

A Novel Fluorescent Dipyrido[3,2-a:2',3'-c]phenazine (dppz) Derivative Prepared by Amide Bonding

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Received March 10, 2006

A novel fluorescent dipyrido[3,2-a:2',3'-c]phenazine (dppz) derivative, 7-(4-methoxybenzoylamino) dppz (**1**), was synthesized by amide connection to position 7 of the dppz ring. Its fluorescence quantum yield ($\Phi = 0.21$ in dichloromethane) was as high as that of the conventional 7-amino-dppz (**3**), and its fluorescence lifetime was much shorter than that of **3**.

Key Words : Fluorescent materials, Dppz derivative, Amide bonding, Fluorescence quantum yield, Fluorescence lifetime

Introduction

Fluorescent materials are attracting considerable interest for their potential sensory, biochemical, medical, and photo-electronic applications, among other possible uses.¹

In particular, fluorescent materials with the 2,2'-bipyridine (bpy) unit have been studied because of their excellent properties as bidentate ligands and as hydrogen bond acceptors.² Furthermore, it has been reported that the 7-aminodipyrido[3,2-a:2',3'-c]phenazine (7-amino-dppz) with a bpy unit exhibits a relatively higher fluorescence quantum yield compared to other dppz derivatives.³ In a previous report, the essence of the fluorescent molecular design was that a known fluorescent dye, 2-aminophenazine (2-aphz), was integrated with a nonfluorescent bpy. The existing synthetic strategy for the relatively high fluorescent species, however, is limited to only dppz rings with 2-aphz. Thus, in this experiment, to find the superior fluorescent dppz derivatives connected by amide bonding, the dppz derivatives connected to 7-(4-methoxybenzoylamino)dppz (**1**) with the methoxy electron-donating group and 7-(4-nitrobenzoylamino)dppz (**2**) with the nitro electron-withdrawing group, respectively, were synthesized. Herein, it was discovered that a novel compound **1** has a relatively high fluorescence quantum yield comparable to that of the 7-amino-dppz, despite being a nonrigid π -conjugated system. It is also possible to overwhelm the low fluorescence that occurs frequently in the less rigid and extended structure through the connection of the aromatic ring with an electron-donating group (-OCH₃) to position 7 of the dppz ring by amide bonding. This paper, therefore, represents the first report on the synthetic strategy of the novel fluorescent dppz derivative and the spectroscopic properties of its absorption, emission, and fluorescence emission decay compared to those of other dppz derivatives.

Experimental Section

Materials. The distilled solvents (CH₃CN, MeOH, and EtOH) were used in reaction. Dichloromethane, acetonitrile, and ethanol were used the spectrophotometric grade of Aldrich for the spectroscopic measurement. All other reagents used in reaction were obtained commercially from Aldrich and used as received. Compound **3**, **4**, **5**, and **6** were synthesized according to a previously reported procedure.³

Measurements. The ¹H-NMR spectrum of sample in DMSO was recorded on a Varian Mercury 400 NMR spectrometer (USA). The absorption spectra were measured on a Hitachi U-3300 spectrophotometer. The fluorescence spectra were measured on a SLM8100 spectrofluorometer (Aminco, USA) with a Xe-arc lamp light source using 4 or 8 nm band pass excitation and emission monochromators, in which the rhodamine B solution was used as a reference to correct for variation of the Xe light source with time and wavelength.

Every spectroscopic measurement was carried out in the concentration of 5×10^{-6} mol dm⁻³ in dichloromethane

Fluorescence quantum yield (Φ_{rel}) was calculated according to the following equation⁴; $\Phi_{unk} = \Phi_{std}(I_{unk}/A_{unk})(A_{std}/I_{std})(\eta_{unk}/\eta_{std})^2$, where Φ_{unk} is the fluorescence quantum yield of the sample, Φ_{std} is the fluorescence quantum yield of the standard (an ethanol solution of 2-aminopyridine, $\Phi_F = 0.37$, excitation at 285 nm),⁵ I_{unk} and I_{std} are the integrated fluorescence intensities of the sample and the standard, respectively, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength, respectively, η_{unk} and η_{std} are the refractive indexes of the corresponding solutions.

The time-resolved emission measurements were performed with an Edinburgh FL-900 and a femtosecond mode-locked Ti-sapphire laser pumped by a Nd:YVO₄ laser. Laser

output has a 200 fs pulse width with a repetition rate, 76 MHz, and it can span the excitation wavelength in the range of 235-300 and 350-490 nm by using nonlinear optical crystals. The laser pulse power was minimized to be 1.2 μW /pulse by passing through pulse picker. Temporal profiles of the fluorescence decays were measured by using time-correlated single photon counting method (TCSPC).⁶ The instrumental response function was measured by detecting the scattered laser pulse of *ca.* 200 fs with quartz crystal.

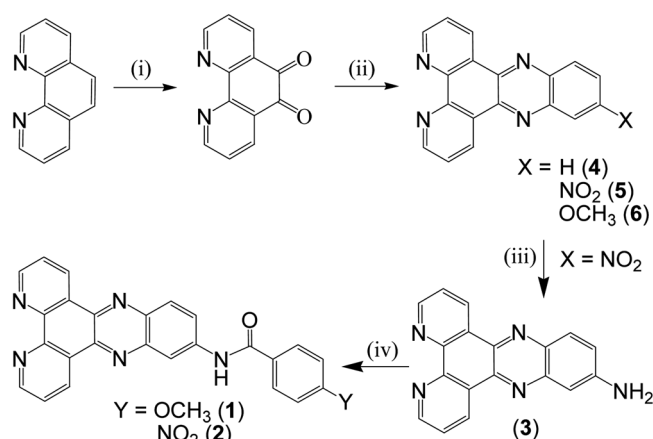
Syntheses of dppz derivatives.

7-(4-Methoxybenzoylamino)dipyrido[3,2-a:2',3'-c]phenazine (1): To a dry acetonitrile containing triethylamine, 7-amino-dppz (3) and 4-methoxybenzoyl chloride were dissolved and refluxed for 3 h under inert atmosphere. The precipitate was collected by filtration, washed with acetonitrile, and dried *in vacuo* at 80 °C; yellow powder 89% m.p. = 321-322 °C δ_{H} (300 MHz; DMSO- d_6) 3.83 (3H, s), 7.10 (2H, d, $J = 7.7$ Hz), 7.90 (2H, m), 8.02 (2H, d, $J = 7.7$ Hz), 8.30 (2H, s), 8.97 (1H, s), 9.15 (2H, m), 9.45 (2H, q, $J = 8.2$ Hz), 10.71 (1H, s), Found: C, 72.40; H, 4.12; N, 16.41. Calc. for $\text{C}_{26}\text{H}_{17}\text{N}_5\text{O}_2$: C, 72.38; H, 3.97; N, 16.23. Mass (FAB) m/z , 432 $[\text{M}+\text{H}]^+$.

7-(4-Nitrobenzoylamino)dipyrido[3,2-a:2',3'-c]phenazine (2): To a dry acetonitrile containing triethylamine, 7-amino-dppz (3) and 4-nitrobenzoyl chloride were dissolved and refluxed for 7 h under inert atmosphere. The precipitate was collected by filtration, washed with acetonitrile, and dried *in vacuo* at 80 °C; greenish powder 91% m.p. = 320 °C (decomposition) δ_{H} (300 MHz; DMSO- d_6) 6.57 (1H, s), 7.86 (2H, m), 8.22 (2H, d, $J = 7.7$ Hz), 8.29 (2H, s), 8.37 (2H, d, $J = 7.7$ Hz), 8.86 (1H, s), 9.13 (2H, m), 9.36 (2H, q, $J = 8.2$ Hz), Found: C, 67.35; H, 3.21; N, 18.89. Calc. for $\text{C}_{25}\text{H}_{14}\text{N}_6\text{O}_3$: C, 67.26; H, 3.16; N, 18.83. Mass (FAB) m/z , 447 $[\text{M}+\text{H}]^+$.

Results and Discussion

The fluorescent dppz derivative can be successfully synthesized (high-yield yellow compound 1) through simple amide condensation reaction, in which the methoxy electron-donating group, consisting of its compound, plays an important role in the appearance of its relatively high fluorescence quantum yield compared to nonemissive compound 2, with the nitro electron-withdrawing group (Scheme 1). As shown in Figure 1, the absorption spectra of the dppz derivatives 1, 2, 3, and 4 were measured in 5×10^{-6} mol dm^{-3} dichloromethane at 25 °C. The lowest energy absorption bands appeared between 350 and 490 nm. In particular, as shown in Table 1, compounds 1 and 2 showed much longer absorption maxima than did compound 4, with the absorption tail of compound 1 extending to 450 nm, although that of compound 3 was extended to 490 nm. This could be ascribed to the extended aromatic ring by amide bonding. In addition, it could be noted that compound 1 showed a hyperchromic effect that was not observed with other dppz derivatives.



Scheme 1. Syntheses of 7-substituted dppz derivatives. (i) Conc. H_2SO_4 , conc. HNO_3 , KBr, 80-85 °C, 2 h; (ii) 4-X-1,2-diaminobenzene, EtOH, reflux, 4 h; (iii) Pd/C, NaBH_4 , MeOH, 17 h; (iv) 4-Y-benzoylchloride, CH_3CN , NEt_3 , 2 hr, reflux.

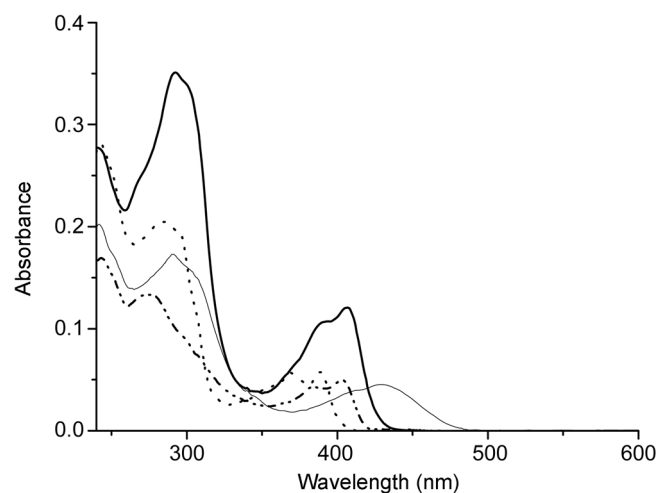


Figure 1. The electronic absorption spectra of 5×10^{-6} mol dm^{-3} compound 1 (—), 2 (— · —), 3 (---) and 4 (·····) in dichloromethane at 25 °C.

Table 1. Absorption and fluorescence maxima in dichloromethane at 25 °C

Compound	$\lambda_{\text{abs}}/\text{nm}$ ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{fl}}/\text{nm}$ (Φ)
1	407 (4.38)	440 (0.21)
2	403 (4.00)	— (0)
3	428 (3.96)	517 (0.24)
4	378 (3.97)	— (0)
5	390 (4.13)	— (0)
6	400 (4.18)	422 (0.03)

As shown in Figure 2 and Table 1, the fluorescence spectra of the dppz derivatives 1, 2, and 3 were measured by the excitation of 365 nm in 5×10^{-6} mol dm^{-3} dichloromethane at 25 °C. The synthesized compound 1 with the methoxy electron-donating group showed a relatively high fluorescence quantum yield ($\Phi = 0.21$ in dichloromethane), comparable to that of compound 3, although the fluorescence

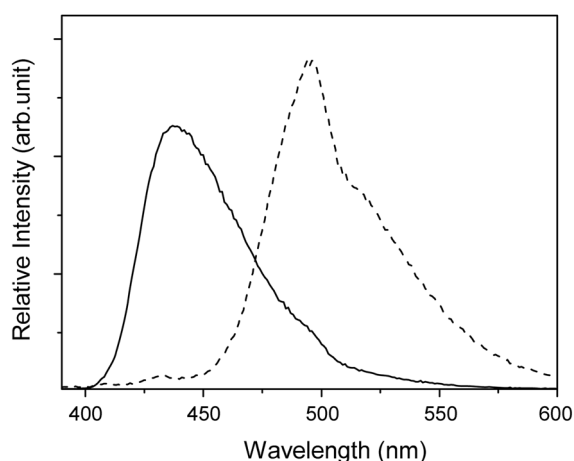


Figure 2. The fluorescence emission spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$) of $5 \times 10^{-6} \text{ mol dm}^{-3}$ compound **1** (—) and **3** (.....) in dichloromethane at $25 \text{ }^\circ\text{C}$.

Table 2. Absorption and fluorescence maxima of compound **1** at $25 \text{ }^\circ\text{C}$

Solvent	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{fl}}/\text{nm}$ (F)
Dichloromethane	407	440 (0.21)
Acetonitrile	406	454 (0.21)
Ethanol	406	470 (0.11)

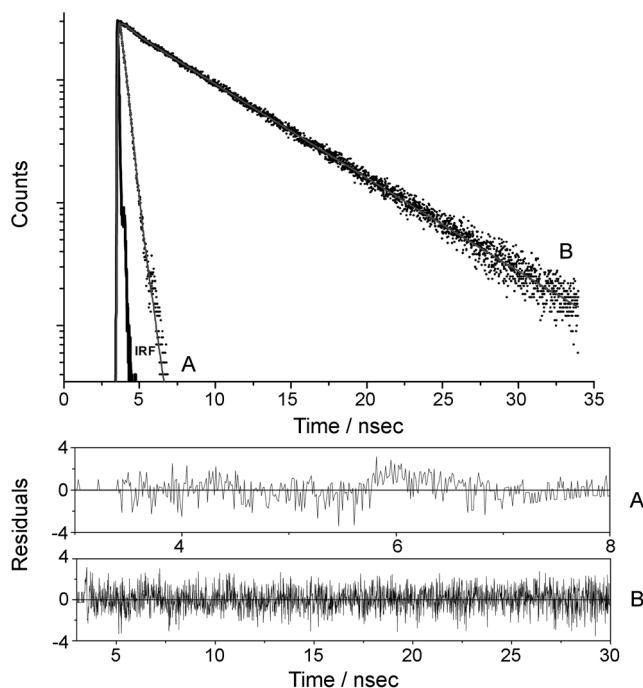


Figure 3. The fluorescence emission decay spectra of compound **1** (A) and **3** (B) monitored at $\lambda_{\text{em}} = 450 \text{ nm}$ and 500 nm , respectively.

maximum of compound **1** that appeared in the wavelength (440 nm) was shorter than that of compound **3** (517 nm). In addition, the fluorescence quantum yield of compound **1** was seven times higher than that of compound **6** ($\Phi = 0.03$ in dichloromethane), with the methoxy electron-donating

group directly in position 7 of the dppz ring.

Meanwhile, the synthesized compound **2** with the nitro electron-withdrawing group produced no emission. The same result was observed with compound **5** with the nitro electron-withdrawing group directly in position 7 of the dppz ring.

As shown in Table 2, the solvent effect of compound **1** was investigated using spectroscopic methods. While its absorption band appeared at almost the same wavelength ($406\text{--}407 \text{ nm}$) irrespective of the solvent's polarity, its fluorescence band red-shifted from 440 nm to 470 nm as a result of increasing polarity.

According to the investigation of time-resolved emission spectroscopy of compounds **1** and **3** (Fig. 3), the fluorescence emission curve of compound **1** showed a much shorter lifetime ($\tau = 0.3 \text{ ns}$) as a single component, while that of compound **3** showed a longer lifetime ($\tau = 5.6 \text{ ns}$) as a single component.

Conclusion

The above results show that the synthesized compound **1** is a novel material whose high level of fluorescence is comparable to that of compound **3**, but with a more extended and less rigid structure. Due to such material property, compound **1** shows much potential in the production of organic light-emitting diodes (OLEDs). The design and synthesis of a number of other superior fluorescent dppz derivatives, moreover, are still in progress.

Acknowledgements. This work was partly supported by a research grant of Kwangwoon University (2005) and by the MIC (Ministry of Information and Communication), Korea, under the ITRC (Information Technology Research Center) Support Program supervised by the IITA (Institute of Information Technology Assessment) (IITA-2005-C1090-0502-0038).

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