



## Near-infrared solid-state fluorescent naphthooxazine dyes attached with bulky dibutylamino and perfluoroalkenyloxy groups at 6- and 9-positions

So-Yeon Park<sup>a</sup>, Yasuhiro Kubota<sup>a</sup>, Kazumasa Funabiki<sup>a</sup>, Motoo Shiro<sup>b</sup>, Masaki Matsui<sup>a,\*</sup>

<sup>a</sup>Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

<sup>b</sup>X-ray Research Laboratory, Rigaku Corporation, 3-9-12 Matubara-cho, Akishima, Tokyo 196-8666, Japan

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### ABSTRACT

No solid-state fluorescence is observed for 9-(diethylamino)benzo[*a*]phenoxazin-5-one (Nile Red). However, 9-dibutylamino-6-{perfluoro[4-methyl-3-(1-methylethyl)-2-penten]-2-oxy}benzo[*a*]phenoxazin-5-one showed fluorescence maximum at 717 nm in solid state with fluorescence quantum yield 0.024. X-ray crystallographic analysis suggests that prevention of network  $\pi$ – $\pi$  interactions by the bulky fluorine-containing and dibutylamino groups is essential to show solid-state fluorescence.

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Survey of solid-state fluorescence of organic compounds is one of the most exciting subjects in connection with emitters in organic electroluminescence (EL) devices<sup>1</sup> and solid-state organic dye laser.<sup>2</sup> 7-(Diarylamino)-4-methylcoumarins,<sup>3</sup> ter(9,9-diarylfluorenes),<sup>4</sup> diphenylanthrazolines,<sup>5</sup>  $\alpha,\beta$ -dicyanostilbenes,<sup>6</sup> diketopyrrolopyrroles,<sup>7</sup> 9,10-disubstituted anthracenes,<sup>8</sup> bisazomethine dye,<sup>9</sup> heterocyclic quinol-type compounds,<sup>10</sup> perylenediimides,<sup>11</sup> and dipyrroboradiazaindacenes<sup>12</sup> have been reported to show solid-state fluorescence. A few reddish solid-state fluorescent compounds such as 4,7-di(2-thienyl)benzothiadiazoles,<sup>13</sup> fumaronitriles,<sup>14</sup> 3,6-dicyanopyrazines,<sup>15</sup> and 2,3-dicyano-6*H*-1,4-diazepins<sup>16</sup> have been reported. However, no near-infrared solid-state fluorescent compounds have been reported so far. To our knowledge, the most bathochromic solid-state fluorescent compound is 4-(dicyanomethylene)-4*H*-pyran derivative, there being the fluorescence maximum ( $F_{\text{max}}$ ) 695 nm.<sup>17</sup> Near-infrared (NIR) solid-state fluorescent compounds have potential application in the field of security technology.

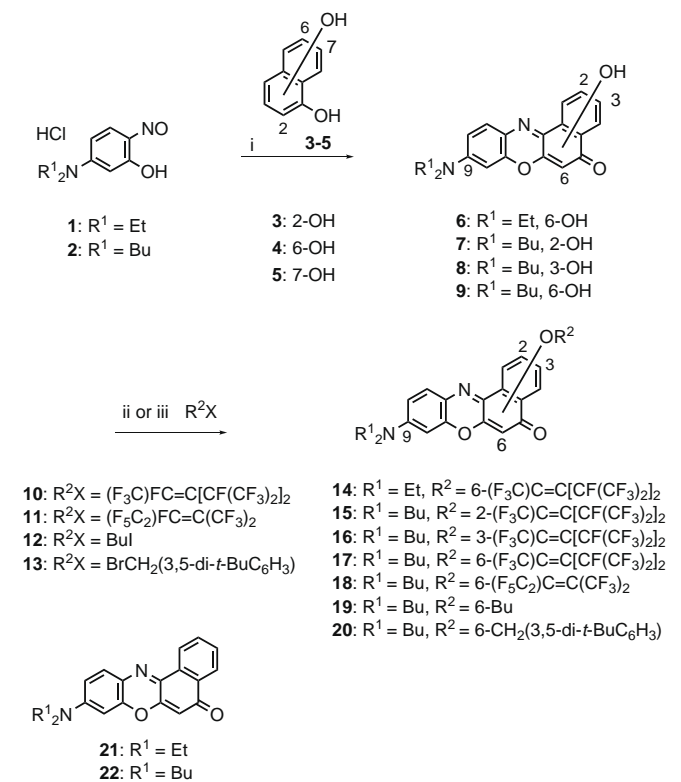
Nile Red is a traditional neutral naphthooxazine dye showing medium fluorescence in solution (fluorescence quantum yield ( $\Phi_f$ ) = 0.59 in ethanol). However, Nile Red does not show fluorescence in solid state. The excited state in condensed and crystalline states is deactivated by strong intermolecular interactions. Therefore, introduction of bulky substituent(s) into fluorophores is good methodology to improve solid-state fluorescence intensity. As fluo-

rine-containing substituents are much more bulky than the corresponding fluorine-free ones, introduction of fluorine-containing group(s) into fluorophores is very effective to depress intermolecular interactions between the molecules. It is clear that perfluoro[4-methyl-3-(1-methylethyl)-2-penten-2-oxy] group derived from perfluoropropylene trimer, in which two perfluoro(isopropyl) and one trifluoromethyl groups are contained in a molecule, is much more bulky than well-known and usually-used *tert*-butyl group. No application of bulky perfluoroalkenyloxy-containing compounds for advanced materials has been reported so far. We thought that introduction of this bulky fluorine-containing group into naphthooxazine dye might be effective to prevent its intermolecular interactions. We report herein NIR solid-state fluorescent naphthooxazine dyes.

9-(Dialkylamino)benzo[*a*]phenoxazin-5-ones **14–20** were prepared as shown in Scheme 1. 5-Dialkylamino-2-nitrosophenol hydrochloric acid salts **1** and **2** were allowed to react with naphthalenediols **3–5** to give the corresponding hydroxy-substituted naphthooxazine intermediates **6–9**. Then, compounds **6–9** were allowed to react with perfluoropropylene trimer **10**, a 1:2 mixture of [(F<sub>3</sub>C)<sub>2</sub>FC]<sub>2</sub>C=CF(CF<sub>3</sub>) and [(F<sub>3</sub>C)<sub>2</sub>FC](F<sub>3</sub>CF<sub>2</sub>C)C=C(CF<sub>3</sub>)<sub>2</sub>, in the presence of sodium hydride to give **14–17**. The former isomer more smoothly reacts with phenoxide ions than the latter one to give a perfluoro(vinylether) product.<sup>18</sup> Compound **9** was allowed to react with perfluoropropylene dimer **11** to give **18** in a 37% yield. Compound **9** also reacted with butyl iodide (**12**) and 3,5-(di-*tert*-butyl)-benzyl bromide (**13**) in the presence of potassium carbonate and 16-crown-6-ether to give **19** and **20**, respectively. Compounds **21**

\* Corresponding author. Tel.: +81 59 293 2601; fax: +81 58 293 2794.

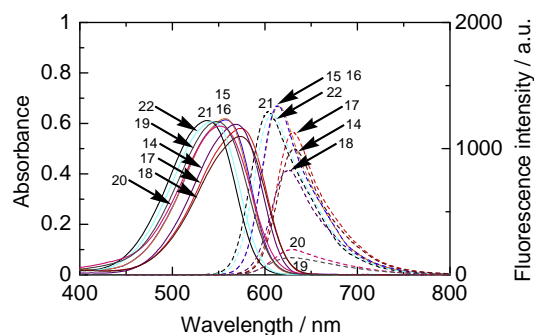
E-mail address: [matsui@apchem.gifu-u.ac.jp](mailto:matsui@apchem.gifu-u.ac.jp) (M. Matsui).



**Scheme 1.** Reagents and conditions: (i) **1** (1.0 equiv) or **2** (1.0 equiv), **3–5** (1.0 equiv), reflux, 4 h, DMF, (ii) **6–9** (1.0 equiv), **10** (2.5 equiv) or **11** (2.5 equiv), NaH (1.0 equiv) or TEA (1.0 equiv), rt, DMF, 2–18 h, (iii) **9** (1.0 equiv), **12** (2.5 equiv) or **13** (2.5 equiv), K<sub>2</sub>CO<sub>3</sub> (1.0 equiv), 18-crown-6-ether, rt, 10 h.

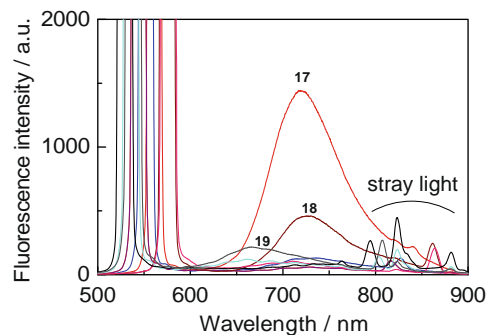
(Nile Red) and **22** were also prepared as described in the literature.<sup>19</sup> The detailed procedure for the synthesis of **14–22** is shown in Supplementary data.

The UV–vis absorption and fluorescence spectra of naphthooxazine dyes in dichloromethane are shown in Figure 1. The results are also listed in Table 1. The absorption maximum ( $\lambda_{\max}$ ) of naphthooxazine dyes was more bathochromic in the following order of compound: **17** (574 nm), **18** (573), **14** (569) > **20** (551), **19** (547) > **22** (543), **21** (538). Thus, introduction of perfluoro(alkenyl-oxo) and alkoxy group caused bathochromic shift due to less stable HOMO energy level. 6-Perfluoro(alkenyl-oxo) derivative **17** (574) was more bathochromic than the 2- and 3-perfluoro(alkenyl-oxo) derivatives **15** (558) and **16** (557). The molar absorption coeffi-



**Figure 1.** UV–vis absorption and fluorescence spectra of **14–22** in dichloromethane measured at the concentration of  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> at 25 °C. Solid and dotted lines represent UV–vis absorption and fluorescence spectra, respectively.

icients ( $\epsilon$ ) of **14–22** were observed in the range of 54,800–61,900 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, there being no significant difference among them. The  $F_{\max}$  was more bathochromic in the order of compound: **17** (632 nm), **18** (631), **20** (630), **19** (627), **14** (625) > **16** (614), **15** (613) > **22** (608), **21** (604). This result is attributed to slightly large Stokes shift of **19** and **20**. The  $\Phi_f$  was larger in the order of compound: **21** (0.87), **22** (0.87) > **16** (0.76), **15** (0.74), **17** (0.69), **18** (0.66), **14** (0.56) > **20** (0.12), **19** (0.11). Thus, 6-unsubstituted derivatives showed the most intense fluorescence followed by perfluoro(alkenyl-oxo) and alkoxy derivatives in solution. Low  $\Phi_f$  of **19** and **20** may come from free rotation of the flexible alkoxy linkage in solution.



**Figure 2.** Fluorescence spectra of **14–22** in solid state.  $\lambda_{\text{ex}}$  was obtained by measuring diffusion reflection spectra given in Kubelka–Munk Units.

**Table 1**  
Optical properties of naphthooxazine dyes

Run	Compd	Dichloromethane <sup>a</sup>			Solid state <sup>d</sup>		
		$\lambda_{\max}(\epsilon)$ (nm)	$F_{\max}$ (nm)	$\Phi_f^b$	SS <sup>c</sup> (nm)	$F_{\max}$ (nm)	$\Phi_f^b$
1	<b>14</b>	569 (58,600)	625	0.54	56	— <sup>e</sup>	— <sup>e</sup>
2	<b>15</b>	558 (61,400)	613	0.74	55	734	0.008
3	<b>16</b>	557 (61,900)	614	0.76	57	729	0.007
4	<b>17</b>	574 (58,000)	632	0.69	60	717	0.024
5	<b>18</b>	573 (54,800)	631	0.66	58	727	0.015
6	<b>19</b>	547 (60,800)	627	0.11	80	666	0.010
7	<b>20</b>	551 (58,900)	630	0.12	79	— <sup>e</sup>	— <sup>e</sup>
8	<b>21</b>	538 (61,000)	604	0.87	66	— <sup>e</sup>	— <sup>e</sup>
9	<b>22</b>	543 (60,700)	608	0.87	65	— <sup>e</sup>	— <sup>e</sup>

<sup>a</sup> Measured at the concentration of  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> at 25 °C.

<sup>b</sup> Determined by a Hamamatsu Photonics Absolute PL Quantum Yield Measurement System C9920-02.

<sup>c</sup> Stokes shift.

<sup>d</sup> Excitation wavelength ( $\lambda_{\text{ex}}$ ) was obtained by measuring diffuse reflectance spectra given in Kubelka–Munk units.

<sup>e</sup> Too weak ( $\Phi_f < 0.003$ ).

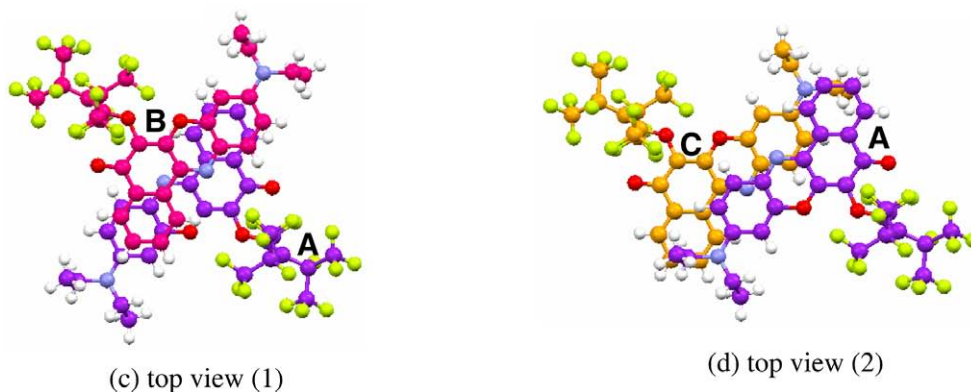
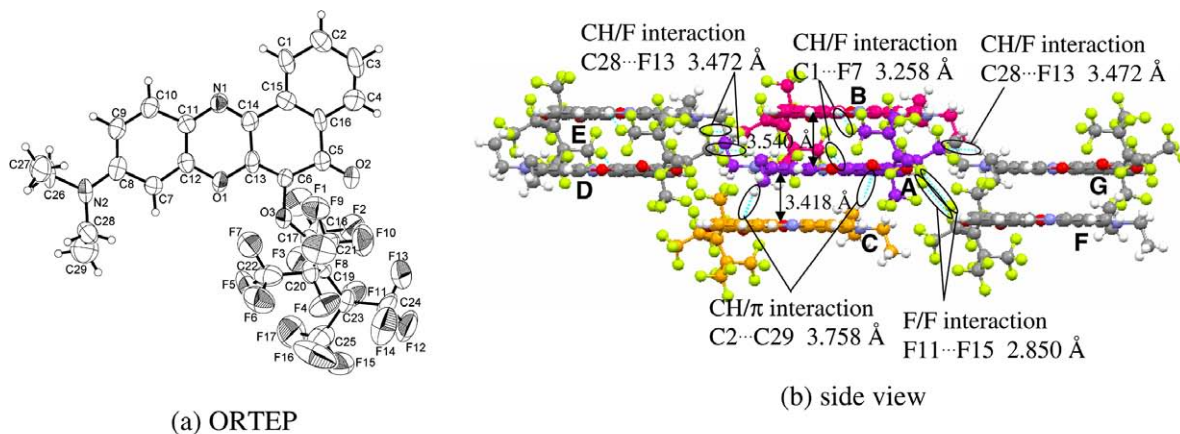


Figure 3. X-ray crystallographic analysis of **22**.

The fluorescence spectra of **14–22** in solid state are shown in Figure 2. The results are also listed in Table 1. No clear solid-state fluorescence was observed for **14**, **15**, **16**, **20**, **21**, and **22**. Interestingly, compounds **17** and **18**, in which a bulky perflu-

oro(alkenyloxy) group is attached at the 6-position, showed  $F_{\max}$  at around 717 and 727 nm with  $\Phi_f$  0.024 and 0.015, respectively. The  $F_{\max}$  of **17** in solid state and in dichloromethane were observed at 717 and 632 nm with half-wavelength of 90 and

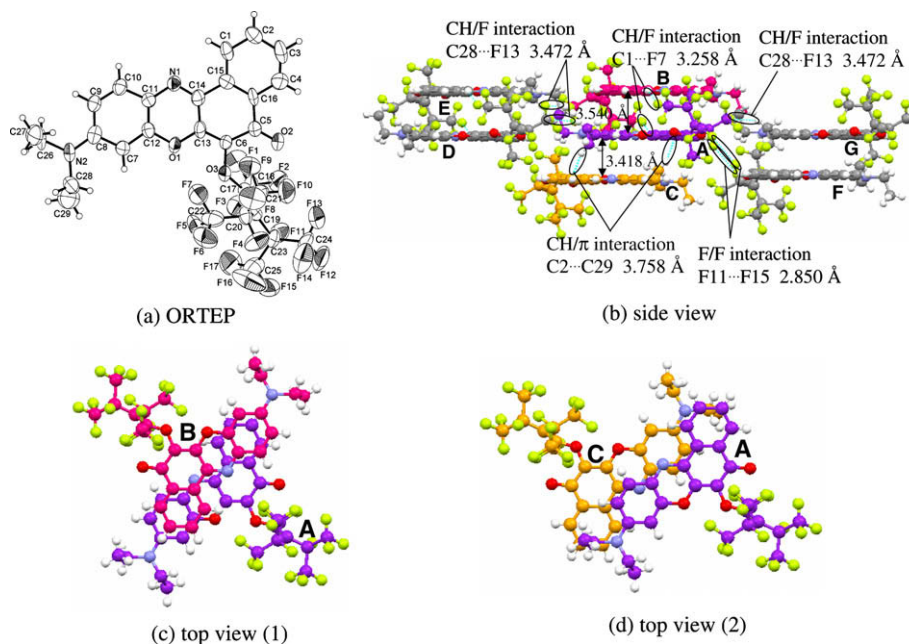


Figure 4. X-ray crystallographic analysis of **14**.

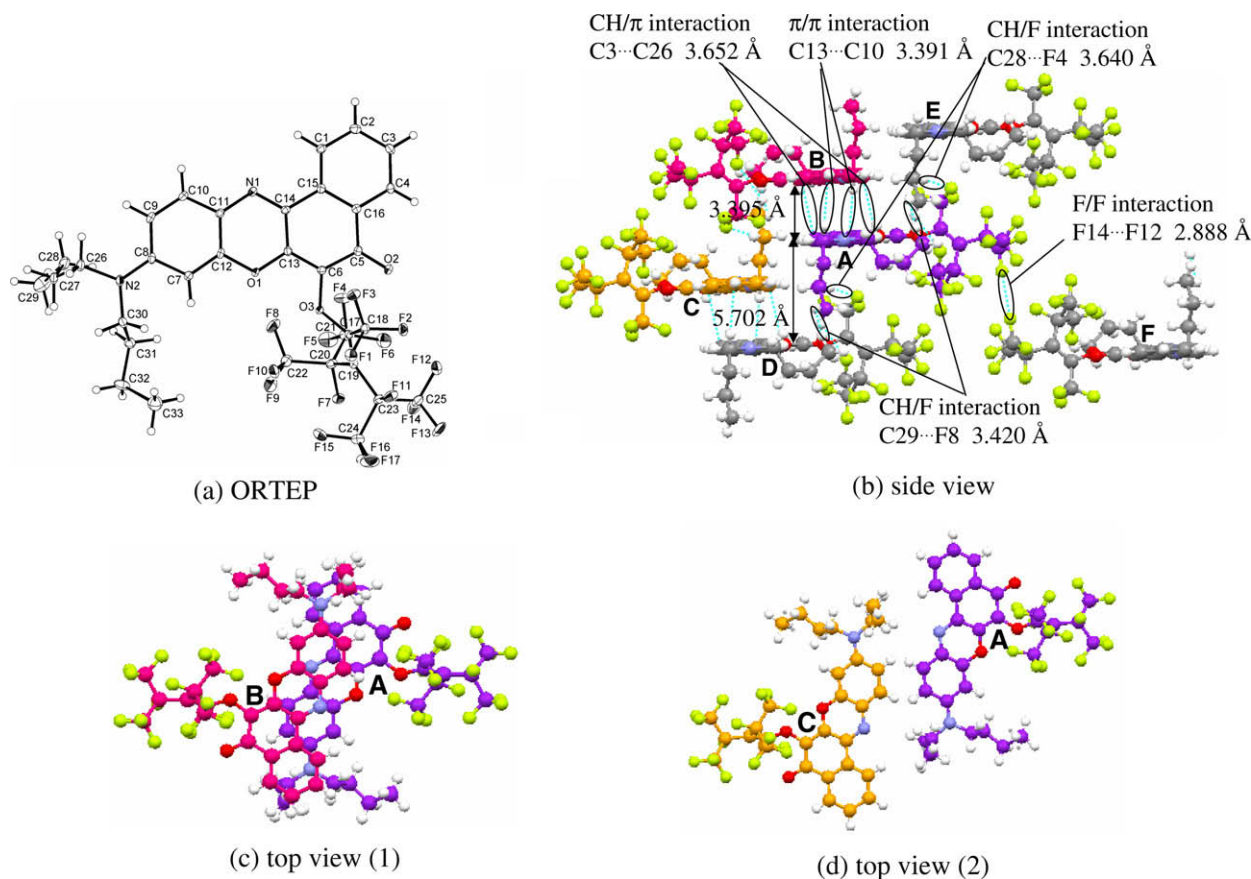


Figure 5. X-ray crystallographic analysis of **17**.

54 nm, respectively. Thus, the solid-state fluorescence spectra were more bathochromic and broad compared with those in dichloromethane due to the intermolecular interactions.

To examine the difference of fluorescence intensity of naphthooxazine dyes **14–22** in solid state, the X-ray crystallographic analysis of **14**, **17**, and **22** was performed.<sup>20</sup>

Figure 3 shows the X-ray crystallography of **22**. In this case, compound is arranged as a herring-bone fashion. Figure 3b shows that molecules A and B are located almost in the same plane. Molecules C and D are packed almost in perpendicular for A. There are six CH/O and four CH/π interactions between A and B. CH/N interactions are observed between A and C and A and D. Figure 3c indicates that molecules A, E, and F are arranged toward the same direction. The interplanar distance among A, E, and F is 3.344 Å. Strong π–π overlapping is observed among A, E, and F as shown in Figure 3d. Thus, compound **22** has strong network π–π stacking.

In the case of compound **14**, a pair of head-to-tail dimer is formed and is arranged as slipped parallel. 6-[(Perfluoro[4-methyl-3-(1-methylethyl)-2-penten]-2-oxy)]benzo[*a*]phenoxazin-5-one group at the 6-position inhibits CH/O intermolecular interactions between adjacent naphthooxazine rings. Figure 4b shows that molecule A is surrounded by B, C, D, E, F, and G. Molecules A, D, and G are located almost in the same plane. CH/F interactions are observed among A, D, and G. Molecules A, B, and C are arranged in parallel. CH/F interactions are observed between A and B. CH/π interactions are observed between A and C. The interplanar distance between A and B and A and C are 3.540 and 3.418 Å, respectively. Figure 4c depicts that molecule A has strong π–π overlapping with B. Figure 4d also shows that molecule A has π–π interactions for C. Thus, compound **14** has network packing.

Compound **17** is arranged as slipped parallel. A pair of head-to-tail dimers is formed in the crystalline, being similar to molecular packing of **14**. Molecule A is surrounded by B, C, D, E, and F as shown in Figure 5b. Molecule B is arranged in parallel to A. There are two π–π and two CH/π interactions between A and B, there being the interplanar distance 3.395 Å. Molecules C and D are also located in parallel for A. The interplanar distance between A and D is 5.702 Å, being too long to have π–π interactions. Strong π–π overlapping is observed between A and B as shown in Figure 5c. Figure 5d shows that no π–π overlapping is observed between A and C. One of butyl groups of dibutylamino group at the 9-position in A can act as a steric moiety for adjacent naphthooxazine molecule.

9-Dibutylamino-6-[(perfluoro[4-methyl-3-(1-methylethyl)-2-penten]-2-oxy)]benzo[*a*]phenoxazin-5-one showed solid-state fluorescence at near-infrared region (717 nm) with  $\Phi_f$  0.024, whereas well-known naphthooxazine dye, Nile Red, does not show fluorescence in the solid state. X-ray crystallographic analysis suggests that absence of network π–π stacking that comes from both bulky dibutylamino group at the 9-position and perfluoro(alkenyloxy) group at the 6-position is essential to show solid-state fluorescence. This is the first report of NIR solid-state fluorescent organic dyes.

#### Supplementary data

Supplementary data (detailed synthetic procedure of **14–22**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.12.081.



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- Single crystals were obtained by recrystallization from ethanol. The diffraction data were collected by using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). The structure was solved by direct methods SIR97, and refined by full-matrix least-squares calculations. Crystal data for **14**: C<sub>29</sub>H<sub>17</sub>F<sub>17</sub>N<sub>2</sub>O<sub>3</sub>, *Mw* = 764.45, triclinic, *P* $\bar{1}$ , *Z* = 2, *a* = 8.099(6), *b* = 12.090(11), *c* = 15.545(19) Å,  $\alpha = 90.88(10)^\circ$ ,  $\beta = 94.02(8)^\circ$ ,  $\gamma = 93.35(7)^\circ$ , *D*<sub>calcd</sub> = 1.675 g cm<sup>-3</sup>, *T* = 296(2) K, *F*(000) = 764,  $\mu = 1.629$  mm<sup>-1</sup>, 11,989 reflections were corrected, 4811 unique (*R*<sub>int</sub> = 0.0669), 4811 observed (*I* > 2 $\sigma$ (*I*)), 536 parameters, *R*<sub>1</sub> = 0.0849, *wR*<sub>2</sub> = 0.2257. Crystal data for **17**: C<sub>33</sub>H<sub>25</sub>F<sub>17</sub>N<sub>2</sub>O<sub>3</sub>, *Mw* = 820.55, triclinic, *P* $\bar{1}$ , *Z* = 2, *a* = 820.55, *b* = 11.169(6), *c* = 17.207(9) Å,  $\alpha = 90.407(9)^\circ$ ,  $\beta = 96.418(8)^\circ$ ,  $\gamma = 92.857(8)^\circ$ , *D*<sub>calcd</sub> = 1.633 g cm<sup>-3</sup>, *T* = 123(2) K, *F*(000) = 828,  $\mu = 0.169$  mm<sup>-1</sup>, 13667 reflections were corrected, 7583 unique (*R*<sub>int</sub> = 0.0359), 7583 observed (*I* > 2 $\sigma$ (*I*)), 513 parameters, *R*<sub>1</sub> = 0.0732, *wR*<sub>2</sub> = 0.1254. Crystal data for **22**: C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>, *Mw* = 374.48, monoclinic, *P*2<sub>1</sub>/*n*, *Z* = 2, *a* = 8.747(5), *b* = 11.169(6), *c* = 17.207(9) Å,  $\alpha = 90.407(9)^\circ$ ,  $\beta = 96.418(8)^\circ$ ,  $\gamma = 92.857(8)^\circ$ , *D*<sub>calcd</sub> = 1.633 g cm<sup>-3</sup>, *T* = 123(2) K, *F*(000) = 828,  $\mu = 0.169$  mm<sup>-1</sup>, 13,667 reflections were corrected, 7583 unique (*R*<sub>int</sub> = 0.0359), 7583 observed (*I* > 2 $\sigma$ (*I*)), 513 parameters, *R*<sub>1</sub> = 0.0732, *wR*<sub>2</sub> = 0.1254. Crystallographic data **14** (CCDC 704025), **17** (CCDC 704026), and **22** (CCDC 705404) have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.