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A facile synthesis of solid-emissive fluorescent dyes: dialkylbenzo[*b*]naphtho[2,1-*d*]furan-6-one-type fluorophores with strong blue and green fluorescence emission properties

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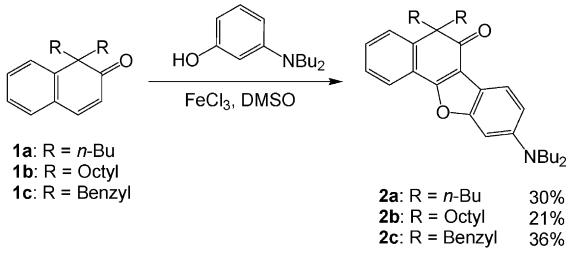
Abstract—A new type of organic fluorophores, dialkylbenzo[*b*]naphtho[2,1-*d*]furan-6-one-type fluorophores, exhibiting strong blue and green emission in the solid state has been easily synthesized by an one-step reaction. The X-ray crystal structure demonstrated that the structural form with a chair-shape with the sterical hindered dialkyl substituents and the 9-dibutylamino group prevents the fluorophores from forming short intermolecular contacts and produces intense solid-state fluorescence emission.

Recently, solid-emissive 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 molecular aggregation in the solid state. In order to develop strong solid-emissive fluorophores, many efforts were made on inhibition of molecular aggregation state causing fluorescence quenching. Fluorescent dyes having non-planar structures with sterical hindered substituents prevent the fluorophores from the close packing causing fluorescence quenching in the solid state and produces intense solid-state fluorescence emission.[5h,8,9] In contrast, we have designed a novel dialkylbenzo[*b*]naphtho[2,1-*d*]furan-6-one-type fluorophores (**2a**–**c**), which consist of π-planar chromophore skeleton with sterical hindered dialkyl substituents prevent the fluorophores from short π–π contacts causing fluorescence quenching in the solid state. In this Letter, we report the preparation of **2a**–**c** by one-step reaction and their photophysical properties in solution and in the solid state. To elucidate the effects of the dialkyl substituents on the solid-state photophysical properties, we have carried out the measurement of the solid-state fluorescence spectra and the X-ray crystallographic analysis of the fluorophores.

The starting 1,1-dialkyl-1*H*-naphthalen-2-one **1a**–**c** were prepared according to the published procedure.[10] Novel dialkylbenzo[*b*]naphtho[2,1-*d*]furan-6-one-type fluorophores **2a**–**c** were easily obtained by the reaction of **1a**–**c** with *m*-(dibutylamino)phenol in the presence of $FeCl_3$ (Scheme 1). However, when metal salt such as $NiCl_2$ or $CuCl_2$ instead of $FeCl_3$ was used, the fluorophores **2** were not obtained. Compounds **2a** and **2c** were obtained as crystals by recrystallization from *n*-hexane, but the compound **2b** was obtained as amorphous.

The spectroscopic properties of **2a**–**c** both in solution and in the solid state are summarized in Table 1.[11]



Scheme 1. Synthetic route of **2a**–**c**.

Keywords: Solid-state fluorescence; Heterocycles; Crystal structures; Dyes; Photophysical property.

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Table 1. Spectroscopic properties of **2a**–**c** in 1,4-dioxane and in the crystalline state

Solvent		In solution			In the crystalline state		
		λ_{max}^{abs}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	λ_{max}^{fl}/nm	Φ	λ_{max}^{ex}/nm	λ_{max}^{fl}/nm	Φ
2a	Cyclohexane	394 (16,100)	440	0.48	446	478	0.40
	1,4-Dioxane	403 (15,000)	489	0.53			
2b	Cyclohexane	394 (15,200)	439	0.50	444[a]	495[a]	0.37[a]
	1,4-Dioxane	402 (15,000)	488	0.52			
2c	Cyclohexane	403 (15,100)	449	0.48	494	526	0.45
	1,4-Dioxane	410 (15,500)	496	0.50			

[a] Amorphous.

The fluorescence spectra of the compounds were recorded by excitation at the wavelengths of the longest absorption maximum. In cyclohexane, the absorption maxima at around 394–403 nm and the fluorescence maxima at around 439–449 nm are both red-shifted by conjugation with the substituent (R) in the order of **2a** ≈ **2b** < **2c**. From these results, it was considered that the π-electron effect of the benzyl group for **2c** caused red-shift of the absorption and fluorescence maxima. On the other hand, the fluorescence quantum yields (Φ) are almost the same among **2a**–**c** (Φ = ca. 0.5). The absorption maxima of **2a**–**c** show a small bathochromic shift of 7–9 nm from cyclohexane to 1,4-dioxane, while the fluorescence maxima show a large bathochromic shift of 47–49 nm, so that the Stokes shift values in polar solvent become larger than that in nonpolar solvent. Similar spectral changes are generally observed for most fluorescent dyes whose dipole moments in the excited state become larger than those in the ground state.

Interesting results have been obtained from the photophysical properties of the crystals. As shown in Figure 1, the crystals of **2a** and **2c** exhibit strong blue and green fluorescence emission, respectively. On the other hand, **2b** was obtained not as crystal but a solid like amorphous, which exhibits strong bluish green fluorescence emission. The fluorescence quantum yields (Φ) of **2a**–**c** are 0.40, 0.37, 0.45, respectively, (Table 1). It is noteworthy that the Φ values of **2a** and **2c** were almost the same in cyclohexane and in the solid state. Consequently, these results also demonstrated that the solid-state photophysical properties of **2a** and **2c** are approaching to their photophysical properties in solution. However, the Φ value of **2b** in the amorphous state is smaller than that of **2b** in cyclohexane. This is presumably due to the disturbance of light scattering of the aggregates in the amorphous state.[12] On the other hand, the wavelengths of the emission maximum of **2a** ($\lambda_{em} = 478$ nm), **2b** ($\lambda_{em} = 495$ nm), and **2c** ($\lambda_{em} = 526$ nm) are red-shifted by 38, 56, and 77 nm compared with that in cyclohexane, respectively. It was considered that the molecular arrangement and orientation in the crystalline state cause the shift of the wavelengths of the solid-state emission maximum.[2–4]

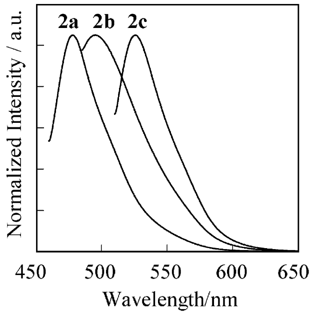

Figure 1. Solid-state emission spectra of the crystals of **2a**–**c**.

To elucidate strong solid-state fluorescence properties of **2a**–**c**, the X-ray crystal structure of **2a** have been determined.[13,14] As shown in Figure 2, the packing structures demonstrate that the molecules are arranged in a

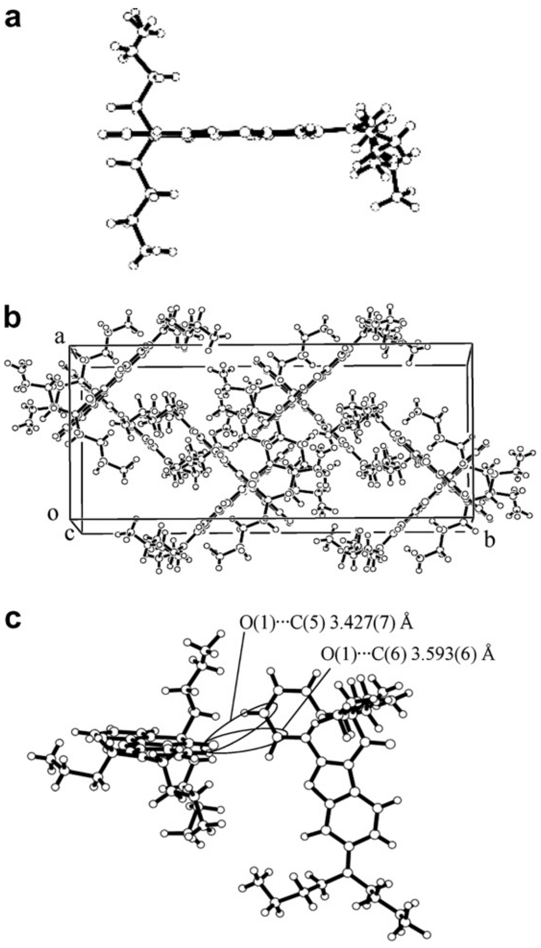

Figure 2. Crystal packing of **2a**: (a) molecular structure (b) a stereoview of the molecular packing structure and (c) the nearest contact between fluorophores.

'herring-bone' fashion. The molecules are packed in the structural form with a chair-shape because one of the butyl group and the 9-dibutylamino group are located on opposite sides of the molecular π-plane, we expected that such stereostructures with sterical hindered substituents (dialkyl and 9-dibutylamino groups) prevent the fluorophores from forming short intermolecular contacts causing fluorescence quenching in the solid state. In fact, fluorophore **2a** has only two edge-to-edge interatomic contacts of less than 3.60 Å between the neighboring fluorophores in the crystal structure.

In conclusion, we have designed and easily synthesized novel dialkylbenzo[*b*]naphtho[2,1-*d*]furan-6-one-type fluorophores with sterical hindered dialkyl substituents and their absorption and fluorescence properties were investigated in solution and in the solid state. As we expected, the X-ray crystal analysis has demonstrated that the chair-shape molecular structure with the sterical hindered dialkyl substituents and the 9-dibutylamino group prevents the fluorophores from forming short intermolecular contacts and produces intense solid-state fluorescence emission. We believe that the design of fluorophores with bulky dialkyl substituents of non-conjugated linkage to the fluorophore skeleton is effective to develop strong solid-emissive fluorescent dyes.

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Supplementary data

Supplementary data associated with this article (Synthetic and experimental details and X-ray crystallographic data) can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.059.

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11. The fluorescence quantum yields (Φ) in solution were determined by using 9,10-bis(phenylethynyl)anthracene ($\Phi = 0.84$, $\lambda_{\mathrm{ex}} = 440$ nm) in benzene as the standard. The solid-fluorescence quantum yields (Φ) were determined by using a calibrated integrating sphere system ($\lambda_{\mathrm{ex}} = 325$ nm).
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13. *Crystal data for* **2a**: $C_{32}H_{43}NO_2$, $M = 473.70$, orthorhombic, $a = 17.964(4)$, $b = 26.276(4)$, $c = 12.005(3)$ Å, $U = 5666(2)$ Å^3, $T = 296.2$ K, space group Pbca (No. 61), $Z = 8$, μ(Mo-Ka) = 0.68 cm^{-1}, 7177 reflections measured, 6498 unique which were used in all calculations. The final R indices were $R_1 = 0.074$, $wR\ (F^2) = 0.239$ (all data).
14. Crystallographic data (excluding structure factors) for the structure of **2a** in this Letter has been deposited with Cambridge Crystallographic Data Centre as supplementary publication number CCDC 648283. Copy of data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].