

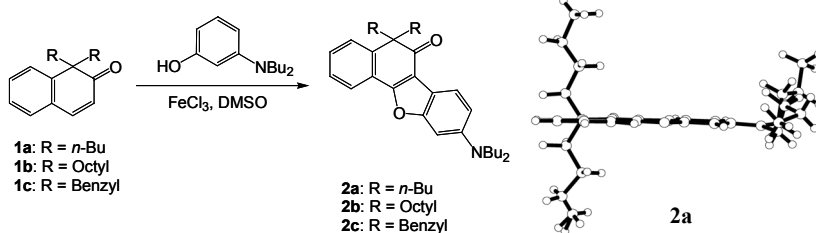
## Graphical Abstract

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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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A New type of organic fluorophores exhibiting strong blue and green emission in the solid state has been easily synthesized by an one-step reaction.



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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. © 2009 Elsevier Science. All rights reserved

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,<sup>1–5</sup> but also their possible applications in the optoelectronics such as light emitting diode and photoelectric conversion.<sup>6,7</sup> 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.<sup>5h, 8, 9</sup> In contrast, we have designed novel dialkylbenzo[*b*]naphtho[2,1-*d*]furan-6-one-type fluorophores (**2a–2c**), which consist of  $\pi$ -planar chromophore skeleton with sterical hindered dialkyl substituents prevent the fluorophores from short  $\pi$ - $\pi$  contacts causing fluorescence quenching in the solid state. In this paper, we report the preparation of **2a–2c** 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-1H-naphthalen-2-one **1a–1c** were prepared according to the published procedure.<sup>10</sup> Novel dialkylbenzo[*b*]naphtho[2,1-*d*]furan-6-one-type fluorophores **2a–2c** were easily obtained by the reaction of **1a–1c** with *m*-(dibutylamino)phenol in the presence of FeCl<sub>3</sub> (Scheme 1). However, when metal salt such as NiCl<sub>2</sub> or CuCl<sub>2</sub> instead of FeCl<sub>3</sub> was used, the fluorophores **2** were not obtained. The 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–2c** both in solution and in the solid state are summarized in Table 1.<sup>11</sup> The fluorescence spectra of the compounds were recorded by excitation at the wavelengths of the longest absorption maximum. In cyclohexane, the absorption maxima at

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

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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  $2\mathbf{a} \approx 2\mathbf{b} < 2\mathbf{c}$ . From these results, it was considered that  $\pi$ -electron effect of the benzyl group for  $2\mathbf{c}$  caused red-shift of the absorption and fluorescence maxima. On the other hand, the fluorescence quantum yields ( $\Phi$ ) are almost the same among  $2\mathbf{a}$ – $2\mathbf{c}$  ( $\Phi = ca. 0.5$ ). The absorption maxima of  $2\mathbf{a}$ – $2\mathbf{c}$  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  $2\mathbf{a}$  and  $2\mathbf{c}$  exhibit strong blue and green fluorescence emission, respectively. On the other hand,  $2\mathbf{b}$  was obtained as not the crystal but the solid like amorphous which exhibits strong bluish green fluorescence emission. The fluorescence quantum yields ( $\Phi$ ) of  $2\mathbf{a}$ – $2\mathbf{c}$  are 0.40, 0.37, 0.45, respectively (Table 1). It is noteworthy that the  $\Phi$  values of  $2\mathbf{a}$  and  $2\mathbf{c}$  were almost the same in cyclohexane and in the solid state. Consequently, these results also demonstrated that the solid-state photophysical properties of  $2\mathbf{a}$  and  $2\mathbf{c}$  are approaching to their photophysical properties in solution. However, the  $\Phi$  value of  $2\mathbf{b}$  in the amorphous state is smaller than that of  $2\mathbf{b}$  in cyclohexane. This is presumably due to the disturbance of light scattering of the aggregates in the amorphous state.<sup>12</sup> On the other hand, the wavelengths of the emission maximum of  $2\mathbf{a}$  ( $\lambda_{em} = 478$  nm),  $2\mathbf{b}$  ( $\lambda_{em} = 495$  nm), and  $2\mathbf{c}$  ( $\lambda_{em} = 526$  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.<sup>2–4</sup>

To elucidate strong solid-state fluorescence properties of  $2\mathbf{a}$ – $2\mathbf{c}$ , the X-ray crystal structure of  $2\mathbf{a}$  have been determined.<sup>13</sup> As shown in Figure 2, the packing structures demonstrate that the molecules are arranged in a “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  $\pi$ -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, the fluorophore  $2\mathbf{a}$  have 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.

### Acknowledgments

This work was partially supported by a Grant-in-Aid for Science and Research from the Ministry of Education, Science, Sport and Culture of Japan (Grant 18350100) and by a Special Research Grant for Green Science from Kochi University.

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11. The fluorescence quantum yields ( $\Phi$ ) in solution were determined by using 9,10-bis(phenylethynyl)anthracene ( $\Phi = 0.84$ ,  $\lambda_{\text{ex}} = 440$  nm) in benzene as the standard. The solid-fluorescence quantum yields ( $\Phi$ ) were determined by using a calibrated integrating sphere system ( $\lambda_{\text{ex}} = 325$  nm).
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13. Crystal data for **2a**:  $\text{C}_{32}\text{H}_{43}\text{NO}_2$ ,  $M = 473.70$ , orthorhombic,  $a = 17.964(4)$ ,  $b = 26.276(4)$ ,  $c = 12.005(3)$  Å,  $U = 5666(2)$  Å<sup>3</sup>,  $T = 296.2\text{K}$ , space group  $\text{Pbca}$  (no.61),  $Z = 8$ ,  $\mu(\text{Mo-K}\alpha) = 0.68$  cm<sup>-1</sup>, 7177 reflections measured, 6498 unique which were used in all calculations. The final R indices were  $R1 = 0.074$ ,  $wR(F^2) = 0.239$  (all data).

### Supplementary data

Synthetic and experimental details and X-ray crystallographic data can be available in the online version. Supplementary data associated with this article can be found in the online version, at doi:xxxxxxxx.

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].

**Figure and Scheme captions**

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

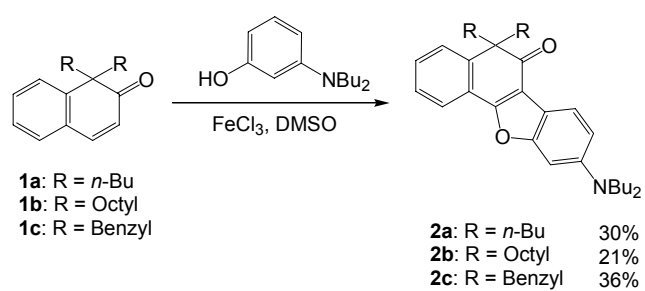
**Figure. 1** Solid-state emission spectra of the crystals of **2a–2c**.

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

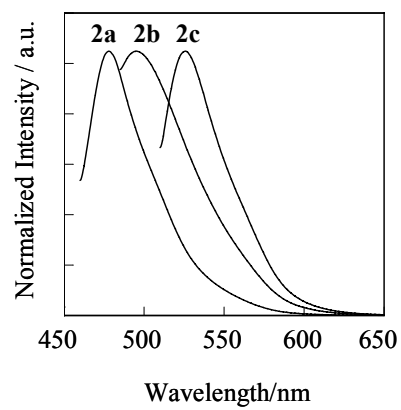
**Table 1** Spectroscopic properties of **2a–2c** in 1,4-dioxane and in the crystalline state

Solvent	in solution			in the crystalline state			
	$\lambda_{\max}^{\text{abs}}/\text{nm}$ ( $\epsilon_{\max}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ )	$\lambda_{\max}^{\text{fl}}/\text{nm}$	$\Phi$	$\lambda_{\max}^{\text{ex}}/\text{nm}$	$\lambda_{\max}^{\text{fl}}/\text{nm}$	$\Phi$	
<b>2a</b>	cyclohexane	394 (16100)	440	0.48	446	478	0.40
	1,4-dioxane	403 (15000)	489	0.53			
<b>2b</b>	cyclohexane	394 (15200)	439	0.50	444 <sup>a</sup>	495 <sup>a</sup>	0.37 <sup>a</sup>
	1,4-dioxane	402 (15000)	488	0.52			
<b>2c</b>	cyclohexane	403 (15100)	449	0.48	494	526	0.45
	1,4-dioxane	410 (15500)	496	0.50			

<sup>a</sup> Amorphous

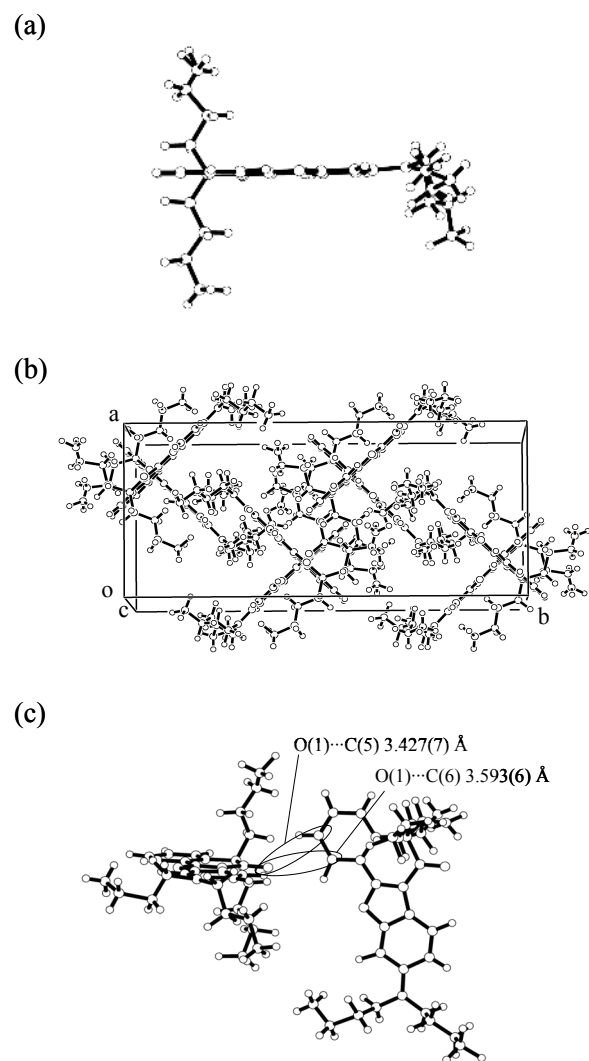


**Scheme 1.** Ooyama et al.



**Figure. 1** Ooyama et al.





**Figure. 2** Ooyama et al.

# **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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## **Experimental Section:**

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 ( $\Phi$ ) were determined by using 9,10-bis(phenylethynyl)anthracene ( $\Phi = 0.84$ ,  $\lambda_{\text{ex}} = 440 \text{ nm}$ )<sup>1</sup> in benzene as the standard. The solid-fluorescence quantum yields ( $\Phi$ ) were determined by using a calibrated integrating sphere system ( $\lambda_{\text{ex}} = 325 \text{ nm}$ ). Elemental analyses were recorded on a Perkin Elmer 2400 II CHN analyzer. <sup>1</sup>H 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).

**General synthetic procedure for the compounds 2a-2c by the reaction of 1, 1-dialkyl-2-naphthalenone 1a-1c with *m*-(dibutylamino)phenol:** To a solution of **1** (7.81 mmol) and FeCl<sub>3</sub> (11.7 mmol) in DMSO (20 ml) was added *m*-(dibutylamino)phenol (11.7 mmol) with stirring at 110 °C. After further stirring for 11-20h, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The precipitate was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extract was washed with water. The CH<sub>2</sub>Cl<sub>2</sub> extract was evaporated and the residue was chromatographed on silica gel (CH<sub>2</sub>Cl<sub>2</sub> : ethyl acetate = 10 : 1 as eluent) to give **2a-2c**.

**5,5-Dibutyl-9-dibutylamino-5H-benzo[b]naphtho[2,1-d]furan-6-one 2a:** Yield 30%: mp 134-136 °C; IR (KBr)/cm<sup>-1</sup> 1631; <sup>1</sup>HNMR(CDCl<sub>3</sub>/TMS)  $\delta$  = 0.54-1.13 (20H, m), 1.35-1.44 (4H, m), 1.57-1.66 (4H, m), 1.74-2.34 (4H, m), 3.47 (4H, t), 6.76 (1H, dd,  $J$  = 2.2 and 8.56 Hz), 6.80 (1H, d,  $J$  = 2.2 Hz), 7.37-7.45, (4H, m), 7.92 -7.96 (1H, m); elemental analysis calcd. For C<sub>32</sub>H<sub>43</sub>NO<sub>2</sub>: C, 81.14; H, 9.15; N, 2.96; Found: C, 81.01; H, 9.28; N, 3.09.

**5,5-Dioctyl-9-dibutylamino-5H-benzo[b]naphtho[2,1-d]furan-6-one 2b:** Yield 21%: IR (KBr)/cm<sup>-1</sup> 1651; <sup>1</sup>HNMR(CDCl<sub>3</sub>/TMS)  $\delta$  = 0.78-1.29 (36H, m), 1.35-1.44 (4H, m), 1.54-1.66 (4H, m), 1.76-1.85 (2H, m), 2.25-2.32 (2H, m), 3.35 (4H, t), 6.75 (1H, dd,  $J$  = 2.2 and 8.8 Hz), 6.80 (1H, d,  $J$  = 2.2 Hz), 7.37-7.41 (1H, m), 7.44 (2H, m), 7.91-7.95 (2H, m); elemental analysis calcd. For C<sub>40</sub>H<sub>59</sub>NO<sub>2</sub>: C, 82.00; H, 10.15; N, 2.39; Found: C, 81.98; H, 10.15; N, 2.53.

**5,5-Dibenzyl-9-dibutylamino-5H-benzo[b]naphtho[2,1-d]furan-6-one 2c:** Yield 36%: mp 135-137 °C; IR (KBr)/cm<sup>-1</sup> 1635; <sup>1</sup>HNMR(CDCl<sub>3</sub>/TMS)  $\delta$  = 0.96 (6H, t), 1.32-1.41 (4H, m), 1.53-1.62 (4H, m), 3.27-3.32 (6H, m), 3.81 (2H, t), 6.60-6.72 (6H, m), 6.84-6.91 (6H, m), 7.31 (1H, m), 7.46 (1H, m), 7.62-7.64 (1H, dd,  $J$  = 1.44 and 7.56 Hz), 7.68-7.70 (1H, d,  $J$  = 7.56 Hz), 7.89 (1H, m); elemental analysis calcd. For C<sub>38</sub>H<sub>39</sub>NO<sub>2</sub>: C, 84.25; H, 7.26; N, 2.59; Found: C, 84.44; H, 7.46; N, 2.88.

### X-ray crystal structure analyses:

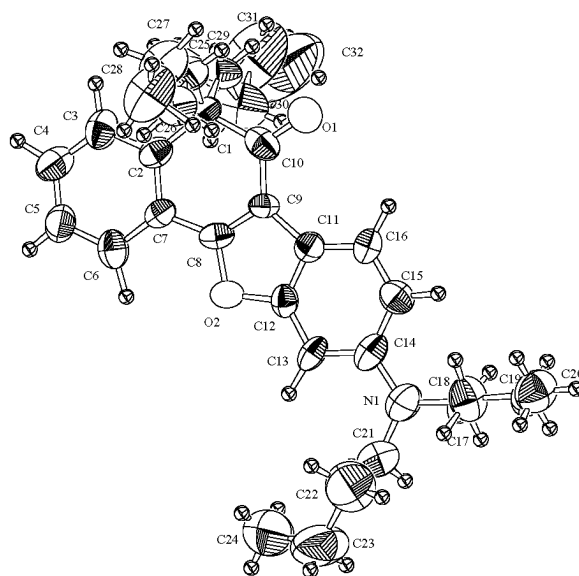
X-ray crystal structure analyses of **2a**: The data sets were collected at 23 ± 1 °C on a Rigaku AFC7S four-circle diffractometer by 2 $\theta$ - $\omega$  scan technique, and using graphite-monochromated Mo-K $\alpha$  ( $\lambda$  = 0.71069 Å) radiation at 50 kV and 30 mA. In all case, the data were corrected for Lorentz and polarization effects. A correction for secondary extinction was supplied. 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<sup>2</sup> crystallographic software package of Molecular Structure Corporation.

Crystal of **2a** was recrystallized from *n*-hexane as light yellow prism, air stable. The one selected had approximate dimensions 0.34×0.34×0.30 mm. The transmission factors ranged from 0.97 to 1.00. The crystal structure was solved by direct methods using SIR 92.<sup>3</sup> The structures were expanded using Fourier techniques.<sup>4</sup> The non-hydrogen atoms were refined

anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.

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<sup>3</sup>,  $T = 296.2$ K, space group  $Pbca$  (no.61),  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.34$  cm<sup>-1</sup>, 7177 reflections measured, 6498 unique which were used in all calculations. The final R indices were  $R1 = 0.073$ ,  $wR(F^2) = 0.237$  (all data).

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**Figure S1** ORTEP diagram including atom number: the compound **2a**.

**Table S1** Crystal data and structure refinement parameter for the compound **2a**.

Compound	<b>2a</b>
Molecular formula	C <sub>32</sub> H <sub>43</sub> NO <sub>2</sub>
Formula weight	473.70
Number of reflection used for unit cell determination (2θ range/°)	12 (22.2-25.0)
Crystal System	orthorhombic
Space group	Pbca
a/Å	17.964(4)
b/Å	26.276(4)
c/Å	12.005(3)
V/Å <sup>3</sup>	5666(2)
Z	8
D <sub>c</sub> /g cm <sup>-3</sup>	1.110
F(000)	2064.00
M(MoKα)/cm <sup>-1</sup>	0.68
Crystal dimensions/nm	0.34×0.34×0.30
Scan mode	ω-2θ
Scan rate in ω/°min <sup>-1</sup>	8.0( up to 5 scans)
Scan width/°	1.42 + 0.30 tanθ
2θ max/°	55.0
Range of indices <i>h</i> ; <i>k</i> ; <i>l</i>	0, 23; 0, 34; -15, 0
Reflections collected (unique)	6498
Reflection observed with I <sub>0</sub> >2σI <sub>0</sub>	1515
Number of parameters	254
R	0.074
R <sub>w</sub>	0.239
w	(σ <sup>2</sup> F <sup>2</sup> ) <sup>-1</sup>
S	1.08
Max. Shift/Error in final cycle	0.07
Max. peak in final diff. map/e Å <sup>-3</sup>	0.38
Min. peak in final diff. map/e Å <sup>-3</sup>	-0.41