DOI 10.5012/bkcs.2010.31.5.1375

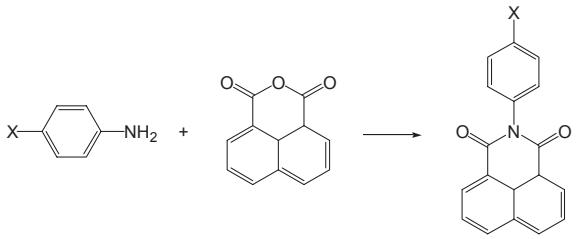
The New Fluorescent Naphthalic Imide Derivatives Having the Inductive Ending Group

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Received November 6, 2009, Accepted February 24, 2010

Key Words: Naphthalic imide, Absorption, Emission, Quantum yield

Photo-materials having emission are attracting considerable interest for their potential sensory, biochemical, medical, and photo-electronic applications, among other possible uses.[1,2] We have been simply and systematically synthesized the aromatic imine conjugated systems[3] showing the emission property by the connection of imine bond through one-pot condensation reaction.[4] Recently, in comparison with aromatic imine systems,[4] the new naphthalic imide systems were synthesized systematically and their photophysical properties were studied. We found for the first time that the new imide systems showed a considerable emission regardless of having the electron withdrawing group in the imide systems. Herein, we report the emission results on the new naphthalic imide systems having electron donating group (X = CH_3, OCH_3, NH_2, $N(CH_3)_2$) and electron withdrawing groups (X = F, Cl, Br), respectively. UV-vis absorption spectra were measured by using a Hitachi U-3300 spectrophotometer. The emission spectra were obtained on a SLM8100 spectrofluorometer (AMINCO, USA) with a Xe-arc lamp light source using 4 nm or 8 nm band pass excitation and emission monochromators. The aromatic imide compounds were synthesized by refluxing 1 eq. of 1,8-naphthalic anhydride and 2 eq. of aniline derivative in methanol at 70 °C, respectively, as shown in Scheme 1. Every product was obtained as a moderate yield (53 ~ 74%) or high yield (82 ~ 88%). As shown in Fig. 1, the absorption peaks of typical imide compounds (X = Cl, Br) having the electron withdrawing group showed at 325 nm and 335 nm, respectively. Meanwhile, in the case of typical imide compounds (X = CH_3, OCH_3, $N(CH_3)_2$), their absorption peaks showed at 330 nm and 355 nm, respectively, having the red shifted band. In particular, their absorption tailing showed until 400 nm. In addition, the naphthalic imide compounds having electron donating group showed the hyperchromic effect. Every experiment of absorption was tried in the chloroform solution (1.00×10^{-5} mol dm^{-3}). As shown in Fig. 2, the normalized emission peaks showed at 355 nm and 380 nm having 395 nm shoulder, respectively, by the excitation wavelength between 335 nm and 350 nm. Herein, the relative quantum yields[5] of the imide derivatives were measured in order to be compared with those of the imine conjugated derivatives



Scheme 1. Syntheses of the naphthalic imide systems; CH_3OH, 70 °C 2 hr, reflux; x = H, CH_3, NH_2, OCH_3, $N(CH_3)_2$, F, Cl, and Br, respectively.

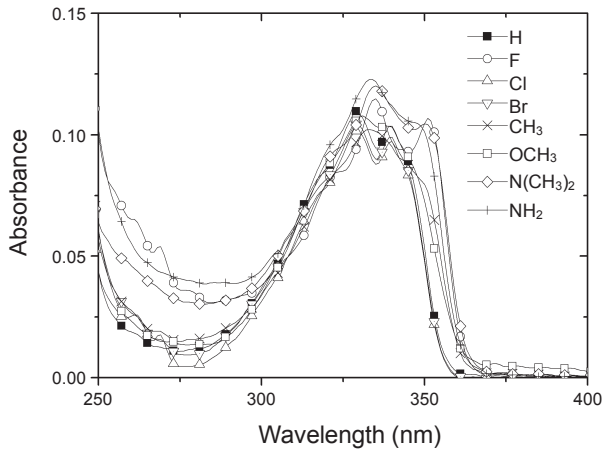


Figure 1. The electronic absorption spectra of 1.00×10^{-5} mol dm^{-3} imide compounds in chloroform at 25 °C.

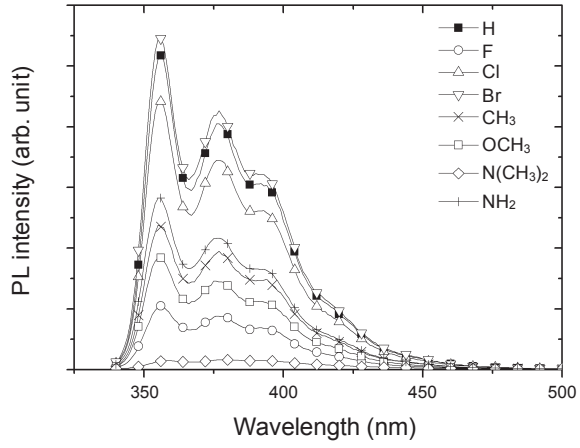


Figure 2. Photoluminescence spectra (λ_{ex} = 340 nm) of 5.00×10^{-6} mol dm^{-3} imide compounds in chloroform at 25 °C.

Table 1. Relative quantum yields (Φrel) of the naphthalic imide derivatives in chloroform at 25 °C

Compound	X	Φrel[a]
1	H	0.74
2	CH_3	0.41
3	NH_2	0.41
4	OCH_3	0.28
5	$N(CH_3)_2$	0.04
6	F	0.19
7	Cl	0.71
8	Br	0.81

[a]Refer to reference **4**. Relative quantum yields of the imine compounds having terminal group **x** are as follows, respectively; x = H (0.56), x = CH_3 (0.53), x = NH_2 (0.47), x = OCH_3 (0.41), x = $N(CH_3)_2$ (0.38), x = F (no emission), x = Cl (no emission), and x = I (no emission).

reported previously,[4] as shown in Table 1. In the case of the imide derivatives having the electron withdrawing groups (x = F, Cl, Br), their relative quantum yields were high even if that of the imide derivative 6 (x = F) was 0.19. However, there was no emission in the case of imine derivatives having the electron withdrawing group. In the compounds having the electron donating group, there was no large different except for the relative quantum yields of the compounds having x = $N(CH_3)_2$. It might be supposed that the heavy atom attached to the aromatic compound causes the more delocalization of the π-conjugated system because it increases the molecular rigidity due to coplanar conformation rather than enhances the intersystem crossing process. In conclusion, we synthesized the naphthalic imide derivatives having the considerable emission through the simple one-pot condensation reaction, and the considerable emission showed in even the imide derivatives bearing electron withdrawing group. As the more advanced and evidenced study for this considerable emission of the imide derivatives, we have an experiment on the emission behavior of the naphthalic imide derivatives introduced the aliphatic part having electron withdrawing group.

Experimental Section

The naphthalic imide derivatives were prepared by refluxing 1 eq. of 1,8-naphthalic anhydride and 2 eq. of aniline derivative in methanol at 70 °C, respectively. Upon refluxing, products were obtained as a precipitate, recrystallized by ether, and dried in vacuum oven at 50 °C. In the case of the preparation of compound **3**, 1 eq. of 1,4-diaminobenzene was added slowly and synthesized in 10 eq. of 1,8-naphthalic anhydride in methanol at 70 °C. Every compound was easily characterized by ^{1}H-NMR and its purity was confirmed by elemental analysis.

***N-p*-Methylphenylnaphthalic imide** (X = CH_3, **2**). Ivory powder, mp 308 °C δ_H (400 MHz; $CDCl_3$) 2.44 (3H, s), 7.21 (2H, d), 7.36 (2H, d), 7.79 (2H, t), 8.28 (2H, d), 8.66 (2H, d), Found: C, 79.61; H, 4.63; N, 4.91 Calc. for $C_{19}H_{13}NO_2$: C,79.43; H, 4.56; N, 4.88.

***N-p*-Aminophenylnaphthalic imide** (X = NH_2, **3**). Yellowish green powder, mp 296.5 °C δ_H (400 MHz; $CDCl_3$) 3.81 (2H, s, C-N), 6.82 (2H, d), 7.09 (2H, d), 7.78 (2H, t), 8.26 (2H, d), 8.65 (2H, d) Found: C, 75.10; H, 4.26; N, 9.85 Calc. for $C_{18}H_{12}N_2O_2$: C, 75.00; H, 4.20; N, 9.72.

***N-p*-Methoxyphenylnaphthalic imide** (X = OCH_3, **4**). Pale brown powder, mp 275.5 °C δ_H (400 MHz; $CDCl_3$) 3.87 (3H, s, O-C), 7.07 (2H, d), 7.25 (2H, d), 7.79 (2H, t), 8.27 (2H, d), 8.65 (2H, d), Found: C, 75.43; H, 4.37; N, 4.63 Calc. for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62.

***N-p*-Dimethylaminophenylnaphthalic imide** (X = $N(CH_3)_2$, **5**). Yellow powder, mp 312 °C δ_H (400 MHz; $CDCl_3$) 3.01 (6H, s, N-C), 6.85 (2H, d), 7.16 (2H, d), 7.77 (2H, t), 8.26 (2H, d), 8.65 (2H, d), Found: C, 76.11; H, 5.17, N, 8.99 Calc. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86.

***N-p*-Fluorophenylnaphthalic imide** (X = F, **6**). Pale white powder, mp 214 °C δ_H (400 MHz; $CDCl_3$) 7.23 (2H, t), 7.30 (2H, m), 7.81 (2H, m), 8.29 (2H, q), 8.65 (2H, d), Calc. for $C_{18}H_{10}NFO_2$: C, 74.22; H, 3.46; N, 4.81.

***N-p*-Chlorophenylnaphthalic imide** (X = Cl, **7**). Pale white powder, mp 234 °C δ_H (400 MHz; $CDCl_3$) 7.27 (2H, d), 7.53 (2H, d), 7.81 (2H, m), 8.31 (2H, q), 8.65 (2H, d), Found: C, 70.30; H, 3.38; N, 4.41 Calc. for $C_{18}H_{10}NClO_2$: C, 70.25; H, 3.28; N, 4.55.

***N-p*-Bromophenylnaphthalic imide** (X = Br, **8**). Pale white powder, mp 233.5 °C δ_H (400 MHz; $CDCl_3$) 7.21 (2H, d), 7.68 (2H, d), 7.81 (2H, m), 8.30 (2H, q), 8.64 (2H, d), Found: C, 61.16; H, 2.93; N 4.01 Calc. for $C_{18}H_{10}NBrO_2$: C, 61.39; H, 2.86; N, 3.98.

Acknowledgments. This work was supported by Kongju National University and Far East University.

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