Dramatic Effects of the Substituents on the Solid-state Fluorescence Properties of Structural Isomers of Novel Benzofuro[2,3-*c*]oxazolocarbazole-type Fluorophores

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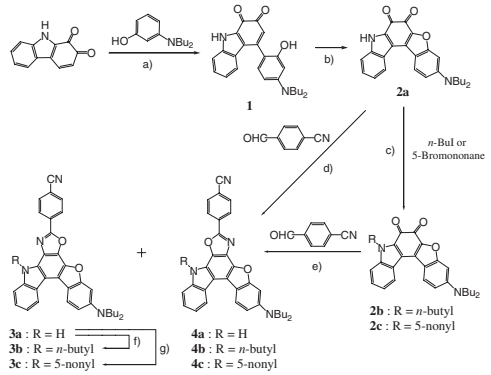
Structural isomers of novel benzofuro[2,3-*c*]oxazolocarbazole-type fluorophores have been synthesized and their photophysical properties in solution and in the solid state were investigated; remarkable differences in the absorption and fluorescence spectra were observed between structural isomers in both states, and a drastic solid-state fluorescence enhancement was found to be caused by N-alkylation of fluorophores.

Solid-state fluorescent dyes have been the focus of considerable interest because of not only attractive materials for the fundamental research of solid-state photochemistry,[1–5] but also their possible applications in the optoelectronics such as light-emitting diode and photoelectric conversion.[6,7] However, organic fluorophores exhibiting strong fluorescence both in solution and in the solid state are relatively limited because most fluorophores undergo fluorescence quenching by aggregation state in the solid state. In this paper, we report structural isomers of novel benzofuro[2,3-*c*]oxazolocarbazole-type fluorophores **3** and **4**, whose photophysical properties in solution and in the solid state were surprisingly different between structural isomers in both states, and a drastic solid-state fluorescence enhancement was found to be caused by N-alkylation of fluorophores.

First, we prepared the starting heteropolycyclic quinones **2a**–**2c** as shown in Scheme 1. Carbazole-1,2-dione was prepared according to published procedure.[8] The quinone **2a** was obtained by the reaction of carbazole-1,2,-dione with *m*-(dibutylamino)-phenol in the presence of $CuCl_2$, followed by intramolecular oxidative-cyclization using $Cu(OCOCH_3)_2$.[9] Next, the heteropolycyclic quinone-type dye **2a** was allowed to react with *p*-cyanobenzaldehyde to give the structural isomers of oxazolocarbazole-type fluorophores **3a** and **4a**. In this reaction, NH_3 resulting from CH_3COONH_4 in the initial stage acts as the nucleophilic reagent to the 6- and/or 7-carbonyl carbon. The reaction of the N-alkylated quinones **2b** or **2c** with *p*-cyanobenzaldehyde afforded preferentially the compound **4b** or **4c**. The fluorophores **3b** and **3c** were prepared by N-alkylation of **3a**.[10] These compounds were completely characterized by ^{1}H NMR, IR, and elemental analysis. A comparison of the observed and calculated UV–vis spectra for compounds **3** and **4** has provided a powerful evidence for identification of the structures **3** and **4**.[10]



Scheme 1. Synthesis of fluorophores **3** and **4**. a) $CuCl_2$, DMSO, 50 °C, 1.5 h, 32%; b) $Cu(OCOCH_3)_2$, DMSO, 80 °C, 1.0 h, 63%; c) **2b**: Na_2CO_3 aq, *N*-methyl-2-pyrrolydone, 90 °C, 10 h, 23%; **2c**: KOH aq, Bu_4NBr, toluene, reflux, 10 h, 26%; d) CH_3COOH, CH_3COONH_4, 90 °C, 1 h, 55% for **3a**, 16% for **4a**; e) **4b**: CH_3COOH, CH_3COONH_4, 90 °C, 2 h, 62%; **4c**: CH_3COOH, CH_3COONH_4, 90 °C, 4 h, 15%; f) *n*-BuLi, *n*-BuI, THF, −108 °C–rt, 1.0–10 h, 41%; g) KOH aq, Bu_4NBr, 5-bromononane, toluene, reflux, 14 h, 14%.

The visible absorption and fluorescence spectral data of **3a**–**3c** and **4a**–**4c** in solution are summarized in Table 1. The effect of N-alkylation of the carbazole ring on photophysical properties of **3** and **4** was negligible, so that the absorption and fluorescence spectra of the fluorophores **3a**–**3c** or **4a**–**4c** resemble very well in each category. In cyclohexane, all compounds exhibit vibronic-structured absorption and emission bands. The fluorophores **3a**–**3c** exhibit an intense absorption band at around 430 and 350 nm and an intense fluorescence band at around 540 nm in

Table 1. Absorption and fluorescence spectral data of **3a**–**3c** and **4a**–**4c** in solution

	Solvent	Absorption[a]	Fluorescence[b]		SS[c]
		λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	λ_{max} /nm	Φ[d]	$\Delta\lambda_{max}$ /nm
3a	Cyclohexane	460(—), 431(—) 410(—), 348(—)[e]	505, 472	—[e]	12
	1,4-Dioxane	428(25900), 350(27300)	539	0.99	111
	THF	429(24100), 350(27100)	582	0.48	153
	Acetone	427(24700), 349(26200)	617	0.16	190
3b	Cyclohexane	469(21600), 438(24400) 415(16600), 355(28600)	513, 480	0.99	11
	1,4-Dioxane	430(26300), 354(32000)	535	0.99	105
3c	Cyclohexane	471(18400), 439(21200) 416(14500), 355(26500)	515, 482	0.99	11
	1,4-Dioxane	430(24000), 359(30900)	534	0.99	104
4a	Cyclohexane	442(—), 390(—), 360(—)[e]	513, 484	—[e]	42
	1,4-Dioxane	430(4700), 359(60200)	575	0.17	145
	THF	430(5900), 359(69200)	623	0.02	193
	Acetone	430(5600), 357(72000)	—[f]	—[f]	—[f]
4b	Cyclohexane	446(5400), 397(19000) 375(24500), 362(41900)	521, 492	0.35	46
	1,4-Dioxane	430(4500), 362(50300)	576	0.17	146
4c	Cyclohexane	445(4200), 398(18000) 375(23000), 361(52400)	522, 492	0.35	47
	1,4-Dioxane	430(4400), 362(49000)	579	0.17	149

[a] 2.0×10^{-5} M. [b] 2.0×10^{-6} M. [c] Stokes shift value. [d] Φ values were determined using 9,10-diphenylanthracene ($\Phi = 0.67$, $\lambda_{ex} = 357$ nm) in benzene as a standard. [e] Poor solubility. [f] Too weak.

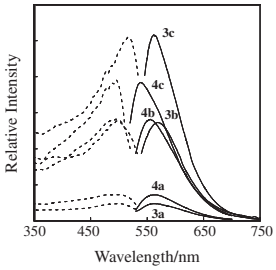


Figure 1. Solid-state excitation (···) and emission (—) spectra of the crystals of **3a**–**3c** and **4a**–**4c**; **3a**: $\lambda_{ex} = 508$ nm, $\lambda_{em} = 566$ nm; **3b**: $\lambda_{ex} = 502$ nm, $\lambda_{em} = 567$ nm; **3c**: $\lambda_{ex} = 515$ nm, $\lambda_{em} = 562$ nm; **4a**: $\lambda_{ex} = 505$ nm, $\lambda_{em} = 562$ nm; **4b**: $\lambda_{ex} = 495$ nm, $\lambda_{em} = 556$ nm; **4c**: $\lambda_{ex} = 497$ nm, $\lambda_{em} = 536$ nm.

1,4-dioxane. The fluorescence quantum yield (Φ) of the fluorophores **3a**–**3c** in 1,4-dioxane were close to 100%. On the other hand, the fluorophores **4a**–**4c** exhibit a weak absorption band at around 430 nm and an intense absorption band at around 360 nm, and relatively weak fluorescence band at around 550 nm ($\Phi = 0.17$) in 1,4-dioxane. The absorption maxima of **3a**–**3c** and **4a**–**4c** are little affected by changing the solvent from 1,4-dioxane to acetone, while these fluorescence maxima show a large bathochromic shift, so that the Stokes shift value in polar solvents becomes larger than that in nonpolar solvents. Significant dependence of the fluorescence quantum yield on the solvent polarity was also observed: the Φ value of **3a** is reduced to ca. 16% with increasing polarity from 1,4-dioxane to acetone, whereas for **4a** an increase in solvent polarity causes a large bathochromic shift and a drastic decrease in the fluorescence intensity. The Φ values of **3a**–**3c** greater than those of **4a**–**4c** suggest that the degree of donor–acceptor conjugation for the former is larger than that for the latter owing to the conjugated linkage of the dibutylamino group to the cyano group in **3a**–**3c**.

Interesting results have been obtained from the photophysical properties of **3a**–**3c** and **4a**–**4c** in the solid state. As shown in Figure 1, the fluorophore **3c** exhibits stronger fluorescence band than the other compounds in the crystalline state. The fluorescence intensity increase in the order of **3c** ($\Phi = 0.20$) > **4c** ($\Phi = 0.17$) > **4b** ($\Phi = 0.11$) ≈ **3b** ($\Phi = 0.10$) ≫ **4a** ($\Phi = 0.03$). Surprisingly, the Φ values of **4c** were almost the same in 1,4-dioxane and in the solid state. The wavelengths of the fluorescence excitation and emission maxima of **3a** ($\lambda_{ex} = 508$ nm, $\lambda_{em} = 566$ nm) and **4a** ($\lambda_{ex} = 505$ nm, $\lambda_{em} = 562$ nm) are largely red-shifted by 48, 60 nm and 61, 49 nm compared with those in cyclohexane, respectively. On the other hand, the emission maxima of **3c** ($\lambda_{em} = 562$ nm) and **4c** ($\lambda_{em} = 536$ nm) show a blue shift with intense fluorescence compared with those of **3a** and **4a**, respectively. These results demonstrated that the solid-state fluorescence enhancement by N-alkylation to fluorophores effectively prevented the intermolecular π–π interaction[4,11,12] and intermolecular hydrogen bonding[11b,13] between fluorophores causing a large red-shift of the absorption and fluorescence maxima and fluorescence quenching in the solid state. However, the fluorescence enhancement and the blue shift of **3c** were relatively small compared to those of **4c**. It was assumed that the intermolecular π–π interaction is strongly formed in the crystals of the donor–acceptor-type fluorophores.

The electrochemical properties of **3a**–**3c** and **4a**–**4c** were determined by cyclic voltammetry (CV) in acetonitrile containing 0.1 M Bu_4NClO_4.[10] These compounds give similar CV curves, and show three oxidation waves at 0.32–0.36, 0.83–0.85, and 0.98–1.01 V vs Ag/Ag^+. The corresponding reduction waves appear at 0.26–0.29, 0.76–0.82, and 0.91–0.96 V and the half-wave potential ($E_{1/2}$) of these compounds are 0.29–0.33, 0.80–0.85, and 0.95–0.99 V. The peak separation between oxidation wave and reduction wave was ca. 60 mV, which show oxidated state of the fluorophores is stable.

In conclusion, we have developed structural isomers of benzofuro[2,3-*c*]oxazolocarbazole-type fluorophores **3** and **4**. The isomers make a marked difference in degree of the donor–acceptor conjugation leading to the quite different absorption and fluorescence spectra in solution. Intense solid-state fluorescence compounds have been prepared by the N-alkylations of the carbazole ring with retaining excellent photophysical property of fluorophores themselves.

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