



Strategy for the increasing the solid-state fluorescence intensity of pyrromethene–BF₂ complexes

Yasuhiro Kubota^{a,*}, Jun Uehara^a, Kazumasa Funabiki^a, Masahiro Ebihara^b, Masaki Matsui^{a,*}

^a Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

^b Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

ARTICLE INFO

Article history:

Received 20 August 2010

Revised 17 September 2010

Accepted 22 September 2010

Available online 27 September 2010

Keywords:

BODIPY

Solid-state fluorescence

Pyrromethene

ABSTRACT

In this study, we attempted to increase the fluorescence quantum yield of pyrromethene–BF₂ complex (BODIPY) in the solid state by introducing bulky groups as substituents at the boron atom. Although the BF₂ complex did not exhibit any fluorescence in the solid state ($\Phi_f = 0.00$), the B(OMe)₂, B(OPh)₂, and BPh₂ complexes did show solid-state fluorescence with quantum yields of 0.02, 0.04, and 0.22, respectively.

© 2010 Elsevier Ltd. All rights reserved.

Solid-state fluorescent dyes have attracted much attention because of their potential applications in optoelectronic materials such as organic electroluminescence devices¹ and solid-state dye lasers.² However, in many cases, fluorescent dyes that show intense fluorescence in solution exhibit decreased fluorescence in the solid state as a result of concentration quenching.³ Therefore, the number of organic dyes that can show intense fluorescence in the solid state is limited and active research is being conducted to develop such dyes.⁴

The pyrromethene–BF₂ complex (BODIPY)⁵ is known as an excellent type of fluorescent dye; it exhibits high fluorescence quantum yield and sharp fluorescence spectra in solution. The fluorescence wavelength of BODIPY dyes can be changed from blue⁶ to near infrared⁷ in solution. Therefore, BODIPY dyes are considered to be strong candidates for the realization of a wavelength-tunable solid-state fluorescent dye. However, most BODIPY dyes hardly fluoresce in the solid state. This has been attributed to their very small Stokes shift (5–20 nm, in most cases) and high planarity.⁸ Recently, some groups⁹ have reported solid-state emissive BODIPY dyes with bulky substituents introduced at the *meso*-position (i.e., 8 position) and/or 3 position. This suggests that the inhibition of molecular aggregation which causes concentration quenching is important, and that the introduction of sterically bulky substituent(s) in the BODIPY core is an effective strategy for improving the solid-state fluorescence intensity of BODIPY dyes. In many

cases, two fluorine atoms are substituted at the boron atom of a BODIPY dye. These fluorine atoms are located above and below the π plane which consists of the pyrromethene skeleton (Fig. S1). Therefore, the substitution of the fluorine atoms by bulky groups is considered as a very effective technique for preventing the π – π stacking of BODIPY dyes. In this Letter, we report a strategy for increasing the solid-state fluorescence intensity of BODIPY dyes by introducing bulky groups at the boron atom in the center.

We selected methoxy, phenoxy, and phenyl groups as the bulky substituents (Fig. 1). We synthesized methoxy derivative **2**, phenoxy derivative **3**, and phenyl derivative **4** using previously reported methods.¹⁰ Compound **1** was allowed to react with methanol and phenol in the presence of AlCl₃ to yield the methoxy derivative **2** and the phenoxy derivative **3**, respectively. The reaction of **1** with phenyl lithium yielded the phenyl derivative **4**.¹¹ The UV–vis absorption and the fluorescence spectra of **1–4** in hexane are shown in Figure 2. The UV–vis absorption spectra of **1–4** show two absorption peaks at wavelengths of around 380 and

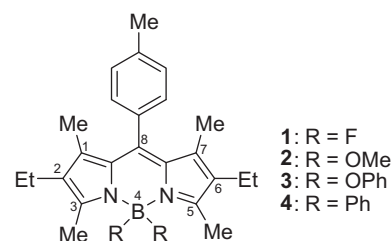


Figure 1. Synthesized BODIPY dyes.

* Corresponding authors. Tel.: +81 59 293 2596; fax: +81 58 230 1893 (Y.K.); tel.: +81 59 293 2601; fax: +81 58 230 1893 (M.M.).

E-mail addresses: kubota@gifu-u.ac.jp (Y. Kubota), matsui@gifu-u.ac.jp (M. Matsui).

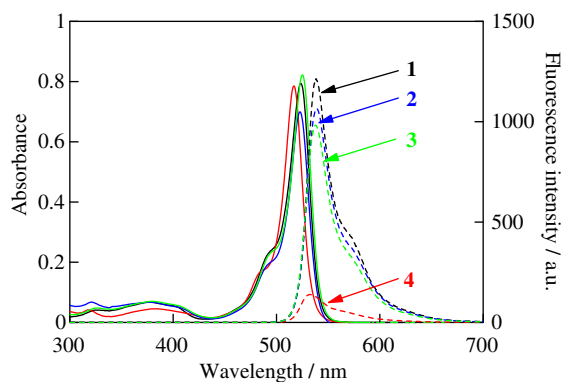


Figure 2. UV-vis and fluorescence spectra of BODIPY dyes **1–4** in hexane at the concentration of 1×10^{-5} mol dm $^{-3}$ at 25 °C. Solid and dotted lines represent UV-vis absorption and fluorescence spectra, respectively.

Table 1
Optical properties of BODIPY dyes **1–4**

Compd	R	Hexane ^a			Solid state ^c	
		λ_{\max} (ϵ) (nm)	F_{\max} (nm)	Φ_f^b	F_{\max} (nm)	Φ_f^b
1	F	524 (79,000)	538	0.56	— ^d	0.00
2	OMe	522 (70,000)	538	0.48	595	0.02
3	OPh	525 (82,000)	538	0.36	580, 617	0.04
4	Ph	517 (79,000)	532	0.03	601, 640	0.22

^a Measured at a concentration of 1.0×10^{-5} mol dm $^{-3}$ at 25 °C.

^b Determined by a Hamamatsu Photonics Absolute PL Quantum Yield Measurement System C9920-02.

^c Excitation wavelength (λ_{ex}) was obtained by measuring the diffuse reflectance spectra given in Kubelka–Munk units.

^d Fluorescence was not observed.

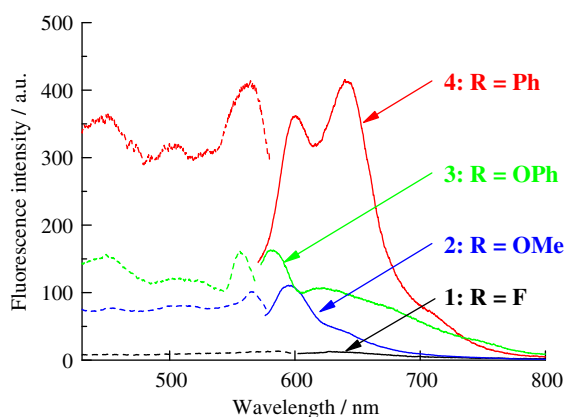


Figure 3. Excitation (dotted line) and fluorescence (solid line) spectra of BODIPY dyes **1–4** in the solid state. The excitation spectra were monitored at 620 nm for **1**, 595 nm for **2**, 617 nm for **3**, and 640 nm for **4**.

520 nm. The weak absorption peaks at around 380 nm are attributable to $S_0 \rightarrow S_2$ transitions. The strong absorption peaks at around 520 nm are typical of $S_0 \rightarrow S_1$ transitions and the shoulder peaks at around 490 nm correspond to the vibrational band of the $S_0 \rightarrow S_1$ transitions.¹² BODIPY dyes **1–4** showed fluorescence maximum at around 540 nm with vibrational transitions. The fluorescence quantum yields in hexane are as follows: **1** = 0.56, **2** = 0.48, **3** = 0.36, and **4** = 0.03 (Table 1). The fluorescence quantum yield of **4** was considerably lower than those of other compounds.

The fluorescence and excitation spectra of **1–4** in the solid state are shown in Figure 3. The solid-state fluorescence intensity shows significant fluctuations depending on the kind of substituent at the boron atom. Compound **1** did not exhibit any fluorescence in the solid state, similar to the behavior of other BODIPY dyes that have been reported so far. On the other hand, **2–4** showed fluorescence in the solid state. Compounds **2**, **3**, and **4** gave the fluorescence maxima at 595, 580, and 640 nm, respectively. The solid-state fluorescence quantum yields for **1**, **2**, **3**, and **4** were 0.00, 0.02, 0.04, and 0.22 (Table 1).

X-ray crystallographic studies were carried out to investigate the difference between **1** (which exhibited no fluorescence) and **4** (which exhibited the most intense fluorescence). The results for **1** and **4** are shown in Figures 4 and 5, respectively.

Two crystallographically independent conformers **4A** and **4B** were identified in the crystals of **4** (Fig. 5). The dihedral angles between the pyrromethene ring and the *meso*-tolyl group of the conformers **4A** and **4B** were almost orthogonal (**4A**: 89.1° and **4B**: 88.5°), whereas the dihedral angle of **1** was 72.5°. Unlike the boron atom of **1**, the boron atom of **4** was not situated in the plane of the pyrromethene ring. The dihedral angles **4A** and **4B** between the plane containing atoms N1, C4, C5, C6, and, N2 and that containing N1, B1, and N2 were 23.1° and 23.4°, respectively (Fig. S2). One of the phenyl rings on the boron atom was oriented almost perpendicular to the plane of the pyrromethene ring. In the crystal packing of **1**, intermolecular π - π interactions were observed; hence, it can be inferred that **1** did not exhibit any fluorescence.¹³ On the other hand, in the crystal packing of **4**, **4A** and **4B** formed independent stacking columns, and the tilt angle between the two columns was 30° (Fig. 6). Although the intermolecular CH/ π interactions between the pyrromethene rings and the tolyl groups were detected, the π - π stacking between adjacent pyrromethene rings was not observed in the crystal packing of **4**. Because the π - π interaction was avoided, **4** exhibited intense fluorescence.

Two peaks were observed on the fluorescence spectra of **4** at around 600 and 640 nm (Fig. 3). It was important to determine whether the observed peaks were attributable to monomer-like fluorescence or excimer-like fluorescence. To achieve this, we investigated the concentration dependence of the excitation and fluorescence spectra of **4**. In sufficiently dilute conditions, **4** is considered to generate the monomer form. We selected potassium bromide (KBr) as the inert material¹⁴ in which to dilute **4**. Mixtures of **4** and KBr with varying dye concentrations (0.01, 0.1, 1, 10, and 100 wt %) were prepared. The fluorescence and excitation spectra of these mixtures were measured (Fig. 7). The spectral shapes of excitation and fluorescence spectra of **4** were not extensively affected by the changes in concentration, suggesting that the observed peaks are not attributable to excimer-like fluorescence. Therefore, the two observed peaks may be attributed to the monomer-like $S_1 \rightarrow S_0$ and the vibrational transitions.

In conclusion, solid-state fluorescence properties of BODIPY dyes with fluorine atoms **1**, methoxy groups **2**, phenoxy groups **3**, and phenyl groups **4** substituted at their boron atom were investigated to clarify the effect of the substituent groups on the solid-state fluorescence quantum yield. The fluorescence quantum yields in the solid state are as follows: **1** = 0.00, **2** = 0.02, **3** = 0.04, and **4** = 0.22. Substitution of the fluorine atoms by more sterically bulky substituents resulted in fluorescence in the solid state. In particular, the BODIPY dye substituted with phenyl groups (i.e., **4**) exhibited the most intense fluorescence in the solid state. X-ray crystallographic analysis of **4** showed that one of the phenyl groups on the boron atom was oriented almost perpendicular to the plane of the pyrromethene ring and that this phenyl group contributed to the prevention of the π - π interaction between the pyrromethene rings. Therefore, the introduction of bulky substituents at the boron atom can be considered as an effective strategy for

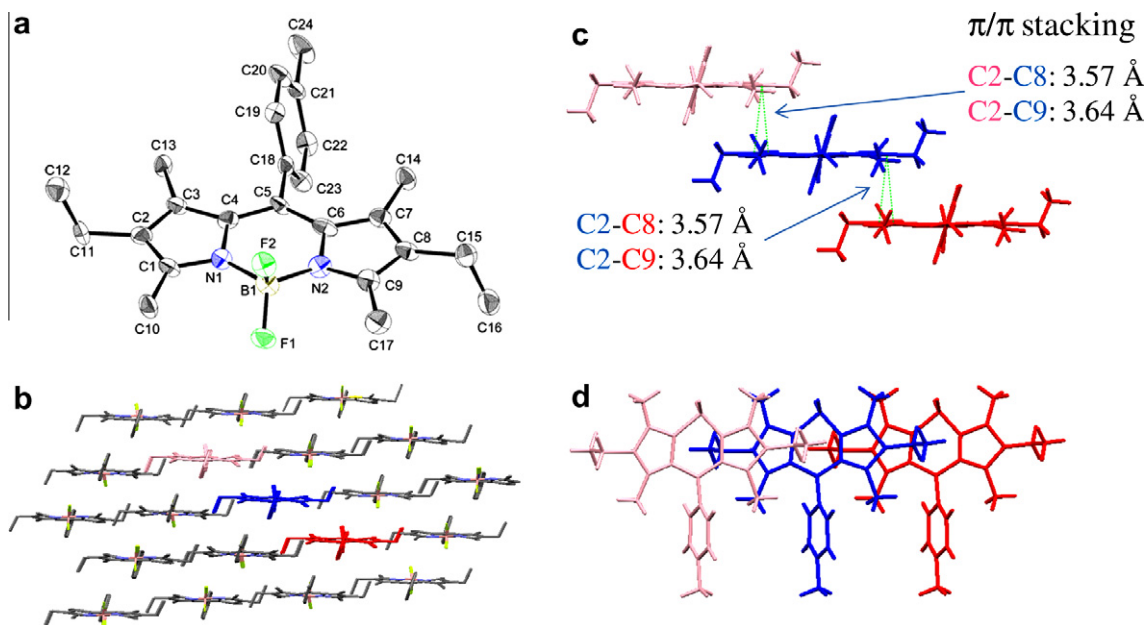


Figure 4. Crystal structure of **1** (CCDC 785006). (a) ORTEP drawing of **1**. (b) Global crystal packing of **1**. (c) Side view of crystal packing of **1**. (d) Top view of crystal packing of **1**. Dotted lines show intermolecular π - π interactions. Hydrogen atoms have been omitted for clarity.

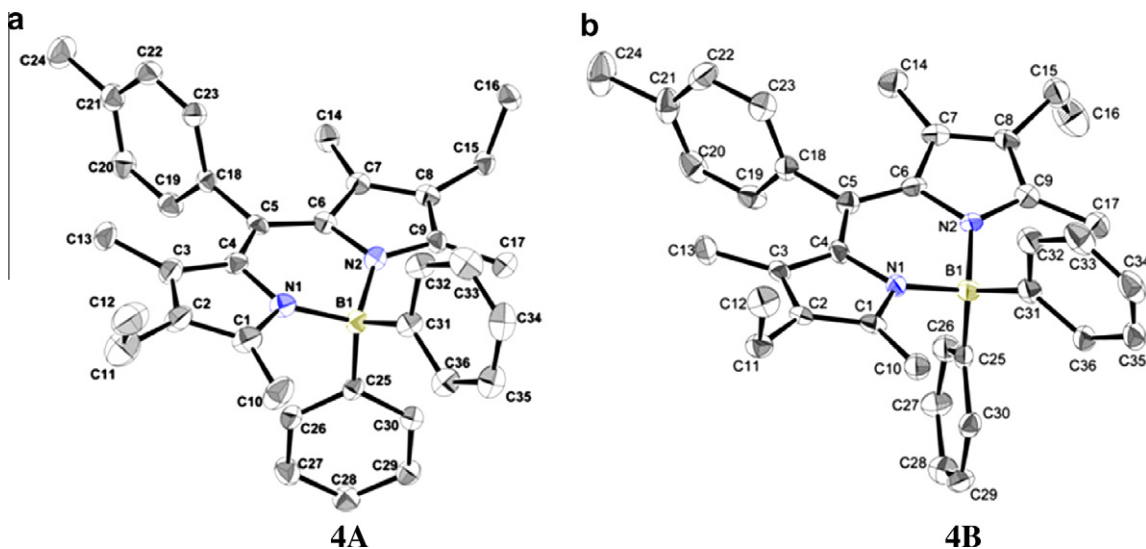


Figure 5. Crystal structure of **4** (CCDC 784322). ORTEP views of (a) **4A** and (b) **4B**. Hydrogen atoms have been omitted for clarity.

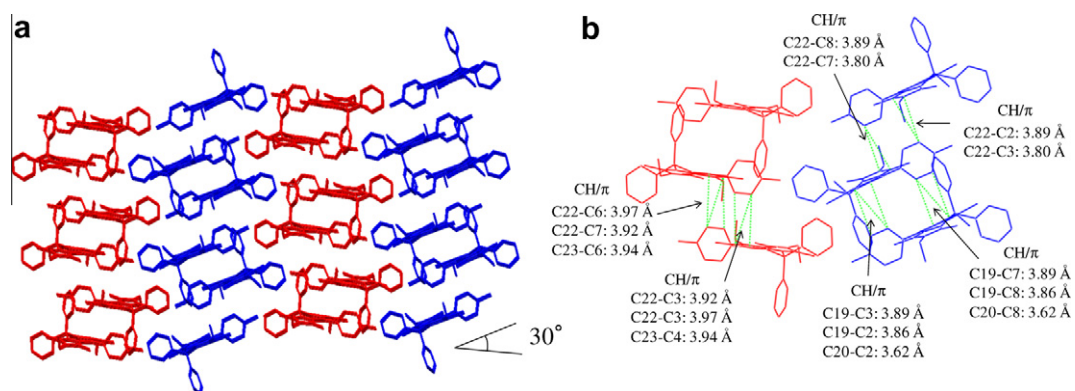


Figure 6. (a) Global crystal packing of **4**. (b) Intermolecular interactions of **4**. Dotted lines show intermolecular CH/ π interactions. Hydrogen atoms have been omitted for clarity. Blue and red molecules represent the conformers **4A** and **4B**, respectively.

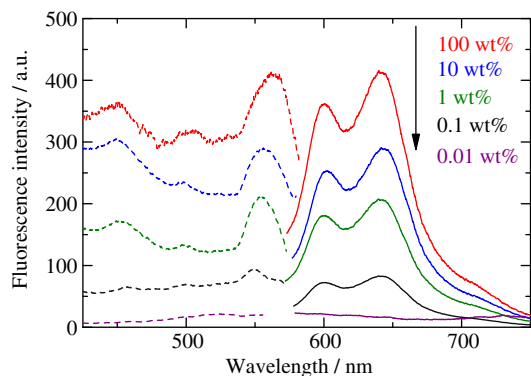


Figure 7. Excitation (dotted line) and fluorescence (solid line) spectra of BODIPY dye **4** in solid state with dye concentrations of 0.01, 0.1, 1, 10, and 100 wt%.

increasing the solid-state fluorescence quantum yield of BODIPY dyes. Further, the applicability of this strategy to other BF_2 complexes is being investigated.

Supplementary data

Supplementary data (synthetic procedures and crystallographic information file) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.09.106.

References and notes

- (a) Ye, S.; Chen, J.; Di, C.; Liu, Y.; Lu, K.; Wu, W.; Du, C.; Liu, Y.; Shuai, Z.; Yu, G. *J. Mater. Chem.* **2010**, *20*, 3186; (b) Liu, Y.; Tao, X.; Wang, F.; Dang, X.; Zou, D.; Ren, Y.; Jiang, M. *Org. Electron.* **2009**, *10*, 1082; (c) Lai, M.-Y.; Chen, C.-H.; Huang, W.-S.; Lin, J. T.; Ke, T.-H.; Chen, L.-Y.; Tsai, M.-H.; Wu, C.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 581; (d) Lee, Y.-T.; Chiang, C.-L.; Chen, C.-T. *Chem. Commun.* **2008**, 217; (e) Gondek, E.; Nizioł, J.; Danel, A.; Kityk, I. V.; Pokladko, M.; Sanetra, J.; Kulig, E. *J. Lumin.* **2008**, *128*, 1831; (f) Ning, Z.; Zhou, Y.; Zhang, Q.; Ma, D.; Zhang, J.; Tian, H. *J. Photochem. Photobiol. A: Chem.* **2007**, *192*, 8; (g) Luo, J.; Zhou, Y.; Niu, Z.-Q.; Zhou, Q.-F.; Ma, Y.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 11314; (h) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.
- (a) Fan, R.; Xia, Y.; Chen, D. *Opt. Express* **2008**, *16*, 9804; (b) Fukuda, M.; Kodama, K.; Yamamoto, H.; Mito, K. *Dyes Pigm.* **2004**, *63*, 115.
- (a) Park, S.-Y.; Kubota, Y.; Funabiki, K.; Shiro, M.; Matsui, M. *Tetrahedron Lett.* **2009**, *50*, 1131; (b) Park, S.-Y.; Ebihara, M.; Kubota, Y.; Funabiki, K.; Matsui, M. *Dyes Pigm.* **2009**, *82*, 258; (c) Ooyama, Y.; Okamoto, T.; Yamaguchi, T.; Suzuki, T.; Hayashi, A.; Yoshida, K. *Chem. Eur. J.* **2006**, *12*, 7827; (d) Shirai, K.; Matsuoka, M.; Fukunish, K. *Dyes Pigm.* **1999**, *42*, 95.
- (a) Gao, F.; Liao, Q.; Xu, Z.-Z.; Yue, Y.-H.; Wang, Q.; Zhang, H.-L.; Fu, H.-B. *Angew. Chem., Int. Ed.* **2010**, *49*, 732; (b) Imai, Y.; Kamon, K.; Tajima, N.; Kinuta, T.; Sato, T.; Kuroda, R.; Matsubara, Y. *J. Lumin.* **2010**, *130*, 954; (c) Shiota, N.; Kinuta, T.; Sato, T.; Tajima, N.; Kuroda, R.; Matsubara, Y.; Imai, Y. *Cryst. Growth Des.* **2010**, *10*, 1341; (d) Shimizu, M.; Takeda, Y.; Higashi, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 3653; (e) Iida, A.; Yamaguchi, S. *Chem. Commun.* **2009**, 3002; (f) Ooyama, Y.; Uwada, K.; Kumaoka, H.; Yoshida, K. *Eur. J. Org. Chem.* **2009**, 5979; (g) Fu, X.-F.; Yue, Y.-F.; Guo, R.; Li, L.-L.; Sun, W.; Fang, C.-J.; Xu, C.-H.; Yan, C.-H. *Cryst. Eng. Commun.* **2009**, *11*, 2268; (h) Mizobe, Y.; Hinoue, T.; Yamamoto, A.; Hisaki, I.; Miyata, M.; Hasegawa, Y.; Tohno, N. *Chem. Eur. J.* **2009**, *15*, 8175; (i) Kitamura, C.; Naito, T.; Yoneda, A.; Kobayashi, T.; Naito, H.; Komatsu, T. *Chem. Lett.* **2009**, 38, 600; (j) Thomas, R.; Varghese, S.; Kulkarni, G. U. *J. Mater. Chem.* **2009**, *19*, 4401; (k) Ooyama, Y.; Nagano, S.; Yoshida, K. *Tetrahedron* **2009**, *65*, 1467; (l) Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 9760; (m) Lai, M. Y.; Chen, C. H.; Huang, W. S.; Lin, J. T.; Ke, T. H.; Chen, L. Y.; Tsai, M. H.; Wu, C. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 581; (n) Sreejith, S.; Divya, K. P.; Ajayaghosh, A. *Chem. Commun.* **2008**, 2903; (o) Kitamura, C.; Matsumoto, C.; Kawatsuki, N.; Yoneda, A.; Asada, K.; Kobayashi, T.; Naito, H. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 754; (p) Ooyama, Y.; Nagano, S.; Okamura, M.; Yoshida, K. *Eur. J. Org. Chem.* **2008**, 5899; (q) Wakamiya, A.; Mori, K.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4273; (r) Mizuyama, N.; Tominaga, Y.; Kohra, S.; Ueda, K.; Hirayama, S.; Shigemitsu, Y. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 602.
- (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891; (b) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184.
- Gómez-Durán, C. F. A.; García-Moreno, I.; Costela, A.; Martín, V.; Sastre, R.; Bañuelos, J.; Arbeloa, F. L.; Arbeloa, I. L.; Peña-Cabrera, E. *Chem. Commun.* **2010**, 5103.
- (a) Umezawa, K.; Nakamura, Y.; Makino, H.; Citterio, D.; Suzuki, K. *J. Am. Chem. Soc.* **2008**, *130*, 1550; (b) Umezawa, K.; Matsui, A.; Nakamura, Y.; Citterio, D.; Suzuki, K. *Chem. Eur. J.* **2009**, *15*, 1096; (c) Nagai, A.; Chujo, Y. *Macromolecules* **2010**, *43*, 193.
- (a) Zhang, D.; Wen, Y.; Xiao, Y.; Yu, G.; Liu, Y.; Qian, X. *Chem. Commun.* **2008**, 4777; (b) Hepp, A.; Ulrich, G.; Schmechel, R.; Von Seggern, H.; Ziessel, R. *Synth. Met.* **2004**, *146*, 11.
- (a) Ozdemir, T.; Atilgan, S.; Kutuk, I.; Yildirim, L. T.; Tulek, A.; Bayindir, M.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 2105; (b) Badré, S.; Monnier, V.; Méallet-Renault, R.; Dumas-Verdes, C.; Schmidt, E. Y.; Mikhaleva, A. I.; Laurent, G.; Georges, G.; Ibanez, A.; Trofimov, B. A.; Pansu, R. B. *J. Photochem. Photobiol., A: Chem.* **2006**, *183*, 238; (c) Vu, T. T.; Badré, S.; Dumas-Verdes, C.; Vachon, J. -J.; Julien, C.; Audebert, P.; Senotrusova, E. Y.; Schmidt, E. Y.; Trofimov, B. A.; Pansu, R. B.; Clavier, G.; Méallet-Renault, R. *J. Phys. Chem. C* **2009**, *113*, 11844.
- (a) Tahtaoui, C.; Thomas, C.; Rohmer, F.; Klotz, P.; Duportail, G.; Mèly, Y.; Bonnet, D.; Hibert, M. *J. Org. Chem.* **2007**, *72*, 269; (b) Ehrenschröder, T.; Wagenknecht, H.-A. *Synthesis* **2008**, 3657; (c) Ulrich, G.; Goze, C.; Goeb, S.; Retailliau, P.; Ziessel, R. *New J. Chem.* **2006**, *30*, 982; (d) Goze, C.; Ulrich, G.; Mallon, L. J.; Allen, B. D.; Harriman, A.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 10231.
- BODIPY dyes **1–4** were able to be stored at room temperature for 5 months without decomposition. Although BODIPY dyes **1–4** were stored in CDCl_3 solution at room temperature for 5 days, any spectral changes were not observed in the ^1H NMR spectra. Therefore, BODIPY dyes **1–4** are considered to be comparatively stable.
- Rihn, S.; Retailliau, P.; Bugsaliewicz, N.; Nicola, A. D.; Ziessel, R. *Tetrahedron Lett.* **2009**, *50*, 7008.
- Matsui, M.; Ikeda, R.; Kubota, Y.; Funabiki, K. *Tetrahedron Lett.* **2009**, *50*, 5047.
- Davis, R.; Kumar, N. S. S.; Abraham, S.; Suresh, C. H.; Rath, N. P.; Tamaoki, N.; Das, S. *J. Phys. Chem. C* **2008**, *112*, 2137.