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Benzene-fused bis(acenaphthoBODIPY)s, stable near-infrared-selective dyes†

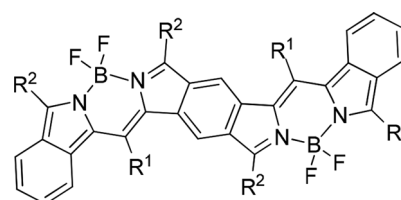
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Benzene-fused bis(acenaphthoBODIPY)s prepared by retro-Diels–Alder reaction of bicyclo[2.2.2]octadiene-fused precursors showed strong absorption bands in the near-infrared region and very weak absorptions in the visible region.

Introduction

Biological and clinical applications of near-infrared (NIR) dyes is an area of great interest because the development of laser-generating techniques enables us to use light of a certain wavelength more easily than before. In the medical fields, NIR light in the so-called optical window region plays a key role in photodynamic therapy for cancer treatment¹ and imaging of mammalian living cells in deep tissue² due to its permeability. In industry, organic NIR dyes are a key material for improving the efficiency of organic solar cells;³ fair amounts of solar energy reach the earth's surface as NIR light. Inorganic NIR dyes are used as cutoff filters for detectors and as ink for NIR-reading machines.⁴ NIR dyes that have no or little absorption in the visible region can be used as invisible NIR ink for humans, whereas panchromatic NIR dyes are ideal for solar-cell application. Many kinds of organic compounds that are used as NIR dyes usually have large π chromophores such as linear cyanine,⁵ cyclic oligopyrroles including porphyrin and phthalocyanine,⁶ squaraine,⁷ rhodamine⁸ and boron dipyrromethene (BODIPY);⁹ however, absorption maxima of their pristine chromophores, except for cyclo[*n*]pyrroles,¹⁰ do not reach the NIR region. Expansion of the core chromophores or efficient introduction of substituents is therefore essential for dyes with NIR absorption. We have approached this subject by fusion and expansion of chromophores. We reported that π -expanded porphyrins,¹¹ π -expanded BODIPYs,¹² π -fused oligoporphyrins¹³ and benzene-fused bisBODIPYs¹⁴ have strong absorption maxima

in the far-red-to-NIR region. Especially in the case of benzene-fused bis(benzoBODIPY)s **1** (Fig. 1), only the absorption maxima with the lowest energy occurred in the NIR region (775 to 903 nm), depending on the substituents. Both panchromatic BODIPYs for solar-cell application¹⁵ and NIR-selective BODIPYs for bio-imaging application⁹ have attracted much attention. Our fusion method for the BODIPY chromophore in the proper direction was proven to be effective for the elongation of absorption maxima into the NIR region with keeping transparency in the visible region. Similar to the π -expanded porphyrins¹¹ and BODIPYs,¹² however, bis(benzoBODIPY)s **1a** and **1b** without electron-withdrawing groups was proven to be unstable. Although introduction of electron-withdrawing groups such as ethoxycarbonyl and cyano groups stabilized the benzene-fused bis(benzoBODIPY) chromophore, the absorption maxima also tended to shift bathochromically. In order to tune absorption maxima of the NIR dyes, stable NIR π systems based on the BODIPY chromophore are necessary. Lash and coworkers reported that the absorption maxima of porphyrin Q bands are remarkably bathochromically shifted in the NIR region by fusion of acenaphtho moieties to β positions of porphyrins.¹⁶ We have also reported the effective elongation of absorption maxima in the case of BODIPYs¹⁷ and cyclo[*n*]pyrroles.¹⁸ This acenaphtho-fusion method was



- 1a:** R¹ = 4-^tBuC₆H₄, R² = H
1b: R¹ = 4-^tBuC₆H₄, R² = CH₃
1c: R¹ = 4-^tBuC₆H₄, R² = CO₂Et
1d: R¹ = 4-^tBuC₆H₄, R² = CN

Fig. 1 Benzene-fused bis(benzoBODIPY)s with NIR absorptions.

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successfully applied to the preparation of bisBODIPYs with stable NIR chromophores.

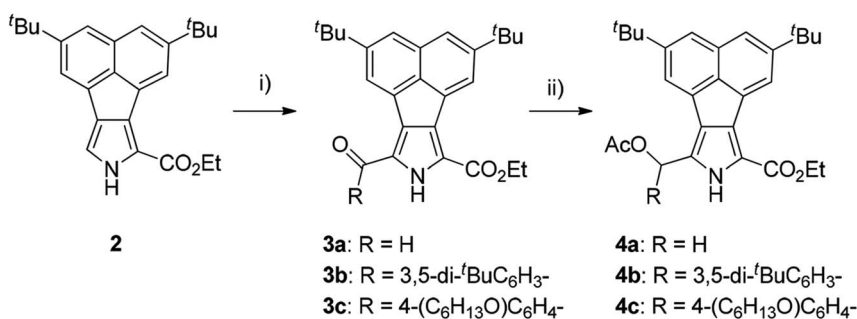
Results and discussion

Our strategy for the preparation of acenaphtho-fused bisBODIPYs (bisANBODIPYs) was based on the retro-Diels–Alder protocol,¹⁹ which was successfully used in the preparation of highly flat, insoluble compounds. This protocol enabled us to treat the intermediary compounds in the synthetic scheme without worrying about their solubility, and it was quite successful when the final targeted compounds did not need to be characterized. In most cases, the solubility of the targeted compounds was required for their full characterization. In order to increase the solubility of the target acenaphtho derivatives in common organic solvents, two *tert*-butyl groups were introduced into acenaphthylene, and the resulting compound was converted to ethylacenaphtho[1,2-*c*]pyrrole-1-carboxylate **2**.¹⁸ Formylation of **2** with the Vilsmeier reagent gave α -formylated compound **3a** in 98% yield (Scheme 1). The formyl group of **3a** was converted to an acetoxymethyl group by reduction with NaBH₄ followed by acetylation with Ac₂O and 4-dimethylaminopyridine (DMAP). Compound **4a** was obtained in 92% yield in two steps.

We have reported that the fusion geometry of two BODIPY chromophores is very important for the elongation of absorption maxima with the lowest energy: fusion of the chromophores in the anti manner was found to be more effective than the *syn* manner.¹⁴ Therefore, we chose bicyclo[2.2.2]octadiene-fused (BCOD-fused) dipyrroles **5** (ref. 20) as the starting material. Double condensation of **4a** with **5** under acidic conditions gave BCOD-fused bis(dipyrrromethene)s **6a** in 66% yield (Scheme 2). Four ester groups of **6a** were transformed to four methyl groups by rigorous reduction with LiAlH₄ in refluxing THF in 37% yield. The rather unstable tetramethyl derivative was then converted to BCOD-fused bis(boron acenaphthodipyrrromethene) (BCOD-bisANBODIPY) **7a** in 27% yield by treatment with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), (*i*-Pr)₂EtN and BF₃·OEt₂. The thermogravimetric experiment on precursor **7a** showed that evolution of ethylene gas started from *ca.* 200 °C and ceased at 250 °C (temperature increase rate of 10 °C min⁻¹). The starting reddish purple color

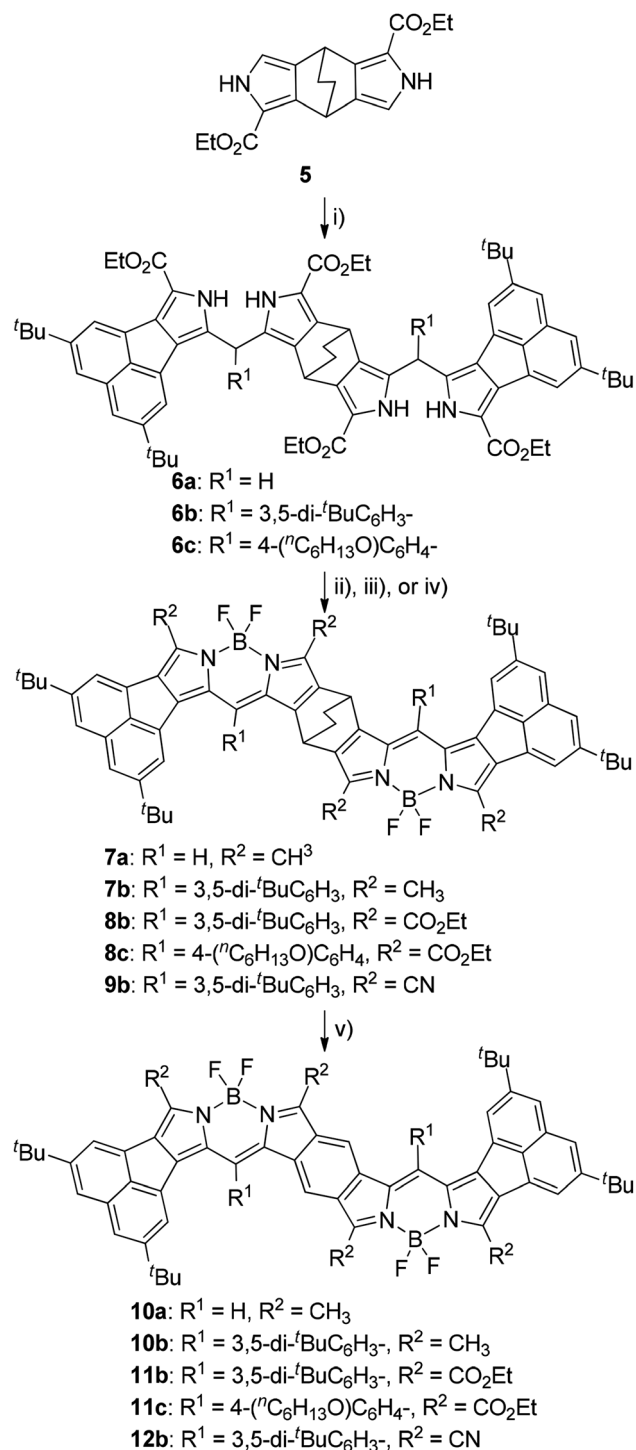
of **7a** turned black. Thus, the bulk thermal conversion of **7a** was performed at 200 °C for 2 h *in vacuo*. The obtained material was poorly soluble and no purification was possible, although the ultraviolet-visible-NIR (UV-vis-NIR) spectrum and matrix-assisted laser-ionization time-of-flight (MALDI-TOF) MS of the material indicated the formation of benzene-fused bisANBODIPY (B-bisANBODIPY) **10a** (Scheme 2).

We next examined the use of solubilizing substituents such as 3,5-di-*tert*-butylphenyl and 4-hexyloxyphenyl groups in order to characterize the B-bisANBODIPYs. Thus, acetoxy(aryl)methyl derivatives **4b** and **4c** were prepared (Scheme 1). Friedel–Crafts acylation of **2** by the mixed anhydrides of 3,5-di-*tert*-butylbenzoic acid and 4-hexyloxybenzoic acid with trifluoroacetic anhydride (TFAA) and trifluoroacetic acid (TFA) afforded α -acylated compounds **3b** and **3c** in respective yields of 80 and 96%.²¹ Reduction of the acyl groups of **3** with NaBH₄ followed by acetylation with Ac₂O gave α -acetoxymethyl derivatives **4b** and **4c** in 69% and 65% yields, respectively. Treatment of **4b** with **5** under acidic conditions afforded a diastereomeric mixture of BCOD-fused bis(dipyrrromethane) **6b** in 58% yield (Scheme 2). Bis(dipyrrromethane) **6b** was transformed into three types of BCOD-bisANBODIPYs: first, bis(dipyrrromethane) **6b** was directly converted to BCOD-bisANBODIPY **8b** with four ester groups in 70% yield by treatment with DDQ, *N,N*-diisopropylethylamine and BF₃·OEt₂. Second, four ester groups of **6b** were transformed to four methyl groups by rigorous reduction with LiAlH₄ in refluxing THF. The rather unstable tetramethyl derivative was then converted to BCOD-bisANBODIPY **7b** in 35% yield by treatment with DDQ, *N,N*-diisopropylethylamine and BF₃·OEt₂. Third, the four ester groups of **6b** were removed by treatment with NaOH in ethylene glycol at 170 °C. The unstable α -free derivative obtained was cyanated with chlorosulfonyl isocyanate (CSI)²² and then transformed to BCOD-bisANBODIPY **9b** with four cyano groups in 5% overall yield from **6b**. Bis(dipyrrromethane) **6c** with two hexyloxyphenyl groups obtained from the reaction of **4c** with **5** (75% yield) was converted to BCOD-bisANBODIPY **8c** with four ester groups at 80% yield. The thermal treatment of **7b**, **8b**, **8c** and **9b** at 200 °C for 2 h or at 250 °C for 30 min *in vacuo* produced almost quantitative yields of B-bisANBODIPYs **10b**, **11b**, **11c** and **12b**, respectively (Scheme 2). Both thermal conditions gave similar results.



Scheme 1 Reagents, conditions and yields: (i) for **3a**: DMF, POCl₃, rt, 1.5 h; 98%; **3b**: 3,5-di-*tert*-butylbenzoic acid, trifluoroacetic anhydride, trifluoroacetic acid, rt, 3 d; 80%; **3c**: 4-hexyloxybenzoic acid, TFAA, TFA, rt, 3 d; 96%. (ii) NaBH₄, THF/EtOH (2/1), 0 °C, 2 h; Ac₂O, DMAP (cat.), CH₂Cl₂, rt, 30 min; **4a**: 92%, **4b**: 69%, **4c**: 65%.





Scheme 2 Reagents, conditions and yields: (i) **4**, TsOH, AcOH, rt, 3 h; **6a**: 63%; **6b**: 58%; **6c**: 75%; (ii) LiAlH₄, THF, reflux, 3 h; DDQ, CH₂Cl₂, rt, 1 h; BF₃·OEt₂, (*i*-Pro)₂EtN, 2 h; **7a**: 27%; **7b**: 35%; (iii) DDQ, CH₂Cl₂, rt, 1 h; BF₃·OEt₂, (*i*-Pro)₂EtN, 2 h; **8b**: 70%; **8c**: 80%; (iv) NaOH, ethylene glycol, 170 °C, 3 h; CSI, DMF/CH₃CN (2 : 1), -50 °C, 1.5 h, then rt, overnight; DDQ, CH₂Cl₂, rt, 1 h; BF₃·OEt₂, *N,N*-diisopropylethylamine, 2 h; 5%; **9b**; (v) 200 °C, 2 h or 250 °C, 30 min; quant.

Electronic spectra of BODIPYs in CH₂Cl₂ were recorded. Fig. 2 shows the UV-vis-NIR and fluorescence spectra of BCOD-bisANBODIPY **7b** and B-bisANBODIPY **10b** as representative

cases. The spectral shapes of other bisANBODIPYs are almost the same as those of **7b** and **10b** (see ESI†). The results are listed in Table 1. In the spectra of BCOD-bisANBODIPYs **7a**, **7b**, **8b** and **8c**, strong absorption bands with the lowest energy can be observed at *ca.* 625 nm, irrespective of substituent difference between tetramethyl and tetra(ethoxycarbonyl). On the other hand, the absorption band was shifted by *ca.* 20 nm to 646 nm by substitution of four cyano groups. In the case of B-bisANBODIPYs, the absorption bands with the lowest energy shifted by *ca.* 200 nm relative to those of the corresponding BCOD-bisANBODIPYs. The absorption maxima of **10a**, **10b**, **11b**, **11c** and **12b** were observed at 828, 824, 835, 836 and 900 nm, respectively. In all cases, these large peaks were accompanied by smaller peaks with shorter wavelengths. In the acenaphtho series, differences in absorption maxima with the lowest energy between tetramethyl **10b**, tetra(ethoxycarbonyl) **11b** and tetracyano **12b** were *ca.* 11 and 64 nm. Therefore, the spectrum of tetra(ethoxycarbonyl) **11b** resembled that of tetramethyl **10b** rather resembling that of tetracyano **14**. In the benzo series **1a**, **1b** and **1c**, the opposite tendency was reported.¹⁴ The spectrum of tetra(ethoxycarbonyl) **1b** resembled that of tetracyano **1c**. The differences of the absorption maxima between **1a**, **1b** and **1c** were 62 and 10 nm.

We carried out time-dependent density functional theory (TD-DFT) calculation of simplified B-bisANBODIPYs **13**, **14**, **15** and **16** (Fig. 3) at the level of B3LYP/6-31G+(d) in order to clarify the difference. The representative results are summarized in Table 2, and the typical calculated spectrum of **15** with the corresponding spectrum of **11b** is illustrated in Fig. 4. In all cases, the two lower excited states with effective oscillator strength consisted of almost one transition between HOMO and LUMO or between HOMO-2 and LUMO. The energy differences between the two states were 0.5144 eV for **13**, 0.6824 eV for **14**, 0.3757 eV for **15** and 0.3938 eV for **16**. These values are quite larger than those observed for **10a-12b** in the UV-vis-NIR spectra. Thus, we concluded that the absorptions accompanying the longest-wavelength maxima were due to vibration. The differences in calculated absorption maxima between tetramethyl **14**, tetra(methoxycarbonyl) **15** and tetracyano **16** were 26 and 28 nm. This tendency for calculated absorption maxima can be explained by the electron-withdrawing ability of ester and cyano groups. However, it is not in accordance with the

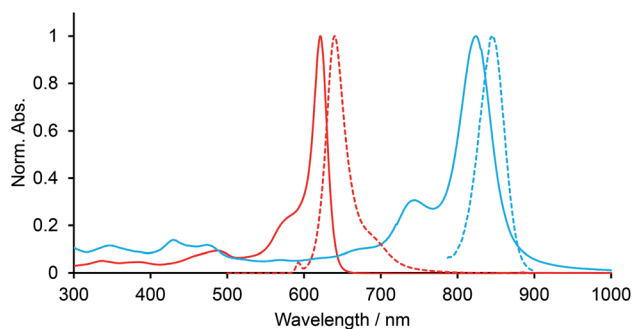


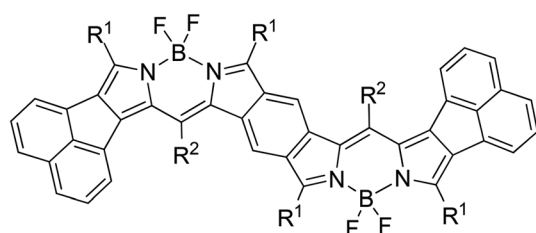
Fig. 2 UV-vis-NIR (solid line) and fluorescence (dotted line) spectra of **7b** (red line) and **10b** (blue line) in CH₂Cl₂.



Table 1 Electronic spectra of bisANBODIPYs in CH₂Cl₂

	UV-vis-NIR			Fluorescence			
	nm ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$) or [relative intensity]			nm (ex. nm)	Φ^a		
7a		486 [0.13]		580 [sh, 0.27]	624 [1.00]	631 (600)	0.40
7b		488 (2.48)		580 (sh, 4.81)	621 (20.1)	640 (580)	0.53
8b	351 (1.83)	422 (1.72)		535 (sh, 3.14)	625 (14.1)	658 (610)	0.07
8c	358 (1.35)	416 (1.82)		540 (3.10)	624 (12.1)	665 (590)	0.10
9b	420 (1.60)	460 (1.78)		— ^b	646 (8.84)	707 (590)	0.02
10a	348 [0.21]	433 [0.20]	475 [0.19]	746 [0.38]	828 [1.00]	838 (790)	0.08
10b	348 (2.36)	430 (2.50)	472 (2.13)	744 (5.54)	818 (16.9)	846 (800)	0.10
11b	356 (2.34)	443 (1.91)	570 (0.94)	756 (5.18)	835 (15.9)	842 (800)	0.05
11c	366 (2.45)	446 (2.10)	572 (1.00)	758 (5.06)	836 (15.9)	850 (780)	0.04
12b	397 [0.19]	490 [0.14]	624 [0.09]	803 [0.34]	900 [1.00]	—	—

^a Absolute quantum yield. ^b The shoulder peak was not observed probably due to broadening of the main peak.



- 13:** R¹ = H, R² = H
14: R¹ = CH₃, R² = Ph
15: R¹ = CO₂CH₃, R² = Ph
16: R¹ = CN, R² = Ph

Fig. 3 Simplified B-bisANBODIPY structures **13–16** for TD-DFT calculation.

Table 2 Two state transitions with the lowest energy and meaningful oscillator strength in TD-DFT calculation for B-bisANBODIPYs

State ^a	The most contributed transition	Energy		
		eV	nm	<i>f</i>
13	HOMO → LUMO	1.7310	716	1.5266
	HOMO-2 → LUMO	2.2568	549	0.1750
14	HOMO → LUMO	1.6445	753	1.449
	HOMO-2 → LUMO	2.2887	541	0.1200
15	HOMO → LUMO	1.6508	751	1.2759
	HOMO-2 → LUMO	2.1253	583	0.1286
16	HOMO → LUMO	1.5679	790	1.1908
	HOMO-2 → LUMO	2.0192	614	0.1473

^a Oscillator strengths of states 2 and 3 are almost zero.

observed tendency: in the case of B-bisANBODIPY series, the difference in absorption energy between tetramethyl and tetra(ethoxycarbonyl) derivatives was small, while that between tetra(ethoxycarbonyl) and tetracyano derivatives was large.

Next, we studied the structure of bisANBODIPYs. Fortunately, single crystals of BCOD- and B-bisANBODIPYs **7b**, **8b**, **10b**, **11b**, **11c** and **12b** were obtained by the solvent-vapor diffusion method: bisANBODIPYs were dissolved in chloroform

or dichloromethane and placed under an atmosphere of a poor solvent such as methanol or acetonitrile. In the case of **11b** and **12b** were dry solvent sets used in order to avoid hydrolysis of a BF₂ unit (*vide infra*). The crystals obtained were subjected to X-ray analysis. Ortep drawings of **8b** and **11b** are respectively illustrated in Fig. 5 and 6 as representative, and others are provided in the ESI.† All crystals except for those from **11c** were proven to involve co-crystallized solvent molecules in a disordered fashion. B-bisANBODIPY **11c**, however, underwent partial hydrolysis during recrystallization from an undried solvent system. The crystal was proven to consist of mono-BF₂-removed **17** and **11c** (**17/11c** ratio of *ca.* 3 : 1; Fig. 7 and S7 in ESI†). There might be fully-hydrolyzed bisdipyrin **18** in the crystal. We could not determine the possibility by the X-ray analysis. When the solvent molecules were not properly modeled, the rest of the molecules were refined by the Platon Squeeze technique.

In the crystal structure of BCOD-bisANBODIPY **8b**, one of the ester parts was disordered. Another ester carbonyl group was directed toward the BF₂ moiety of BODIPY, even though this conformation was thought to be disadvantageous because of the dipole-dipole interaction. Both ester groups were disordered in one BODIPY part of B-bisANBODIPYs **11c** and **17**. On the other hand, no disordered ester group was observed in the other BODIPY part, which consisted of 75% dipyrin and 25% BODIPY. BCOD-bisANBODIPY **8b** adopted the gable shape because of the BCOD skeleton and the dihedral angle between

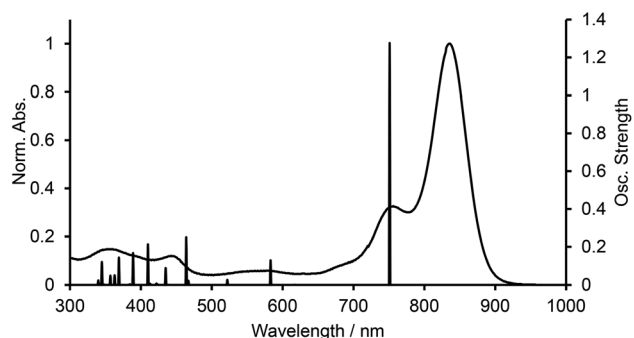


Fig. 4 UV-vis-NIR spectra of **11b** and calculated spectrum of **15**.



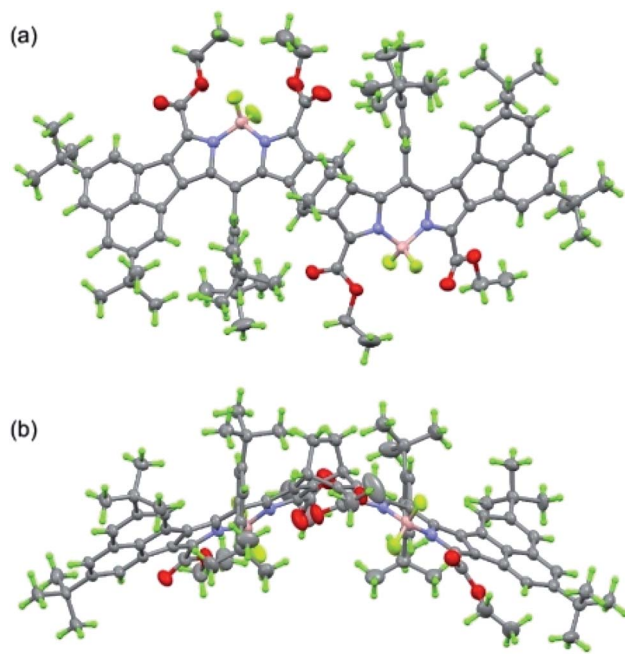


Fig. 5 Ortep drawing of **8b** (top (a) and side (b) views). Solvent molecules (CHCl_3 and *i*-propanol) and disordered substituents with lower occupancies are omitted for clarity.

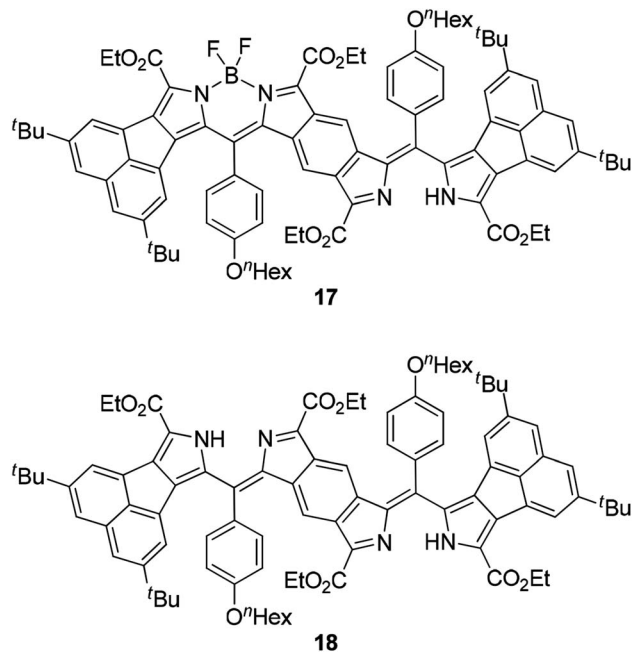


Fig. 7 Mono- BF_2 derivative **17** and bisdipyrrin **18**.

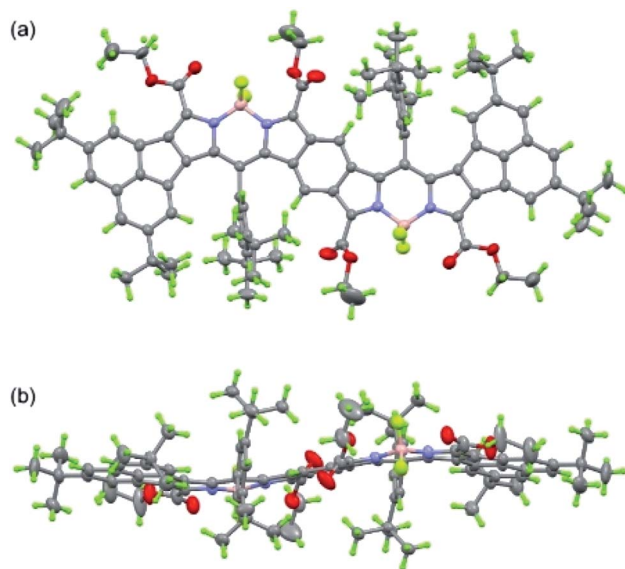


Fig. 6 Ortep drawing of **11b** (top (a) and side (b) views). The structure was refined by the Platon Squeeze technique. Disordered atoms with lower occupancies and refined acetonitrile are omitted for clarity.

the mean planes of twelve BODIPY atoms ($121.1(1)^\circ$; Table 3). Contrary to almost flat structures of **10b** and **12b** (see Fig. S6 and S8[†]), the mixtures of **11c** and **17** adopted slightly waved conformation. The dihedral angle between the BODIPY mean planes was $9.64(4)^\circ$, and those between the mean planes and benzene moiety were $6.47(8)^\circ$ and $3.44(7)^\circ$. Dihedral angles between the ester and BODIPY planes are also listed in Table 3.

The values are rather large probably because of the steric effect of the acenaphtho moiety. This may be the reason for the differences in absorption mentioned earlier. Conjugation of the ester groups to the B-bisANBODIPY chromophore was thought to be poor. Thus, the HOMO and LUMO energy levels were not close enough.

We monitored the UV-vis-NIR spectra of B-bisANBODIPYs **10a**, **10b**, **11b**, **11c** and **12b** in order to test their stability (Fig. 8, S9 and S10[†]). We reported a smooth decomposition pattern showing new strong absorption (614 nm) and emission (619 nm) peaks in the case of tetramethyl B-bis(benzoBODIPY) **1a** (see Fig. S11 and S12[†]).¹⁴ The spectral feature was thought to be due to two benzoBODIPY chromophores, because strength of the absorption was similar to that of **1a**. Moreover, the decomposition was suppressed by protection either from oxygen or light. Taking these facts into an account, singlet oxygen was thought to attack the center benzene moiety forming an *endo*-peroxide species, although decomposition of a BODIPY chromophore by singlet oxygen was reported to proceed by initial attack at its $\text{C}^8\text{-C}^{8a}$ bond forming a dioxetane species.²³ Contrary to the B-bis(benzoBODIPY)s **1**,¹⁴ tetracyano derivative **12b** was revealed to decompose faster than the other derivatives. As Fig. 8c shows, the absorption spectra of tetracyano derivative **12b** only decreased in intensity and no obvious other peak emerged. On the other hand, a new absorption peak slowly appeared at 650 nm in the case of tetramethyl derivative **10a**, similarly to the case of B-bis(benzoBODIPY). In the cases of tetra(ethoxycarbonyl) derivatives **11b** and **11c**, the peaks at 745 nm accompanying with the longest-wavelength absorption maxima (835 and 836 nm) increased (Fig. 8a) and then decreased. After 84 days, the longest-wavelength absorptions completely disappeared and the new large absorptions



Table 3 Dihedral angles in bisANBODIPY tetraesters

	BCOD-bisANBODIPY 8b		B-bisANBODIPY		
	BODIPY-1	BODIPY-2	11b ^a	11c and 17 ^b	
	BODIPY-1	BODIPY-2	BODIPY	BODIPY-1	BODIPY-2 ^c
Benzene	121.1(1) ^d		7.29(8)°	6.47(8)°	3.44(7)°
Proximal ester [occupancy]	29.72(6)° [1.00]	52.09(7)° [1.00]	55.06(3)°	14.91(2)° [0.75] 34.52(4)° [0.25]	10.70(2)° [1.00]
Distal ester [occupancy]	26.69(9)° [0.59] 21.32(10)° [0.41]	29.63(6)° [1.00]	17.81(4)°	24.76(2)° [0.75] 5.57(5)° [0.25]	11.98(3)° [1.00]

^a Compound **11b** occupies a special position (−1). ^b The crystal consisted of ca. 75% of **17** and 25% of **11c**. ^c This BODIPY part consisted of ca. 75% of dipyrin and 25% of BODIPY. ^d The dihedral angle between two BODIPY parts.

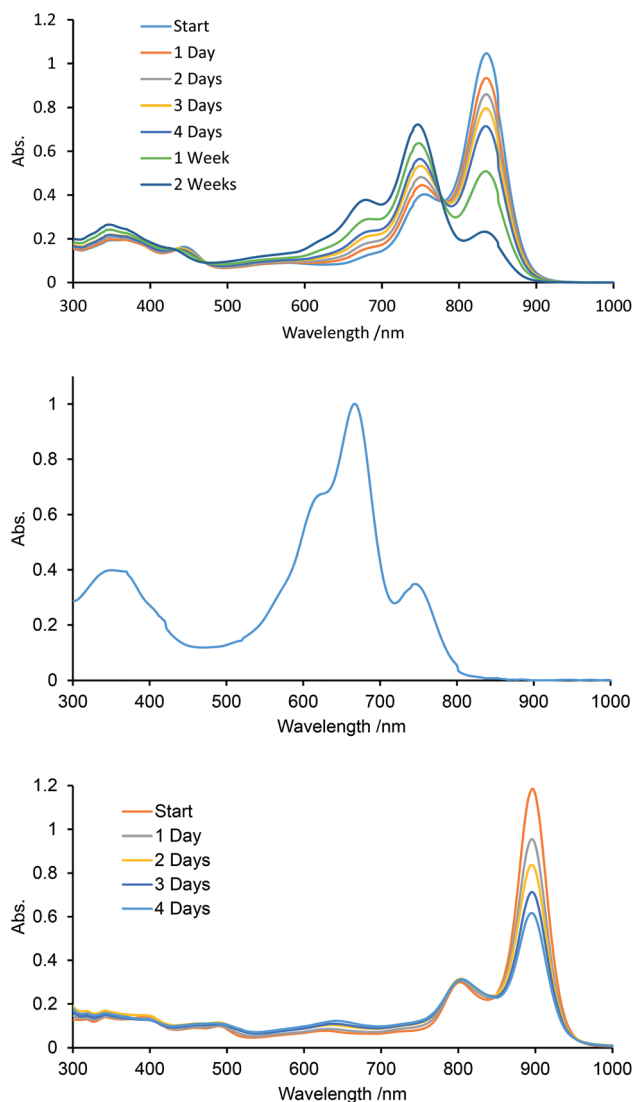


Fig. 8 UV-vis-NIR monitoring of **11c** (upper: after 1–14 days and middle: after 84 days) and **12b** (bottom: after 1–4 days) in spectroscopic-grade CH_2Cl_2 .

appeared at 666 and 620 nm (Fig. 8b). The absorption maxima at 745 and 666 nm were determined to be due to mono-BF₂

derivative **17** and bisdipyrin **18**, respectively, by diagnosis of the X-ray analysis (*vide ante*) and mass spectroscopies (Fig. S14[†]). This decomposition pattern of tetra(ethoxycarbonyl) derivatives was hydrolysis and was different from that of tetramethyl derivatives. As the single crystals of **12b** were obtained from the anhydrous solvent system (*vide ante*), the first decomposition step of **12b** was also thought to be hydrolysis. Substitution of electron-withdrawing groups such as cyano and ethoxycarbonyl groups at 3- and 5-positions of 4-bora-3a,4a-diaza-s-indacene skeleton made the BODIPY chromophore labile toward hydrolysis, although the pristine difluoro BODIPY was robust toward hydrolysis under neutral conditions.²⁴ Alkyl and/or aryl substituted BODIPYs was only hydrolyzed to dipyrins under strongly acidic or basic conditions.²⁵

Next, B-bisANBODIPYs **10a**, **10b**, **11b**, **11c** and **12b** were subjected to a cyclic voltammetry experiment (results are summarized in Table 4). In all cases, one reversible oxidation and two reversible reduction peaks were observed. The oxidation half-wave potentials ($E_{1/2}$) of **10b**, **11b**, **11c** and **12b** were 0.472, 0.922, 0.944 and 1.273 V, respectively. These values were sufficiently high for resisting oxidation by air. Therefore, the smooth decomposition observed with tetra(ethoxycarbonyl) and tetracyano derivatives could not be ascribed to oxidation. In the case of tetra(ethoxycarbonyl) derivatives **11b** and **11c**, the decomposition could be due to hydrolysis of the difluoro-diazaborindine to dipyrin moieties by moisture in the spectroscopic-grade dichloromethane. The spectrum after four days was similar to that of the mother liquor obtained in the

Table 4 CV data for B-bisANBODIPYs^a

B-bis(ANBODIPY)	$E_{1/2}/\text{V}$			
	2nd Ox.	1st Ox.	1st Red.	2nd Red.
10b	0.903	0.472	−1.040	−1.401
11b	—	0.922	−0.528	−0.874
11c	—	0.940	−0.505	−0.854
12b	—	1.273	−0.083	−0.499

^a The measurement was performed in CH_2Cl_2 by using Pt as electrodes, Ag/Ag⁺ reference electrode, tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte, and Fc^{+/0}/Fc as a standard.



case of single-crystal synthesis of **11c**, and the amounts of **11b** and **11c** almost did not decrease in the dehydrated solvents. Moreover, mass peaks due to the corresponding mono-hydrolyzed products were observed in the MS spectra of **11b**, **11c** and **12b**. Although the decomposition pathway of **12b** was ambiguous at that time, we believed that the first stage of decomposition was hydrolysis.

Conclusion

We prepared B-bisANBODIPYs with very strong NIR absorption. The strength of other absorptions in the visible region was less than 15% relative to that of the corresponding absorption maximum at the longest wavelength. Although B-bisANBODIPYs with electron-withdrawing groups were rather labile toward hydrolysis, they proved to be robust toward oxidation by air. Therefore, B-bisANBODIPYs are promising candidates for stable NIR-selective dyes in non-aqueous media such as resins.

Experimental

General

Melting points were measured on a Büchi M-565 apparatus and were uncorrected. NMR spectra were obtained with an AL-400 spectrometer at ambient temperature by using CDCl₃ as a solvent and tetramethylsilane as an internal standard for ¹H and ¹³C, unless otherwise indicated. IR spectra were obtained on a Thermo Scientific Nicolet iS5 FT-IR spectrometer with an iD5 ATR diamond plate. UV-vis-NIR and fluorescence spectra were recorded on Jasco V-570 and Hitachi F-4500 spectrophotometers, respectively. Absolute quantum yields were measured with a Hamamatsu Photonics C 9920-03G spectrophotometer. Mass spectra were obtained either with a JEOL JMS-700 (EI, 70 eV; FAB⁺, *p*-nitrobenzyl alcohol) or with a JEOL JMS-S3000 (MALDI-TOF). Elemental analyses were performed with a Yanaco MT-5 elemental analyzer at ADRES, Ehime University. Preparative GPC using LC-911 or LC-916 with Jaigel-1H and 2H was performed by Japan Analytical Industry Ltd. Co. Dehydrated solvents were purchased from Kanto Chemical Co. and used without further purification. Commercially available materials were used without further purification.

X-ray measurement

X-ray measurements of the single crystals at −173 °C were done with Rigaku VariMax Saturn-724 (1.2 kW Mo rotating anode) or a Rigaku VariMax R-AXIS Rapid (1.2 kW Cu rotating anode). Single crystals for X-ray analysis were obtained by the diffusion method: compounds in a soluble solvent were placed in a vapor of a poor solvent. The X-ray diffraction data were processed by using Crystal Clear 1.6.3 or Rapid Auto followed by Crystal Structure Ver. 4.2.5.²⁶ Structures were solved by using the processed data with SIR-2004 or SIR-2011,²⁷ and then refined by Shelxl-64 (Shelx-2013).²⁸ Final structures were validated by Platon CIF check.²⁹

Ethyl 2,5-bis(1,1-dimethylethyl)-9-formyl-8*H*-acenaphtho[1,2-*c*]pyrrole-7-carboxylate (**3a**)

POCl₃ (1.9 mL, 23.6 mmol) was added to dry DMF (2.2 mL, 24.5 mmol) at 0 °C under an argon atmosphere, and the mixture was stirred at rt for 30 min. After acenaphthopyrrole **2** (ref. 18) (6.22 g, 16.6 mmol) in dry CH₂Cl₂ (115 mL) was added at rt, the mixture was stirred for 90 min. The reaction was quenched by addition of an aqueous saturated solution of sodium acetate (16 mL) and then the mixture was stirred for 30 min. The organic layer was separated and the aqueous layer was extracted with CHCl₃. The combined organic layer was washed with an aqueous saturated solution of NaHCO₃, water and brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residual solid was triturated in hexane to give 6.52 g (16.2 mmol, 98%) of the title compound as a pale yellow powder: mp 230–233 °C (decomp.); ¹H NMR δ 10.20 (s, 1H), 9.55 (br s, 1H), 8.25 (d, *J* 1.4 Hz, 1H), 8.02 (d, *J* 1.4 Hz), 7.82 (d, *J* 1.4 Hz, 1H), 7.78 (d, *J* 1.4 Hz, 1H), 4.55 (d, *J* 7.2 Hz, 2H), 1.60 (t, *J* 7.2 Hz, 3H), 1.50 (s, 18H); ¹³C NMR δ 179.1, 161.0, 151.5, 151.2, 137.1, 134.2, 133.7, 130.4, 130.0, 129.7, 126.4, 122.6, 122.2, 122.0, 120.9, 120.1, 61.7, 35.6, 35.5, 31.7, 31.6, 14.7; IR ν_{max} 3263, 2963, 1682, 1664 cm^{−1}; MS (FAB⁺) *m/z* 404 [M⁺ + 1], 403 [M⁺]. Anal. calcd for C₂₆H₂₉NO₃ + 1/5H₂O: C, 76.70; H, 7.28; N, 3.44. Found; C, 76.68; H, 7.24; N, 3.31%.

Ethyl 2,5-bis(1,1-dimethylethyl)-9-{3',5'-bis(1'',1''-dimethylethyl)benzoyl}-8*H*-acenaphtho[1,2-*c*]pyrrole-7-carboxylate (**3b**)

To a stirred solution of 3,5-bis(1,1-dimethylethyl)benzoic acid (11.1 g, 45.0 mmol) in dry CH₂Cl₂ (30 mL) was added trifluoroacetic anhydride (6.64 mL, 47.4 mmol) at rt under an argon atmosphere, and the mixture was stirred for 15 min. After trifluoroacetic acid (8.53 mL, 111.5 mmol) was added and stirred for an additional 5 min, acenaphthopyrrole **2** (5.94 g, 15.8 mmol) in dry CH₂Cl₂ was added and the mixture was stirred for 3 days. After the reaction was quenched with a saturated aqueous solution of NaHCO₃, the mixture was extracted with CHCl₃. The organic extract was washed with a saturated aqueous solution of NaHCO₃, water and brine, dried over Na₂SO₄, and concentrated *in vacuo*. The residual solid was triturated in MeOH to give 7.49 g (12.7 mmol; 80%) of the title compound as a pale yellow powder: mp 252–255 °C; ¹H NMR δ 9.56 (br s, 1H), 8.27 (s, 1H), 7.74–7.72 (m, 4H), 7.65 (s, 1H), 6.72 (s, 1H), 4.56 (q, *J* 7.2 Hz, 2H), 1.60 (t, *J* 7.2 Hz, 3H), 1.49 (s, 9H), 1.31 (s, 18H), 1.21 (s, 9H); ¹³C NMR δ 188.5, 160.9, 151.6, 151.0, 150.6, 138.7, 135.1, 134.4, 133.9, 130.5, 130.5, 129.5, 126.6, 126.3, 123.1, 122.1, 121.8, 121.7, 121.6, 118.8, 61.4, 35.5, 35.2, 35.0, 31.6, 31.5, 31.3, 14.7; IR ν_{max} 3238, 2961, 1720, 1626 cm^{−1}; MS (FAB⁺) *m/z* 592 [M⁺ + 1], 591 [M⁺]. Anal. calcd for C₄₀H₄₉NO₃ + 1/3H₂O: C, 80.36; H, 8.37; N, 2.34. Found; C, 80.42; H, 8.33; N, 2.37%.

Ethyl 2,5-bis(1,1-dimethylethyl)-9-(4-(hexyloxy)benzoyl)-8*H*-acenaphtho[1,2-*c*]pyrrole-7-carboxylate (**3c**)

The reaction of 4-(hexyloxy)benzoic acid (3.35 g, 15.0 mmol) and **2** (1.92 g, 5.00 mmol) was performed according to the



procedure described above to give 2.80 g (4.82 mmol, 80%) of the title compound as a gray powder: mp 162–164 °C (decomp.); ¹H NMR δ 9.63 (s, 1H), 8.28 (d, *J* 1.3 Hz, 1H), 7.98 (m, 2H), 7.72 (d, *J* 1.3 Hz, 1H), 7.66 (d, *J* 1.3 Hz, 1H), 7.01 (m, 2H), 6.83 (d, *J* 1.3 Hz, 1H), 4.55 (q, *J* 7.2 Hz, 2H), 4.04 (t, *J* 6.4 Hz, 2H), 1.84 (m, 2H), 1.60 (t, *J* 7.2 Hz, 3H), 1.52–1.46 (m, 11H), 1.40–1.32 (m, 4H), 1.24 (s, 9H), 0.93 (t, *J* 7.2 Hz, 3H); ¹³C NMR δ 185.8, 163.1, 160.9, 151.2, 150.7, 134.2, 133.9, 133.8, 131.6, 130.8, 130.7, 130.4, 129.5, 126.2, 121.9, 121.9, 121.7, 121.6, 118.7, 114.6, 68.2, 61.4, 35.5, 35.3, 31.6, 31.5, 31.3, 29.1, 25.7, 22.6, 14.7, 14.0; IR ν_{max} 3290, 2950, 2925, 2866, 1687, 1634 cm⁻¹; MS (MALDI-TOF) *m/z* 582.9, 581.9, 580.9, 579.9; Anal. calcd for C₃₈H₄₅NO₄ + 1/7H₂O: C, 78.37; H, 7.84; N, 2.41. Found: C, 78.36; H, 7.77; N, 2.43%.

Ethyl 9-acetoxymethyl-2,5-bis(1,1-dimethylethyl)-8H-acenaphtho[1,2-*c*]pyrrole-7-carboxylate (4a)

To a stirred solution of **3a** (7.26 g, 18.0 mmol) in a mixture of dry THF (180 mL) and dry EtOH (60 mL) was added NaBH₄ (2.44 g, 64.5 mmol) at 0 °C under an argon atmosphere, and the mixture was allowed to warm to rt. After 2 h, water was added and the mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residual solid was triturated in hexane to give a quantitative amount of ethyl 9-hydroxymethyl-2,5-(1,1-dimethylethyl)-8H-acenaphtho[1,2-*c*]pyrrole-7-carboxylate as a pale yellow powder: mp 228–231 °C (decomp.); ¹H NMR δ 9.32 (br s, 1H), 8.17 (d, *J* 1.4 Hz, 1H), 7.70 (d, *J* 1.4 Hz, 1H), 7.63 (m, 2H), 5.56 (d, *J* 5.7 Hz, 2H), 4.49 (q, *J* 7.2 Hz, 2H), 2.39 (br s, 1H), 1.58 (t, *J* 7.2 Hz, 3H), 1.46 (s, 18H) IR ν_{max} 3432, 3196, 2961, 1662 cm⁻¹; MS (MALDI-TOF) *m/z* 407.8 [M⁺ + 2], 406.7 [M⁺ + 1], 405.7 [M⁺]. Anal. calcd for C₂₆H₃₁NO₃: C, 77.01; H, 7.71; N, 3.45. Found: C, 76.84; H, 7.68; N, 3.43%. The hydroxymethyl derivative (7.30 g, 18.0 mmol) and DMAP (0.338 g, 2.77 mmol) were dissolved in CHCl₃ (252 mL) under an argon atmosphere and then Ac₂O (17.1 mL, 180 mmol) was added with stirring. After 30 min, water was added. The organic layer was separated and the aqueous phase was extracted with CHCl₃. The organic phase was washed with an aqueous saturated solution of NaHCO₃ (three times), water and brine, dried over anhydrous Na₂SO₄, and concentrated. The residual solid was triturated in ether to give 7.44 g (16.6 mmol, 92%) of the title compound as a pale yellow powder: mp 195 °C (decomp.); ¹H NMR δ 9.05 (br s, 1H), 8.18 (d, *J* 1.4 Hz, 1H), 7.73 (d, *J* 1.4 Hz, 1H), 7.70 (d, *J* 1.4 Hz, 1H), 7.66 (d, *J* 1.4 Hz, 1H), 5.40 (s, 2H), 4.49 (q, *J* 7.2 Hz, 1H), 2.16 (s, 3H), 1.58 (t, *J* 7.2 Hz, 3H), 1.47 (s, 9H), 1.46 (s, 9H); ¹³C NMR δ 171.4, 161.5, 151.2, 150.9, 134.3, 133.5, 131.4, 131.3, 129.7, 129.6, 123.7, 121.4, 121.3, 120.3, 118.1, 115.4, 60.9, 58.2, 35.5, 35.5, 31.7, 31.6, 20.9, 14.8; IR ν_{max} 3257, 2951, 1734, 1673 cm⁻¹; MS (FAB⁺) *m/z* 447 [M⁺], 388 [M - (CH₃CO₂⁻)]. Anal. calcd for C₂₈H₃₃NO₄: C, 75.14; H, 7.43; N, 3.13. Found: C, 75.20; H, 7.31; N, 3.20%.

Ethyl 9-(1'-acetoxy-3,5-bis(1'',1''-dimethylethyl)benzyl)-2,5-bis(1,1-dimethylethyl)-8H-acenaphtho[1,2-*c*]pyrrole-7-carboxylate (4b)

The reaction of **3b** (5.91 g, 10.0 mmol) with NaBH₄ (1.26 g 33.3 mmol) was carried out according to the procedure described above

to afford a quantitative amount of ethyl 9-(1'-hydroxy-{3,5-bis(1'',1''-dimethylethyl)benzyl}-2,5-bis(1,1-dimethylethyl)-8H-acenaphtho[1,2-*c*]pyrrole-7-carboxylate) as a pale yellow powder: mp 224–226 °C; ¹H NMR δ 9.40 (br s, 1H), 8.19 (s, 1H), 7.64 (s, 1H), 7.49 (s, 1H), 7.46 (s, 1H), 7.40 (s, 1H), 6.54 (s, 1H), 6.10 (s, 1H), 4.48 (q, *J* 7.2 Hz, 2H), 1.57 (t, *J* 7.2 Hz, 3H), 1.46 (s, 9H), 1.25 (s, 18H), 1.22 (s, 9H); ¹³C NMR δ 151.6, 150.8, 150.4, 140.1, 134.2, 131.7, 131.5, 129.3, 126.4, 123.1, 122.1, 121.13, 122.10, 119.4, 118.8, 113.8, 72.0, 60.7, 35.5, 35.2, 34.9, 31.7, 31.5, 31.4, 14.9, and three sp² carbon signals were not identified due to overlap; IR ν_{max}/cm⁻¹ 3384 (br), 2951, 1660; MS (MALDI-TOF) *m/z* 595.7, 594.9, 593.8. Anal. calcd for C₄₀H₅₁NO₃: C, 80.90; H, 8.66; N, 2.36. Found: C, 80.76; H, 8.55; N, 2.35%. Acetylation of the alcohol (5.93 g, 10 mmol) was performed according to the procedure described above to give 4.40 g (6.92 mmol, 69%) of the title compound as a pale yellow powder: mp 187 °C (decomp.); ¹H NMR δ 8.92 (br s, 1H), 8.19 (s, 1H), 7.68 (s, 1H), 7.58 (s, 1H), 7.44 (s, 1H), 7.41 (s, 2H), 7.20 (s, 1H), 7.12 (s, 1H), 4.49 (q, *J* 7.2 Hz, 2H), 2.21 (s, 3H), 1.58 (t, *J* 7.2 Hz, 3H), 1.47 (s, 9H), 1.33 (s, 9H), 1.26 (s, 18H); ¹³C NMR δ 170.1, 161.5, 151.4, 151.0, 150.7, 136.5, 134.4, 134.2, 131.6, 131.4, 129.6, 128.2, 127.9, 123.0, 121.9, 121.2, 120.0, 119.2, 114.5, 71.73, 60.8, 35.5, 35.4, 34.9, 31.7, 31.7, 31.4, 21.2, 14.8; IR ν_{max} 3286, 2959, 1748, 1658 cm⁻¹; MS (FAB⁺) *m/z* 636 [M⁺ + 1], 576 [M - (CH₃CO₂⁻)]. Anal. calcd for C₄₂H₅₃NO₄: C, 79.33; H, 8.40; N, 2.20. Found: C, 79.13; H, 8.51; N, 2.21%.

Ethyl 9-(1'-acetoxy-4-hexyloxybenzyl)-2,5-bis(1,1-dimethylethyl)-8H-acenaphtho[1,2-*c*]pyrrole-7-carboxylate (4c)

The reaction of **3c** (2.80 g, 4.82 mmol) with NaBH₄ (1.13 g, 28.3 mmol) was carried out according to the procedure described above to afford a quantitative amount of ethyl 2,5-bis(1,1-dimethylethyl)-9-(1'-hydroxy-4-hexyloxybenzyl)-8H-acenaphtho[1,2-*c*]pyrrole-7-carboxylate as a gray powder: mp 193–197 °C (decomp.); ¹H NMR δ 9.29 (s, br, 1H), 8.19 (m, 1H), 7.64 (m, 1H), 7.50 (m, 1H), 7.47 (m, 2H), 6.92 (m, 2H), 6.44 (m, 1H), 6.06 (d, *J* 4.5 Hz, 1H), 4.50 (q, *J* 7.2 Hz, 2H), 3.93 (t, *J* 6.7 Hz, 2H), 2.43 (d, *J* 4.5 Hz, 1H), 1.77 (m, 2H), 1.59 (t, *J* 7.2 Hz, 3H), 1.48–1.42 (m, 11H), 1.40–1.30 (m, 4H), 1.24 (s, 9H), 0.91 (t, *J* 7.1 Hz, 3H); ¹³C NMR δ 159.7, 150.9, 150.6, 134.0, 133.2, 131.7, 131.4, 129.4, 126.3, 121.2, 119.3, 119.0, 114.9, 113.8, 70.9, 67.9, 60.7, 35.5, 35.2, 31.7, 31.5, 31.3, 29.2, 25.7, 22.6, 14.9, 14.0, and five sp² carbon signals were not identified due to overlap; IR ν_{max} 3378, 3205, 2956, 2872, 1665 cm⁻¹; MS (MALDI-TOF) *m/z* 581.9 [M⁺], 564.9 [M⁺ - OH]. Anal. calcd for C₃₈H₄₇NO₄: C, 78.45; H, 8.14; N, 2.41. Found: C, 78.39; H, 8.06; N, 2.40%. Acetylation of the alcohol (2.80 g, 4.82 mmol) was performed according to the procedure described above to give 1.96 g (3.11 mmol, 65%) of the title compound as a pale yellow powder: mp 187 °C (decomp.); ¹H NMR δ 9.06 (s, br, 1H), 8.18 (m, 1H), 7.66 (m, 1H), 7.55 (m, 1H), 7.48 (d, *J* 8.7 Hz, 2H), 7.14 (m, 1H), 6.90 (d, *J* 8.7 Hz, 2H), 6.69 (m, 1H), 4.50 (q, *J* 7.2 Hz, 2H), 3.92 (t, *J* 6.4 Hz, 2H), 2.20 (s, 3H), 1.76 (m, 2H), 1.59 (t, *J* 7.2 Hz, 3H), 1.50–1.40 (m, 11H), 1.35–1.30 (m, 4H), 1.29 (s, 9H), 0.90 (t, *J* 6.7 Hz, 3H); ¹³C NMR δ 170.2, 161.7, 159.6, 150.9, 150.7, 134.2, 134.2, 131.5, 131.2, 129.5, 129.3, 129.3, 129.3, 128.3, 127.9, 121.3, 121.2, 119.8, 119.5, 114.7, 114.5, 71.2, 67.8, 60.9, 35.5, 35.3, 31.6, 31.5, 31.4, 29.2, 25.7, 22.5, 21.2, 14.8, 14.0; IR ν_{max} 3272, 2953, 1695,



1673, 1225 cm^{-1} ; MS (FAB⁺) m/z 623 [M⁺], 564 [M - (CH₃CO₂⁻)]. Anal. calcd for C₄₀H₄₉NO₄: C, 77.01; H, 7.92; N, 2.25. HRMS (FAB⁺): calcd for C₄₀H₄₉NO₅, 623.3611. Found 623.3587.

General procedure for BCOD-fused bis(dipyrromethane) tetracarboxylates

To a stirred solution of acenaphthopyrrole-7-carboxylate **4** (2.0 mmol) and BCOD-fused dipyrrole ester **5** (0.3328 g, 1.05 mmol) in acetic acid (20 mL) was added *p*-toluenesulfonic acid monohydrate (119 mg, 0.56 mmol) at rt, and the mixture was stirred for 3 h. After the reaction was quenched with water, the mixture was extracted with EtOAc. The organic extract was washed with an aqueous saturated NaHCO₃ (three times), water and brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residual solid was triturated to give a diastereomeric mixture of BCOD-fused bis(dipyrromethane) derivative as a cream-yellow powder.

Bis(dipyrromethane)tetracarboxylate **6a** was obtained in 63% yield (0.724 g, 0.66 mmol) from **4a** (0.897 g, 2.0 mmol) and **5** (0.3328 g, 1.05 mmol) as a cream powder: MS (FAB⁺) m/z 1102.6, 1074.6, 1057.5. Further identification was not performed because of the low solubility.

Bis(3,5-di-*tert*-butylphenyl)-substituted bis(dipyrromethane)tetracarboxylate **6b** was obtained in 58% yield (0.429 g, 0.291 mmol) from **4b** (0.647 g, 1.02 mmol) and **5** (0.164 g, 0.502 mmol) as a white powder: mp > 250 °C (decomp.); ¹H NMR δ 8.54 (br s, 2H), 8.19 (m, 2H), 8.11 (m, 2H), 7.63 (m, 2H), 7.47 (m, 2H), 7.25 (m, 2H), 7.18 (m, 4H), 6.54 (m, 2H), 5.87 (m, 2H), 4.44–3.90 (m, 10H), 1.46–1.19 (m, 88H); ¹³C NMR (typical signals) δ 151.8, 150.9, 150.5, 137.1, 134.1, 131.9, 131.6, 129.4, 129.0, 127.2, 126.5, 122.8, 122.0, 121.1, 119.3, 118.5, 113.9, 113.8, 60.5, 89.9, 43.4, 35.5, 35.2, 34.9, 31.7, 35.2, 34.9, 31.7, 31.5, 31.3, 30.8, 14.6, 14.1; IR ν_{max} 3452, 3335, 2960, 2904, 2867, 1697, 1659 cm^{-1} ; MS (MALDI-TOF) m/z 1480, 1479, 1453, 1452, 1451. Anal. calcd for C₉₈H₁₁₈N₄O₈: C, 79.53; H, 8.04; N, 3.79. Found: C, 79.50; H, 8.24; N, 3.76%.

Bis(4-hexyloxyphenyl)-substituted bis(dipyrromethane)tetracarboxylate **6c** was obtained in 75% yield (1.69 g, 1.16 mmol) from **4c** (1.89 g, 3.0 mmol) and **5** (0.504 g, 1.55 mmol) as a white powder: mp > 250 °C (decomp.); ¹H NMR δ 8.43–8.39 (s, 1H), 8.29–8.18 (m, 4H), 7.64 (m, 2H), 7.51–7.48 (m, 2H), 7.35–7.29 (m, 5H), 6.87–6.82 (m, 4H), 6.37–6.28 (m, 2H), 5.65–5.62 (m, 2H), 4.45–4.35 (m, 6H), 4.15–4.09 (m, 4H), 3.91 (m, 4H), 3.93–3.89 (m, 4H), 1.80–1.72 (m, 4H); ¹³C NMR (diastereomer mixture, typical signals) δ 161.6, 158.9, 158.9, 150.9, 150.8, 150.8, 150.7, 150.7, 137.5, 134.1, 134.0, 132.0, 131.9, 131.9, 131.4, 131.3, 130.5, 130.2, 130.2, 130.0, 130.0, 129.9, 129.7, 129.5, 129.5, 128.4, 128.4, 128.3, 127.7, 127.6, 127.5, 127.4, 121.3, 121.1, 119.6, 119.4, 118.8, 115.3, 114.1, 113.8, 113.4, 113.3, 68.0, 67.9, 60.7, 60.7, 60.6, 60.1, 59.9, 43.1, 43.0, 42.6, 35.5, 35.2, 35.2, 35.2, 31.7, 31.6, 31.4, 31.4, 31.2, 31.1, 30.7, 29.2, 27.3, 27.1, 25.7, 22.6, 14.8, 14.8, 14.7, 14.4, 14.3, 14.3, 14.0; IR ν_{max} 3434, 3305, 2954, 1692, 1663, 1240 cm^{-1} ; MS (FAB⁺) m/z 1455 [M⁺]. HRMS (FAB⁺): calcd for C₉₄H₁₁₀N₄O₁₀⁺, 1454.8222. Found: 1454.8247.

General procedure for BF₂ complexation of bis(dipyrromethane)

To a stirred solution of BCDO-fused bis(dipyrromethane) (0.5 mmol) in dry CH₂Cl₂ (30 mL) was added DDQ (0.379 g, 1.20 mmol) at room temperature in the dark. After the mixture was stirred for 1 h, (i-Pr)₂EtN (3.0 mL, 20 mmol) was added and the mixture was stirred for 10 min at rt. BF₃·OEt₂ (3.0 mL, 23 mmol) was added and the mixture was stirred for 2 h at rt. The reaction was quenched with water, and the mixture was filtered through a Celite pad, which was washed with EtOAc. The filtrate was extracted with EtOAc. The combined organic extract was washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residual solid was purified by chromatography on silica gel (CH₂Cl₂) and preparative GPC.

BCOD-bisANBODIPY **7a**

To a stirred solution of **6a** (0.173 g, 0.157 mmol) in dry THF (10 mL), LiAlH₄ (0.179 g, 4.72 mmol) was added at rt in the dark. The mixture was then heated to reflux for 3 h. After cooling to 0 °C, the reaction was quenched by slow addition of an aqueous saturated sodium tartrate. The mixture was filtered through a Celite pad, which was washed with EtOAc. The filtrate was extracted with EtOAc. The combined organic phase was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residual material was filtered with CH₂Cl₂ through a short silica-gel column, and the filtrate was concentrated *in vacuo* to give 0.051 g (0.0585 mmol, 37%) of tetramethyl bis(dipyrromethane), which was used without further purification. The complexation with BF₂ was performed according to the general procedure to provide 0.028 g (0.0156 mmol, 27%) of **7a** as a reddish purple powder: mp 170 °C (decomp.); ¹H NMR (CD₂Cl₂) δ 7.99 (s, 2H), 7.76 (s, 2H), 7.69 (s, 2H), 7.62 (s, 2H), 7.55 (s, 2H), 4.59 (s, 2H), 2.78 (s, 6H), 2.59 (s, 6H), 1.84–1.66 (m, 4H), 1.45 (s, 18H), 1.38 (s, 18H); UV-vis-NIR (CH₂Cl₂) λ_{max} [relative int.] 486 [0.13], 580 [sh, 0.27], 624 [1.00] nm; fluorescence (CH₂Cl₂) λ_{max} 631 nm (excitation 600 nm; $\Phi = 0.4$); IR ν_{max} 2954, 2926, 2865 cm^{-1} ; MS (FAB⁺) m/z 963, 935; HRMS calcd for C₆₂H₆₄B₂F₄N₄: 962.5253. Found: 962.5238.

BCOD-bisANBODIPY with four methyl and two 3,5-di-*tert*-butylphenyl group **7b**

The reduction of **6b** (0.100 g, 0.090 mmol) with LiAlH₄ (0.170 g, 4.72 mmol) was carried out according to the procedure described above to afford 0.079 g of crude bis(dipyrromethane) with four methyl and two 3,5-di-*tert*-butylphenyl groups, which was used without further purification. Complexation with BF₂ was performed according to the general procedure to give 0.043 g (0.032 mmol, 35%) of **7b** as a reddish purple powder: mp 200 °C (decomp.); ¹H NMR (CD₂Cl₂) δ 7.86 (m, 2H), 7.75 (m, 2H), 7.67 (m, 2H), 7.63 (m, 2H), 7.55 (s, 2H), 7.38 (s, 2H), 5.75 (s, 2H), 3.13 (s, 2H), 2.96 (s, 6H), 2.18 (s, 6H), 1.63 (m, 4H), 1.53 (s, 9H), 1.48 (s, 9H), 1.29 (s, 9H), 1.21 (s, 9H); ¹³C NMR δ 152.9, 151.1, 151.0, 150.9, 149.8, 149.3, 148.3, 145.2, 141.4, 137.1, 136.3, 135.1, 133.0, 131.9, 131.2, 129.2, 128.9, 128.7, 128.2, 124.9, 124.0, 123.2, 122.5, 120.8, 118.3, 35.5, 35.4, 32.0, 31.6, 31.6, 31.5,



29.7, 28.5, 14.4, 12.5; UV-vis-NIR (CH_2Cl_2 , $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$) λ_{max} 488 (2.48), 580 (sh, 4.81), 621 (20.1) nm; fluorescence (CH_2Cl_2) λ_{max} 640 nm (excitation 580 nm; $\Phi = 0.53$); IR ν_{max} 2957, 1491, 1150, 1012 cm^{-1} ; MS (FAB⁺) m/z 1340 [$\text{M}^+ + 1$], 1311 [$\text{M}^+ - \text{C}_2\text{H}_4$]; HRMS calcd for $\text{C}_{90}\text{H}_{104}\text{B}_2\text{F}_4\text{N}_4$: 1338.8383. Found: 1338.8337. Anal. calcd for $\text{C}_{90}\text{H}_{104}\text{B}_2\text{F}_4\text{N}_4 + \text{CH}_3\text{CN} + 2\text{H}_2\text{O}$: C, 78.01; H, 7.90; N, 4.94. Found: C, 77.90; H, 8.40; N, 4.99%. Single crystals were obtained by diffusion of hexane into a chloroform solution of **7b**. CCDC No. 1821923.

BCOD-bisANBODIPY with four ethoxycarbonyl and two 3,5-di-*tert*-butylphenyl groups **8b**

The complexation of **6b** (0.213 g, 0.14 mmol) with BF_2 was performed according to the general procedure to give 0.155 g (0.0986 mmol, 70%) of **8b** as a reddish purple powder: mp 230 °C (decomp.); ¹H NMR δ 8.21 (d, J 1.4 Hz, 2H), 7.87 (m, 2H), 7.70 (m, 2H), 7.69 (m, 2H), 7.46 (m, 2H), 7.31 (m, 2H), 5.70, (d, J 1.4 Hz, 2H), 4.61, (m, 4H), 4.35 (q, J 7.1 Hz, 4H), 3.84 (m, 2H), 1.60 (m, 4H), 1.56 (t, J 7.1 Hz, 6H), 1.51 (s, 18H), 1.45 (s, 18H), 1.43 (t, J 7.1 Hz, 6H), 1.22 (s, 18H), 1.20 (s, 18H); ¹³C NMR δ 161.1, 160.3, 153.3, 151.2, 150.8, 150.7, 150.7, 150.6, 147.8, 140.6, 139.1, 139.0, 137.2, 133.9, 133.5, 131.6, 131.2, 130.8, 129.5, 129.2, 126.0, 125.6, 125.2, 124.1, 122.6, 122.4, 121.5, 61.9, 61.5, 35.54, 35.52, 35.2, 35.1, 32.9, 32.0, 31.6, 31.4, 31.2, 28.5, 14.4, 13.9; UV-vis-NIR (CH_2Cl_2 , $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$) λ_{max} 351 (1.83), 422 (1.72), 535 (sh, 3.14), 625 (14.1) nm; fluorescence (CH_2Cl_2) λ_{max} 658 nm (excitation 610 nm; $\Phi = 0.07$); IR ν_{max} 2955, 2903, 2867, 1750, 1702 cm^{-1} ; MS (FAB⁺) m/z 1594 [$\text{M} + \text{Na}^+$], 1572 [$\text{M}^+ + 1$], 1552 [$\text{M} - \text{F}^-$], 1543 [$\text{M} + \text{H}^+ - \text{C}_2\text{H}_4$]; Anal. calcd for $\text{C}_{98}\text{H}_{112}\text{B}_2\text{F}_4\text{N}_4\text{O}_8$: C, 74.90; H, 7.18; N, 3.57. Found: C, 74.94; H, 7.39; N, 3.51%. Single crystals were obtained by diffusion of 2-propanol into a chloroform solution of **8b**. CCDC No. 1821927.

BCOD-bisANBODIPY with four ethoxycarbonyl and two 4-hexyloxyphenyl groups **8c**

The complexation of **6c** (0.400 g, 0.27 mmol) was performed according to the general procedure to afford 0.346 g (0.22 mmol, 80%) of **8c** as a reddish purple powder: mp 217 °C (decomp.); ¹H NMR δ 8.25 (d, J 1.2 Hz, 2H), 7.71 (s, 4H), 7.48 (m, 2H), 7.40 (m, 2H), 7.29 (m, 2H), 7.22 (m, 2H), 5.68 (m, 2H), 4.64 (q, J 7.2 Hz, 4H), 4.56–4.42 (m, 4H), 4.26–4.15 (m, 4H), 3.42 (br s, 2H), 1.97 (m, 4H), 1.61 (m, 4H), 1.59 (t, J 7.2, 6H), 1.54 (s, 18H), 1.49 (t, J 7.0 Hz, 6H), 1.48–1.42 (m, 12H), 1.23 (s, 18H) 0.98 (t, J 7.2 Hz, 6H); ¹³C NMR δ 161.3, 161.0, 160.9, 151.9, 151.3, 150.9, 148.9, 140.0, 139.4, 139.2, 138.8, 133.5, 131.6, 131.3, 130.8, 130.2, 129.5, 129.1, 127.3, 126.8, 124.9, 124.5, 122.9, 122.6, 116.7, 116.2, 68.2, 62.0, 61.8, 35.6, 35.5, 33.2, 31.7, 31.6, 31.6, 31.2, 29.4, 27.4, 26.0, 22.7, 14.4, 14.1; UV-vis-NIR (CH_2Cl_2 , $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$) λ_{max} 358 (1.35), 416 (1.82), 540 (3.10), 624 (12.1) nm; fluorescence (CH_2Cl_2) λ_{max} 665 nm (excitation 590 nm; $\Phi = 0.10$); IR ν_{max} 2654, 2933, 2867, 1748, 1704 cm^{-1} ; MS (FAB⁺) m/z 1586 [$\text{M} + \text{K}^+$], 1570 [$\text{M} + \text{Na}^+$], 1528 [$\text{M} - \text{F}^-$], 1519 [$\text{M} + \text{H}^+ - \text{C}_2\text{H}_4$]. Anal. calcd for $\text{C}_{94}\text{H}_{104}\text{B}_2\text{F}_4\text{N}_4\text{O}_{10} + \text{C}_6\text{H}_{14}$: C, 73.52; H, 7.28; N, 3.43. Found C, 73.82; H, 7.00; N, 3.72%.

BCOD-bisANBODIPY with four cyano and two 3,5-di-*tert*-butylphenyl groups **9b**

To a suspension of **6b** (0.4415 g, 0.29 mmol) in ethylene glycol (10 mL) was added NaOH (0.28 g, 7.0 mmol) under an argon atmosphere. The mixture was heated at 170 °C for 3 h in the dark. After the mixture was cooled to rt, water was added. The mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The residual solid was chromatographed on silica gel (40% EtOAc/hexane) to give the compound without esters, which was directly used without identification. This material was dissolved in a mixture of dry DMF (11 mL) and dry CH_3CN (4.5 mL) and then cooled to -50 °C. CSI (0.17 mL, 1.97 mmol) in acetonitrile (2 mL) was added dropwise at the same temperature. The mixture was stirred at -50 °C for 1.5 h and then at rt overnight. The reaction was quenched by addition of water, and the mixture was extracted with EtOAc. The organic extract was washed with an aqueous saturated NaHCO_3 solution, water and brine, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The residual material was chromatographed on silica gel (40% EtOAc/hexane) to give the tetracyano compound, which was directly used without identification. The complexation of the tetracyanide with BF_2 was achieved through the general procedure. The target BCOD-fused tetracyano bis(acenaphthoBODIPY) **9** was obtained in 5% yield (21 mg, 0.015 mmol) as a reddish purple powder: mp 200 °C (decomp.) ¹H NMR δ 8.10 (d, J 1.1 Hz, 2H), 8.00 (t, J 1.8 Hz, 2H), 7.86 (d, J 1.2 Hz, 2H), 7.83 (d, J 1.2 Hz, 2H), 7.51 (t, J 1.8 Hz, 2H), 7.32 (t, J 1.8 Hz, 2H), 5.90 (s, 2H), 3.54 (2H), 1.53 (s, 18H), 1.46 (m, 20H), 1.29 (m, 20H), 1.20 (s, 18H); ¹³C NMR δ 155.0, 152.2, 152.1, 151.9, 150.6, 149.3, 148.7, 142.2, 147.4, 133.1, 132.8, 132.6, 131.5, 130.0, 129.5, 127.5, 127.1, 126.7, 125.4, 124.7, 124.1, 122.0, 120.7, 119.2, 116.6, 111.5, 110.3, 35.7, 35.6, 35.6, 35.4, 32.3, 31.9, 31.5, 31.5, 31.3, 28.0; IR ν_{max} 2957, 2225, 1490, 1129, cm^{-1} ; UV-vis-NIR (CH_2Cl_2) [relative int.] λ_{max} 417 [0.17], 461 [0.20], 570 [sh, 0.36], 647 [1.00] nm; fluorescence (CH_2Cl_2) λ_{max} 707 nm (excitation 590 nm; $\Phi = 0.02$); IR ν_{max} 2957, 2225, 1490, 1129 cm^{-1} ; MS (FAB⁺) m/z 1383, 1364, 1355, 1338, 1336. Anal. calcd for $\text{C}_{90}\text{H}_{92}\text{B}_2\text{F}_4\text{N}_8 + 3\text{H}_2\text{O}$: C, 75.20; H, 6.87; N, 7.80. Found; C, 75.28; H, 6.69; N, 7.67%.

General procedure for thermal conversion of BCOD-bisANBODIPY to B-bisANBODIPY

BCOD-bisANBODIPY was weighed in a microtube, which was placed in a test tube. The test tube was evacuated by an oil rotary pump and placed in a glass tube oven, which was pre-heated at the indicated temperature. After the indicated time, the test tube was removed and cooled to rt. The conversion was quantitative.

B-bisANBODIPY **10a**

The conversion of **7a** (5.0 mg) was performed at 200 °C for 2 h to afford 4.9 mg (94%) of **10a** as a black powder: UV-vis-NIR [CH_2Cl_2 , relative int.] λ_{max} 348 [0.21], 433 [0.20], 475 [0.19], 746 [0.38], 828 [1.00] nm; FL (CH_2Cl_2) λ_{max} , 838 nm; MS (MALDI-



TOF) m/z 937.4, 936.3, 935.3; HRMS calcd for $C_{60}H_{60}B_2F_4N_4$: Me 934.4940. Found: Ma 934.4942.

B-bisANBODIPY 10b

The conversion of **7b** (4.3 mg) was performed at 200 °C for 2 h to afford 4.1 mg (97%) of **10b** as a black powder: mp > 300 °C (decomp.); 1H NMR δ 7.93 (t, $J = 1.7$ Hz, 2H), 7.69 (d, $J = 1.3$ Hz, 2H), 7.58 (d, $J = 1.3$ Hz, 2H), 7.55 (d, $J = 1.3$ Hz, 2H), 7.47 (d, $J = 1.8$ Hz, 4H), 5.90 (d, $J = 1.3$ Hz, 2H), 5.77 (s, 2H), 2.93 (s, 6H), 2.68 (s, 6H), 1.45 (s, 18H), 1.38 (s, 36H), 1.17 (s, 18H); ^{13}C NMR δ 158.3, 153.5, 150.9, 150.9, 143.0, 141.1, 136.1, 135.4, 134.0, 133.7, 133.3, 132.3, 131.8, 131.4, 129.9, 129.4, 127.0, 123.3, 123.1, 122.4, 122.0, 119.9, 117.4, 117.2, 35.5, 35.4, 35.3, 31.9, 31.7, 31.6, 14.1, 12.6; IR ν_{max} 2953, 1506, 1149, 1105 cm^{-1} ; UV-vis-NIR (CH_2Cl_2 , $\epsilon \times 10^{-4} M^{-1} cm^{-1}$) λ_{max} 348 (2.36), 430 (2.50), 472 (2.13), 744 (5.54), 818 (16.9) nm; FL (CH_2Cl_2) λ_{max} , 846 nm; MS (FAB $^+$) m/z 1311 ($M^+ + 1$); HRMS calcd for $C_{88}H_{100}B_2F_4N_4$: 1310, 8070. Found: 1310.8045. Anal. calcd for $C_{88}H_{100}B_2F_4N_4 + H_2O$: C, 79.51; H, 7.73; N, 4.21. Found: C, 79.27; H, 7.93; N, 4.29%. Single crystals were obtained by diffusion of acetonitrile into a dichloromethane solution of **10b**. CCDC No. 1821919.

B-bisANBODIPY 11b

The conversion of **8b** (5.0 mg) was performed at 250 °C for 30 min to afford 4.9 mg (98%) of **11b** as a black powder: mp > 300 °C (decomp.); 1H NMR δ 8.34 (m, 2H), 7.91 (m, 2H), 7.68 (m, 4H), 7.43 (d, $J = 1.7$ Hz, 4H), 6.09 (s, 2H), 5.86 (d, $J = 1.2$ Hz, 2H), 4.67–4.58 (m, 8H), 1.62–1.58 (m, 12H), 1.46 (s, 18H), 1.36 (s, 36H), 1.18 (s, 18H); ^{13}C NMR δ 161.1, 159.7, 153.5, 151.1, 150.7, 147.6, 143.6, 142.8, 138.7, 134.7, 134.1, 132.9, 132.8, 132.3, 131.4, 130.1, 129.5, 129.2, 124.3, 124.0, 123.3, 122.9, 122.6, 122.5, 121.9, 119.7, 63.0, 61.5, 35.5, 35.5, 35.4, 35.3, 32.0, 31.9, 31.8, 31.6, 31.4, 31.4, 31.3, 14.5, 13.9; UV-vis-NIR (CH_2Cl_2 , $\epsilon \times 10^{-4} M^{-1} cm^{-1}$) λ_{max} 356 (2.34), 443 (1.91), 570 (0.94), 756 (5.18), 835 (15.9) nm; fluorescence (CH_2Cl_2) λ_{max} 846 nm; IR ν_{max} 2952, 2905, 2868, 1726, 1705 cm^{-1} ; MS (MALDI-TOF) m/z 1543.8 [$M^+ + 1$], 1496.8 [$M - BF_2 + H + 1$]; Anal. calcd for $C_{96}H_{108}B_2F_4N_4O_8$: C, 74.70; H, 7.05; N, 3.63. Found: C, 74.71; H, 7.27; N, 3.56%. Single crystals were obtained by diffusion of acetonitrile into a chloroform solution of **11b**. CCDC No. 1821922.

B-bisANBODIPY 11c

The conversion of **8c** (13.0 mg) was performed at 250 °C for 30 min to afford 12.6 mg (97%) of **11c** as a black powder: mp > 300 °C (decomp.); 1H NMR δ 8.33 (d, $J = 1.3$ Hz, 2H), 7.69 (m, 2H), 7.66 (m, 2H), 7.51 (m, 4H), 7.33 (m, 4H), 6.62 (s, 2H), 5.72 (s, 2H), 4.69–4.56 (m, 8H), 4.23 (m, 4H), 1.98 (m, 4H), 1.68–1.60 (m, 10H), 1.55 (t, $J = 7.3$ Hz, 6H), 1.47 (m, 26H), 1.22 (s, 18H), 1.00 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR δ 161.2, 160.8, 159.9, 151.1, 150.7, 148.1, 143.5, 141.5, 138.7, 134.1, 132.8, 132.5, 132.4, 132.3, 131.1, 130.6, 129.9, 129.2, 126.7, 123.7, 123.3, 122.7, 122.6, 122.1, 120.0, 116.7, 68.2, 63.1, 61.5, 35.5, 35.4, 31.7, 31.7, 31.6, 31.2, 31.1, 29.5, 22.7, 14.7, 14.1; UV-vis-NIR (CH_2Cl_2 , $\epsilon \times 10^{-4} M^{-1} cm^{-1}$) λ_{max} 366 (2.45), 446 (2.10), 572 (1.00), 758 (5.06), 836 (15.9) nm; fluorescence (CH_2Cl_2) λ_{max} 844 nm; IR ν_{max} 2952, 2867, 1722, 1696 cm^{-1} ; MS (MALDI-TOF) m/z 1519.6 [M^+],

1500.6 [$M - F^-$], 1471.6 [$M^+ - BF_2$]. Anal. calcd for $C_{92}H_{100}B_2F_4N_4O_{10}$: C, 72.72; H, 6.63; N, 3.69. Found: C, 72.57; H, 6.62; N, 3.85%. Single crystals were obtained by diffusion of 2-propanol into a chloroform solution of **11c**. CCDC No. 1821920.

B-bisANBODIPY 12b

The conversion of **9** (6.9 mg) was performed at 250 °C for 5 h to afford 6.8 mg (100%) of **12b** as a black powder: mp > 300 °C (decomp.); 1H NMR δ 8.11 (m, 2H), 8.09 (s, 2H), 7.83 (s, 2H), 7.82 (s, 2H), 7.45 (m, 4H), 6.11 (s, 2H), 5.98 (s, 2H), 1.47 (s, 18H), 1.41 (s, 36H), 1.19 (s, 18H); ^{13}C NMR (typical signals) δ 171.7, 168.6, 155.0, 152.0, 133.4, 131.7, 35.8, 35.6, 35.5, 35.4, 31.7, 31.5, 31.4; UV-vis-NIR (CH_2Cl_2 , relative int.) λ_{max} 397 [0.19], 490 [0.14], 624 [0.09], 803 [0.34], 900 [1.00] nm; IR ν_{max} 2957, 2905, 2869, 2221 cm^{-1} ; MS (FAB $^+$) m/z 1355 [$M^+ + 1$], 1336 [$M - F^-$], 1308 [$M - BF_2 + H + H^+$], 1307 [$M - BF_2 + H^+$]. Anal. calcd for $C_{88}H_{88}B_2F_4N_8 + 5/2H_2O$: C, 75.48; H, 6.69; N, 8.00. Found: C, 75.54; H, 6.50; N, 8.00%. Single crystals were obtained by diffusion of dry acetonitrile into a dry chlorobenzene solution of **12b**. CCDC No. 1821205.

Conflicts of interest

There are no conflicts to declare.

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