# Fluorescence Enhancement in Imide Compounds by Introducing Steric Electron-Donor Groups

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## I. Introduction

Organic fluorescent materials can be applied in many fields such as displays, light emitting devices (LEDs), and spectrum convertors for solar cells (**Fig.1**). Recently, polyimide (PI), a thermally and chemically stable polymer, has been attracting much interests due to its potential applications as novel fluorescent materials. Previously, we have proposed a molecular design concept for highly fluorescent PIs [1]. Moreover, we found that imide compounds having an electron-donor group e.g. hydroxyl (-OH) and amino (-$NH_2$) group in the anhydride moieties exhibit enhanced fluorescence properties compared with *N*-cyclohexylphthalimide (NHPI, without electron-donor group; **Fig.2**) [2] owing to enhancement of locating excited $\pi$-$\pi^*$ transition. However, fluorescence intensities of these compounds are significantly reduced in the solid state due to self-absorptions or intermolecular interactions. Since fluorescence materials are usually used in solid states, novel materials exhibiting intense fluorescence intensities in the solid states are strongly demanded.

In this study, imide compounds substituted by a steric electron-donor group (piperidine and pyrrolidine) at the anhydride moieties, which is expected to suppress the intermolecular quenching mentioned above [3], were newly synthesized (4-PiNHPI, 4-PyrNHPI; **Fig.2**), and their fluorescence properties were examined in solution and solid states.

## II. Experimental

The absorption/fluorescence spectra were measured by using a Jasco V-670 spectrophotometer and a Hitachi F-7000 spectrofluorometer. Fluorescence quantum yields ($\Phi$) were estimated by using an integrating sphere.

## III. Results and Discussion

The $\Phi$ values observed for chloroform solutions (1.0 x$10^{-4}$ M) of 4-PiNHPI and 4-PyrNHPI are shown in **Fig. 2**. It should be noted that both 4-PiNHPI and 4-PyrNHPI showed higher $\Phi$ values of 0.89 than NHPI ($\Phi$=0.01) originating from the larger spatial overlaps between HOMO and LUMO. In the solid state, 4-PiNHPI showed larger $\Phi$ value of 0.51 than 4-PyrNHPI ($\Phi$=0.18). In order to clarify this reason, X-ray diffractions (XRD) for crystalline samples of these compounds were measured. According to the crystal structures, 4-PiNHPI has a larger steric hindrance at the amine substituent than 4-PyrNHPI, which can suppress intermolecular quenching (**Fig. 3**). In conclusion, the introduction of steric amine structures into imide compounds significantly enhances fluorescence properties both in solution and in solid state.

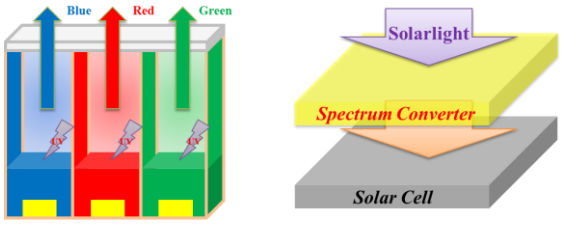


**Fig.1.** Applications of fluorescent materials.

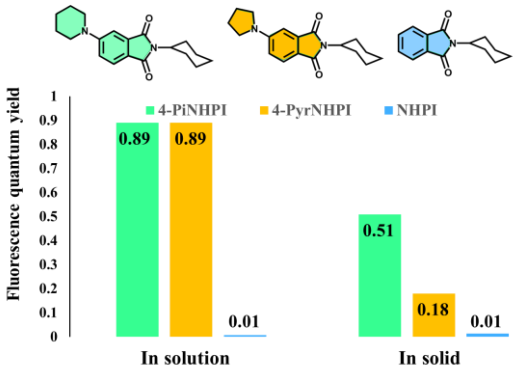


**Fig.2.** Chemical structures and fluorescence quantum yields of NHPI, 4-PiNHPI, and 4-PyrNHPI.

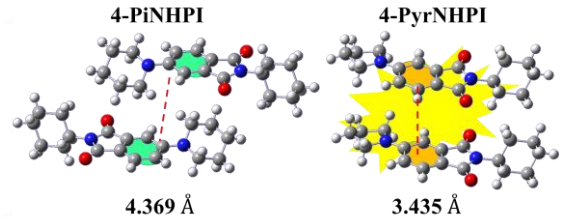


**Fig.3.** Crystal structures of 4-PiNHPI and 4-PyrNHPI. The numbers refer to the closest distances between neighboring molecules.

## References

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[2] Kenta Kanosue and Shinji Ando*, "Fluorescence emissions of imide compounds and end-capped polyimides enhanced by intramolecular double hydrogen bonds", Phys. Chem. Chem. Phys, **17**, pp. 30659-30669, October 2015.

[3] M. Shimizu, Y. Takeda, M. Higashi, and T. Hiyama, "1,4-Bis(alkenyl)-2,5-dipiperidinobenzenes: Minimal fluorophores exhibiting highly efficient emission in the solid state," Angew. Chemie - Int. Ed., vol. 48, no. 20, pp. 3653–3656, 2009.