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Optical Properties and Emission Mechanisms of Highly Fluorescent Polyimides Applicable to Spectrum Converter for Solar Cells

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Introduction

Thermally stable fluorescent polymers have been attracting attentions for use in spectrum converter for Si-type solar cells. The efficiency of fluorescent mission *(i.e.* quantum yield, ϕ) of conventional polyimides (PIs) is very low (<0.05) due to their strong intra- and intermolecular charger transfer (CT).[1] In this study, excited-state proton transfer (ESIPT) mechanism occurring at intramoleuclar hydrogen bonding was introduced into phthalimide and pyromellitic diimide moieties in model compounds and at the termini of a highly fluorescent PI (HFPI) to enhance the fluorescence intensity and Stoke's shift of HFPI films.

Results & Discussion

An HFPI prepared from 4,4'-oxidiphthalic dianhydride and 4,4'-diaminocyclohexyl-methane was end-capped with 3-hydroxyphthalic anhydride (Fig.1). The colorless PI films exhibit two characteristic emission peaks at 400 (weak) and 530 nm (strong). The former is attributable to the inherent LE(π–π*) emission from the main chain, and the latter is to an ESPIT emission from the termini caused by efficient energy transfer from the main chain. Due to mixing of these two emissions, the PI films show gradated multicolor (blue, light-blue, white, light-green) emission depending on the amount of termini, whilst maintaining good transparency and colorlessness.[2] The Stokes' shift is as large as 9800−10700 cm^{-1}. Furthermore, *N*,*N*'-dicyclohexyl-3,6-dihydroxypyromellitimide (36DHPMDI, Fig.2) exhibits red-color emission consisting of two fluorescent peaks at 457 nm (weak) and 637 nm (strong) with excitation at 432 nm. The former is attributable to emission from the excited enol form, and the latter is to the excited mono-keto form via ESIPT (the Stokes' shift is ca. 8000 cm^{-1}). Although 36DHPMDI show a weak absorption around 430 nm, the strong red emission with near-UV excitation is highly suitable to spectrum converter. In addition, 36DHPMDI dissolved in methanol exhibits red emission at 634 nm with excitation at 526 nm which is attributed to direct excitation of keto form existing in the ground state. This compound shows significant solvato-chromism and high pH sensitivity in solution due to deprotonation of –OH groups. 'ESIPT mechanism' is an effective and versatile tool to control and enhance the fluorescence of imides and HFPIs.

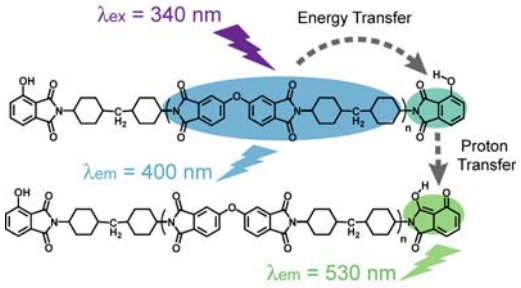

Figure 1. Emission mechanism of a highly fluorescent polyimide films having ESIPT moiety at the termini.

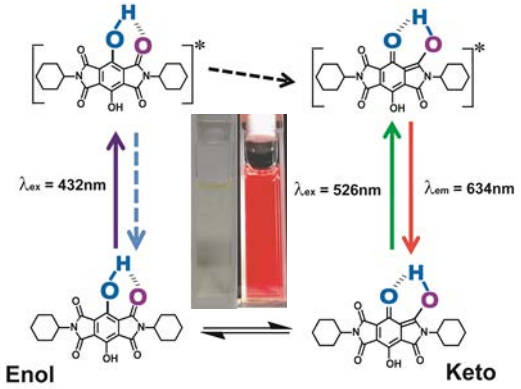

Figure 2. Photophysical processes via ESIPT of an imide compound which forms two intramolecular hydrogen bondings. Bright red fluorescence is observed.

References

1) J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B.*, **113**, 15212 (2009).
2) J. Wakita, S. Inoue, N. Kawanishi, S. Ando, *Macromolecues*, **43**, 3594 (2010).