

Variable Color Fluorescence of *N*-Cyclohexylphthalimides Substituted by Amino and Acylamino Groups with Different Acidity

Takehiko KAMBARA (神原武彦), Kenta KANOSUE (鹿末健太),
Ryohei ISHIGE (石毛亮平), and Shinji ANDO (安藤慎治)

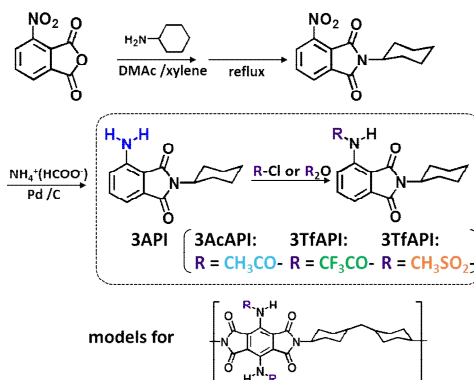
Department of Chemical Science and Engineering, Tokyo Institute of Technology (Tokyo Tech),
2-12-1-E4-5, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Abstract: A series of *N*-cyclohexylphthalimides having an amino- or acylamino-groups, such as acetylamino, trifluoroacetylamino, and sulfonylamino groups with a wide range of acidities, were synthesized as model compounds for exploring the enhanced fluorescent emission of highly fluorescent polyimides with large Stokes shifts via excited state intramolecular proton transfer (ESIPT). The optical absorption and fluorescence spectra of these compounds as well as quantum yields of luminescence were measured in solution and in the solid state, and the relationships between the acidity of amino- and acylamino groups and the variable color enhanced fluorescence are discussed. Moreover, the solvent and temperature dependences of the fluorescent properties are investigated.

Keywords: Cyclohexylphthalimides / Acylamino-group / Fluorescence / Acidity / ESIPT / Stokes shift

1. Introduction

Solid-state emissive organic materials recently attract much of interests because of their potentials for applications such as opto-electronic devices¹, organic fluorescent sensors¹, and solar spectrum converters. We have developed a wide range of polyimides (PIs) exhibiting intense fluorescent emission based on the molecular design strategy of using (1) alicyclic diamines and (2) dianhydrides with extended π -conjugation.² On the other hand, incorporation of push-pull structure² is a versatile way to synthesize fluorescent compounds.



Scheme 1 Synthetic scheme of compounds.

Introduction of electron-donating and electron-accepting groups into π -conjugated molecules effectively enhances the intramolecular charge transfer (ICT) character in the excited states, which endows characteristic properties such as large extinction coefficients³, solvato-chromic emission, and enlarged Stokes shifts with the push-pull compounds. Moreover, the formation of intramolecular hydrogen bonding (*int*-HB) between electron-donating and accepting groups in imides and polyimides causes a specific nuclear relaxation, *i.e.* excited state intramolecular proton transfer (ESIPT).⁴⁻⁸ In general, fluorescent emission from a proton-transferred structure (*keto* form) in compounds forming *int*-HB is observed at a much longer wavelength than that from the pristine state (*enol* form).

In this study, four kinds of model compounds for highly fluorescent PIs⁵⁻⁸ were synthesized, in which four different amino/acylamino groups are introduced as electron donating groups (Scheme 1). Their optical absorption and fluorescent properties were investigated, and the effects of acidities with different acylamino groups on the potential tendency of ESIPT was discussed.

2. Experimental

Synthetic schemes of the model compounds are summarized in Scheme 1. The compounds were purified twice by recrystallization from ethanol. Fluorescence spectra were measured with Hitachi F-7100 spectrophotometer, and fluorescence quantum yield (Φ) was evaluated using an integral sphere.

3. Results and Discussion

The optical absorption and fluorescence spectra of the model compounds dissolved in CHCl_3 (5.0×10^{-5} M) are shown in Figure 1, and their experimental data are summarized in Table 1. All the compounds exhibited bright fluorescence emissions, though unsubstituted *N*-cyclohexylphthalimide (not shown) is almost non-fluorescent⁵ due to the $n-\pi^*$ character of S_0-S_1 transition. These results indicate that introduction of electron-donating amino and acylamino groups effectively transform the forbidden S_0-S_1 ($n-\pi^*$) transitions to allowed $\pi-\pi^*$ transitions, which leads to the bright fluorescent emissions.

Two emissive bands were clearly observed in 3TfAPI and 3SAPI, which are a very weak emission around 400 nm and an intense emission around 570 nm with a very large Stokes shift ($\Delta\nu$) via ESIPT. These bands are assignable to the radiative relaxations from the excited enol-form and the excited keto-forms with a proton transfer, respectively. In contrast, 3API and 3AcAPI, which are substituted by less acidic amino- and acylamino groups, exhibited only one emissive band at 410 and 445 nm. These facts clearly indicate that the ESIPT behaviors of the phthalimides forming *int*-HB is essentially dominated by the acidity of protic groups.

The values of Φ for fluorescent emission of the acylamino-substituted compounds (3AcAPI, 3TfAPI and 3SAPI) were smaller than that of 3API, irrespective of the occurrence of ESIPT. The decrease in Φ values reflects fast radiationless decay paths associated with the *int*-HBs formed between acylamino group and imide group.

4. Conclusions

It was clarified that *N*-cyclohexylphthalimides substituted with different amino/acylamino groups at the C3 position exhibit variable color bright fluorescence. The ESIPT behaviors of amino- and acylamino-substituted phthalimide compounds essentially depends on the acidity of protic groups.

References

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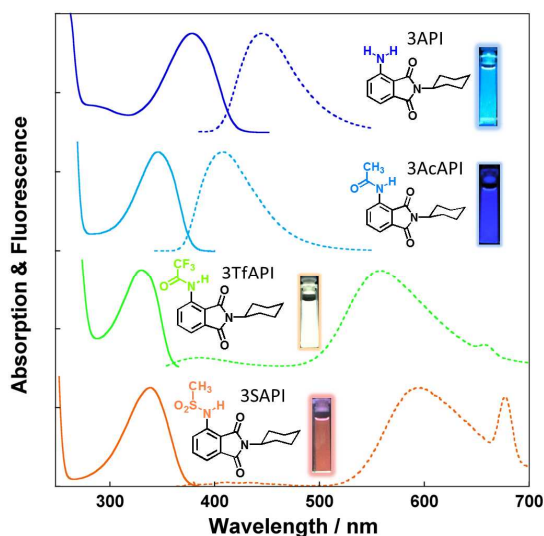


Figure 1 Optical absorption and fluorescence spectra of the model compounds.

Table 1 Optical absorption wavelengths λ_{abs} , fluorescence wavelengths λ_{FL} , Stokes shifts $\Delta\nu$, and fluorescence quantum yields Φ of model compounds.

	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{FL}} / \text{nm}$	$\Delta\nu / \text{cm}^{-1}$	Φ
3API	379	445	3913	0.76
3AcAPI	350	410	4181	0.08
3TfAPI	330	556	12317	0.12
3SAPI	339	595	12692	0.02