules*, **2010**, *43*, 3594; *Phys. Chem. Chem. Phys.*, **2015**, *17*, 30659; *Macromolecules*, **2015**, *48*, 1777; *Macromolecules*, **2016**, *49*, 1848; *Phys. Chem. Chem. Phys.*, **2018**, *20*, 16033; *J. Photopolym. Sci. Technol.* **2019**, *32*, 449; *ACS Appl. Polym. Mater.* **2021**, *3*, 3911; *Mater. Chem. Front.* **2022**, *6*, 24;

[3] *ACS Macro Lett.*, **2016**, *5*, 1301; *Mater. Chem. Front.* **2019**, *3*, 39, *ACS Omega* **2020**, *5*, 14831; *ChemPhotoChem*, **2023**, e202200310.

[4] *Mater. Adv.* **2021**, *2*, 5629; *Polymers (Basel)*. **2021**, *13*, 4050;