Unique Fluorescent Properties of 1-Aryl-3,4-diphenylpyrido[1,2-*a*]benzimidazoles

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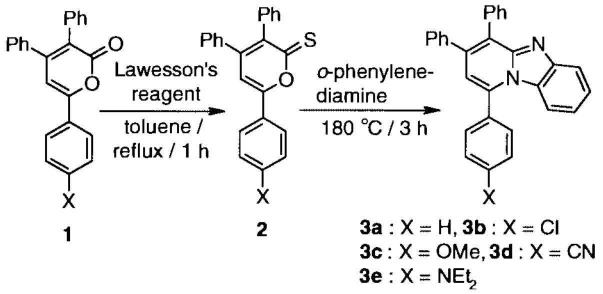
Novel fluorophores, 1-aryl-3,4-diphenylpyrido[1,2-*a*]benzimidazoles were synthesized. They emit intense blue to green fluorescence in solution (Φ: ca. 0.7) and show weak negative solvatofluorochromism by about 10 nm which was caused by the combination of π–π* and n–π* transitions. In the powdered form, they emit intense fluorescence whose intensity is at least two times stronger than that of Alq_3.

Fluorescent organic compounds have been the focus of considerable interest because of their potential applications to a variety of fields, including their use as fluorescent probes and in optoelectronics.[1,2] We previously reported on a new series of fluorophores, 3,4,6-triaryl-α-pyrone derivatives (**1**), which show intense blue to orange fluorescence only in the solid state.[3,4] In order to develop the efficient fluorescence both in solution and the solid states, novel 1-aryl-3,4-diphenylpyrido[1,2-*a*]benzimidazoles were newly synthesized. In this paper we report on their synthesis and unique fluorescent properties.

Although α-pyrones **1** did not react with *o*-phenylenediamine to afford pyridobenzimidazoles **3**, a reaction employing their thione derivatives **2** gave the desired product as shown in Scheme 1.[5] The results of them are summarized in Table 1 and the structures of **3** were determined by ^1H, ^{13}C NMR, and X-ray crystallographic analysis. When the reaction temperature was raised to 200 °C, the polymerization of *o*-phenylenediamine was dominant and the yields of **3** decreased extensively. In case of α-pyrones, the intermolecular interaction was observed due to short interplaner distance which was clarified by X-ray structure analysis.[4] However, such packing effect was not observed for **3a**, whose ORTEP drawing is shown in Figure 1.[6]



Scheme 1.

Table 1. Characterization of the compounds **3a**–**3e**

Compound	X	Yield/%[a]	mp/°C	λ_{abs}/nm[b]	λ_{flu}/nm[c]	Φ
3a	H	45	>250	380	489	0.72
3b	Cl	39	221	380	488	0.48
3c	MeO	42	241	381	492	0.78
3d	CN	28	>250	384	518	0.66
3e	Et_2N	35	212	387	514	0.57

[a] Overall yields from **1**. [b] Absorption spectra were obtained in ca. 10^{-4} M toluene solutions. [c] Emission spectra were recorded in 10^{-6} M toluene solutions and excited at their absorption maxima.

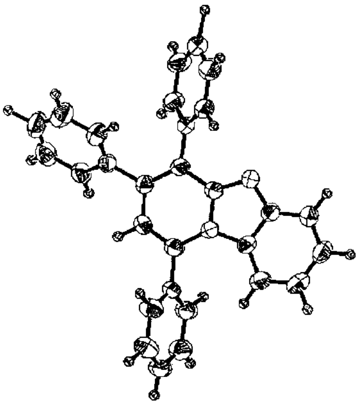


Figure 1. ORTEP drawing of **3a**.

Their absorption and fluorescent spectra were measured in toluene. The life-time of fluorescence was not influenced by the oxygen. The absorption and fluorescent maxima of **3d** and **3e**, the X groups of which are strong electron-withdrawing and donating, were slightly red-shifted, as compared to those of **3a**–**3c**. However, these shifts caused by the substituent X were much smaller than those of triphenyl-α-pyrones. It indicates that no strong electron donor–acceptor interactions occur in the molecules.

They emit intense blue to green luminescence, the quantum yields of which are relatively high and the Stokes shifts are greater than 100 nm. Surprisingly, these compounds exhibit weak negative solvatochromism in their spectra and the fluorescent maxima are blue-shifted with increase in the polarity of the solvent except for **3e**. The results are listed in Table 2 and Figure 2 shows the absorption and fluorescent spectra of **3a** in toluene and ethanol. The spectral shapes of other derivatives

Table 2. Absorption and emission data of **3a** in a series of solvents

Solvent	λ_{abs}/nm[a]	log ε	λ_{flu}/nm[b]	Φ
cyclohexane	381	0.74	483	0.71
toluene	381	0.84	487	0.72
diethylether	377	0.85	488	0.69
THF	376	0.85	489	0.65
CH_2Cl_2	373	0.76	485	0.74
EtOH	368	0.75	482	0.63

[a] Absorption spectra were obtained in ca. 10^{-4} M solutions. [b] Emission spectra were recorded in 10^{-6} M solutions and excited at their absorption maxima.

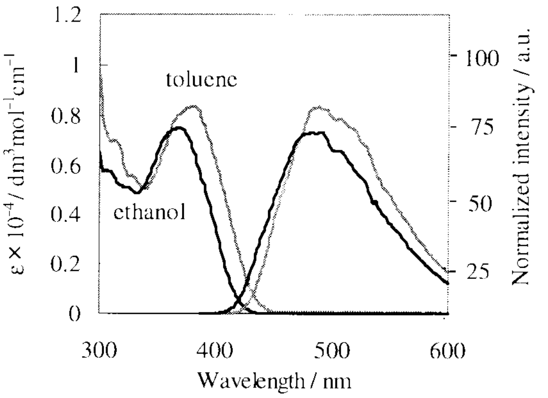


Figure 2. Absorption and normalized fluorescent spectra of **3a** in toluene and ethanol.

were almost same as those of **3a**. The spectral shift of **3a** was analyzed by means of the Lippert–Mataga equation 1,[7,8]

$$\Delta\nu = \nu_{abs} - \nu_{flu} = 2(\Delta\mu)^2\Delta f/hca^3 + \text{const},$$
$$\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1), \qquad (1)$$

where Δν is the difference between the fluorescence and absorption maxima, Δμ the difference between the excited and ground state dipole moments, Δ*f* the Lippert's solvent polarity parameter, *h* Planck's constant, *c* the concentration of the compounds, *a* an effective radius of the Onsager cavity of the compounds, and ε and *n* are the relative permittivity and the optical reflective index of the solvents, respectively. Since the value of Δν showed nearly linear dependence on Δ*f* as shown in Figure 3, it is expected that the lowest excitation bands of them were assigned not to an n–π* but, rather, a π–π* transition. The *a* and Δμ for **3a** are estimated to be ca. 5.0 Å and 4.0 D, respectively, which are reasonable for compounds without donor–acceptor units in their molecular structures. The quantum yields of **3a** in polar solvents are slightly lower than those in nonpolar ones. Accordingly, it is expected that the transition of these compounds consists, not only of a π–π* transition, but also to some extent of an n–π* transition in polar solvents and **3a**–**3d** showed weak, negative solvatofluorochromism. This solvatochromism is mainly dependent on the ground state energy level in each solvent. On the other hand, **3e** has highly polar diethylamino group and is not classified in this type of compounds.

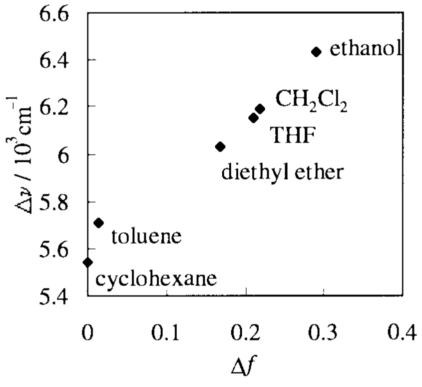


Figure 3. Plots of Δν vs Δ*f* of **3a**.

Finally, the relative fluorescence intensity was evaluated in the solid state with excitation at 380 nm using Alq_3 as the reference.[9] Except for **3d** (λ_{flu} = 511 nm, relative intensity : 0.02) and **3e** (535 nm, 0.22), **3a**, **3b**, and **3c** showed more intense fluorescence than Alq_3 as shown in Figure 4. Therefore, these compounds are of considerable promise for use in EL applications instead of Alq_3.

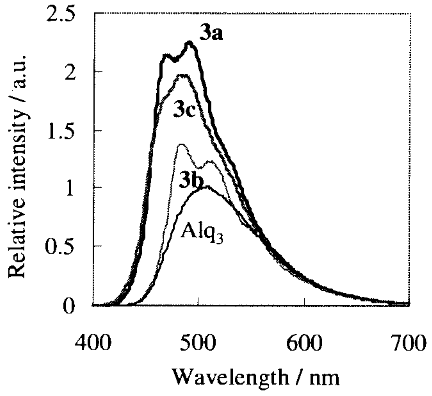


Figure 4. Fluorescent spectra of **3a**, **3b**, **3c**, and Alq_3 in the powdered form.

In summary, novel fluorophores, 1-aryl-3,4-diphenylpyrido-[1,2-*a*]benzimidazoles were synthesized and their fluorescent properties were investigated in solution and the solid state. It was found that their weak negative solvatofluorochromism was caused by the combination of π–π* and n–π* in polar solvents. In the solid state, they also emit highly efficient fluorescence and have potential for use as a fluorescent pigment and in EL devices. These issues are currently under investigation.

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References and Notes

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6 X-ray crystallographic data : $C_{29}H_{20}N_2$, M_r = 396.49, yellow, prismatic, triclinic, space group $P1$ (#2), a = 10.295(3) Å, b = 11.238(4) Å, c = 10.260(2) Å, α = 102.91 (2)°, β = 99.66 (2)°, γ = 110.52(3)°, V = 1043.4(6) Å^3, Z = 2, D_c 1.262 g/cm, $F(000)$ = 416.00, μ(Mo Kα) = 0.74 cm^{-1}, graphite monochromated Mo Kα (λ = 0.71069 Å), T = 23 °C, final discrepancy factor: R = 0.087 and R_w = 0.070. The structure was solved by direct method (SAPI92).
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9 Samples were injected into the space between two plain glass slides and their fluorescence was measured. The relative intensities were evaluated by comparing them with that of Alq_3 whose intensity was set as 1.