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OPTICAL ABSORPTION AND FLUORESCENCE PROPERTIES OF *N*-CYCLOHEXYLPHTHALIMIDES SUBSTITUTED WITH ACYLAMINO GROUPS

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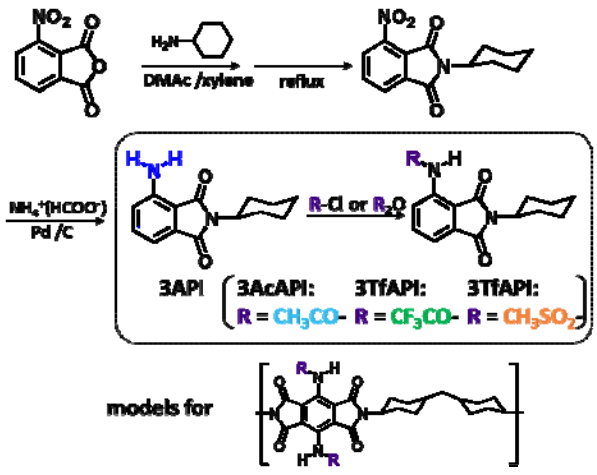
Introduction

Solid-state emissive organic materials recently attract much of interests because of their potentials for applications such as opto-electronic devices[1], organic fluorescent sensors[1], and spectrum converters. We have developed a wide series of polyimides (PIs) exhibiting intense fluorescent emission based on the molecular design strategy consisting of (1) Use of alicyclic diamines, and (2) Use of dianhydrides with extended conjugation.[2]

Building of push-pull structure[2] is a versatile way to synthesize fluorescent 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. The ICT character endows characteristic properties such as large extinction coefficients[3], solvatochromic emission, and enlarged Stokes shifts with the push-pull type compounds. Moreover, formation of intramolecular hydrogen bonding (int-HB) between electron-donating and electron-accepting groups sometimes causes specific nuclear relaxation, *i.e.* excited state intramolecular proton transfer[4] (ESIPT). In general, fluorescent emission from a proton-transferred structure (keto form) is observed at a much longer wavelength than that from the pristine structure (enol form).



Scheme 1 Synthetic scheme of model compounds.

In this study, four kinds of model compounds for highly fluorescent PIs 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.

Experimental

Synthetic schemes of the model compounds are summarized in Scheme 1. Model compounds were purified twice by recrystalization from ethanol prior to preparing solution for optical measurements. Fluorescence quantum yield (Φ) was evaluated using an integral sphere (HAMAMATSU).

Results and Discussion

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

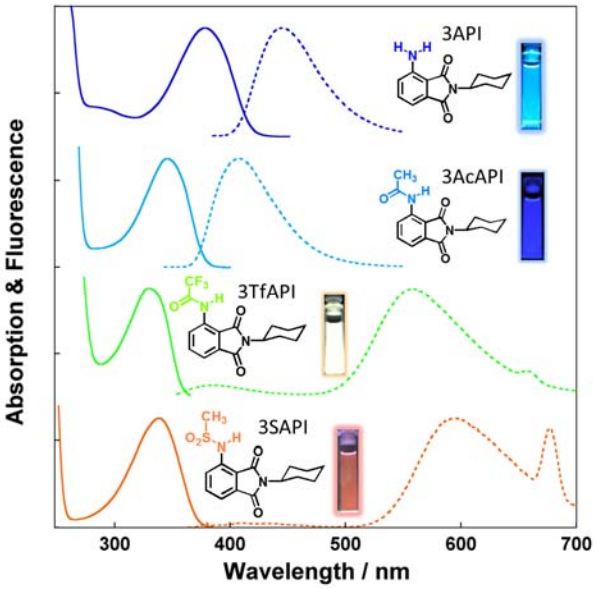


Figure 1 Optical absorption and fluorescencce spectra of the model compounds.

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

	λ_{abs} / nm	λ_{FL} / nm	$\Delta\nu$ / 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

For 3TfAPI and 3SAPI, two emissive bands are observed: a very weak emission around 400 nm and an intense emission around 570 nm with a very large Stokes shift ($\Delta\nu$). These bands are assignable to radiative relaxations from the excited enol/keto forms, respectively. In contrast, 3API and 3AcAPI having less acidic amino/acylamino groups exhibited only one emissive band at shorter wavelengths. According to these results, the potential tendency for ESIPT of the imide compounds, which form int-HB, is essentially dominated by the acidity of the proton donating (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 the fast radiationless decay paths associated with the int-HBs between acylamino group and imide group.

In conclusion, it was revealed that *N*-cyclohexylphthalimides subtituted with different amino/acylamino groups at the C3 position exhibit a variety of fluorescent properties. And it was clarified that the potential tendency of ESIPT of amino- and acylamino-substituted imide compounds primarily depends on the acidity of the protic groups.

References:

1. M. Shimizu and T. Hiyama, *Chem. Asian J.*, **2010**, 5, 1516.
2. J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **2009**, 19, 15212.
3. X. Liu, Z. Xu and J. Cole, *J. Phys. Chem. C*, **2013**, *117*, 16584.
4. J. E. Kwon and S. Y. Park., *Adv. Mater.*, **2011**, 23, 3615.
5 J. Wakita, S. Inoue, N. Kawanishi and S. Ando, *Macromolecules*, **2010**, 43, 3594