Tetrahedron Letters 51 (2010) 1600–1602

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of a new type of dibenzopyrromethene–boron complex with near-infrared absorption property

Yuji Kubo[a,*], Yu Minowa[a], Takayuki Shoda[b], Kimiya Takeshita[b]

[a] *Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan*
[b] *Mitsubishi Chemical Group Science and Technology Research Center, 1000 Kamoshida, Aoba, Yokohama, Kanagawa 227-8502, Japan*

ARTICLE INFO

Article history:
Received 18 December 2009
Revised 20 January 2010
Accepted 21 January 2010
Available online 28 January 2010

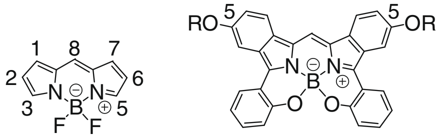
ABSTRACT

A new type of π-extended 4-bora-3a,4a-diaza-*s*-indacene (BODIPY dye), bis(isoindole)-derived benzo-[1,3,2]oxazaborinine **1**, has been synthesized by seven-step procedure from 2-methoxybenzoic acid methyl ester. The benzannulation of the pyrrole ring and the formation of a structurally strained intramolecular B–O ring enable the dye to absorb near-infrared light at ca. 750 nm with a molecular extinction coefficient (ε) of ca $8.3 \times 10^4\ M^{-1}\ cm^{-1}$ in THF. The absorption properties are discussed on the basis of DFT calculations. Interestingly, a film of 5,5-dihexyloxy derivative **1b**, which was fabricated by a spin-coating procedure on a glass plate, exhibited a dramatic bathochromic shift of absorbance as compared to the solution, with λ_{max} of 922 nm.

Functional dyes capable of absorbing near-infrared light beyond 700 nm[1] have attracted increasing attention in recent years, and such dyes are expected to find applications in optical recording media, laser filters, thermal writing displays, photodynamic therapy, solar cells, and so on. In particular, the demand for such dyes for applications in solar cells has increased considerably because approximately 50% of the radiation intensity of sunlight is in the near-infrared region from 700 to 2000 nm.[2] Although many near-infrared absorbing dyes such as azo dyes,[3] cyanine dyes,[4] quinone dyes,[5] and phthalocyanine dyes[6] have been developed so far, the synthetic exploration of related dyes with high molecular extinction coefficients in the near-infrared region as well as photostability remains as an area of concern. It has occurred to us that the use of BODIPY might be an advantageous approach toward this end because it serves as a stable dye which has strong absorption bands in the UV/vis spectrum as well as a sharp fluorescence emission with high quantum yield.[7] Despite the highly synthetic versatility, the development of near-infrared absorbing BODIPY remains in its infancy.[8]

In this study, in order to synthesize the desired BODIPY dyes, we considered several approaches to realize shifts to longer wavelengths in the absorption spectra: (1) the introduction of styryl units at 3,5-positions (see Chart 1);[9] (2) the replacement of methine with N at the *meso*-position;[8b,c] (3) rigid system of aryl-substituted BODIPY;[8a,10] (4) benzannulation of pyrrole;[8b,11] and (5) the formation of a benzo[1,3,2]oxazaborinine based on intramolecular B,O-chelation.[8c,12] Among these approaches, we chose (4) and (5), the combination of which would contribute to the extension of π-conjugation in the BODIPY scaffold, thus allowing us to target the synthesis of **1**. In addition, our proposed synthetic path to obtain the target enables us to introduce an alkoxy group at the 5-position of the isoindole ring (Chart 1); this is feasible for tuning the solubility as well as the stability. In this Letter, we report the synthesis and absorption properties of **1**, and discuss its properties on the basis of DFT calculations. Interestingly, as described below, a film of 5,5-dihexyloxy derivative **1b** was found to exhibit a significant absorption band at 922 nm.

The synthetic path of **1** is shown in Scheme 1; methyl 2-methoxybenzoate **2** was allowed to react with hydrazine hydrate[13] to yield **3**, followed by condensation with 1-(2-hydroxy-4-methoxyphenyl)ethanone. The obtained product **4** was oxidized with lead tetraacetate[14] and then condensed with ammonia to afford tetramethoxy-substituted and benzo-fused dipyrrin **6**. Subsequently BF_2-chelation with **6** using $BF_3{\cdot}Et_2O$ was carried out to afford F-BODIPY with a bis(isoindole)methene core **7**.[15] Then, demethylation of **7** with BBr_3 allows spontaneous cyclization to



BODIPY core

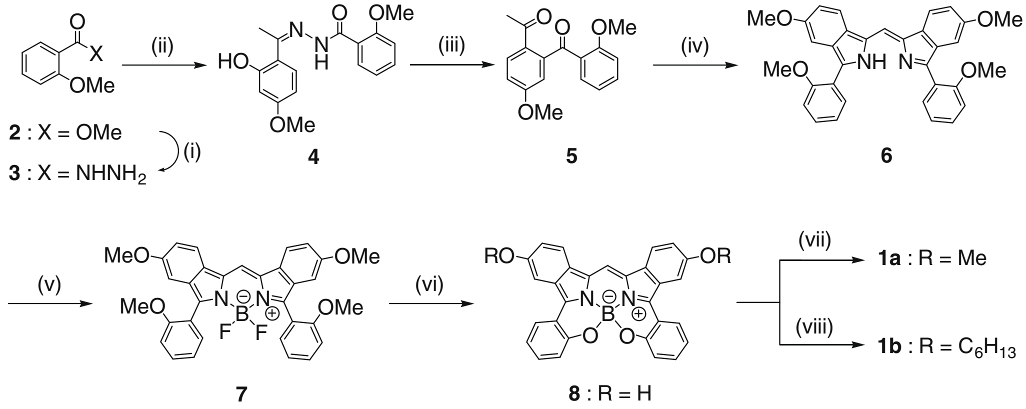
1a : R = Me
1b : R = C_6H_{13}

Chart 1.

---

[*] Corresponding author. Tel./fax: +81 42 677 3134.
E-mail address: yujik@tmu.ac.jp (Y. Kubo).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.01.070



Scheme 1. Synthesis of **1**. Reagents and conditions: (i) $N_2H_4{\cdot}H_2O$, dry EtOH, reflux, 4 h, (94%); (ii) 1-(2-hydroxy-4-methoxyphenyl)ethanone, dry EtOH, reflux, 44 h, (86%); (iii) $Pb(OAc)_4$, THF, rt, 2 h, (87%); (iv) NH_4OH, AcOH, MeOH, rt, 2 days, (24%); (v) $BF_3{\cdot}Et_2O$, NEt_3, dry toluene, 80 °C, 1.5 h, (91%); (vi) BBr_3, CH_2Cl_2, 0 °C to rt, 3 days, (66%); (vii) MeI, K_2CO_3, dry DMF, 50 °C, 36 h, (59%); (viii) $C_6H_{13}I$, NaH, dry DMF, rt, 2 h, (39%).

afford a constrained benzo[1,3,2]oxazaborinine **8**. Because the dye was found to be relatively unstable in a solution, we then converted it to the corresponding dialkoxy derivatives **1a**[16] and **1b**[17] using Williamson synthesis with MeI and $C_6H_{13}I$, respectively.

Anisole-annulated F-BODIPY **7** absorbs visible light at 654 nm ($\varepsilon = 8.67 \times 10^4\ M^{-1}\ cm^{-1}$) in THF (Fig. 1). When compared to the corresponding F-BODIPY **9**[12], because compound **10** has not been reported so far (Chart 2), a significant red-shift by 104 nm was observed.[18] Although anisole-annulation of the BODIPY scaffold is advantageous in that it affords a dye capable of absorbing longer wavelength light, the absorption band of **7** does not reach the near-infrared region. However, further modification based on the intramolecular B–O ring formation led to a significant bathochromic shift in the absorption spectra. As a result, **1a** absorbs near-infrared light having a wavelength of 746 nm in THF ($\varepsilon = 8.29 \times 10^4\ M^{-1}\ cm^{-1}$). In addition, the hexyloxy derivative **1b** exhibits a similar absorption property at 748 nm in THF ($\varepsilon = 8.34 \times 10^4\ M^{-1}\ cm^{-1}$). In this way, we have succeeded in synthesizing near-infrared absorbing BODIPY analogues.

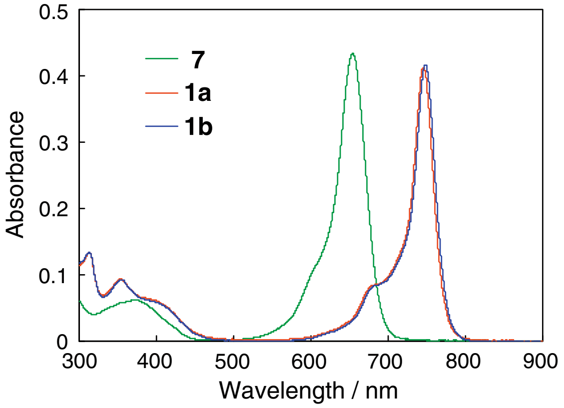


Figure 1. Absorption spectra of **7** (5.0 μM), **1a** (5.0 μM), and **1b** (5.0 μM) in THF at 25 °C.

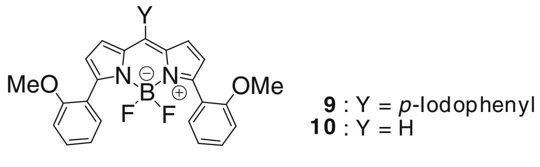


Chart 2.

For better understanding of the spectra properties, the molecular orbitals were analyzed on the basis of DFT calculations. A geometry optimization was carried out using B3LYP hybrid function with 6-31G (d,p) basis set (Fig. 2). Although the first absorption band is characterized as a mixture of several configurations, it can mainly be ascribed to the HOMO–LUMO transition. The energies of the HOMO and LUMO of scaffold **10** are calculated to be −5.072 and −2.429 eV, respectively. The anisole-annulation at the pyrrole ring leads to significant unstabilization of the HOMO level, possibly due to the π-extended electron-donor nature of the segment. Alternatively, it is interesting to note that intramolecular B–O ring formation results in the stabilization of both HOMO and LUMO whereby the LUMO level is relatively more stabilized than the HOMO level. Taken together, the calculation not only supports our design principle in this study but also contributes to the synthesis of related dyes based on the BODIPY scaffold.

As the next stage, dye films were fabricated by spin-coating a THF solution of **1** (5.8 mg mL^{-1}) onto a glass plate. Each film is composed by 100% dye. Although film **1a** absorbs Vis–NIR light with λ_{max} of 664 nm, we could obtain a greenish film of **1b**. Surprisingly, the **1b** film exhibited an intense absorption band up to 1060 nm with λ_{max} of 922 nm (Fig. 3). A large bathochromic shift by 174 nm was obtained as compared to the solution (vide supra). This spectral behavior might be attributable to dye aggregation in the film. Studies aimed at the structural analysis are thus underway.

In conclusion, we have developed new near-infrared absorbing BODIPY analogues. It is noteworthy that film **1b** exhibits a significant absorption band up to 1060 nm; an investigation of the

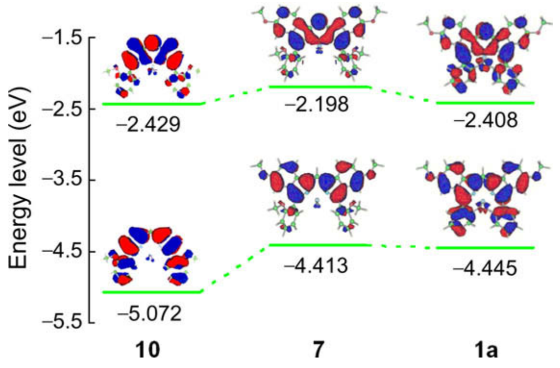


Figure 2. Diagrams showing HOMO and LUMO levels of **10**, **7**, and **1a**.

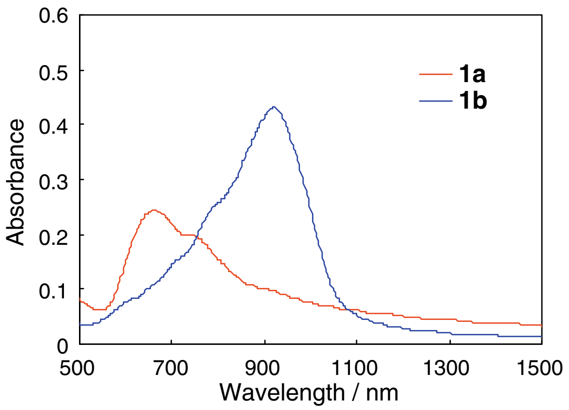


Figure 3. Absorption spectra of films **1a** and **1b** on a glass plate.

electronic and photophysical properties of the film should be of interest in the field of materials science. Also, the advantage of the proposed synthetic path enables us to introduce functional groups at the 5-position in the isoindole ring. We have been synthesizing derivatives in line with the strategy in our laboratory.

References and notes

1. (a) Fabian, J.; Zahradník, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677–694; (b) *Infrared Absorbing Dyes*; Matuyoka, M., Ed.; Plenum Press: New York, 1990; (c) Fabian, J.; Nakazumi, H.; Matsuoka, M. *Chem. Rev.* **1992**, *92*, 1197–1226; (d) *Near-Infrared Dyes For High Technology Applications (NATO Science Partnership Sub-Series: 3)*; Daehne, S., Rensch-Genger, U., Wolfbeis, O. S., Eds.; Kluwer Academic Publishers: Dortrecht, 1998.
2. Yanagida, M.; Onozawa-komatsuzaki, N.; Kurashige, M.; Sayama, K.; Sugihara, H. *Sol. Energy, Mater. Sol. Cells* **2010**, *94*, 297–302.
3. (a) Li, Y.; Patrick, B. O.; Dolphin, D. *J. Org. Chem.* **2009**, *74*, 5237–5243; (b) Salvador, M. A.; Almeida, P.; Reis, L. V.; Santos, P. F. *Dyes Pigments* **2009**, *82*, 118–123.
4. (a) Yagi, S.; Ohta, T.; Akagi, N.; Nakazumi, H. *Dyes Pigments* **2008**, *77*, 525–536; (b) Descalzo, A. B.; Rurack, K. *Chem. Eur. J.* **2009**, *15*, 3173–3185.
5. (a) Kubo, Y.; Yoshida, K.; Adachi, M.; Nakamura, S.; Maeda, S. *J. Am. Chem. Soc.* **1991**, *113*, 2868–2873; (b) Barthram, A. M.; Cleary, R. L.; Kowallick, R.; Ward, M. D. *Chem. Commun.* **1998**, 2695–2696.
6. (a) Arslanoğlu, Y.; Sevim, A. M.; Hamuryudan, E.; Gül, A. *Dyes Pigments* **2006**, *68*, 129–132; (b) Modibane, D. K.; Nyokong, T. *Polyhedron* **2009**, *28*, 479–484; (c) Li, H.; Nguyen, N.; Fronczek, F. R.; Vicente, M. G. H. *Tetrahedron* **2009**, *65*, 3357–3363.
7. Reviews, see: (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891–4932; (b) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184–1201.
8. (a) Zhao, W.; Carreira, E. M. *Chem. Eur. J.* **2006**, *12*, 7254–7263; (b) Donyagina, V. F.; Shimizu, S.; Kobayashi, N.; Lukyanets, E. A. *Tetrahedron Lett.* **2008**, *49*, 6152–6154; (c) Loudet, A.; Bandichhor, R.; Burgess, K.; Palma, A.; McDonnell, S. O.; Hall, M. J.; O'Shea, D. F. *Org. Lett.* **2008**, *10*, 4771–4774; (d) Umezawa, K.; Matsui, A.; Nakamura, Y.; Citterio, D.; Suzuki, K. *Chem. Eur. J.* **2009**, *15*, 1096–1106.
9. Saki, N.; Dinc, T.; Akkaya, E. U. *Tetrahedron* **2006**, *62*, 2721–2725.
10. Chen, J.; Burghart, A.; Derecskei-Kovacs, A.; Burgess, K. *J. Org. Chem.* **2000**, *65*, 2900–2906.
11. (a) Kang, H. C.; Haugland, R. P. U. S. Patent 5,433,896, July 18, 1995.; (b) Wu, Y.; Klaubert, D. H.; Kang, H. C.; Zhang, Y.-z. U. S. Patent 6,005, 113, 1999.; (c) Wada, M.; Ito, S.; Uno, H.; Murashima, T.; Ono, N.; Urano, T.; Urano, Y. *Tetrahedron Lett.* **2001**, *42*, 6711–6713.
12. Kim, H.; Burghart, A.; Welch, M. B.; Reibenspies, J.; Burgess, K. *Chem. Commun.* **1999**, 1889–1890. Arylation of the *meso*-position has no spectral effect on the absorption wavelength.[7a].
13. Khan, K. M.; Rasheed, M.; Ullah, Z.; Hayat, S.; Kaukab, F.; Choudhary, M. I.; ur-Rahman, A.; Perveen, S. *Bioorg. Med. Chem.* **2003**, *11*, 1381–1387.
14. Kotali, A.; Lafazanis, I. S.; Harris, P. A. *Tetrahedron Lett.* **2007**, *48*, 7181–7183.
15. Difluoro[5-methoxy-1-[[5-methoxy-3-(2-methoxyphenyl)-2*H*-isoindole-1-yl]methylene]-3-(2-methoxyphenyl)-1*H*-isoindolate-N^1,N^2]boron **7**; ^{1}H NMR (270 MHz, DMSO-d_6) δ 3.69–3.75 (12H, m), 6.56 (2H, d, $J = 1.7$ Hz), 6.99 (1H, t, $J = 7.4$ Hz), 7.06 (1H, t, $J = 7.4$ Hz), 7.15–7.21 (4H, m), 7.37 (1H, d, $J = 7.4$ Hz), 7.43–7.50 (3H, m), 8.02 (2H, dd, $J = 8.8$, 1.1 Hz), 8.44 (1H, s); ^{13}C NMR (68 MHz, DMSO-d_6) δ 55.25, 55.43, 101.61, 111.41, 115.64, 115.79, 119.22, 119.45, 119.72, 119.87, 120.68, 121.14, 127.00, 127.12, 128.15, 128.27, 130.95, 131.11, 131.18, 131.86, 147.34, 147.60, 157.14, 157.21; FAB MS (*m*/*z*) 564 [M^+]. Anal. Calcd for $C_{33}H_{27}BF_2N_2O_4{\cdot}0.2CH_2Cl_2$: C, 68.18; H, 4.75; N, 4.82; B, 1.86. Found: C, 68.00; H, 4.89; N, 4.92; B, 1.8.
16. Boron chelated [5-methoxy-1-[[5-methoxy-3-(2-hydroxyphenyl)-2*H*-isoindole-1-yl]methylene]- 3-(2-hydroxyphenyl)-1*H*-isoindole **1a**; ^{1}H NMR (270 MHz, DMSO-d_6) δ 3.98 (6H, s), 6.90 (2H, d, $J = 8.2$ Hz), 7.23 (2H, t, $J = 7.6$ Hz), 7.30 (2H, dd, $J = 8.8$, 1.8 Hz), 7.42 (2H, t, $J = 7.6$ Hz), 7.75 (2H, d, $J = 1.9$ Hz), 8.13 (2H, d, $J = 8.9$ Hz), 8.38 (1H, s), 8.46 (2H, d, $J = 7.7$ Hz); ^{13}C NMR (68 MHz, DMSO-d_6) δ 55.69, 102.90, 119.03, 119.83, 120.44, 120.96, 121.46, 126.17, 127.29, 128.25, 128.45, 131.93, 140.68, 152.45, 158.10; FAB MS (*m*/*z*) 496 [M^+]. Anal. Calcd for $C_{31}H_{21}BN_2O_4{\cdot}0.3H_2O$: C, 74.21; H, 4.34; N, 5.58; B, 2.15. Found: C, 74.08; H, 4.23; N, 5.53; B, 2.1.
17. Boron chelated [5-hexyloxy-1-[[5-hexyloxy-3-(2-hydroxyphenyl)-2*H*-isoindole-1-yl]methylene]-3-(2-hydroxyphenyl)-1*H*-isoindole **1b**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.930–0.958 (6H, m), 1.37–1.42 (8H, m), 1.52–1.57 (4H, m), 1.88 (4H, quint, $J = 7.2$ Hz), 4.08 (2H, dt, $J = 8.7$, 6.6 Hz), 4.13 (2H, dt, $J = 8.7$, 6.6 Hz), 6.99 (2H, d, $J = 8.0$ Hz), 7.15 (2H, dd, $J = 8.8$, 2.0 Hz), 7.19 (2H, t, $J = 7.6$ Hz), 7.37 (2H, app. td, $J = 7.8$, 1.4 Hz), 7.51 (2H, d, $J = 1.8$ Hz), 7.53 (1H, s), 7.79 (2H, d, $J = 8.9$ Hz), 8.15 (2H, dd, $J = 7.8$, 1.3 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 14.23, 22.81, 25.98, 29.51, 31.85, 68.57, 103.69, 109.64, 119.95, 120.17, 120.74, 120.93, 125.87, 127.99, 128.81, 129.52, 131.71, 141.50, 153.56, 157.80; FAB MS (*m*/*z*) 636 [M^+]. Anal. Calcd for $C_{41}H_{41}BN_2O_4$: C, 77.36; H, 6.49; N, 4.40; B, 1.7. Found: C, 77.29; H, 6.48; N, 4.26; B, 1.8.
18. The absorption spectrum of dye **9** was measured in $CHCl_3$.[12]