Synthesis, X-ray crystal structures, and solid-state fluorescence properties of 3-dibutylamino-6-alkoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one derivatives**

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Dedicated to ... on the occasion of ... (optional)

Keywords: Fluorescent dyes / Crystal structures / Pi-Pi interaction / Substituent effects / Solid-state fluorescence

Heterocyclic fluorophores, 3-dibutylamino-6-alkoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (**2a–2g**) with the different chain length of alkoxy substituents linked non-conjugate to the chromophore skeleton have been derived from the quinol-type compound **1** and their photophysical properties have been investigated in solution and in the solid state. The fluorophores **1** and **2a–2g** exhibit similar fluorescence properties in solution. However, the fluorophores **2a–2g** exhibit stronger solid-state fluorescence properties compared with the quinol **1**. Furthermore, the fluorescence quantum yields (Φ) of **2** in the solid state are higher than that of **1** in solution, and considerable differences in the solid-state fluorescence were observed among the alkoxy derivatives **2a–2g**. To elucidate the dramatic effect of the alkoxy substituents, we have performed the semi-empirical molecular

orbital calculations (AM1 and INDO/S) and the X-ray crystallographic analysis. On the basis of the results of the calculations and the X-ray crystal structures, the relations between the solid-state photophysical properties and the chemical and crystal structures of **1** and **2a–2g** were discussed. It was confirmed that the introduction of a long alkoxy chain such as butoxy and pentoxy groups of non-conjugated linkage to the chromophore can efficiently prevent the short π – π contact between the fluorophores in molecular aggregation states and cause a dramatic solid-state fluorescence enhancement.

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Introduction

During the last decade, there has been a gradual accumulation of information about solid-state fluorescence of organic fluorophores, which is the subject of great interest to the optoelectronics industry such as light emitting diode^[1] and photoelectric conversion.^[2] Some studies suggested that the key point in designing new organic fluorescent dyes exhibiting strong solid emission properties is to remove the intermolecular interactions between fluorophores causing fluorescence quenching in molecular aggregation states. For example, the introduction of bulky substituents to the original fluorophores,^[1f, 1j, 3, 4] and the construction of a non-planar structures with sterical hindered substituents^[4d, 5] are known to be very useful methods for solving the problem of fluorescence quenching by aggregation. However, it is difficult to make a systematic study to investigate the relation between the chemical structures and the solid-state emission properties for appearance of strong solid-state fluorescence of organic fluorescent dyes.

In the previous paper,^[6] we have reported the solid-state fluorescence properties of novel benzofurano[3,2-*b*]naphthoquinol-type fluorophore (**1**) and the alkoxy derivative (**2b**) with butoxy substituent of non-conjugated linkage to the chromophore (Scheme 1). Dramatic substituent effects on the solid-state photophysical properties were observed, which has been elucidated by means of the X-ray crystallographic analysis. It was confirmed that the introduction of butoxy substituent of non-conjugated linkage to the chromophore can efficiently prevent the short π – π contact between the fluorophores in molecular aggregation states and cause a dramatic solid-state fluorescence enhancement. This fact suggests that the solid-state fluorescence of the fluorophore is significantly dependent on the steric factor of the alkoxy substituent of non-conjugated linkage to the chromophore skeleton at 6-position of **2**. Here, we report the photophysical properties in solution and in the crystalline state of the heterocyclic fluorophores, 3-dibutylamino-6-alkoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (**2**) with different chain length of alkoxy substituents. To elucidate the steric effect of the alkoxy substituents on the solid-state fluorescence excitation and emission spectra, we have performed the X-ray crystallographic analysis.

Results and Discussion

Synthesis of 3-dibutylamino-6-alkoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one fluorophores (**2a–2g**)

It is known that dialkylamino-substituted triphenylcarbinol analogs undergo dehydroxylation under acidic conditions to give triaryl carbocation salts.^[7] In order to prepare alkoxy derivatives of the quinol, we tried the dehydroxylation of quinol **1**. The reaction of **1** with boron trifluoride ($\text{BF}_3\text{-OEt}_2$) gave the cationic salt in 93% yield (Scheme 1). The cationic salt was then dissolved in alcohols with heating to give the corresponding alkoxy derivatives **2a-2g** in high yield (55–86%).

<Scheme 1. here>

Spectroscopic properties of **1** and **2** in solution

The visible absorption and fluorescence spectral data of **1** and **2** in various solvents are summarized in Table 1. The fluorescence spectra of the compounds were recorded by excitation at the wavelengths of the longest absorption maximum. Because of the non-conjugated linkage of the alkoxy and hydroxyl groups to the chromophore skeleton, the absorption and fluorescence spectra of the fluorophores **1** and **2** resemble very well one another. The quinol **1** exhibits two distinct absorption bands at around 391 and 321 nm in benzene, and exhibit a weak fluorescence band at around 540 nm ($\Phi = 0.056$). The effect of solvent polarity on the absorption spectrum of **1** is small, whereas that on the fluorescence spectrum is big: an increase in solvent polarity causes a large bathochromic shift and a drastic decrease in the fluorescence intensity. The fluorescence intensity was too weak to allow determination of the maximum wavelengths and the quantum yields in acetonitrile and 95% ethanol. The Stokes shift values for **1** are large, even in a solvent of low polarity. The absorption spectra of **2** are little affected by increasing the solvent polarity, while these fluorescence spectra show a large bathochromic shift and a reduction of fluorescence intensity. The photophysical properties of **2** were similar to that of the quinol **1**.

<Table 1. here>

Semi-empirical MO calculations (AM1, INDO/S)

The photophysical spectra of **1** and **2** were analyzed by using semi-empirical molecular orbital (MO) calculations. The molecular structures were optimized by using MOPAC/AM1 method^[8], and then the INDO/S method^[9] was used for spectroscopic calculations. The calculated absorption wavelengths and the transition character of the first absorption bands are collected in Table 2. The calculated absorption wavelengths and the oscillator strength values are relatively good compatible with the observed spectra in benzene, although the calculated absorption spectra are blue shifted. This deviation of the INDO/S calculations, giving high transition energies compared with the experimental values, has been generally observed.^[10] The calculations show that the longest excitation bands for **1** and **2** are mainly assigned to the transition from the HOMO to the LUMO, where HOMO were mostly localized on the 3-dibutylaminobenzofurano moiety, and the LUMO were mostly localized on the naphthoquinol moiety (Figure 1). The values of the dipole moments in the ground states are 2.79 for **1** and 3.11–3.38 for **2**. The differences between the dipole moments ($\Delta\mu$) of the first excited (HOMO→LUMO) and the ground states are 12.37 for **1** and 11.54–12.04 for **2**. The changes in the calculated electron density accompanying the first electron excitation are shown in Figure 2, which shows a strong migration of intramolecular charge-transfer character in **1** and **2**. On the other hand, the differences between the dipole moments ($\Delta\mu$) of the second excited (HOMO→LUMO + 1) and the ground states are 6.83 for **1** and 5.65–6.71 for **2**. These calculations indicate that the

compounds **1** and **2** have similar large dipole moments in the excited state, which explains well the experimental observations that the compounds showed a large bathochromic shift of their fluorescence maxima in polar solvents and that the Stokes shift values for the compounds **1** and **2** in ethanol are much larger than those in benzene. The calculated data for **2** are quite similar to those for **1**, which is also in good agreement with the observation that these compounds exhibit similar Stokes shift values.

< Figures 1 and 2. here> <Table 2. here>

Spectroscopic properties of **1** and alkoxy derivatives **2** in the solid state

Of particular interest are the photophysical properties of the crystals of **1** and alkoxy derivatives **2**. Crystals of **1**, **2a**, **2b**, **2c**, **2f** and **2g** were obtained by recrystallization from ethanol solution. However, the compound **2d** was obtained as amorphous by recrystallization from various solutions (ethanol, *n*-hexane, acetonitrile, dichloromethane, benzene, and acetone solutions). On the other hand, crystals of **2e** were obtained by dissolving in a minimum quantity of dichloromethane and reprecipitating with *n*-hexane. Figure 3 and Table 3 show the spectroscopic properties of the crystals of the fluorophores **1**, **2a**, **2b**, **2c**, **2e**, **2f** and **2g**. Many remarkable differences are seen when the absorption and fluorescence spectra in the crystalline state are compared to those in solution. The longest wavelength of the excitation maximum of **1** is located at around 504 nm, which are red-shifted by 113 nm in comparison with the values of the absorption maxima in benzene. The fluorescence maximum of **1** is located at around 569 nm, which is red-shifted by 29 nm in comparison with the fluorescence maxima in benzene. On the other hand, the longest excitation maxima of the crystals of **2** are located at around 444–503 nm, which is red-shifted by 55–128 nm in comparison with the longest absorption maximum of those in benzene. The solid-state fluorescence maximum of **2** are located at around 525–561 nm, which are red-shifted by 1–39 nm in comparison with the fluorescence maximum in benzene. The red-shift values of **2** except **2g** from solution to the solid state are smaller than that of **1**. Furthermore, a big difference is clear in the fluorescence intensity between the compounds **1** and **2**. The compounds **2** exhibit stronger fluorescence band than the compound **1** in the crystalline state, which is quite different from the behaviour in solution: the fluorescence quantum yields of **1** and **2** are in the order of **2e** ($\Phi = 0.51$) > **2b** ($\Phi = 0.26$) > **2c** ($\Phi = 0.11$) > **2a** ($\Phi = 0.04$) $\approx$ **1** ($\Phi = 0.04$) in the crystalline state. The fluorophores **2b** and **2e** exhibited much stronger fluorescence in the solid state than in solution. It had been reported that non-radiative decay is accelerated by free rotation of substituents in solution.^[4d] Since the rotation of the alkoxy substituents is restricted in the solid state, the fluorescence quantum yields are higher in the solid states than in solution. The difference in the fluorescence quantum yields among various alkoxy derivatives in the crystalline state is discussed on the bases of the X-ray crystal structures in the next section.

< Figure 3. here> <Table 3. here>

X-ray crystal structures of **1**, **2a**, **2b**, **2c** and **2f**

To understand the dramatic substituent effect on the solid state photophysical properties, the X-ray crystal structures of the compound **1** and the alkoxy derivatives **2a**, **2b**, **2c** and **2f** have been determined and shown in Figures 4–8, respectively. The crystal systems of **1** and the alkoxy derivatives **2** are summarized in Table

4. The packing structures show that the molecules of **1**, **2a**, **2b**, **2c** and **2f** are arranged in a “bricks in a wall” fashion.

The packing structures demonstrate that the crystal of **1** is built up by a centrosymmetric dimer unit which is composed of a pair of quinol enantiomers bound cofacially by intermolecular hydrogen bonds between the hydroxy group and the carbonyl group on both sides of the dimer unit. The hydrogen bond angle OH...O is 179(3)° and the O...O distance is 2.811(2) Å. The two hydrogen bonds hold the enantiomers in close proximity, leading to close π - π overlapping. As shown in Figure 4(c), there are 8 (= 4 × 2) short interatomic π - π contacts for **1**. The π -overlaps were observed between the naphthoquinol moieties. The interplanar distances between the naphtho[2,3-*b*]benzofuran planes are *ca.* 3.57 Å, which suggests strong π - π interactions between the fluorophores.

< Figure 4. here >

On the other hand, in the case of the alkoxy derivatives, there are no intermolecular hydrogen bonds between the enantiomers. The phenyl group is twisted out of the plane of the naphtho[2,3-*b*]benzofuran moiety by *ca.* 90° and the alkoxy chain is also almost perpendicularly extended to the π -plane. In the crystal of **2a**, a continuous π -stacking of the equal enantiomers of *R*- and *S*-isomers was formed in independent columns in which π -overlaps were observed between the naphtho moiety and the 9-dibutylaminobenzo moiety of the adjacent equal enantiomers (Figure 5). The interplanar distances between the naphtho[2,3-*b*]benzofuran planes are *ca.* 3.42 Å. There are 6 short interatomic π - π contacts of less than 3.6 Å in a pair of enantiomers, which suggests π - π interactions between the fluorophores. In the case of **2b**, there are no short non-bonded interatomic π - π contacts of less than 3.60 Å as shown in Figure 6. The phenyl group is twisted out of the plane of the naphtho[2,3-*b*]benzofuran moiety by 90.24° and the butoxy chain is also almost perpendicularly extended to the quinol plane. The shortest distance for non-bonded overlapping atoms is 3.81(3) Å (for C(11)*...C(12) and C(11)...C(12)*), which suggests a considerable reduction in the intermolecular π - π interactions between neighbouring fluorophores. The packing structures of **2c** and **2f** resemble very well one another as shown in Figures 7 and 8. There are 3 short interatomic π - π contacts of less than 3.6 Å in a pair of equal enantiomers. The inclination between the naphtho[2,3-*b*]benzofuran planes in the pair of equal enantiomers are 27° for **2c** and 28° for **2f**, respectively. These results demonstrated that alkoxylation to fluorophores can effectively prevent the intermolecular π - π interaction^[3b, 5, 4, 11-14] and intermolecular hydrogen bonding^[2b, 15] between fluorophores in molecular aggregation state and thus cause a dramatic enhancement in the solid-state fluorescence.

< Figures 5–8. here >

From the stereostructures of **2a**, **2b**, **2c** and **2f**, we noticed that the chain length of alkoxy substituents affect the crystal structure (Figure 9). Consequently, the degree of the reduction in the intermolecular π - π interactions and the interplanar distances between neighbouring fluorophores are deeply related to the length of alkyl chain in alkoxy substituents. In the case of **2a**, a continuous π -stacking of the equal enantiomers of *R*- and *S*-isomers was found in independent columns because a short chain of ethoxy substituent can not efficiently prevent the short π - π contact between the fluorophores in molecular aggregation states. In the cases of **2c** and **2f**, some short interatomic π - π contacts of less than 3.6 Å in a pair of equal enantiomers were still observed because the isobutoxy and neopentoxy substituents are not enough to prevent the short π - π contact between the fluorophores. On the contrary, in the case of **2b**, there are no short interatomic π - π

contacts of less than 3.60 Å. This result indicates that the butoxy substituent can efficiently prevent the short π - π contact between the fluorophores and lead to much stronger solid-state fluorescence emission. As shown above, a good-correlation between the solid-state fluorescence intensity and the molecular stacking structure was observed. In addition, it was demonstrated that the penthoxy substituent of **2e** is effective for appearance of strong solid-state fluorescence, although the high-quality single crystal of **2e** was not obtained. On the other hand, Ooyama *et al.* reported that for benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole-type fluorescent dyes, the introduction of sterically hindered substituents to carbazole ring situated on the centre of chromophores skeleton can efficiently prevent the short π - π contact between the fluorophores in molecular aggregation states and cause a dramatic solid-state fluorescence enhancement.^[16] In the case of the compounds **2**, it was demonstrated that the introduction of bulky 6, 6-disubstituents (such as phenyl group and a long alkoxy group) of non-conjugated linkage to the centre of chromophore skeleton have large effect for the improvement of the solid-state fluorescence.

Conclusions

We have synthesized heterocyclic fluorophores, 3-dibutylamino-6-alkoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (**2**) with phenyl group and various alkoxy substituents linked non-conjugate to the chromophore skeleton at 6-position and evaluated their absorption and fluorescence properties in solution and in the solid state. It was confirmed that the introduction of a long chain alkoxy substituents of non-conjugated linkage to the centre of chromophore skeleton can efficiently prevent the short π - π contact between the fluorophores in molecular aggregation states and cause a dramatic solid-state fluorescence enhancement.

< Figure 9. here >

Experimental Section

General: Melting points were measured with a Yanaco micro melting point apparatus MP-500D. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer for samples in KBr pellet form. Absorption spectra were observed with a JASCO U-best30 spectrophotometer and fluorescence spectra were measured with a JASCO FP-777 spectrophotometer. Single-crystal X-ray diffraction was performed on Rigaku AFC7S diffractometer. For the measurement of the solid-state fluorescence excitation and emission spectra of the crystals, a JASCO FP-777 spectrometer equipped with a JASCO FP-1060 attachment was used. The fluorescence quantum yields (Φ) in solution were determined using 9,10-diphenylanthracene (Φ = 0.67, λ_{ex} = 357 nm)^[17] in benzene as the standard. The solid-fluorescence quantum yields (Φ) were determined by using a calibrated integrating sphere system (λ_{ex} = 325 nm). Elemental analyses were recorded on a Perkin Elmer 2400 II CHN analyzer. ¹H NMR spectra were recorded on a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Column chromatography was performed on silica gel (KANTO CHEMICAL, 60N, spherical, neutral). Semi-empirical molecular orbital (MO) calculations were performed on FUJITSU FMV-ME4/657 by using the WinMOPAC Ver. 3 package (Fujitsu, Chiba, Japan).

General Synthetic Procedure for 3-(dibutylamino)-6-alkoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (**2a–2g**) by Dehydroxybutoxylation of **1**:

Compound **1** (0.3 g) was dissolved in a solution of 47% BF₃·OEt₂ (17 ml) and stirred for 15 min at room temperature. The reaction mixture was poured into water and the resulting precipitate was filtered and dried to afford a cationic salt as a dark green

powder; 0.37 g (93% yield). The cationic salt (0.3 g) was dissolved in alcohol and stirred for 30 min at 60 °C. The reaction mixture was neutralized with aq. Na₂CO₃ and extracted with CHCl₃. The organic extract was washed with water and evaporated. The residue was chromatographed on silica gel (CH₂Cl₂ as eluent) and was further purified by recrystallization from a mixture of CH₂Cl₂–*n*-hexane to give **2a–2g** as yellow and orangish yellow crystals.

3-(dibutylamino)-6-ethoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (2a): Yield: 79%; m.p. 160–163 °C; ¹H NMR (400 MHz, [D₃]chloroform, TMS): δ = 0.93 (t, 6H), 1.18 (t, 3H), 1.33–1.62 (m, 8H), 3.10–3.40 (m, 6H), 6.76 (d, *J* = 2.2 Hz, 1H), 6.86 (dd, *J* = 2.2 and 8.8 Hz, 1H), 7.22–7.66 (m, 8H), 7.92 (d, *J* = 8.7 Hz, 1H), 8.25 (dd, *J* = 1.0 and 7.6 Hz, 1H); IR (KBr): $\tilde{\nu}$ = 1667 cm^{−1}; elemental analysis calcd (%) for C₃₂H₃₅NO₃ (481.63): C 79.80, H 7.32, N, 2.91; found: C 79.74, H 7.54, N 3.03.

3-(dibutylamino)-6-butoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (2b): Yield: 86%; m.p. 115–117 °C; ¹H NMR (400 MHz, [D₃]chloroform, TMS): δ = 0.84 (t, 3H), 0.95 (t, 6H), 1.26–1.61 (m, 12H), 3.04–3.21 (m, 2H), 3.29 (t, 4H), 6.69 (d, *J* = 2.2 Hz, 1H), 6.75 (dd, *J* = 2.2 and 8.8 Hz, 1H), 7.21–7.54 (m, 8H), 8.01 (d, *J* = 8.5 Hz, 1H), 8.33 (dd, *J* = 1.2 and 7.8 Hz, 1H); IR (KBr): $\tilde{\nu}$ = 1660 cm^{−1}; elemental analysis calcd (%) for C₃₄H₃₉NO₃ (509.68): C 80.12, H 7.71, N 2.75; found: C 80.19, H 7.92, N 2.89.

3-(dibutylamino)-6-isobutoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (2c): Yield: 68%; m.p. 123–126 °C; ¹H NMR (400 MHz, [D₆]acetone, TMS): δ = 0.88–0.97 (m, 12H), 1.26–1.61 (m, 8H), 1.90–1.93 (m, 1H), 2.78–2.99 (m, 2H), 3.29 (t, 4H), 6.70–6.77 (m, 2H), 7.22–7.55 (m, 8H), 8.02 (d, *J* = 8.5 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H); IR (KBr): $\tilde{\nu}$ = 1662 cm^{−1}; elemental analysis calcd (%) for C₃₄H₃₉NO₃ (509.68): C 80.12, H 7.71, N 2.75; found: C 80.22, H 7.91, N 2.88.

3-(dibutylamino)-6-*tert*-butoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (2d): Yield: 62%; m.p. 42–45 °C; ¹H NMR (400 MHz, [D₆]acetone, TMS): δ = 0.58–0.93 (m, 15H), 1.36–1.60 (m, 8H), 3.32 (t, 4H), 6.76–6.86 (m, 2H), 7.25–7.59 (m, 8H), 7.90–7.93 (m, 1H), 8.25–8.28 (m, 1H); IR (KBr): $\tilde{\nu}$ = 1658 cm^{−1}; elemental analysis calcd (%) for C₃₄H₃₉NO₃ (509.68): C 80.12, H 7.71, N 2.75; found: C 80.35, H 8.05, N 2.79.

3-(dibutylamino)-6-pentoxo-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (2e): Yield: 54%; m.p. 107–109 °C; ¹H NMR (400 MHz, [D₃]chloroform, TMS): δ = 0.85 (t, 3H), 0.95 (t, 6H), 1.26–1.61 (m, 14H), 3.04–3.20 (m, 2H), 3.29 (t, 4H), 6.69 (d, *J* = 2.2 Hz, 1H), 6.74 (dd, *J* = 2.2 and 8.8 Hz, 1H), 7.22–7.54 (m, 8H), 8.01 (d, *J* = 8.8 Hz, 1H), 8.32 (dd, *J* = 1.2 and 7.8 Hz, 1H); IR (KBr): $\tilde{\nu}$ = 1665 cm^{−1}; elemental analysis calcd (%) for C₃₅H₄₁NO₃ (523.70): C 80.27, H 7.89, N 2.67; found: C 80.33, H 7.62, N 2.81.

3-(dibutylamino)-6-neopentoxo-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (2f): Yield: 55%; m.p. 123–126 °C; ¹H NMR (400 MHz, [D₃]chloroform, TMS): δ = 0.92–0.96 (m, 15H), 1.32–1.38 (m, 4H), 1.53–1.59 (m, 4H), 2.77 (m, 2H), 3.26–3.31 (4H, m), 6.69–6.77 (m, 2H), 7.2–7.29 (m, 4H), 7.43–7.54 (m, 4H), 8.02 (d, *J* = 8.78 Hz, 1H), 8.32 (d, *J* = 6.3 Hz, 1H); IR (KBr): $\tilde{\nu}$ = 1662 cm^{−1}; elemental analysis calcd (%) for C₃₅H₄₁NO₃ (523.70): C 80.27, H 7.89, N 2.67; found: C 80.09, H 8.01, N 2.72.

3-(dibutylamino)-6-phenoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (2g): Yield: 71%; m.p. 226–228 °C; ¹H NMR (400 MHz, [D₆]acetone, TMS): δ = 0.92 (t, 6H), 1.3–1.6 (m, 8H), 3.36 (t, 4H), 6.74–6.78 (m, 2H), 7.03–7.35 (m, 10H), 7.41 (dd, *J* = 1.24 and 7.80 Hz, 1H), 7.51 (dd, *J* = 1.24 and 7.32 Hz, 1H), 7.58 (dd, *J* = 1.48 and 7.32 Hz, 1H), 7.91 (d, *J* = 8.76 Hz, 1H), 8.32 (dd, *J* = 1.48 and 7.56 Hz, 1H); IR (KBr): $\tilde{\nu}$ = 1637

cm^{−1}; elemental analysis calcd (%) for C₃₆H₃₅NO₃ (529.67): C 81.63, H 6.66, N 2.64; found: C 81.70, H 6.60, N 2.70.

X-ray Crystallographic Studies: The reflection data were collected at 23 ± 1 °C on a Rigaku AFC7S four-circle diffractometer by 2θ–ω scan technique, and using graphite-monochromated MoK_α (λ = 0.71069 Å) radiation at 50 kV and 30 mA. In all case, the data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The reflection intensities were monitored by three standard reflections for every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. All calculations were performed using the teXsan^[18] crystallographic software package of Molecular Structure Corporation. CCDC-172461 (**1**), CCDC-635416 (**2a**), CCDC-172462 (**2b**), CCDC-635417 (**2c**), and CCDC-635418 (**2f**) contain the supplementary crystallographic data (see Table 4) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 1: Crystals of **1** were recrystallized from ethanol as orange prism, air stable. The transmission factors ranged from 0.98 to 1.00. The crystal structure was solved by direct methods using SIR 88.^[19] The structures were expanded using Fourier techniques.^[20] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.

Compound 2a: Crystals of **2a** were recrystallized from ethanol as yellow prism, air stable. The transmission factors ranged from 0.93 to 1.00. The crystal structure was solved by direct methods using SAPI 91.^[21] The structures were expanded using Fourier techniques.^[20] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.

Compound 2b: Crystals of **2b** were recrystallized from ethanol as yellow prism, air stable. The transmission factors ranged from 0.97 to 1.00. The crystal structure was solved by direct methods using SIR 92.^[22] The structures were expanded using Fourier techniques.^[20] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.

Compound 2c: Crystals of **2c** were recrystallized from ethanol as yellow prism, air stable. The transmission factors ranged from 0.95 to 1.00. The crystal structure was solved by direct methods using SIR 88.^[19] The structures were expanded using Fourier techniques.^[20] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.

Compound 2f: Crystals of **2f** were recrystallized from ethanol as yellow prism, air stable. The transmission factors ranged from 0.95 to 1.00. The crystal structure was solved by direct methods using SIR 88.^[19] The structures were expanded using Fourier techniques.^[16] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.

Computational methods: All calculations were performed on FUJITSU FMV-ME4/657. The semi-empirical calculations were carried out with the WinMOPAC Ver. 3 package (Fujitsu, Chiba, Japan). Geometry calculations in the ground state were carried out using the AM1 method.^[8] All geometries were completely optimized (keyword PRECISE) by the eigenvector following routine (keyword EF). Experimental absorption spectra of the compounds were studied with the semi-empirical method INDO/S (intermediate neglect of differential overlap/spectroscopic).^[9] All INDO/S calculations were performed using single excitation full SCF/CI (self-consistent field/configuration interaction), which includes the configuration with one electron excited from any occupied orbital to any unoccupied orbital, 225 configurations were considered for the configuration interaction [keyword CI (15 15)].

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

Dramatic 6-alkoxy substituent effects on the solid-state photophysical properties of novel heterocyclic fluorophores, 3-dibutylamino-6-alkoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one (**2**), have been discussed on the basis of the X-ray crystal structures.

Solid-state fluorescent dyes

Y. Ooyama*, T. Mamura, K. Yoshida* Page No. – Page No.

Synthesis, X-ray crystal structures, and solid-state fluorescence properties of 3-dibutylamino-6-alkoxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one derivatives

Keywords: Fluorescent dyes / Crystal structures / Pi-Pi interaction / Substituent effects / Solid-state fluorescence

Table 1. Absorption and fluorescence spectral data of **1** and **2a–2g** in various solvents.

Compound	Solvent	Absorption (obs.) ^[a]	Fluorescence(obs.) ^[b]		SS ^[d]
		$\lambda_{\text{max}} / \text{nm}$ ($\epsilon_{\text{max}} / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em}} / \text{nm}$	Φ ^[c]	$\Delta\lambda_{\text{max}}/\text{nm}$
1	Cyclohexane	371 (1730), 317 (17400)	480	0.12	109
	Benzene	391 (1600), 321 (17300)	540	0.056	149
	1,4-Dioxane	384 (1480), 320 (16200)	547	0.045	163
	Tetrahydrofuran	385 (1230), 320 (17500)	555	0.020	170
	Chloroform	398 (1260), 324 (17100)	566	0.006	168
	Acetonitrile	388 (1310), 322 (16700)	— ^[e]	— ^[e]	— ^[e]
	95%Ethanol	391 (1390), 320 (17700)	— ^[e]	— ^[e]	— ^[e]
	Benzene	383 (1660), 321 (17700)	536	0.118	153
2b	Cyclohexane	378 (1840), 317 (19000)	481	0.20	103
	Benzene	392 (1700), 323 (18400)	537	0.11	145
	1,4-Dioxane	388 (1660), 321 (18300)	568	0.077	180
	Tetrahydrofuran	388 (1600), 321 (17800)	572	0.037	184
	Chloroform	396 (1480), 325 (17200)	585	0.008	189
	Acetonitrile	388 (1460), 323 (17200)	— ^[e]	— ^[e]	— ^[e]
	95%Ethanol	392 (1440), 321 (19300)	— ^[e]	— ^[e]	— ^[e]
	Benzene	391 (1620), 321 (17200)	537	0.112	146
2c	Benzene	389 (1700), 322 (17900)	525	0.10	136
2e	Benzene	383 (1900), 321 (19100)	535	0.111	152
2g	Benzene	380 (2320), 324 (18500)	522	0.198	142

[a] 5.0×10^{-5} M. [b] 1.0×10^{-6} M. [c] Φ values were determined using 9,10-diphenylanthracene ($\Phi = 0.67$, $\lambda_{\text{ex}} = 357$ nm) in benzene as the standard. [d] Stokes shift value. [e] Too weak to be measured.

Table 2. Calculated absorption wavelengths (λ_{max}) and difference in dipole moments ($\Delta\mu$) for **1** and **2a–2g**.

Compound	$\mu/D^{[a]}$	Absorption (calc.)		CI component ^[c]	$\Delta\mu/D^{[d]}$
		$\lambda_{\text{max}} / \text{nm}$	$f^{[b]}$		
1	2.79	356	0.12	HOMO→LUMO (87%)	12.37
		298	0.70	HOMO→LUMO + 1 (66%)	6.83
2a	3.16	352	0.11	HOMO→LUMO (87%)	11.57
		296	0.66	HOMO→LUMO + 1 (65%)	5.67
2b	3.19	355	0.11	HOMO→LUMO (87%)	12.04
		298	0.69	HOMO→LUMO + 1 (67%)	6.44
2c	3.11	352	0.11	HOMO→LUMO (87%)	11.54
		296	0.67	HOMO→LUMO + 1 (66%)	5.76
2e	3.14	352	0.11	HOMO→LUMO (87%)	11.57
		296	0.66	HOMO→LUMO + 1 (65%)	5.65
2f	3.22	352	0.12	HOMO→LUMO (87%)	11.54
		296	0.67	HOMO→LUMO + 1 (66%)	5.80
2g	3.38	357	0.13	HOMO→LUMO (88%)	11.56
		299	0.64	HOMO→LUMO + 1 (70%)	6.71

[a] The values of the dipole moment in the ground state. [b] Oscillator strength. [c] The transition is shown by an arrow from one orbital to another, followed by its percentage CI (configuration interaction) component. [d] The values of the difference in the dipole moment between the excited and the ground states.

Table 3. Spectroscopic properties of **1** and **2** in the crystalline state

Compound	$\lambda_{\text{max}}^{\text{ex}}/\text{nm}$	$\lambda_{\text{max}}^{\text{fl}}/\text{nm}$	Φ ^[a]
1	504	569	0.04
2a	448	525	0.03
2b	495	547	0.26
2c	503	540	0.11
2e	444	527	0.51
2g	508	561	0.11

[a] The solid-fluorescence quantum yields (Φ) were determined by using a calibrated integrating sphere system ($\lambda_{\text{ex}} = 325 \text{ nm}$).

Table 4. Crystal data and structure refinement parameters for the compounds **1** and **2**.

Compound	1	2a	2b	2c	2f
molecular formula	C ₃₀ H ₃₁ NO ₃	C ₃₂ H ₃₅ NO ₃	C ₃₄ H ₃₉ NO ₃	C ₃₄ H ₃₉ NO ₃	C ₃₅ H ₄₁ NO ₃
formula weight	453.58	481.63	509.69	509.69	523.71
crystal size[nm]	0.55×0.10×0.70	0.20×0.05×0.20	0.30×0.10×0.40	0.60×0.30×0.25	0.25×0.30×0.40
refine (2 θ range, [°])	25 (27.2-29.6)	9 (6.6-17.5)	25 (22.4-24.9)	25 (20.1-25.4)	25 (22.1-24.0)
crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	C2/c	C2/c
<i>a</i> [Å]	11.738(2)	10.131(6)	9.061(1)	26.377(4)	26.429(7)
<i>b</i> [Å]	12.244(2)	15.851(6)	20.227(2)	11.253(4)	11.321(1)
<i>c</i> [Å]	10.879(2)	8.247(5)	8.751(1)	21.601(4)	21.860(8)
α [°]	90.69(2)	93.96(5)	101.52(1)		
β [°]	116.39(1)	91.22(6)	114.30(1)	114.79(1)	113.10(2)
γ [°]	64.73(1)	84.87(4)	87.75(1)		
<i>V</i> [Å ³]	1235.8(10)	1315(1)	1430.6(4)	5821(2)	6016(2)
<i>Z</i>	2	2	2	8	8
ρ_{calcd} [g cm ⁻³]	1.219	1.216	1.183	1.163	1.156
<i>F</i> (000)	484.00	516.00	548.0	2192.0	2256.0
μ (MoK α) [cm ⁻¹]	0.78	0.77	0.74	0.73	0.72
<i>T</i> [K]	296.2	296.2	296.2	296.2	296.2
scan mode	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
scan rate [° min ⁻¹]	4.0 ^[b]	4.0 ^[b]	4.0 ^[b]	4.0 ^[b]	4.0 ^[b]
scan width [°]	1.68 + 0.30 tan θ	1.37 + 0.30 tan θ	1.10 + 0.30 tan θ	1.78 + 0.30 tan θ	0.94 + 0.30 tan θ
2 θ max [°]	50.0	50.0	50.0	50.0	50.0
<i>hkl</i> range	-13/0, -14/13, -11/12	0/12, -18/18, -9/9	0/10, -24/24, 10/9	0/31, 0/13, -25/23	0/28, -12/12, -23/21
reflections measured	4577	4914	5385	5243	7824
unique reflns	4345	4629	5036	5122	4916
reflns observed with $I_0 > 2\sigma I_0$	2631	1336	2304	1606	2060
<i>R</i> _{int}	0.015	0.104	0.045	0.062	0.066
no. of parameters	432	398	432	374	389
<i>R</i>	0.0406	0.0856	0.0803	0.1287	0.1027
<i>R</i> _w	0.0986	0.1613	0.1700	0.2552	0.2162
<i>w</i>	($\sigma^2 F^2$) ⁻¹	($\sigma^2 F^2$) ⁻¹	($\sigma^2 F^2$) ⁻¹	($\sigma^2 F^2$) ⁻¹	($\sigma^2 F^2$) ⁻¹
<i>S</i>	1.19	1.04	1.33	1.78	1.60
max. shift/error in final cycle	0.01	0.01	0.01	0.00	0.01
max. peak in final diff. map [e Å ⁻³]	0.34	0.43	0.41	0.78	0.45
min. peak in final diff. map [e Å ⁻³]	-0.28	-0.46	-0.32	-0.66	-0.38

[a] Number of reflections used for unit cell determination. [b] Up to five scans.

Figure and Scheme captions

Scheme 1. Synthesis of **2**.

Figure 1. a) HOMOs and b) LUMOs for **1** and **2b**. The black and white lobes denote the negative and positive signs of the coefficients of the molecular orbital. The size of each lobe is proportional to the MO coefficient.

Figure 2. Calculated electron density changes accompanying the first electronic excitation of **1** and **2b**. The black and white lobes signify the decrease and increase in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change.

Figure 3. Solid-state excitation (dotted line) and emission (solid line) spectra of the crystals of **1** and **2a**, **2b**, **2c**, **2f** and **2g**; **1**: $\lambda_{\text{ex}} = 504$ nm, $\lambda_{\text{em}} = 569$ nm; **2a**: $\lambda_{\text{ex}} = 448$ nm, $\lambda_{\text{em}} = 525$ nm; **2b**: $\lambda_{\text{ex}} = 495$ nm, $\lambda_{\text{em}} = 547$ nm; **2c**: $\lambda_{\text{ex}} = 503$ nm, $\lambda_{\text{em}} = 540$ nm; **2e**: $\lambda_{\text{ex}} = 444$ nm, $\lambda_{\text{em}} = 527$ nm; **2f**: $\lambda_{\text{ex}} = 491$ nm, $\lambda_{\text{em}} = 536$ nm; **2g**: $\lambda_{\text{ex}} = 508$ nm, $\lambda_{\text{em}} = 561$ nm.

Figure 4. Crystal packing and hydrogen bonding pattern of **1**; a) a stereoview of the molecular packing structure, b) a schematic structure, c) a side view, and d) a top view of the pairs of fluorophores.

Figure 5. Crystal packing of **2a**; a) a stereoview of the molecular packing structure, b) a schematic structure, c) a side view, and d) a top view of the pairs of fluorophores.

Figure 6. Crystal packing of **2b** (a) a stereoview of the molecular packing structure, (b) a schematic structure, (c) a side view, and (d) a top view of the pairs of fluorophores.

Figure 7. Crystal packing of **2c**; a) a stereoview of the molecular packing structure, b) a schematic structure, c) a side view, and d) a top view of the pairs of fluorophores.

Figure 8. Crystal packing of **2f**; a) a stereoview of the molecular packing structure, b) a schematic structure, c) a side view, and d) a top view of the pairs of fluorophores.

Figure 9. Schematic representation of the effects of the substituents on interplanar distances between a pair of fluorophores for **1**, **2a**, **2b**, **2c** and **2f**.

Scheme 1. Synthesis of **2**.

a)

b)

Figure 1. a) HOMOs and b) LUMOs for **1** and **2b**. The black and white lobes denote the negative and positive signs of the coefficients of the molecular orbital. The size of each lobe is proportional to the MO coefficient.

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Figure 5. Crystal packing of **2a** (a) a stereoview of the molecular packing structure, (b) a schematic structure, (c) a side view, and (d) a top view of the pairs of fluorophores.

Figure 6. Crystal packing of **2b** (a) a stereoview of the molecular packing structure, (b) a schematic structure, (c) a side view, and (d) a top view of the pairs of fluorophores.

Figure 7. Crystal packing of **2c** (a) a stereoview of the molecular packing structure, (b) a schematic structure, (c) a side view, and (d) a top view of the pairs of fluorophores.

(c)

(d)

(c)

(d)

Figure 8. Crystal packing of **2f** (a) a stereoview of the molecular packing structure, (b) a schematic structure, (c) a side view, and (d) a top view of the pairs of fluorophores.

(c)

(d)

(c)

(d)

Figure 8. Crystal packing of **2f** (a) a stereoview of the molecular packing structure, (b) a schematic structure, (c) a side view, and (d) a top view of the pairs of fluorophores.

Figure 9. Schematic representation of the effects of the substituents on interplanar distances between a pair of fluorophores for **1**, **2a**, **2b**, **2c** and **2f**.