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Bis(BF_2)-2,2′-Bidipyrrins (BisBODIPYs): Highly Fluorescent BODIPY Dimers with Large Stokes Shifts

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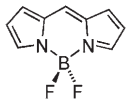
Abstract: Four new dimeric bis(BF_2)-2,2′-bidipyrrins (bisBODIPYs), and their corresponding BODIPY monomers, have been prepared and studied with respect to their structural and photophysical properties. The solid-state molecular structure of the dimers and the relative orientation of the subunits have been revealed by an X-ray diffraction study, which showed that the molecules contain two directly linked BODIPY chromophores in a conformationally fixed, almost orthogonal arrangement. Two of the fluorine atoms are in close contact with each other and the ^{19}F NMR spectra show a characteristic through-space coupling in solution. The new chromophores all exhibit a clear exciton splitting in the absorption spectra with maxima at about 490 and 560 nm, and are highly luminescent with an intense emission band at around 640 nm. The Stokes shift, which is the difference between the maximum of the lowest-energy absorption band and the maximum of the emission band, has a typical value of 5 to 15 nm for simple BODIPYs, whereas this value increases to 80 nm or more for the dimers, along with a slight decrease in fluorescence quantum yields and lifetimes. These properties indicate potential uses of these new fluorophoric materials as functional dyes in biomedical and materials applications and also in model compounds for BODIPY aggregates.

Keywords: bidipyrrins · boron · dyes/pigments · fluorescence · porphyrinoids

Introduction

Boron dipyrrins (BODIPYs, also called boron dipyrromethene or boraindacene) constitute a class of boron chelates with a dipyrrin ligand[1] that are currently attracting multifacetted interest in many research areas owing to their advantageous photophysical properties. BODIPYs are very versatile and are used as light-stable functional dyes in a variety of different fields, such as laser dyes,[2,3] light harvesters,[4–6] fluorescent switches,[7] biomolecular labels,[8] cation sensors,[9–17] and so on.[18–24] The fluorescence properties of BODIPYs can be fine-tuned preparatively by using several different approaches. The introduction of functional substituents on the carbon framework, enlargement of the chromophore, substitution of the fluorine atoms for O- or C-donors, or replacing the *meso* CH position with a nitrogen bridge has produced a plethora of interesting fluorophores from this class of molecule. Very recently, two comprehensive reviews of the field have appeared in the literature.[25,26]



BODIPY core

Despite the enormous number of publications about different aspects of BODIPY dyes, reports on other oligopyrrolic boron complexes have remained scarce. Macrocyclic tetra-,[27–31] hexa-, and octapyrroles[29] have only been used as ligands for BF_2 groups during the last decade, and in two instances open-chain tetrapyrroles of the bilin and urobilin type have been employed.[32,33] Oligomeric dipyrrins would be of interest as ligands for BF_2 groups because of their potential to form covalent BODIPY aggregates.[34–36] Formal dipyrrin dimers, such as 2,2′-bidipyrrins, are particularly appealing in this context owing to their straightforward synthesis, high stability, and known ability to form mono- and dinuclear transition-metal chelates of different structures.[37–43]

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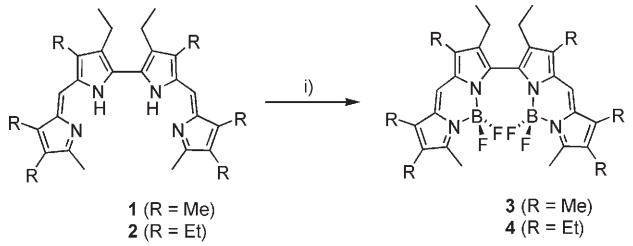
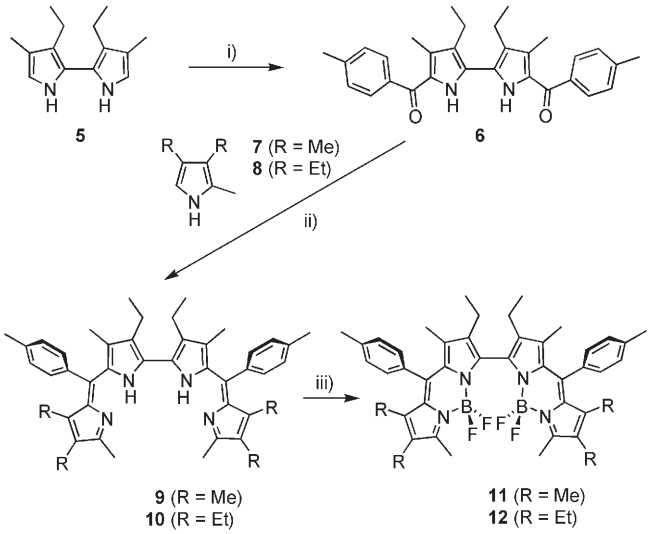
We have successfully used 2,2′-bidipyrrins as starting materials for conceptually new bisBODIPY fluorophores and report herein the preparation, structural determination, and basic photophysical characterization of these dyes.

Results and Discussion

Preparation of fluorophores: The syntheses of dimeric bisBODIPYs **3**, **4**, **11**, and **12** were achieved by a two-fold BF_2-coordination of the free-base ligands **1**, **2**, **9**, and **10**, as depicted in Schemes 1 and 2. Two different types of 2,2′-bidipyrrins were employed for this study, namely, those with and without *meso*-aryl substituents. Tetrapyrroles **1** and **2** (Scheme 1) have been reported previously, whereas *meso*-arylated ligands **9** and **10** (Scheme 2) were unknown, but were easily prepared by known procedures from bipyrrole **5** via two-fold-substituted compound **6** and trialkylpyrroles **7** or **8** with an overall yield of 34 and 32%, respectively.



Scheme 1. Preparation of *meso*-unsubstituted bisBODIPYs **3** (44% yield) and **4** (45% yield). i) BF_3·Et_2O, 2,6-lutidine, diethyl ether.

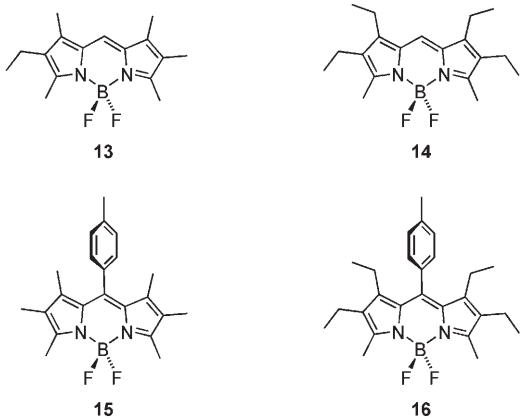


Scheme 2. Preparation of *meso*-aryl-substituted bisBODIPYs **11** and **12**. i) *N*-4-Methylbenzoylmorpholine, $POCl_3$, 1,2-dichloroethane, 48%; ii) $POCl_3$, Δ, 70 (**7**) and 67% (**8**); iii) BF_3·Et_2O, 2,6-lutidine, diethyl ether, 65%.

The preparation of BODIPYs in high yields from dipyrrins and excess boron trifluoride etherate is usually performed at ambient temperature in a mixture of dichloromethane and triethylamine. For 2,2′-bidipyrrins **1**, **2**, **9**, and **10**, however, the desired bisBODIPYs were only formed in a yield of about 10% under these conditions, and no improvement in yield was observed upon changing the reaction time, solvent, or reagent concentration. Indeed, a larger excess of boron trifluoride and an increased reaction temperature were found to decompose the product with time. The *meso*-unsubstituted bisBODIPYs (**3** and **4**) were particularly sensitive to these conditions.

We assumed that the formation of basic fluoride anions in the reaction mixture, and their attack at the *meso*-position of both the free-base ligands and the bisBODIPYs, was responsible for the observed decomposition processes. Therefore, water-saturated diethyl ether was employed as the reaction medium to reduce the basicity of the fluoride ions. The yields improved significantly and after some further optimization the desired dimeric BODIPYs were obtained in reasonable yields of up to 65% (Schemes 1 and 2). The new compounds were obtained as analytically pure ruby-colored powders after chromatographic purification on silica gel. In solution the novel fluorophores are characterized by a violet color and an intense red fluorescence.

For comparison, monomeric BODIPYs **13**–**16**, which have similar peripheral substituents as dimeric **3**, **4**, **11**, and **12**, were also studied herein. The monomers were prepared according to published procedures for *meso*-unsubstituted (**13** and **14**)[44] or *meso*-aryl substituted compounds (**15** and **16**).[45] Analytical and spectroscopic data were as previously reported for known compound **14** and are similar to literature analogues for the new derivatives.



Conformation of bisBODIPYs: Single crystals suitable for X-ray diffraction studies were grown from **12**, **13**, and **16**. The results of this study are presented in Figures 1, 2, and 3, and crystallographic and molecular details are summarized in Tables 1 and 2. The C_9BN_2 frameworks of **13** and **16** (Figure 1) are essentially flat, with the boron atom displaced from the median plane by only 0.07 and 0.092 Å, respectively. Typical B–N and B–F bond lengths of 1.54–1.55 and 1.39–1.40 Å, respectively, are present throughout, and as ex-

Table 1. Selected crystallographic data for **12**, **13**, and **16**.

	12	**13**	**16**
formula	$C_{48}H_{56}B_2F_4N_4$	$C_{16}H_{21}BF_2N_2$	$C_{26}H_{33}BF_2N_2$
M_r [g mol^{-1}]	786.59	290.16	422.35
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a [Å]	13.6933(16)	8.8728(8)	11.1044(9)
b [Å]	17.1625(18)	11.9386(14)	18.348(2)
c [Å]	19.050(2)	14.0937(13)	11.9364(11)
α [°]	94.680(14)	90	90
β [°]	98.435(14)	90.313(11)	109.857(6)
γ [°]	103.149(13)	90	90
V [Å^3]	4281.6(9)	1492.9(3)	2287.4(4)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	1.220	1.291	1.226
μ [mm^{-1}] ($Mo_{K\alpha}$)	0.083	0.093	0.082
2θ limits [°]	1.73–26.23	2.71–25.89	2.13–25.90
measured reflns	34034	11117	11740
independent reflns	15769	2847	4399
observed reflns[a]	9097	1839	2860
no. parameters	1088	196	287
$R1$[b]	0.0559	0.0444	0.0324
w$R2$[c] (all data)	0.1604	0.1306	0.0644
max/min peaks	0.878/−0.352	0.287/−0.240	0.180/−0.172

[a] Oberservation criterion: $I > 2\sigma(I)$.
[b] $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. [c] $wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$

Table 2. Selected bond lengths [Å], distances [Å], and bond angles [°] for **13**, **16**, and **12**.

	13	**16**	**12**[a]	
			(B1)	(B2)
B−N1[b]	1.546(3)	1.5461(19)	1.544(3)	1.538(3)
B−N2	1.538(3)	1.5457(19)	1.540(3)	1.535(3)
B−F1	1.394(3)	1.3935(15)	1.384(3)	1.368(3)
B−F2	1.402(2)	1.3951(18)	1.383(3)	1.384(4)
C2−N1	1.348(2)	1.3502(17)	1.341(3)	1.344(3)
N1−C5	1.391(2)	1.4014(17)	1.402(3)	1.403(3)
C5−C6	1.378(3)	1.4084(19)	1.387(3)	1.383(3)
C6−C7	1.378(3)	1.4008(19)	1.405(3)	1.413(3)
C7−N2	1.396(2)	1.4016(16)	1.401(3)	1.400(3)
N2−C10	1.356(2)	1.3483(17)	1.365(3)	1.361(3)
B···C6	2.961	3.010	2.992	2.987
N1···N2	2.492	2.478	2.480	2.475
N1-B-N2	107.76(15)	106.55(10)	107.1(2)	107.3(2)
N1-B-F1	110.37(17)	110.29(11)	109.2(2)	110.7(2)
N1-B-F2	109.90(16)	110.28(11)	108.8(2)	108.5(2)
N2-B-F1	109.51(16)	110.58(11)	110.8(2)	110.8(2)
N2-B-F2	110.28(17)	109.94(11)	111.0(2)	110.5(2)
F1-B-F2	109.01(16)	109.18(11)	109.9(2)	109.0(2)

[a] Data given for molecule B only. (B1) and (B2) denominate the monomeric subunit that contains atom B1 or B2, respectively. [b] A unified numbering system, which was analogous to the BODIPY system, was used for the subunits of dimer **12**. For a better comparison, see Figures 1 and 2.

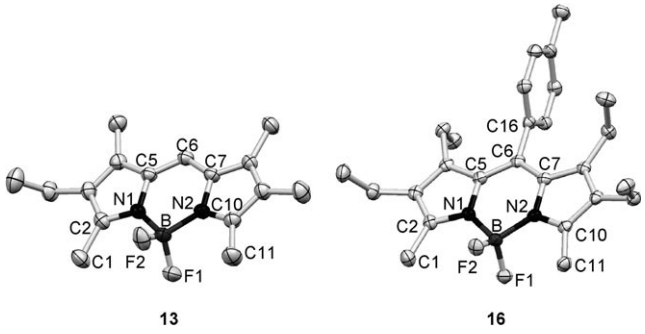


Figure 1. Molecular structure of BODIPYs **13** and **16** (ellipsoids set at the 50% probability level; hydrogen atoms omitted for clarity).

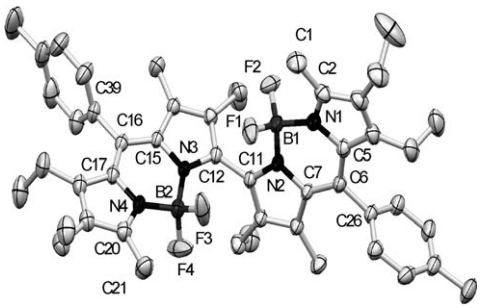


Figure 2. Molecular structure of bisBODIPY **12** (molecule B; ellipsoids set at the 50% probability level; hydrogen atoms omitted for clarity).

pected the angles around the boron atom have values close to the tetrahedral angle of 109.5° (Table 2). The influence of the 4-methylphenyl substituent of **16** on the molecular structure is very small. The mean plane of this group is at a dihedral angle of 82.88° with respect to the mean C_9BN_2 plane, which means that these subunits are electronically decoupled. The steric influence is mainly visible in the metrics of the central six-membered C_3BN_2 ring, in which **16** has longer C5−C6 and C6−C7 bonds, a larger C6···B distance, a smaller N1···N2 distance, and a slightly reduced N1-B-N2 angle than **13**. The C−C and C−N bond lengths within the dipyrrin backbone of **13** and **16** indicate strongly delocalized and almost symmetric π-systems, without any clear distinction between single and double bonds. These findings are characteristic for most BODIPYs and have been reported previously.[46]

BisBODIPY **12** crystallizes with two independent (though very similar) molecules, A and B, in the asymmetric unit, but only molecule B will be discussed herein (Figure 2). In general, the monomeric subunits of **12** follow the structural behavior of the monomers described above. However, an element of asymmetry is present within the C_{meso}−$C_{pyrrole}$ bonds. The C6−C7 and C15−C16 bond lengths are 0.018 and 0.030 Å longer than C5−C6 and C16−C17, respectively (Figure 2), and the planarity of the two slightly different C_9BN_2 subunits is less pronounced in **12** than it is in **13** or **16**. However, all other bond lengths, angles, and distances within the BODIPY subunits of **12**, which includes the almost perpendicular orientation of the 4-methylphenyl substituents (B1 subunit: 89.07°; B2 subunit: 85.10°), are very similar to the results from the monomers, particularly **16** (Table 2).

The intramolecular interactions of the monomeric subunits of **12** deserve special attention. The subunits are joined at C11−C12 with a bond length of 1.471 Å, which is typical for a single C(sp^2)−C(sp^2) bond, and a dihedral angle of 96.52° between the mean C_9BN_2 planes (Figure 3). In this ar-

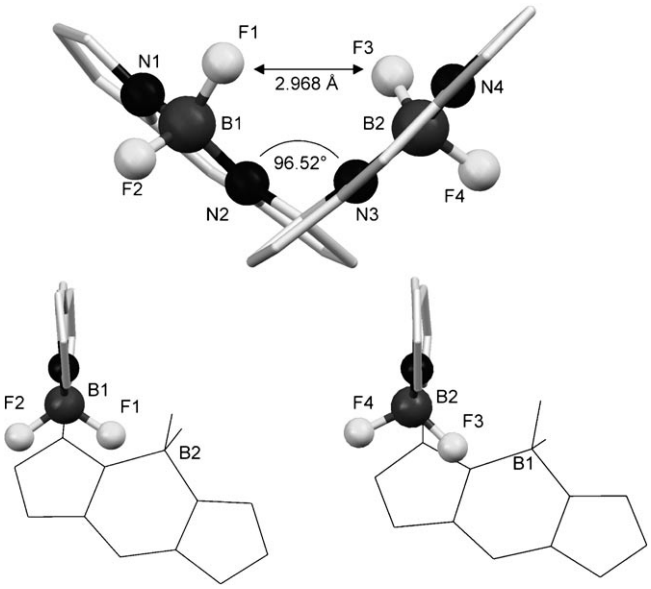


Figure 3. Selected views of the molecular conformation of bisBODIPY **12** (substituents removed).

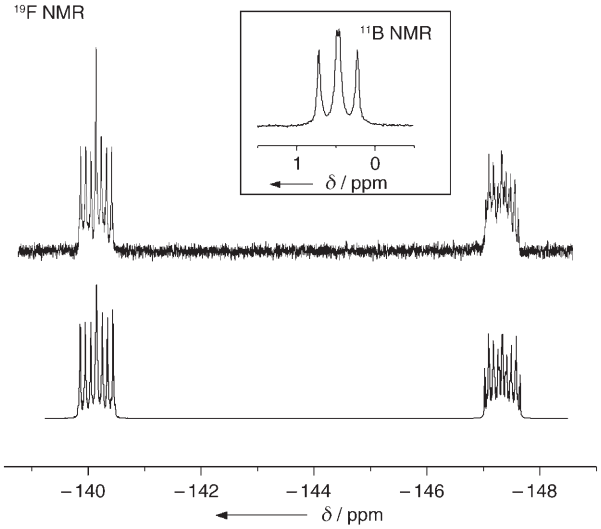


Figure 4. Top: A ^{19}F NMR spectrum (376 MHz) of **3** obtained experimentally. Bottom: simulated ^{19}F NMR spectrum of **3**. Inset: ^{11}B NMR spectrum (128 MHz) of **3**. Spectra were recorded in CD_2Cl_2.

rangement, the inward-pointing fluorine atoms F1 and F3 are situated in close contact (a distance of only 2.968 Å), and the BF_2 subunits are displaced outwards from the mean C_9BN_2 planes by 0.049 and 0.145 Å to reduce the steric interaction in the center of the molecule. The other two fluorine atoms, F2 and F4, show short F···H distances to a methyl group proton of the same subunit (2.482 (F2···H) and 2.541 Å (F4···H), compared with 2.481 and 2.561 Å for **13** and **16**, respectively) and to an ethyl group proton of the other subunit (2.552 (F2···H) and 2.479 Å (F4···H)). This data indicates very intimate interactions, but also the absence of significant intermolecular strain between the locked subunits of **12**.

BODIPYs, such as **13**–**16**, show very characteristic ^{19}F and ^{11}B NMR spectra, with a quartet signal at $\delta \approx -140$ ppm in the ^{19}F NMR spectrum, a triplet at $\delta \approx 0.5$ ppm in the ^{11}B NMR spectrum, and a coupling constant of ^{1}J(B,F) ≈ 34 Hz. However, owing to the reduced local symmetry in bisBODIPYs **3**, **4**, **11**, and **12**, the fluorine atoms are no longer magnetically equivalent and show a strong ^{2}J(F,F′) coupling of 103 to 106 Hz. This leads to two complex multiplet signals in the ^{19}F NMR spectra at $\delta \approx -140$ and -147 ppm and the observation of a doublet of doublets signal in the ^{11}B NMR spectra (Figure 4). A more detailed analysis of the ^{19}F signals reveals that the low-field absorption can be fully explained as a doublet of quartets signal with ^{1}J(B,F) and ^{2}J(F1,F2) coupling, whereas the high-field signal displays a more complex pattern. This pattern can be understood if the presence of a second J(F,F) coupling between the spatially related F1 and F3 atoms is assumed. Such through-space coupling (as opposed to through-bond coupling) is known for inflexible systems such as this, in which a fluorine atom is locked at a van der Waals distance from a second NMR-active nucleus.[47–50] A simulation of the ^{19}F NMR spectrum of **3** that assumes an F1,F3 coupling of 25 Hz provides a good first-order fit of the experimental data (Figure 4, bottom). Therefore, the locked conformation of the bisBODIPY framework found in the crystalline state also appears to be present and stable under ambient conditions in solution.

Photophysical characterization: BisBODIPYs **3**, **4**, **11**, and **12** were examined by absorption and steady-state fluorescence spectroscopy in toluene. For comparison, data for monomers **13** to **16** were recorded under identical conditions, and the results are summarized in Table 3. Figure 5 shows typical spectra of both monomeric and dimeric BODIPYs.

The absorption spectrum of **12** is characterized by two major bands at 490 and 559 nm, and similar spectra are obtained for all dimers (see Table 3). A comparison of the extinction coefficient and the energy of the longest-wavelength absorption band with those of **16**, which is a similarly substituted monomer, at 529 nm clearly indicates the presence of exciton splitting for bisBODIPYs. Such behavior was expected for the dimer, given the close spatial relationship of the subchromophores of **12** and the fact that, in the observed conformation, the transition dipole moments of the component units do not cancel each other out.[51] To confirm that the observed phenomenon have a molecular origin rather than a supramolecular one, several control experiments were performed at a range of concentrations from 3×10^{-4} to 7×10^{-6} mol L^{-1}. Identical spectra were observed and it can be safely assumed that no dimerization or other aggregation phenomena are present under the working conditions.

The luminescence spectra of the bisBODIPYs display a broad emission band that is notably shifted by a Stokes shift of 79 to 83 nm with respect to the lowest-energy absorption

Table 3. Spectroscopic and luminescence data for compounds **3**, **4**, and **11**–**16** in toluene.

Compound	Absorption	Emission		
	λ_{max} [nm]	ε [10^4 M^{-1} cm^{-1}]	λ_{max}[a] [nm]	Φ_{fl}[b]
bisBODIPY **3**	393	1.66	648	0.71
	492	6.44		
	565	7.36		
bisBODIPY **4**	393	1.55	650	0.76
	494	6.46		
	567	7.15		
bisBODIPY **11**	394	1.62	638	0.67
	489	6.71		
	558	7.71		
bisBODIPY **12**	395	1.70	638	0.69
	490	7.20		
	559	8.26		
BODIPY **13**	381	0.74	540	1.00
	534	8.20		
BODIPY **14**	380	0.78	540	1.00
	535	8.89		
BODIPY **15**	378	0.70	538	0.88
	526	7.26		
BODIPY **16**	380	0.71	538	0.80
	529	7.75		

[a] Derived from corrected emission spectra. [b] Luminescence quantum yields in air-free toluene, determined by comparing corrected emission spectra and using *N*,*N*′-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide) in aerated dichloromethane as a standard (Φ_{fl} = 0.99).[52] Excitation at 490 nm.

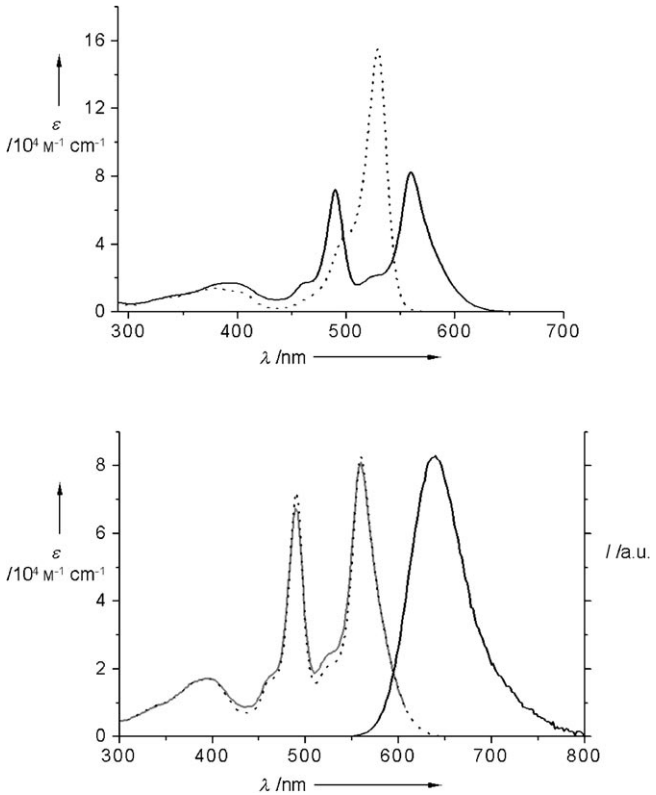


Figure 5. The spectroscopic properties of bisBODIPY **12** and BODIPY **16** in toluene. Top: absorption spectra of **12** (——) and **16** (•••••). To allow a better comparison, the absorption coefficient of **16** is multiplied by two. Bottom: absorption (•••••) and emission spectra (——) of **12** after excitation at 490 nm. The normalized excitation spectrum recorded at 640 nm is also shown (gray line).

transition. Excitation spectra registered on the emission maxima of the bisBODIPYs perfectly match the absorption spectra, which indicates a genuine emission of the dimeric species. The large Stokes shift of the emission, which for simple monomeric BODIPYs is typically in the range of 5 to 15 nm, and the relatively broad shape of the emission band are indicative of a large geometric displacement of the excited state with respect to the ground state and/or of some excimer-like character in the excited state of the covalent dimers. The fluorescence quantum yields (Φ_{fl}) of dimers **3**, **4**, **11**, and **12** have been determined to be between 0.67 and 0.76 (Table 3). These values are lower than those of the analogous monomers (**13**–**16**, Table 3), but still remarkably high. An enhancement of the intersystem crossing efficiency, with a consequent loss of fluorescence yield, has been reported for composite molecules that exhibit exciton splitting, and this situation could also apply here.[51] The presence of aryl substituents decreases the luminescence of the bisBODIPYs and that of the corresponding BODIPY monomer models by around 10%, which is likely to be caused by an enhancement of the nonradiative rate constants of the singlet excited state.[53,54] Exchanging methyl for ethyl substituents, on the other hand, does not markedly influence the photophysics. These observations are well-known for monomeric BODIPYs.[26] The time evolution of the luminescence is described by a single exponential decay under an experimental resolution of 10 ps and the measured lifetime is (3.4 ± 0.1) ns for all dimers. The luminescence lifetime of the monomers is exponential and ranges from 4 to 6 ns. The shorter lifetime of the dimers can be accounted for by enhanced intersystem crossing, which is the result of the population of an exciton-split excited state, as discussed above. To fully characterize the systems, in-depth spectroscopic and photophysical studies under different conditions are underway. It should be stressed that the monomers and dimers show very high photostability, both in air-equilibrated and air-free solutions. Indeed, the dimers are even more stable than the monomers under high-power laser irradiation.

Conclusion

In summary, we have reported the preparation, structure determination, and spectroscopic characterization of a set of highly fluorescent covalent BODIPY dimers (bisBODIPYs). As a result of the specific conformation of these species, which is present in the solid state and in solution, the photophysical properties deviate significantly from those of the monomers. In particular, the increased Stokes shift and the reduced fluorescence lifetime of the novel fluorophores are of interest in this context. These properties indicate potential uses of these new fluorophoric compounds as functional

dyes for biomedical applications and materials and also in model compounds for BODIPY aggregates.

Experimental Section

General: Solvents were dried according to standard procedures and then saturated with argon. All reagents were purchased from commercial sources and used as received, unless stated otherwise. Compounds **1**,[55] **2**,[56] **5**,[57] **7**,[58] **8**,[59] and **14**[60] were prepared as previously reported. NMR spectra were obtained by using Bruker ARX-300 or Bruker DRX-400 spectrometers. Chemical shifts (δ) are given in ppm relative to residual solvent resonances (^{1}H, ^{13}C NMR spectra) or to external standards ($BF_3{\cdot}Et_2O$ for ^{11}B and $CFCl_3$ for ^{19}F NMR spectra). High-resolution ESI mass spectra were recorded by using an IonSpec Ultima or a QStar Pulsar i. Combustion analyses (C,H,N) were performed by using an Elementar Vario EL instrument. Spectroscopic-grade toluene was used for photophysical and spectroscopic determinations. A Perkin–Elmer Lambda 9 UV/Vis spectrophotometer and a Spex Fluorolog II spectrofluorimeter were used to acquire absorption and emission spectra. Reported luminescence spectra are corrected for the photomultiplier response. Emission quantum yields were determined after correction for the photomultiplier response, with reference to an air-equilibrated toluene solution of *N*,*N*′-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide) in aerated CH_2Cl_2 with a Φ_{fl} value of 0.99.[52] Luminescence lifetimes were recorded by using IBH single-photon counting equipment (excitation at $\lambda = 465$ nm from a pulsed diode source; resolution 0.3 ns). The presence of fast components was excluded by exciting the sample with the second harmonic of a picosecond Nd/YAG laser ($\lambda = 532$ nm) and collecting the emissions with a Streak Camera; the overall resolution of the system was 10 ps. Further details on the spectroscopy/photophysics experimental setup can be found in the literature.[61,62] Single-crystal X-ray diffraction studies were performed by using Stoe IPDS-1 (**12**, **13**) or Stoe IPDS-2 (**16**) instruments. Suitable crystals were obtained by layering solutions of the compounds in CH_2Cl_2 with hexane and allowing slow diffusion at −20 °C. All of the structures were solved and refined by using the SHELXS programs for crystal structure determination[63] and refinement.[64] Crystal data and experimental details are given in Table 1. CCDC 669710, 669711, and 669712 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3,3′-Diethyl-4,4′-dimethyl-5,5′-di-4-methylbenzoyl-2,2′-bipyrrole (6): *N*-4-Methylbenzoylmorpholine (16.42 g, 80 mmol) and phosphorous oxytrichloride (16 mL, 171 mmol) were mixed under an argon atmosphere and heated at 65 °C for 3.5 h. Then, a solution of 3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole (4.32 g, 20 mmol) in 1,2-dichloroethane (80 mL) was added at RT and the mixture was heated at reflux for 4 h. The reaction was quenched with saturated Na_2CO_3 solution (600 mL) and heated for an additional hour at 80 °C. After phase separation, the aqueous layer was extracted thoroughly with dichloromethane. The combined organic extracts were dried (Na_2SO_4) and evaporated to dryness in vacuo. The brownish residue was purified by column chromatography on silica gel (CH_2Cl_2/diethyl ether 1:0 to 20:1). The brownish-yellow fraction was collected and gave **6** as a shiny yellow powder after recrystallization from dichloromethane/hexane (4.26 g, 48 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.80 (s, 2H; N*H*), 7.61 (d, $J = 8.0$ Hz, 4H; H_{ar}), 7.27 (d, $J = 8.0$ Hz, 4H; H_{ar}), 2.53 (q, $J = 7.6$ Hz, 4H; CH_2CH_3), 2.43 (s, 6H; CH_3), 2.11 (s, 6H; CH_3), 1.11 ppm (t, $J = 7.6$ Hz, 6H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 186.2$, 142.1, 137.0, 129.2, 129.1, 128.7, 127.8, 127.5, 125.6, 21.7, 18.0, 15.6, 11.7 ppm; HRMS (ESI+): *m*/*z*: calcd for $C_{30}H_{32}N_2O_2Na$ $[M+Na]^+$: 475.2356; found: 475.2358.

General procedure for 9 and 10: A solution of **6** (575 mg, 1.27 mmol) and **7** or **8** (3.80 mmol) in phosphorous oxytrichloride (10 mL) was heated at reflux for 5 h. After cooling to 60 °C and removal of all volatile compounds in vacuo, the residual dark-green tar was redissolved in methanol (300 mL). The product was precipitated by slow addition of triethylamine until the blue color of the solution faded (≈2 mL). After stirring for 1 h, the product was filtered off and washed with cold MeOH until the washings were colorless. Recrystallization from MeOH/CH_2Cl_2 gave **9** or **10** as fine, dark green powders with a metallic sheen.

2,2′-Bidipyrrin ***9***: Prepared from **7** (562 mg, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.38$ (s, 2H; N*H*), 7.25–7.21 (m, 8H; H_{ar}), 2.82 (q, $J =$ 7.5 Hz, 4H; CH_2CH_3), 2.45 (s, 6H; CH_3), 2.28 (s, 6H; CH_3), 1.84 (s, 6H; CH_3), 1.31 (s, 6H; CH_3), 1.23 (s, 6H; CH_3), 1.20 ppm (t, $J = 7.5$ Hz, 6H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.2$, 141.9, 138.0, 137.9, 137.2, 136.7, 135.9, 134.6, 132.7, 130.7, 129.8, 129.3, 128.7, 21.6, 18.3, 15.6, 15.4, 12.8, 11.4, 9.8 ppm; HRMS (ESI+): *m*/*z*: calcd for $C_{44}H_{51}N_4$ $[M+H]^+$: 635.4108; found: 635.4099; elemental analysis calcd (%) for $C_{44}H_{50}N_4{\cdot}1.5\,MeOH$: C 80.02, H 8.26, N 8.20; found: C 80.43, H 7.96, N 8.40.

2,2′-Bidipyrrin ***10***: Prepared from **8** (588 mg, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 13.53$ (br s, 2H; N*H*), 7.29 (d, $J = 7.9$ Hz, 4H; H_{ar}), 7.22 (d, $J = 7.9$ Hz, 4H; H_{ar}), 2.84 (q, $J = 7.4$ Hz, 4H; CH_2CH_3), 2.45 (s, 6H; CH_3), 2.30 (s, 6H; CH_3), 2.29 (q, $J = 7.5$ Hz, 4H; CH_2CH_3), 1.60 (q, $J = 7.3$ Hz, 4H; CH_2CH_3), 1.26 (s, 6H; CH_3), 1.18 (t, $J = 7.4$ Hz, 6H; CH_2CH_3), 1.04 (t, $J = 7.5$ Hz, 6H; CH_2CH_3), 0.671 ppm (t, $J = 7.3$ Hz, 6H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 156.9$, 143.6, 139.8, 138.9, 138.0, 137.4, 135.9, 135.6, 133.9, 133.6, 131.6, 130.0, 128.8, 21.6, 19.0, 18.4, 17.8, 16.8, 15.6, 15.2, 15.1, 11.5 ppm; HRMS (ESI+): *m*/*z*: calcd for $C_{48}H_{59}N_4$ $[M+H]^+$: 691.4734; found: 691.4727; elemental analysis calcd (%) for $C_{48}H_{58}N_4{\cdot}1.5\,MeOH$: C 80.44, H 8.73, N 7.58; found: C 80.66, H 8.46, N 7.70.

General procedure for 3, 4, 11, and 12: 2,6-Lutidine (5 mL), and then $BF_3{\cdot}Et_2O$ (12 mL), were added dropwise to an ice-cooled solution of **1**, **2**, **9**, or **10** (0.12 mmol) in Et_2O (100 mL). Then the ice bath was removed and the mixture was stirred for 10 min. The ice bath was then replaced and the reaction was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (50 mL). The aqueous layer was extracted with Et_2O, then the combined organic layers were washed with a saturated aqueous solution of Na_2CO_3 (3×20 mL), dried over $MgSO_4$, and evaporated to dryness in vacuo. The reddish residue was purified by column chromatography on silica gel (CH_2Cl_2). The strongly fluorescent red fraction contained the product. Recrystallization from CH_2Cl_2/hexane gave **3**, **4**, **11**, or **12** as analytically pure ruby-colored powders.

BisBODIPY ***3***: Prepared from **1** (29 mg, 44 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.17$ (s, 2H; CH_{meso}), 2.36 (s, 6H; CH_3), 2.33 (q, $J = 7.6$ Hz, 4H; CH_2CH_3), 2.31 (s, 6H; CH_3), 2.19 (s, 6H; CH_3), 1.92 (s, 6H; CH_3), 1.03 ppm (t, $J = 7.6$ Hz, 6H; CH_2CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta =$ 160.7, 142.8, 140.0, 134.9, 134.7, 133.6, 132.7, 127.7, 120.2, 18.1, 13.8, 13.0, 9.9, 9.5, 8.8 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -140.2$ (dq, $J(F^1,F^2) =$ 103 Hz, $J(B,F) = 34$ Hz, 2F; F^1,BF^2), −147.0–−147.6 ppm (m, 2F; F^1,BF^2); ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta = 0.52$ ppm (dd, $J(B,F^1)$, $J(B,F^2) = 34$ Hz; 2B); HRMS (ESI+): *m*/*z*: calcd for $C_{30}H_{36}B_2F_4N_4Na$ $[M+Na]^+$: 573.2954; found: 573.2957; elemental analysis calcd (%) for $C_{30}H_{36}B_2F_4N_4$: C 65.48, H 6.59, N 10.18; found: C 65.21, H 6.33, N 10.23.

BisBODIPY ***4***: Prepared from **2** (34 mg, 45 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.15$ (s, 2H; CH_{meso}), 2.74 (q, $J = 7.6$ Hz, 4H; CH_2CH_3), 2.63 (q, $J = 7.6$ Hz, 4H; CH_2CH_3), 2.39 (s, 6H; CH_3), 2.41–2.32 (m, 8H; 2× CH_2CH_3), 1.29 (t, $J = 7.6$ Hz, 6H; CH_2CH_3), 1.21 (t, $J = 7.6$ Hz, 6H; CH_2CH_3), 1.06 (t, $J = 7.6$ Hz, 6H; CH_2CH_3), 1.04 ppm (t, $J = 7.6$ Hz, 6H; CH_2CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 160.4$, 145.8, 143.3, 141.5, 133.7, 133.3, 133.1, 132.1, 120.2, 18.3, 18.1, 17.9, 17.2, 16.8, 16.7, 14.7, 14.3, 12.9 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -140.4$ (dq, $J(F^1,F^2) =$ 103 Hz, $J(B,F) = 34$ Hz, 2F; F^1BF^2), −146.6–−147.2 ppm (m, 2F; F^1BF^2); ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta = 1.10$ ppm (dd, $J(B,F^1)$, $J(B,F^2) = 34$ Hz; 2B); HRMS (ESI+): *m*/*z*: calcd for $C_{36}H_{48}B_2F_4N_4Na$ $[M+Na]^+$: 657.3893; found: 657.3898; elemental analysis calcd (%) for $C_{36}H_{48}B_2F_4N_4$: C 68.16, H 7.63, N 8.83; found: C 67.85, H 7.64, N 8.77.

BisBODIPY ***11***: Prepared from **9** (57 mg, 65 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.37$–7.25 (m, 8H; H_{ar}), 2.47 (s, 6H; CH_3), 2.42 (s, 6H; CH_3), 2.29–2.21 (m, 4H; CH_2CH_3), 1.85 (s, 6H; CH_3), 1.44 (s, 6H; CH_3), 1.35 (s, 6H; CH_3), 0.95 ppm (t, $J = 7.6$ Hz, 6H; CH_2CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 158.7$, 142.6, 142.2, 141.4, 139.1, 136.8, 134.8, 132.8, 132.6, 131.7, 129.9, 129.8, 128.4 (2C), 128.2, 21.2, 18.1, 13.9, 13.0, 12.3,

12.2, 8.8 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -137.2$ (dq, $J(F^1,F^2) = 103$ Hz, $J(B,F) = 34$ Hz, 2F; F^1BF^2), -147.1 – -147.6 ppm (m, 2F; F^1BF^2); ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta = 1.00$ ppm (dd, $J(B,F^1)$, $J(B,F^2) = 34$ Hz; 2B); HRMS (ESI+): *m/z*: calcd for $C_{44}H_{48}B_2F_4N_4Na$ $[M+Na]^+$: 753.3893; found: 753.3893; elemental analysis calcd (%) for $C_{44}H_{48}B_2F_4N_4$: C 72.34, H 6.62, N 7.67; found: C 71.91, H 6.81, N 7.58.

BisBODIPY ***12***: Prepared from **10** (61 mg, 65%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.40$–7.32 (m, 8H; H_{ar}), 2.47 (s, 6H; CH_3), 2.43 (s, 6H; CH_3), 2.32 (q, $J = 7.5$ Hz, 4H; CH_2CH_3), 2.28–2.21 (m, 4H; CH_2CH_3), 1.79–1.66 (m, 4H; CH_2CH_3), 1.39 (s, 6H; CH_3), 1.02 (t, $J = 7.5$ Hz, 6H; CH_2CH_3), 0.94 (t, $J = 7.6$ Hz, 6H; CH_2CH_3), 0.72 ppm (t, $J = 7.5$ Hz, 6H; CH_2CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 158.8$, 147.5, 142.8, 142.2, 139.1, 137.1, 134.9, 134.4, 132.2, 131.9, 131.8, 129.4, 129.3, 128.7, 128.5, 21.2, 18.7, 18.1, 17.0, 16.1, 14.6, 13.9, 12.8, 12.2 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -139.2$ (dq, $J(F^1,F^2) = 106$ Hz, $J(B,F) = 34$ Hz, 2F; F^1BF^2), -146.2 – -146.9 ppm (m, 2F; F^1BF^2); ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta = 0.05$ ppm (dd, $J(B,F^1)$, $J(B,F^2) = 34$ Hz; 2B); HRMS (ESI+): *m/z*: calcd for $C_{48}H_{56}B_2F_4N_4Na$ $[M+Na]^+$: 809.4519; found: 809.4526; elemental analysis calcd (%) for $C_{48}H_{56}B_2F_4N_4$: C 73.29, H 7.18, N 7.12; found: C 72.90, H 7.25, N 6.95.

Preparation of BODIPY 13: NEt_3 (9.6 mL) and $BF_3{\cdot}Et_2O$ (12 mL) were added to a solution of 4-ethyl-3,3′,4′,5,5′-pentamethyldipyrrin hydrobromide[65] (647 mg, 2 mmol) in CH_2Cl_2 (200 mL). After stirring for 1 h, the mixture was added to a saturated solution of Na_2CO_3. After phase separation, the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with a saturated aqueous solution of Na_2CO_3 (3×20 mL), dried over Na_2SO_4, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/pentane 1:2). Compound **13** was obtained as a red powder after recrystallization (CH_2Cl_2/MeOH) of the residue obtained from the strongly fluorescent greenish-yellow fraction (403 mg, 69%). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.06$ (s, 1H; CH_{meso}), 2.49 (s, 3H; CH_3), 2.48 (s, 3H; CH_3), 2.44 (q, $J = 7.6$ Hz, 2H; CH_2CH_3), 2.22 (s, 3H; CH_3), 2.20 (s, 3H; CH_3), 1.97 (s, 3H; CH_3), 1.11 ppm (t, $J = 7.6$ Hz, 3H; CH_2CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 155.1$, 154.4, 137.6, 137.0, 132.3, 131.8, 125.5 (2C), 118.8, 17.3, 14.4, 12.5, 12.3, 9.4, 9.2, 8.7 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -146.4$ ppm (q, $J(B,F) = 34$ Hz, 2F; B*F*); ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta = 0.73$ ppm (t, $J(B,F) = 34$ Hz, 1B; *B*F); HRMS (ESI+): *m/z*: calcd for $C_{16}H_{22}BF_2N_2$ $[M+H]^+$: 291.1839; found: 291.1838; elemental analysis calcd (%) for $C_{16}H_{21}BF_2N_2$: C 66.23, H 7.29, N 9.65; found: C 66.11, H 7.23, N 9.76.

General procedure for *meso* aryl-substituted BODIPYs: A mixture of **7** or **8** (6 mmol) and 4-methylbenzoylchloride (3 mmol) in CH_2Cl_2 (60 mL) was stirred at RT for 4 d. NEt_3 (18 mmol) and $BF_3{\cdot}Et_2O$ (24 mmol) were added and the mixture was stirred for an additional day. The mixture was then poured into a saturated aqueous solution of $NaHCO_3$. After phase separation, the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (3×20 mL), dried with Na_2SO_4, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/pentane 1:1). The product was obtained as orange needles after recrystallization (CH_2Cl_2/MeOH) of the residue obtained from the strongly fluorescent greenish-yellow fraction.

BODIPY ***15***: Prepared from **7** (423 mg, 42%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.34$–7.27 (m, 4H; H_{ar}), 2.48 (s, 6H; CH_3), 2.44 (s, 3H; CH_3), 1.86 (s, 6H; CH_3), 1.31 (s, 6H; CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 153.7$, 140.8, 139.2, 138.9, 132.7, 130.9, 129.8, 128.2, 126.5, 21.2, 12.5, 11.9, 8.7 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -146.2$ ppm (q, $J(B,F) = 34$ Hz, 2F; B*F*); ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta = 0.03$ ppm (t, $J(B,F) = 34$ Hz, 1B; *B*F); HRMS (ESI+): *m/z*: calcd for $C_{22}H_{25}BF_2N_2Na$ $[M+Na]^+$: 389.1971; found: 389.1973; elemental analysis calcd (%) for $C_{22}H_{25}BF_2N_2{\cdot}0.25\,H_2O$: C 71.27, H 6.93, N 7.56; found: C 71.10, H 6.72, N 7.65.

BODIPY ***16***: Prepared from **8** (570 mg, 45%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.36$–7.17 (m, 4H; H_{ar}), 2.48 (s, 6H; CH_3), 2.44 (s, 3H; CH_3), 2.32 (q, $J = 7.6$ Hz, 4H; CH_2CH_3), 1.61 (q, $J = 7.5$ Hz, 4H; CH_2CH_3), 1.04 (t, $J = 7.6$ Hz, 6H; CH_2CH_3), 0.68 ppm (t, $J = 7.5$ Hz, 6H; CH_2CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 154.2$, 145.6, 140.9, 139.1, 132.6, 132.0, 130.2, 128.9, 128.7, 21.3, 18.6, 17.0, 16.3, 14.9, 12.4 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -145.7$ ppm (q, $J(B,F) = 34$ Hz, 2F; B*F*); ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta = 0.23$ ppm (t, $J(B,F) = 34$ Hz, 1B; *B*F); HRMS (ESI+): *m/z*: calcd for $C_{26}H_{33}BF_2N_2Na$ $[M+Na]^+$: 445.2597; found: 445.2604; elemental analysis calcd (%) for $C_{26}H_{33}BF_2N_2{\cdot}1.5\,H_2O$: C 69.49, H 8.02, N 6.24; found: C 69.37, H 7.76, N 5.96.

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