DOI: 10.1002/zaac.200900435

Solution and Solid State Structure of a BisBODIPY Fluorophor

Martin Bröring,*[a] Yuan Yuan,[a] Robin Krüger,[a] Christian Kleeberg,[a] and Xiulan Xie[a]

Keywords: Fluorescence; NMR spectroscopy; X-ray diffraction; Conformation; BODIPY; Tetrapyrroles

Abstract. The solution and solid-state structures of 3,3'-diethyl-4,4',8,8',9,9',10,10'-octamethyl-6,6'-di-*p*-tolyl-bisBODIPY, a potent fluorescent dye, were examined by X-ray diffraction and NMR spectroscopy. The crystallographic analysis resulted in two different conformations for the fluorophor with dihedral angles between the C_9N_2B subunits of 91.9 and 96.8°. The presence of two different conformations is a consequence of the crystal packing as the 3D structure is composed of alternating layers of BisBODIPY molecules with and without cocrystallized solvent. In solution NMR spectroscopic studies the compound displays intramolecular and distance dependant *through space* C–F and F–F couplings, which were used to analyze the solution structure. This analysis suggests a single minimum conformation and a rigid, but unstrained structure in solution. The fluorescence properties of the BisBODIPY and in particular the high quantum yields found for this class of luminophores are qualitatively in agreement with the latter result, and better described by the solution structure than by the solid-state structure.

Introduction

BisBODIPYs [1] are potent novel fluorophors that can be prepared by the action of boron trifluoride diethyletherate and a base on a certain class of artificial open-chain tetrapyrroles, the 2,2'-bidipyrrins [2]. These tetrapyrroles are very versatile in coordination compounds and have been used before as ligands in helical transition metal complexes [3], in helicates [4], and in polynuclear complexes [5]. They also show much potential as precursors in the oxidative macrocyclization to metallocorroles [6] and other macrocyclic non-natural porphyrinoids [7]. In this sense, BisBODIPYs can be regarded as dinuclear difluoridoboron complexes of 2,2'-bidipyrrin ligands. Their properties, however, relate more to those of the mononuclear entities, the so-called BODIPYs (BOron-DIPYrrins), which are of great technological interest due to their unique photophysical properties [8].

The photophysical properties of BisBODIPYs are governed by a narrow excitation-coupled longest wavelength absorption and by a large Stokes shift of about 70 nm. These features are present in addition to the high fluorescence quantum yield of ≥ 70 % that is typical for most BODIPY dyes [9]. Such high quantum yields are usually only present in rigid compounds, which are devoid of significant intramolecular motion, as vibrations and rotations quench the exited states through non-radiative processes [10]. The structural data obtained on solid BisBODIPYs so far, however, are not in agreement with the photophysical findings. In fact, three different molecular conformations with dihedral angles between the monomeric BODIPY subunits of 79.9, 91.4, and 96.5° are realized in the structural determinations known to date. This structural finding indicates a significant degree of conformational freedom in these molecules and the presence of several low-energy conformers in the solid state (Figure 1). The molecular structures also prove the presence of very short intramolecular F···F and F···CH_2 distances close to the centers of the molecules, which are at or even below the van der Waals limits in most instances [1, 6e]. In solution, these contacts are documented by the pres-

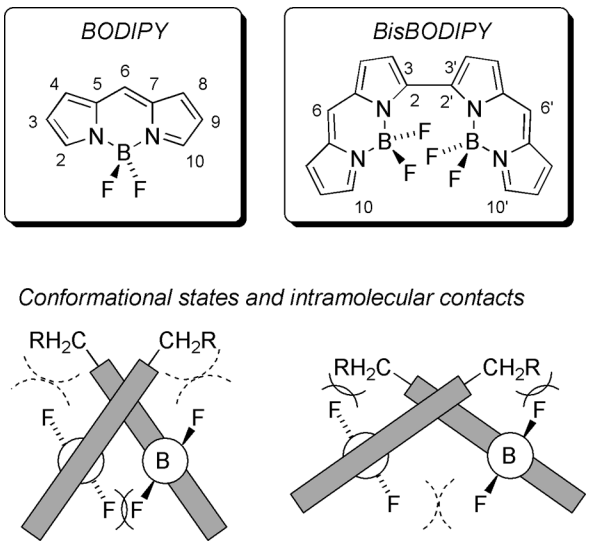


Figure 1. General formulae of BODIPYs and BisBODIPYs with numbering schemes, and intramolecular conformations of the latter with respect to the dihedral angle between monomeric subunits.

* Prof. Dr. M. Bröring
Fax: +49-6421-282-5653
E-Mail: broering@staff.uni-marburg.de
[a] Fachbereich Chemie
Philipps-Universität
Hans-Meerwein-Straße
35032 Marburg, Germany

Zeitschrift für anorganische und allgemeine Chemie ZAAC Journal of Inorganic and General Chemistry

ence of *through-space* F···F and F···C couplings in the ^{19}F and ^{13}C NMR spectra [11]. In principle, the size of such *through-space* coupling constants depends on the distance between the coupling nuclei [12] and can thus be used in order to assign solution conformations and dynamics in molecular systems [13]. We applied both, the NMR spectroscopic method of solution structure determination as well as a single-crystal X-ray diffraction experiment to BisBODIPY (**1**) (Figure 2) and report herein on our results.

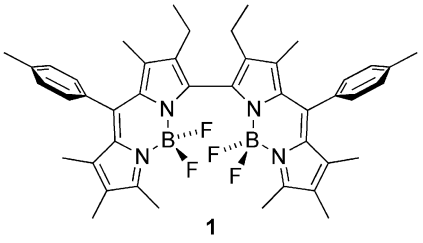


Figure 2. 3,3'-Diethyl-4,4',8,8',9,9',10,10'-octamethyl-6,6'-di-*p*-tolyl-bisBODIPY (**1**).

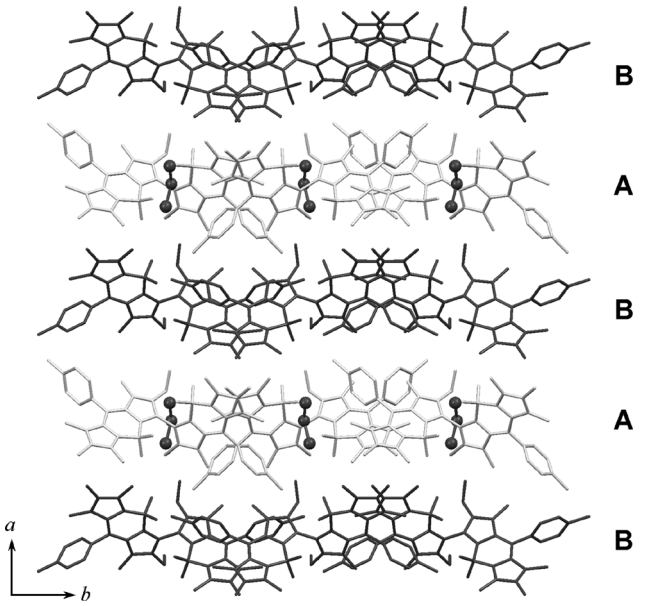


Figure 3. Packing pattern of **1** (view in crystallographic *c* direction; hydrogen atoms removed for clarity). Molecules with different conformations **A** and **B** are given in bright and dark gray, respectively. The solvent sites inside layer **A** are marked as dark gray ball-and-stick items.

Results and Discussion

Crystallographic Investigation

Compound **1** was prepared by the treatment of the tetrapyrrole with BF_3 diethyletherate as detailed in an earlier instance [1]. A single crystal of **1** grew from a dichloromethane/methanol solution at 4 °C. The compound crystallizes in purple blocks. The asymmetric unit contains two molecules of **1** and 0.7 dichloromethane molecules, and the molecular parameters of the two distinct BisBODIPY molecules in the unit cell and their conformations differ slightly from each other. The layered packing pattern in the crystal is shown in Figure 3. Figure 4 provides selected views of the conformations of molecules **A** and **B**, and Table 1 summarizes molecular parameters for both molecules of **1**.

The crystal of **1** is composed of two alternating undulated layers **A** and **B**, which are packed in the *a* direction. Layers **A** contain BisBODIPY molecules (**1**) of the conformation **A** and solvent sites that are occupied by dichloromethane molecules to 70 %. Both axial chiral enantiomers of **1A** are present in a 1:1 ratio. Layers **B** contain only BisBODIPY molecules (**1**) of the conformation **B**, again as the racemate, and no solvent sites. As apparent from Figure 3 and from the presence of the solvent molecules in only one of the layers, the packing within the layers differs slightly. The finding of two different molecular conformations of **1** in the single crystal can thus be assigned to a genuine packing effect.

The BisBODIPY molecules (**1**) themselves also appear slightly strained and forced to non-ideal conformations in the crystal. Compared to the typically almost planar C_9BN_2 subunit and the symmetric binding of the boron atom to both nitrogen donors in monomeric BODIPYs and related compounds [1, 6a, 14] some elements of distortion are present here (Figure 4 and Table 1). The B–N distances within one BODIPY

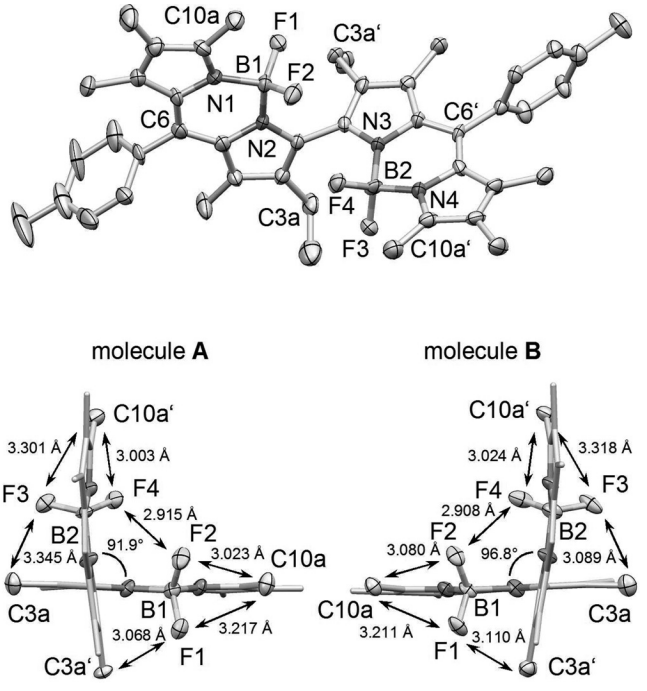


Figure 4. Molecular structure of **1**. Top: View of the complete molecule **A** (hydrogen atoms removed). Bottom: Views along the central pyrrole–pyrrole bonds of molecules **A** and **B**, with intramolecular short contacts and dihedral angles (hydrogen and selected substituent carbon atoms removed for clarity).

subunit differ from each other by 0.008–0.058 Å, and the C_9BN_2 subunits of **1** are bowl-shaped rather than planar. All other bond lengths, angles, and distances within the BODIPY

Table 1. Selected bond lengths /Å and angles /° for molecules **A** and **B** of BisBODIPY (**1**).

	Molecule **A**		Molecule **B**	
	B1[a)]	B2[a)]	B1[a)]	B2[a)]
B–N1[b)]	1.575(8)	1.556(9)	1.539(8)	1.578(9)
B–N2	1.524(10)	1.564(9)	1.565(9)	1.520(10)
B–F1	1.401(8)	1.386(10)	1.381(9)	1.400(9)
B–F2	1.363(8)	1.367(8)	1.369(9)	1.368(9)
C6–C7	1.403(10)	1.394(9)	1.392(10)	1.377(10)
C5–C6	1.423(9)	1.420(8)	1.395(9)	1.412(9)
C2–C2'	1.488(7)		1.485(8)	
N1–B–N2	106.0(5)	106.1(5)	106.7(5)	106.4(5)
N1–B–F1	108.1(5)	107.7(5)	108.6(5)	108.0(6)
N1–B–F2	110.6(6)	111.6(6)	110.5(6)	109.5(6)
N2–B–F1	109.9(6)	110.7(6)	110.0(6)	111.5(6)
N2–B–F2	111.6(5)	111.1(5)	111.2(5)	111.2(6)
F1–B–F2	110.5(6)	109.5(6)	109.8(5)	110.0(5)

a) Monomeric subunit containing the atom B1 etc.b) C atom numbering scheme adopted from Figure 1. N1, N2, F1, F2 and C*X* in subunit B1 used equivalent to N4, N3, F3, F4 and C*X*' in subunit B2, respectively.

subunits of **1**, including the almost perpendicular orientations of the *p*-tolyl substituents (conformer **A**: B1 side: 86.39°; B2 side: 75.21°; conformer **B**: B1 side: 84.46°; B2 side: 81.33°), however, are very similar to the findings on related monomers.

The intramolecular interactions in **1** deserve special attention. The subunits are bound together at C2–C2' in typical distances for $C(sp^2)$–$C(sp^2)$ single bonds of 1.489 and 1.484 Å, and with dihedral angles of 91.91° and 96.18° between the C_9BN_2 mean squares planes of conformers **A** and **B**, respectively (Figure 4). By this arrangement the inwards pointing fluorine atoms F2 and F4 are situated in close contact of only 2.915 and 2.908 Å, and the BF_2 subunits are displaced outwards from their C_9BN_2 mean planes by up to 0.178 Å in order to reduce the steric interaction in the centre of the molecules. The other two fluorine atoms F1 and F3 show short F–C distances to the methyl group carbon atom C10a of the same subunit (F1–C10a: 3.217/3.211 Å; F3–C10a': 3.301/3.318 Å) and to an ethyl group carbon atom of the *other* side (F1–C3a': 3.068/3.110 Å; F3–C3a: 3.345/3.089 Å). This data indicates very intimate interactions, but also proofs the absence of significant intramolecular strain between the locked subunits of **1**.

NMR Examination and Solution Conformation

The close spatial relationship of the NMR active carbon and fluorine nuclei stated above results in the observation of additional signal splitting in the heteronuclear NMR spectra of **1**. As mentioned in the introduction, distance dependant *through space* coupling interactions are responsible for these findings, and their analysis generally allows a conformational analysis of **1** in solution. Therefore, all signals and coupling constants observed in the ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra of **1** were assigned and quantified.

The ^1H NMR spectrum of **1** contains five singlet signals for the different methyl group protons as expected for a BisBODIPY molecule with an effective C_2 symmetry. These signals could be assigned to specific positions by using proximity information through NOE observation. The 3-ethyl substituent produces a triplet signal at 0.95 ppm (3H, $^3J_{HH}$ = 7.6 Hz) and a multiplet signal at 2.20–2.31 ppm, indicating a weak diastereotopic splitting of the methylene protons. For the same reason the four aromatic protons of the *p*-tolyl substituents give rise to a complex higher order signal. The assignment of the ^{13}C NMR resonances was achieved using C–H correlation spectra (HSQC, HMBC). All ^1H and ^{13}C chemical shifts of **1** are listed in Table 2.

Figure 5 provides a detailed view on the aliphatic region of the ^{13}C NMR spectrum of **1**. Both signals of the ethyl group carbon atoms C3a and C3b are split to doublet signals with coupling constants of 4.2 and 2.0 Hz, respectively, whereas for C10a only a broadened signal without a clearly resolved fine structure is recorded. The gated $^{13}C\{^1H\}$ NMR spectrum shows a triplet of double quartets for C3a (J = 127.5, 4.2, 4.2 Hz) and a quartet of double triplets for C3b (J = 126.2, 4.6, 2.6 Hz). The corresponding ^1H-coupled $^{13}C\{^{19}F\}$ NMR spectra reveal a triplet of quartets (J = 127.5, 4.2 Hz) and a quartet of triplets (J = 126.2, 2.6 Hz) for C3a and C3b, respectively. These experiments indicate that both C3a *and* C3b couple with one ^{19}F nucleus of the outwards pointing fluorine atom, with coupling constants of 4.4 and 2.4 Hz. For C10a, the ^1H-coupled $^{13}C\{^{19}F\}$ NMR experiment unraveled the coupling with two different fluorine nuclei with coupling constants of $\leq$ 2.0 and $\leq$ 1.0 Hz.

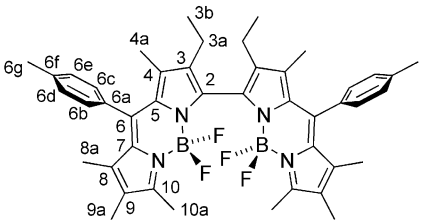
C–F *through space* coupling was explained to be due to a direct interaction between a fluorine lone pair orbital and the σ* orbital of a sterically opposed C–H bond, whereby the former operates as electron donor and the latter as electron acceptor. *Hsee* et al [12e] measured the through-space ^{13}C–^{19}F coupling constant J^{TS}_{CF} in a series of polycyclic aromatic hydrocarbons and drew a relationship between J^{TS}_{CF} (in Hz) and the non-bonded H–F distance d_{HF} (in Å) as:

$$J_{CF}^{TS} = 5541 \cdot e^{-2.44 d_{HF}}$$

With the observed ^{13}C–^{19}F *through space* coupling constants and by using Equation (1), the distances between the fluorine-

Zeitschrift für anorganische und allgemeine Chemie ZAAC Journal of Inorganic and General Chemistry

Table 2. ^{1}H- and ^{13}C NMR signal assignments for **1**.



Position	δ^{1}H /ppm	J_{HH} /Hz	δ^{13}C /ppm	J_{CF} /Hz
2	–		142.90	
3	–		135.07	
3a	2.20–2.31 (m)	15.0/7.6	18.37 (d)	4.4
3b	0.95 (t)	7.6	14.21 (d)	2.4
4	–		137.13	
4a	1.45		12.57	
5	–		131.96	
6	–		142.43	
6a	–		132.88	
6b/c	7.25–7.27 (m), 7.20–7.33 (m)		128.72/128.46	
6d/e	7.35–7.37 (m)		130.18/130.11	
6f	–		139.39	
6 g	2.47		21.53	
7	–		133.11	
8	–		141.74	
8a	1.35		12.45	
9	–		128.72	
9a	1.85		9.07	
10	–		159.00	
10a	2.42		13.25 (br.s)	

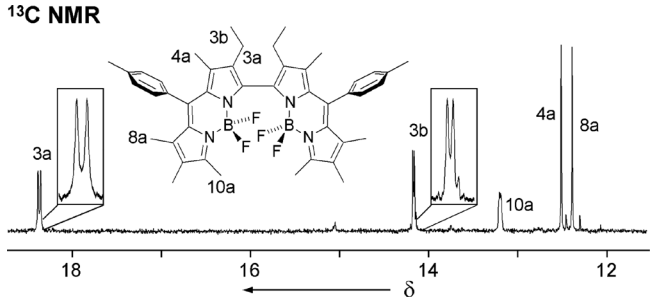


Figure 5. Details from the ^{13}C NMR spectrum of **1** (400 MHz, CD_2Cl_2) with assignments.

and hydrogen atoms attached to the corresponding carbon atoms were calculated. Equation (1) was optimized for molecules, in which only CH groups were considered. For our compounds CH_3 and CH_2 groups are concerned, so that a certain approximation is necessary in order to compare these data with the crystallographic findings. For the structure determination of biological macromolecules *Wüthrich* et al. introduced the concept of pseudoatoms. These are to be created as points of reference for proton–proton distance constraints for the individual protons in methylene or methyl groups in the absence of a stereospecific resonance assignment [15]. In the case here, the distances between the fluorine- and hydrogen atoms of several methylene and methyl groups are concerned. By using the crystallographic data and the Tripos program package Sybyl [16], pseudoatoms H* were added to the methylene and methyl groups at C3a, C3b and C10a, and fluorine-proton distances were measured between the fluorine atoms and the corresponding pseudoatoms H*. Applying these concepts, the distances between the fluorine and H* atoms of **1** in solution and in the solid are calculated to $d(F_{out}–H_{C3a}*)$ = 2.9/3.1 Å, $d(F_{out}–H_{C3b}*)$ = 3.2/4.0 Å, $d(F_{out}–H_{C10a}*)$ = 3.5/3.1 Å, and $d(F_{in}–H_{C10a}*)$ = 3.2/3.4 Å, respectively. As a general trend, the F–H* distances appear shorter in solution than in the solid state and indicate either a more stretched or a more compact and rigid overall molecular shape. The drastically shortened distance $d(F_{out}–H_{C3b}*)$, on the other hand, can only be explained by a significantly different conformation of the ethyl substituents which stay in close contact to the outwards pointing fluorine atoms F1 and F3 in solution.

For the description of the relative orientation and distance of the fluorine atoms at the inner core of **1** in solution, heteronuclear ^{11}B and ^{19}F NMR experiments were performed (Figure 6). The ^{11}B NMR spectrum shows a double doublet signal at 0.0 ppm with couplings J = 29.0 and 34.2 Hz. The splitting of the signal is due to two $^{1}J_{BF}$ couplings as only a singlet is observed in a $^{11}B\{^{19}F\}$ NMR experiment. The inwards and outwards pointing fluorine atoms of **1** produce two multiplet signals at –138.9 and –146.3 ppm in the ^{19}F NMR spectrum. Because of the close spatial relationship of the BF_2 subunits in BisBODIPY (**1**) this spin system is of higher order and was analyzed with the Bruker program DAISY. A simulated spectrum with $^{1}J(F_{out}B)$ = 34.2, $^{1}J(F_{in}B)$ = 29.0, $^{2}J(F_{out}F_{in})$ = 105.0 Hz, and $J^{TS}(F_{in}F_{in'})$ = 24.1 Hz is shown in Figure 6. The remaining differences between the observed and fitted spectra of **1** are due to contributions from the ^{10}B nucleus.

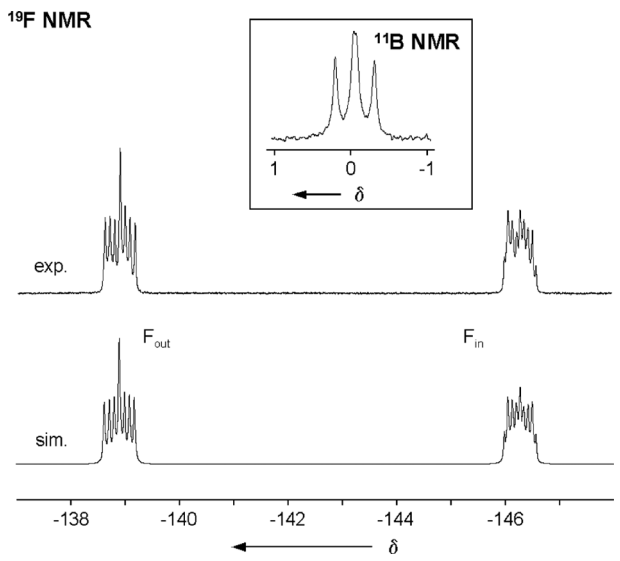


Figure 6. ^{19}F NMR spectrum (376 MHz; top trace) with simulation (bottom) and ^{11}B NMR spectrum (128 MHz; inset) of **1** (both in CD_2Cl_2).

A quantitative analysis of the observed F–F *through space* coupling allows calculating the fluorine–fluorine distance d_{FF} and thus provides the desired conformational information. Similar to the above described ^{13}C–^{19}F coupling case, *through space* ^{19}F–^{19}F coupling is caused by an overlap of two lone-pair orbitals of fluorine substituents in close proximity, and J^{TS}_{FF} decays exponentially with d_{FF}. Nevertheless, in this case two different models have been published [12c, 13b], which were fitted for fluorine-substituted unsaturated hydrocarbons and coupling constants below 100 Hz. These models are given in Equation (2) and Equation (3) below.

$$J^{TS}_{FF} = 6800 \cdot e^{-1.99 d_{FF}}$$

$$J^{TS}_{FF} = 1.70 \times 10^{7} \cdot e^{-4.96 d_{FF}}$$

The application of these models to the NMR spectroscopic data of BisBODIPY (**1**) results in F_{in}–F_{in} distances of 2.84 and 2.72 Å, respectively, as opposed to 2.91 and 2.92 Å in the solid. As before, the solution values are smaller than the data observed from the crystal structure analysis. This result is inconsistent with a stretched conformation in solution, but confirms the above suggestion, that **1** resides in a more compact and rigid conformation in solution, presumably with almost planar C_9BN_2 subunits and only slightly displaced BF_2 groups.

Conclusions

In summary we have presented the results of structural analyses of the BisBODIPY (**1**) in the solid and in solution and could show that significant differences occur for this class of luminophores. In the crystal the compound forms a layered structure with **1** in two different, but slightly strained conformations, while in solution a single, compact minimum conformation prevails. The finding of the more rigid form in solution rather than in the solid may be explained by a shallow energy potential for the rotation around the central C–C bond. In the solid, this shallow potential allows the observed finding of several slightly different conformers while in solution a fast dynamic process superimposes all conformers to one observed single minimum. The uniformity of BisBODIPY (**1**) in solution relates directly to the photophysical properties and in particular to the high fluorescence quantum yields. In this light, the structural differences observed in the solid state appear to be induced by the crystal packing. BisBODIPYs do indeed not crystallize readily and realize different packing pattern for all known derivatives. The solution structural study described here thus helps explain the photophysical properties of these compounds better than the solid-state structures.

Experimental Section

Collection and Reduction of X-ray Data

Intensity data for **1** were collected from a single crystal at 100(2) K, using a Stoe IPDS-II X-ray diffractometer. Graphite monochromated Mo-K_α radiation (0.71073 Å) was used. The structure was solved by direct methods with SIR-2004 [17]. The crystal is twinned by pseudo-merohedry, and the twin ratio refines to 65:35. The twinning emulates an orthorhombic Laue symmetry. No splitting of the reflections could be observed. Refinements were carried out by full-matrix least-squares techniques against $F2$ using SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions.

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-724077. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223) 336-033; E-Mail: deposit@cam.ac.uk].

Crystal data for 1: $C_{44}H_{48}B_2F_4N_4 \cdot 0.352CH_2Cl_2$, 760.42, monoclinic, space group Pc, a = 16.462(8), b = 19.974(7), c = 12.188(6) Å, $\alpha = \beta = \gamma = 90°$, V = 4008(3) Å^3, Z = 4, ρ_{calc} = 1.26 g·cm^{-3}, μ(Mo-K_α) = 0.130 cm^{-1}, θ_{min} = 1.60°, θ_{max} = 25.19°, 16457 reflections measured, 6807 independent, 5214 observed with $I > 2\sigma(I)$, 1026 parameters, 3 restraints, R_1 [$I > 2\sigma(I)$] = 0.0481, wR_2 (all data) = 0.0981, max./min. peak = 0.293/–0.254 e·Å^{-3}.

Analytical data for 1 [1]: 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 %.

NMR Measurements

An amount of **1** (20 mg) was dissolved in CD_2Cl_2 (0.7 mL). The ^{11}B NMR spectra, ^{13}C NMR spectra with ^1H decoupling and with gated ^1H decoupling (denoted as gated $^{13}C\{^1H\}$), with ^{19}F decoupling (denoted as $^{13}C\{^{19}F\}$), and ^{19}F NMR spectra were recorded with a Bruker 5 mm BBO probe on a DRX-400 spectrometer. For all ^{13}C NMR experiments, a relaxation delay of 2.0 s was used and transients between 20000 and 24000 were recorded. ^{11}B NMR spectra with and without ^{19}F decoupling (denoted as $^{11}B\{^{19}F\}$) were recorded with a relaxation delay of 300 ms and 256~512 transients. In order to have accurate coupling constants through simulation, ^{19}F NMR spectra with high quality were taken on diluted samples (10 mg of **1** in 0.7 mL of CD_2Cl_2), with a relaxation delay of 3 s and 512 transients. Two-dimensional spectra were recorded at room temperature with a Bruker Avance 600 MHz spectrometer equipped with a 5 mm inverse probe with z-gradient. NOESY spectra were taken on complex **1** at a mixing time of 1.5 s. DQF-COSY and NOESY experiments were performed in phase-sensitive mode using States-TPPI. Spectra were collected with 8 transients, 4096 points in the F_2 dimension and 512 increments in the F_1 dimension. A phase-sensitive gradient-selected HSQC experiment was performed with sensitivity enhancement [19]. Spectra were recorded with 8 transients, 2048 points in the F_2 dimension and 512 increments in the F_1 dimension, with spectral width of 10 ppm in the ^1H dimension and 130 ppm in the ^{13}C dimension. The gradient-selected HMBC experiment [20] was optimized for a coupling constant of 8 Hz, without decoupling on ^{13}C during acquisition. Spectra were taken with 16 transients, 2048 points in the F_2 dimension and 512 increments in the F_1 dimension, with spectral widths of 10 ppm in the ^1H dimension and 165 ppm in the ^{13}C dimension. ^1H and ^{13}C chemical shifts were referenced to the solvent signals. ^{19}F and ^{11}B chemical shifts were referenced to external standards CCl_3F and $BF_3 \cdot Et_2O$, respectively. All spectra were processed with a Bruker TOPSPIN 2.1.

Acknowledgement

We gratefully acknowledge the *Deutsche Forschungsgemeinschaft* for funding the Bruker AVANCE 600 spectrometer and the *VW Founda-*

tion as well as the *Deutsche Forschungsgemeinschaft* for supporting the preparative work.

References

[1] M. Bröring, R. Krüger, S. Link, C. Kleeberg, S. Köhler, X. Xie, B. Ventura, L. Flamigni, *Chem. Eur. J.* **2008**, *14*, 2976–2983.

[2] A. W. Johnson, R. Price, *J. Chem. Soc.* **1960**, 1649–1653; H. Falk, H. Flödl, U. G. Wagner, *Monatsh. Chem.* **1988**, *119*, 739–749; M. Bröring, *Synthesis* **2000**, 1291–1294; M. Bröring, D. Griebel, C. Hell, A. Pfister, *J. Porphyrins Phthalocyanines* **2001**, *5*, 708–714; L. Simkhovich, I. Goldberg, Z. Gross, *Org. Lett.* **2003**, *5*, 1241–1244; H. S. Gill, I. Finger, I. Bozidarevic, F. Szydlo, M. J. Scott, *New J. Chem.* **2005**, *29*, 68–72.

[3] a) M. Bröring, C. D. Brandt, J. Lex, H.-U. Humpf, J. Bley-Escrich, J.-P. Gisselbrecht, *Eur. J. Inorg. Chem.* **2001**, 2549–2556; b) M. Bröring, C. D. Brandt, J. Bley-Escrich, J.-P. Gisselbrecht, *Eur. J. Inorg. Chem.* **2002**, 910–917; c) M. Bröring, C. D. Brandt, *Monatsh. Chem.* **2002**, *133*, 623–630; d) M. Bröring, S. Köhler, S. Link, O. Burghaus, C. Pietzonka, H. Kelm, H.-J. Krüger, *Chem. Eur. J.* **2008**, *14*, 4006–4016; e) M. Bröring, S. Köhler, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1469–1471.

[4] a) M. Bröring, S. Link, C. D. Brandt, E. Cónsul Tejero, *Eur. J. Inorg. Chem.* **2007**, 1661–1670; b) Y. Zhang, A. Thompson, S. J. Rettig, D. Dolphin, *J. Am. Chem. Soc.* **1998**, *120*, 13537–13538.

[5] a) M. Bröring, A. Pfister, K. Ilg, *Chem. Commun.* **2000**, 1407–1408; b) M. Bröring, C. D. Brandt, E. Cónsul Tejero, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1793–1798; c) M. Bröring, E. Cónsul Tejero, *J. Organomet. Chem.* **2005**, *690*, 5290–5299.

[6] a) M. Bröring, C. Hell, *Chem. Commun.* **2001**, 2336–2337; b) M. Bröring, F. Brégier, E. Cónsul Tejero, C. Hell, M. C. Holthausen, *Angew. Chem.* **2007**, *119*, 449–452; *Angew. Chem. Int. Ed.* **2007**, *46*, 445–448; c) M. Bröring, C. Hell, C. D. Brandt, *Chem. Commun.* **2007**, 1861–1862; d) M. Bröring, C. Hell, M. Steiner, C. D. Brandt, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1082–1086; e) M. Bröring, F. Brégier, R. Krüger, C. Kleeberg, *Eur. J. Inorg. Chem.* **2008**, 5505–5512.

[7] a) M. Bröring, E. Cónsul Tejero, A. Pfister, C. D. Brandt, J. J. Pérez Torrente, *Chem. Commun.* **2002**, 3058–3059; b) M. Bröring, C. Hell, C. D. Brandt, E. Cónsul Tejero, *J. Porphyrins Phthalocyanines* **2003**, *7*, 214–219; c) M. Bröring, C. Hell, F. Brégier, O. Burghaus, E. Cónsul Tejero, *Inorg. Chem.* **2007**, *46*, 5477–5479; d) M. Bröring, S. Köhler, C. Kleeberg, *Angew. Chem.* **2008**, *120*, 5740–5743; *Angew. Chem. Int. Ed.* **2008**, *47*, 5658–5661.

[8] a) A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891–4932; b) R. Ziessel, G. Ulrich, A. Harriman, *New J. Chem.* **2007**, *31*, 496–501; c) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem.* **2008**, *120*, 1202–1219; *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201.

[9] B. Ventura, G. Marconi, M. Bröring, R. Krüger, L. Flamigni, *New J. Chem.* **2009**, *33*, 428–438.

[10] B. Valeur, *Molecular Fluorescence – Principles and Applications*, Wiley-VCH, Weinheim, Germany, **2001**.

[11] Similar couplings have been observed and used in modified BODIPYs before: J. Chen, J. Reibenspies, A. Derecskei-Kovacs, K. Burgess, *Chem. Commun.* **1999**, 2501–2502.

[12] a) F. B. Mallory, *J. Am. Chem. Soc.* **1973**, *95*, 7747–7752; b) J. Hilton, L. H. Sutcliffe, *Prog. NMR Spectrosc.* **1975**, *10*, 27–39; c) J. Hilton, L. H. Sutcliffe, *Spectrochim. Acta* **1976**, *32A*, 201–213; d) F. R. Jerome, K. L. Servis, *J. Am. Chem. Soc.* **1972**, *94*, 5896–5897; e) L. C. Hsee, D. J. Sardella, *Magn. Reson. Chem.* **1990**, *28*, 688–692.

[13] a) M. C. Ruiz de Azua, A. C. Diz, C. G. Giribert, R. H. Contreras, I. D. Rae, *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1986**, *20*, 585–601; b) F. B. Mallory, C. W. Mallory, K. E. Butler, M. B. Lewis, A. Q. Xia, E. D. Luzik, L. E. Fredenburgh, M. M. Ramanjulu, Q. N. Van, M. M. Francl, D. A. Freed, C. C. Wray, C. Hann, M. Nerz-Stormes, P. J. Carroll, L. E. Chirlian, *J. Am. Chem. Soc.* **2000**, *122*, 4108–4116; c) P. Szczecinski, J. Zachara, *J. Organomet. Chem.* **1993**, *447*, 241–249; d) T. Miyake, Y. Koyama, *Carbohydr. Res.* **1994**, *258*, 11–26; e) K. Matsubara, A. Oba, U. Yoshihiro, *Magn. Reson. Chem.* **1998**, *36*, 761–765.

[14] a) Y.-H. Yu, A. B. Descalzo, Z. Shen, H. Röhr, Q. Liu, Y.-W. Wang, M. Spieles, Y.-Z. Li, K. Rurack, X.-Z. You, *Chem. Asian J.* **2006**, *1–2*, 176–187 b) M. Bröring, R. Krüger, C. Kleeberg, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1555–1559.

[15] K. Wüthrich, M. Billeter, W. Braun, *J. Mol. Biol.* **1983**, *169*, 949–961.

[16] *Sybyl7.3.* Tripos Inc., 1699 South Hanley Rd., St. Louis, Missouri, 63144 USA.

[17] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidoria, R. Spagna, *J. Appl. Crystallogr.* **2005**, *38*, 381–388.

[18] G. Sheldrick, *SHELXL-97*, Program for Structure Refinement, Universität Göttingen, Germany, **1997**.

[19] J. Schleucher, M. Schwendinger, M. Sattler, P. Schmidt, O. Schedletzky, S. J. Glaser, O. W. Sorensen, C. Griesinger, *J. Biomol. NMR* **1994**, *4*, 301–306.

[20] W. Willker, D. Leibfritz, R. Kerssebaum, W. Bermel, *Magn. Reson. Chem.* **1993**, *31*, 287–292.

Received: September 11, 2009
Published Online: December 17, 2009

