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B,*B*-Diporphyrinbenzyloxy-BODIPY Dyes: Synthesis and Antenna Effect

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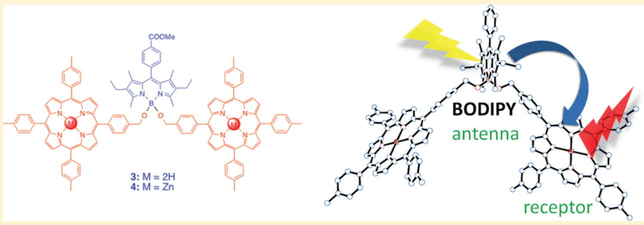
S *Supporting Information*

ABSTRACT: *B*,*B*-Diporphyrinbenzyloxy-BODIPY derivatives have been prepared in high yields, and the photophysical properties are reported. Singlet energy transfers from BODIPY to the porphyrin units have been analyzed.



The B−F bonds of BODIPY are convenient functions for the design of light-harvesting devices based on this dye.[1] Despite numerous efforts, there are only a few examples reported so far including the 4,4-dialkoxy- or 4,4-diaryloxydiaza-*S*-indacene(BODIPY)-containing antennas.[1u,2] In this respect, some *B*-methoxy (*B*-OMe) BODIPYs were successfully prepared by reacting the corresponding BF_2 compound with sodium methoxide in methanol.[2a] The absorption and emission spectra of the corresponding alkoxy products reveal no change compared to the BODIPY itself, indicating that the introduction of substituents on the B-atom had little effect on the electronic states of the boroindacene core.[2a] *B*-OR BODIPYs systems have also been obtained *via* the treatment of the corresponding BODIPY with various alcohols in the presence of aluminum trichloride.[2b] Furthermore, a difluoroboron dipyrrin was subsequently converted into dioxyboron dipyrrin derivatives by treatment with dihydroxy benzaldehyde in the presence of aluminum trichloride and provided access to donor−acceptor−acceptor and antenna−donor−acceptor type triads.[1u] We report here the synthesis and characterization of B,B-diporphyrinbenzyloxy-BODIPY derivatives (Chart 1). Evidence for singlet energy transfer from BODIPY to the porphyrin unit is provided.

The target model compound **1** and the dyad system **3** were readily obtained in only one step from benzyl alcohol and porphyrin **2** (obtained by reduction of 5-(4-(carboxy)phenyl)-10,15,20-tritolylporphyrin zinc)) in 61 and 86% yield, respectively (Scheme 1). The zinc insertion into the free base **3** followed by purification by column chromatography over silica with dichloromethane as the solvent gave the diporphyrin biszinc complex **4** in an almost quantitative yield. The experimental conditions and spectroscopic data for **1**−**4** are provided in the Supporting Information and Experimental Section. The HR-MS data of **3** and **4** reveal the presence of only one ion attributed to the monosodium adduct. In both cases, the perfect match between experimental and simulated ionic patterns undoubtedly confirms the structure of **3** and **4** (see the Supporting Information). For example, the calculated mass for the monosodium adduct of **4** ($C_{121}H_{99}BN_{10}NaO_4Zn_2$) is equal to 1917.6436 Da, in agreement with the experimental value found at 1917.6396 Da ($[M + Na]^+$).

Table 1 summarizes the UV−vis data for all compounds in THF. Compound **1** exhibits two bands characteristic of BODIPY; the S_0−S_1 band at 526 and the S_0−S_2 band at 382 nm, both assigned to spin-allowed π−π^* transitions. The UV−vis spectrum of the free base porphyrin **2** and Zn(TPP) (TPP = 5,10,15,20-tetraphenylporphyrin) are characterized by one Soret band, two Q bands for Zn(TPP), and five Q bands for **2**. It appears that absorption spectra of the multichromophoric species **3** and **4** correspond to the sum of the absorption spectra of the individual components, **1** and **2** for compound **3**, and **1** and **Zn(TPP)** for compound **4** (Figures S6 and S7, Supporting Information) indicating that the interchromophoric interactions are minimal. The positions of the absorption spectra of compound **1** and **Zn(TPP)** indicate that BODIPY and the porphyrin units are the S_1 energy donor and acceptor, respectively.

The photophysical data are summarized in Table 2. One example of the fluorescence spectra is provided in Figure 1. BODIPY **1** shows an intense fluorescence at 544 nm with a quantum yield, Φ_F, of 0.62 and a lifetime, τ_F, of 3.7 ns. The emission spectra of the porphyrin subunits exhibit two characteristic bands respectively at 653 and 718 nm for compound **2** (τ_F = 11.0 ns), and 605 and 655 nm for **Zn(TPP)** (τ_F = 1.9 ns).

When dyad **3** is irradiated at 530 nm where the BODIPY chromophore absorbs the most, almost exclusively the fluorescence of the porphyrin unit is observed. The excitation

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Chart 1

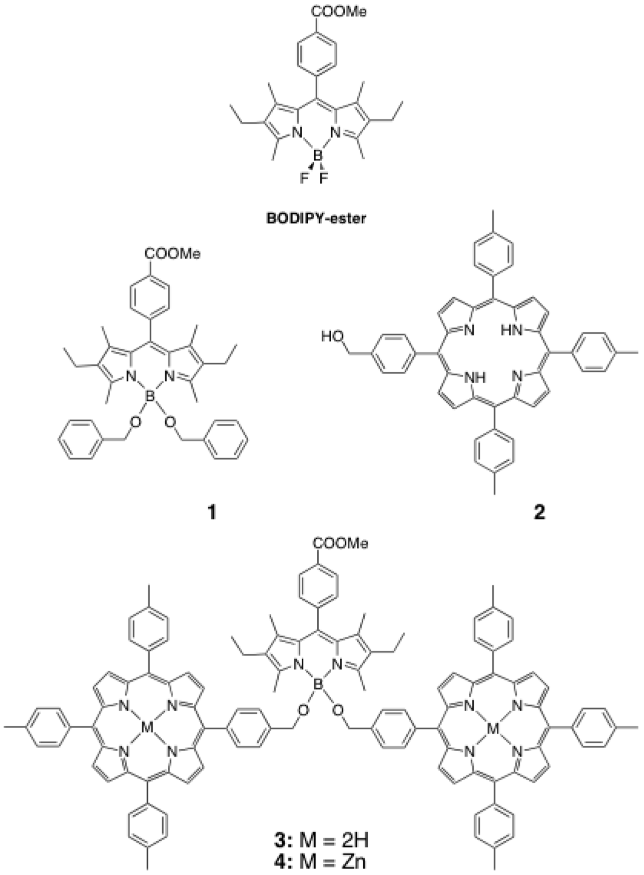

Table 1. UV−vis Absorption Data in THF at 298 K

	λ_{max} (nm) ($\varepsilon \times 10^{-3}$ M^{-1} cm^{-1})			
	porphyrin chromophore		BODIPY chromophore	
compd	Soret band	Q bands	S_2 band	S_1 band
1			382 (3.3)	526 (32.5)
2	417 (312)	649 (3.4)		
		593 (4.1)		
		550 (7.5)		
		515 (14.0)		
		484 (3.2)		
3	418 (816)	648 (8.6)		526 (69.1)
		592 (10.3)		
		546 (27.8)		
4	423 (104)	559 (36.7)		528 (60.0)
		598 (15.9)		
Zn(TPP)	423 (606)	594 (7.1)		
		555 (21.7)		

spectrum exhibits a perfect match with the absorption (Figure 2 and Supporting Information). These two properties indicate clearly an efficient S_1 energy transfer from BODIPY to porphyrin, following excitation of the BODIPY subunit.

The τ_F data were used to extract the S_1 energy transfer rates, k_{ET}. Again, compounds **3** and **4** exhibit two fluorophores, BODIPY and porphyrins (as a free base or a zinc(II) complex), again assigned as the S_1 energy donor and acceptor, respectively. The Φ_F data of the acceptor remain relatively the same regardless the presence or the absence of the S_1 energy donor at 298 and 77 K. This observation indicates that the anchoring of the porphyrin unit onto BODIPY does not

Scheme 1

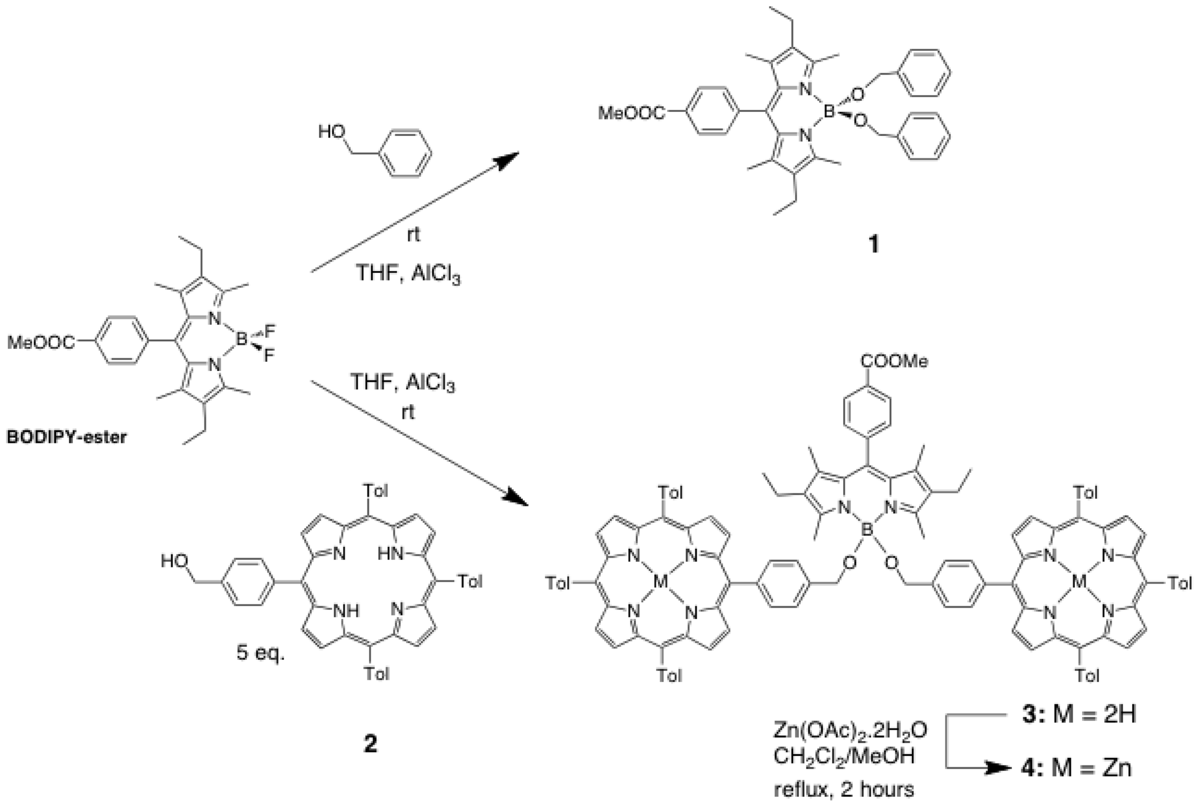

Table 2. Fluorescence Lifetimes, τ_F, in 2MeTHF at 298 and 77 K

			2MeTHF					
			298 K			77 K		
compd	$\Phi_F{}^{a}$ 298 K	λ_{em} (nm)	λ_{exc} (nm)	τ_F (ns)	k_{ET} (s^{-1})	λ_{exc} (nm)	τ_F (ns)	k_{ET} (s^{-1})
1	0.62	544	530	3.7		530	8.1	
2	0.089	653, 718	548	11.0		548	13.6	
3	0.068[b]	653	530	*c*	[c]	530	4.5	1×10^8
			590	12.6		590	14.5	
4	0.039[b]	655	530	3.3	3×10^7	530	4.6	1×10^8
			560	1.9		560	2.3	
Zn(TPP)	0.037	605, 655	563	1.9		563	2.6	

[a] Quantum yields were measured in 2MeTHF at 298 K, using Rhodamine 6G as reference[3] (Φ_F = 0.94 in MeOH, λ_{exc} = 488 nm). All Φ are corrected for changes in refractive index.[4] [b] Total quantum yield (BODIPY and porphyrins). [c] Not measured.

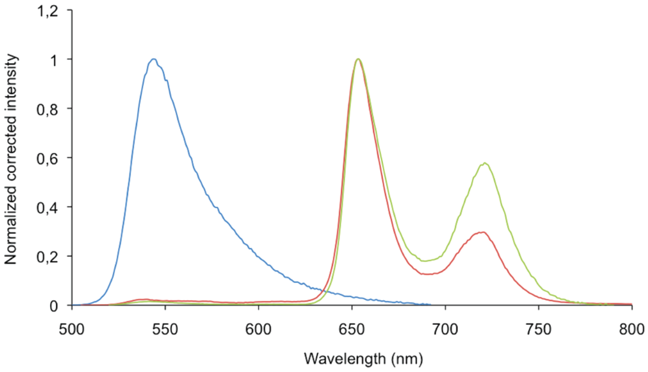

Figure 1. Emission spectra of compounds **2** (red, λ_{exc} = 500 nm), **3** (green) and **1** (blue, λ_{exc} = 530 nm) in 2MeTHF at 298 K.

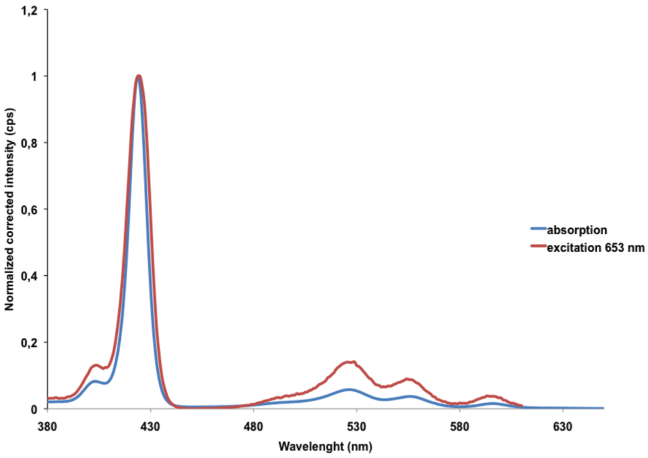

Figure 2. Absorption and excitation spectra of compound **4** (λ_{exc} = 653 nm).

increase the rates for the nonradiative processes internal conversion, k_{ic}, and intersystem crossing, k_{isc}. On the other hand, a decrease in τ_F of the donor is noted, particularly at 77 K (by a factor of approximately 2). Using the equation $k_{ET} = 1/\tau_{F(donor)} - 1/\tau_{F°(donor)}$ where τ_F and $\tau_{F°}$ are the fluorescence lifetimes of the donor in the presence and absence of acceptor, respectively, then the approximate k_{ET} is $\sim 1 \times 10^8$ s^{-1} for both **3** and **4**. Despite the obvious decrease in total Φ_F (going from 0.62 for **1** to 0.068 and 0.039 for **3** and **4**, respectively, at 298 K), the through space energy transfer rates of 1×10^8 s^{-1} are considered modest with respect to other dyads ($\sim 10^9 - 10^{10}$ s^{-1}).[5] The reason for this is most likely due to the nonparallel orientation of the transition moments between the donor and the acceptor according to a Förster mechanism[6] (see the graphical abstract which corresponds to a minimized geometry of **4**; PC Model). In line with a Förster mechanism,[6] the fact that the k_{ET} data is strongly temperature dependent (k_{ET} $\sim 3 \times 10^7$ s^{-1} at 298 K) is consistent with this explanation where a relative change in conformation occurs *via* the rotation about the B−O and O−C single bonds upon changing the temperature.

In conclusion, the good spectral overlap between the donor fluorescence (BODIPY) and acceptor absorption (porphyrin) leading to a notable quenching of the former is observed and clearly demonstrates the BODIPY dye as a good chromophore for the antenna effect. However, the current dyad design can be improved from a gain in appropriate relative orientation of the transition moments between the donor and acceptor.

■ EXPERIMENTAL SECTION

Instrumentation. ^{1}H NMR spectra were recorded on a 300 MHz spectrometer at the Pôle Chimie Moléculaire (Université de Bourgogne); chemical shifts are expressed in ppm relative to chloroform. ^{13}C NMR spectra were recorded on a 300 MHz spectrometer at the Université de Sherbrooke. Mass spectra were obtained in the MALDI/TOF reflectron mode using dithranol as a matrix or by ESI on an Orbitrap spectrometer. The measurements were made at the Pôle Chimie Moléculaire (Université de Bourgogne). UV−vis spectra were recorded on a diode array apparatus. Emission and excitation spectra were obtained using a double monochromator instrument. Fluorescence and phosphorescence lifetimes were measured on a apparatus incorporating a nitrogen laser as the source and a high-resolution dye laser (fwhm = 1.4 ns). Fluorescence lifetimes were obtained from high-quality decays and deconvolution or distribution lifetime analysis. The uncertainties ranged from 20 to 40 ps on the basis of multiple measurements. Phosphorescence lifetimes were determined using an apparatus incorporating a 1 μs tungsten flash lamp (fwhm ~1 μs). Flash photolysis spectra and transient lifetimes were measured using the 355 nm line of a YAG laser from Continuum (Serulite; fwhm =13 ns).

Quantum Yield Measurements. For measurements at 298 K, all samples were prepared in a glovebox, under argon (O_2 < 12 ppm), by dissolution of the compounds in 2MeTHF, using 1 cm^3 quartz cells with a septum. Three different measurements (*i.e.*, different solutions) were performed for each set of photophysical data (quantum yield). The sample concentrations were chosen to correspond to an absorbance of ~0.05 at the excitation wavelength. Each absorbance value was measured three times for better accuracy in the measurements of emission quantum yields. Tetraphenylporphyrin (0.10 in THF)[7] or tetraphenylporphyrin zinc(II) (0.033 in THF) was used as reference.[8]

Chemicals and Reagents. Unless otherwise noted, all chemicals and solvents were of analytical reagent grade and used as received.

Silica gel (70−120 μm) was used for column chromatography. Analytical thin-layer chromatography was performed with 60 F_{254} silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by thin-layer chromatography, UV/vis spectroscopy, and MALDI/TOF mass spectrometry.

5-(4-Carboxyphenyl)-10,15,20-tritolylporphyrin Zinc. To a solution of 4-carboxybenzaldehyde (2.20 g, 14.6 mmol) in 250 mL of $CHCl_3$ were added 4.56 g (19.3 mmol) of 5-*p*-tolyldipyrromethane and 590.0 mg (5.0 mmol) of 4-methylbenzaldehyde. The solution was degassed under nitrogen bubbling for 15 min, shielded from light. Boron difluoride diethyl etherate (325 μL, 2.5 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 1 h 30 min p-chloranil (2.40 g, 9.7 mmol) was then added under stirring. After 2 h, the solvent was evaporated under reduced pressure. The residue thus obtained was chromatographed on silica gel using CH_2Cl_2/MeOH (100/5), and the first purple fraction was isolated. After evaporation of the solvent under vacuum, the residue was redissolved in 250 mL of chloroform, and the solution was treated with 100 mL of a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (2.40 g, 30.0 mmol) in the presence of sodium acetate (2.40 g, 30.0 mmol). The mixture was heated at 75 °C, and the reaction was monitored by TLC, UV−vis, and MALDI/TOF mass spectrometry. After 2 h and cooling to room temperature, the reaction mixture was washed three times with water (750 mL), dried over magnesium sulfate, and concentrated. The residue obtained was chromatographed on silica gel (CH_2Cl_2/MeOH, 100/5). The red-pink fraction was isolated, and the solvent was removed under reduced pressure to give the title compound in 27% yield (2.00 g, 2.67 mmol) Mp > 300 °C. UV/vis (CH_2Cl_2): λ_{max} (nm) ($\varepsilon \times 10^{-3}$ L mol^{-1} cm^{-1}) = 422.0 (135), 551.0 (6), 588.0 (3). ^{1}H NMR ($CDCl_3$, 298 K): δ (ppm) = 2.61 (s, 9H), 7.54 (d, *J* = 7.8 Hz, 6H), 8.08 (d, *J* = 7.8 Hz, 6H), 8.32 (d, *J* = 8.1 Hz, 2H), 8.47 (d, *J* = 8.1 Hz, 2H), 8.91 (m, 8H). MS (MALDI-TOF): *m/z* = 762.18 $[M]^{+\bullet}$, 762.19 calcd for $C_{48}H_{34}N_4O_2Zn$.

***B*,*B*-Bisbenzoyl-1,3,7,9-tetramethyl-2,8-diethyl-5-(*p*-methylbenzoyl)-BODIPY (1).** To a solution of BODIPY ester (70.0 mg, 160 μmol) in dry CH_2Cl_2 (25 mL) was added, under nitrogen, aluminum trichloride (175.0 mg, 1.31 mmol). The solution was heated to 40 °C for 30 min (the color of the solution turned from pale-orange to red) and then cooled to room temperature. Benzyl alcohol (85 μL, 820 μmol) was then added, and the reaction mixture was stirred at room temperature for 1 h. After filtration over alumina in order to remove $AlCl_3$, all the volatiles were evaporated under reduced pressure. After purification by chromatography on silica (EtOAc), the title compound was isolated as a red oil in 61% yield (60.0 mg, 97 mmol). UV/vis (CH_2Cl_2): λ_{max} (nm) ($\varepsilon \times 10^{-3}$ L mol^{-1} cm^{-1}) = 418.0 (880), 525.0 (77), 592.0 (10), 649.0 (10). ^{1}H NMR ($CDCl_3$, 298 K): δ (ppm) = 0.87 (t, *J* = 7.4 Hz, 6H), 1.17 (s, 6H), 2.15 (q, *J* = 7.4 Hz, 4H), 2.42 (s, 6H), 4.02 (s, 3H), 4.49 (s, 4H), 7.15 (m, 10H), 7.40 (d, *J* =8.4 Hz, 2H), 8.13 (d, *J* =8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ (ppm) = 11.9, 12.7, 14.7, 17.1, 29.7, 30.2, 31.4, 52.4, 64.5, 124.5, 126.3, 127.5, 127.7, 129.0, 130.2, 136.2, 141.5, 154.9. HR-MS (ESI): *m/z* = 637.3178 $[M + Na]^+$, 637.3214 calcd for $C_{39}H_{43}BNaN_2O_4$.

5-(4-(Hydroxymethyl)phenyl)-10,15,20-tritolylporphyrin (2). To a suspension of $LiAlH_4$ (75.0 mg, 1.97 mmol) in dry tetrahydrofuran (35 mL) was added dropwise at −80 °C a solution of 5-(4-carboxyphenyl)-10,15,20-tritolylporphyrin zinc (500.0 mg, 0.65 mmol) in dry tetrahydrofuran (35 mL). The mixture was stirred at −80 °C for 10 min, warmed to room temperature for 1 h, and then quenched with water (5 mL). After evaporation of the solvent in vacuum, the residue was extracted with $CHCl_3$, washed three times with water (10 mL), dried over magnesium sulfate, filtered, and evaporated. The residue obtained was chromatographed on silica (CH_2Cl_2/MeOH, 100/2). The fractions were collected, and the solvent was evaporated under reduced pressure. The solid was dissolved in CH_2Cl_2 (100 mL), and 2.0 mL of trifluoroacetic acid was added dropwise under stirring. After 2 h, the reaction mixture was washed with saturated hydrogen carbonate solution and two times with water (100 mL) and then dried over magnesium sulfate. After all volatiles were removed under reduced pressure, the title compound **2** was isolated in 57% yield (254.0 mg, 0.37 mmol) as a purple powder. Mp > 300 °C. UV/vis (CH_2Cl_2): λ_{max} (nm) ($\varepsilon \times 10^{-3}$ L mol^{-1} cm^{-1}) = 416.0 (330), 514.0 (13), 550.0 (8), 590.0 (4), 646.0 (3). ^{1}H NMR (pyridine-d_5, 298 K): δ (ppm) = −2.27 (s, 2H), 2.61 (s, 9H), 5.36 (s, 2H), 7.60 (d, *J* = 7.6 Hz), 8.07 (d, *J* = 7.9 Hz, 2H), 8.27 (d, *J* = 7.6 Hz, 6H), 8.47 (d, *J* = 7.9 Hz, 2H), 9.14 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ (ppm) = 14.1, 21.5, 29.7, 30.3, 65.4, 120.2, 125.3, 127.4, 131.0, 134.5, 137.3, 139.3. MS (MALDI-TOF): *m/z* = 686.3122 $[M]^{+\bullet}$, 686.3040 calcd for $C_{48}H_{38}N_4O$.

***B*,*B*-Bis(1-benzyloxy-10,15,20-tritolylporphyrinyl)-1,3,7,9-tetramethyl-2,8-diethyl-5-(*p*-methylbenzoyl)-BODIPY (3).** To a solution of BODIPY ester (23.0 mg, 52 μmol) in dry THF (50 mL) was added, under nitrogen, aluminum trichloride (55.0 mg, 412 μmol). The solution was heated to 40 °C for 30 min (the color of the solution turned from pale-orange to red) and then cooled to room temperature. 5-(4-(Hydroxymethyl)phenyl)-10,15,20-tritolylporphyrin **2** (170.0 mg, 250 μmol) was then added, and the reaction mixture was stirred at room temperature for 1 h 30 min. After filtration over alumina in order to remove $AlCl_3$, all of the volatiles were evaporated under reduced pressure. After purification by chromatography on silica (EtOAc/heptane, 30/70), the compound was crystallized in a CH_2Cl_2/heptane mixture to afford the title compound **3** as a purple solid in 84% yield (78.0 mg, 44 mmol). Mp > 300 °C. UV/vis (CH_2Cl_2): λ_{max} (nm) ($\varepsilon \times 10^{-3}$ L mol^{-1} cm^{-1}) = 418.0 (880), 525.0 (77), 592.0 (10), 649.0 (10). ^{1}H NMR ($CDCl_3$, 298 K): δ (ppm) = −2.77 (s, 4H), 1.05 (t, *J* = 7.4 Hz, 6H), 1.42 (s, 6H), 2.42 (q, *J* = 7.4 Hz, 4H), 2.68 (s, 18H), 2.88 (s, 6H), 3.98 (s, 3H), 4.57 (s, 4H), 7.54 (d, *J* = 7.9 Hz, 12H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 4H), 8.08 (d, *J* = 7.9 Hz, 12H), 8.10 (d, *J* = 8.0 Hz, 4H), 8.24 (d, *J* = 8.4 Hz, 2H), 8.83 (s, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ (ppm) = 12.1, 13.2, 14.9, 17.3, 21.5, 29.7, 52.4, 64.8, 120.0, 120.3, 126.2, 127.4, 129.1, 130.3, 130.9, 131.8, 133.3, 134.3, 134.5, 155.1. HR-MS (ESI): *m/z* = 886.4219 $[M + 2H]^{2+}$, 886.4209 calcd for $C_{121}H_{103}BN_{10}O_4$.

***B*,*B*-Bis(zinc(II)-1-benzyloxy-10,15,20-tritolylporphyrinyl)-1,3,7,9-tetramethyl-2,8-diethyl-5-(*p*-methylbenzoyl)-BODIPY (4).** To a solution of BODIPY-diporphyrin **3** (50.0 mg, 28 μmol) in 10 mL of CH_2Cl_2 was added a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (24.0 mg, 109 μmol) and sodium acetate (20.0 mg, 243 μmol), and the mixture was heated under reflux for 2 h. The reaction was monitored by TLC, UV−vis, and MALDI/TOF mass spectrometry. After cooling to room temperature, the reaction mixture was washed three times with water (10 mL), dried over magnesium sulfate, and filtered. The title compound **4** was obtained in almost quantitative yield as a purple solid (53.0 mg, 28 μmol) after recrystallization in a CH_2Cl_2/heptane mixture. Mp > 300 °C. UV/vis (CH_2Cl_2): λ_{max} (nm) ($\varepsilon \times 10^{-3}$ L mol^{-1} cm^{-1}) = 422.0 (810), 529.0 (56), 590.0 (6). ^{1}H NMR ($CDCl_3$, 298 K): δ (ppm) = 1.07 (t, *J* = 7.4 Hz, 6H), 1.44 (s, 6H), 2.44 (q, *J* = 7.4 Hz, 4H), 2.69 (s, 18H), 2.90 (s, 6H), 3.97 (s, 3H), 4.58 (s, 4H), 7.54 (d, *J* = 7.9 Hz, 12H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 4H), 8.09 (d, *J* = 7.9 Hz, 12H), 8.11 (d, *J* = 8.0 Hz, 4H,), 8.23 (d, *J* = 8.4 Hz, 2H), 8.94 (s, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ (ppm) = 12.1, 13.2, 14.9, 17.3, 21.5, 29.7, 52.4, 64.8, 121.1, 126.1, 127.3, 129.1, 131.8, 134.1, 137.0, 139.9, 140.1, 150.3. MS (MALDI-TOF): *m/z* = 1895.28 $[M + H]^+$, 1895.66 calcd for $C_{121}H_{100}BN_{10}O_4Zn_2$. HR-MS (ESI): *m/z* = 1917.6396 $[M + Na]^+$, 1917.6436 calcd for $C_{121}H_{99}BN_{10}NaO_4Zn_2$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra and mass spectra (HR-MS) of compounds **1**−**4** (Figures S1−S12). Absorption spectra of **1**, ZnTPP, and **4** in MeTHF at 298 K (Figure S13). Absorption spectra of **1**−**3** in MeTHF at 298 K (Figure S14). Emission spectra of **4**, **1**, and ZnTPP in MeTHF at 298 K (Figure S15). Emission spectra of **2**, **3**, and **1** in MeTHF at 298 K (Figure S16). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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