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Functional Porphyrinoids from a Biomimetically Decorated Bipyrrole

Martin Bröring,*[a] Frédérique Brégier,[a] Robin Krüger,[a] and Christian Kleeberg[a]

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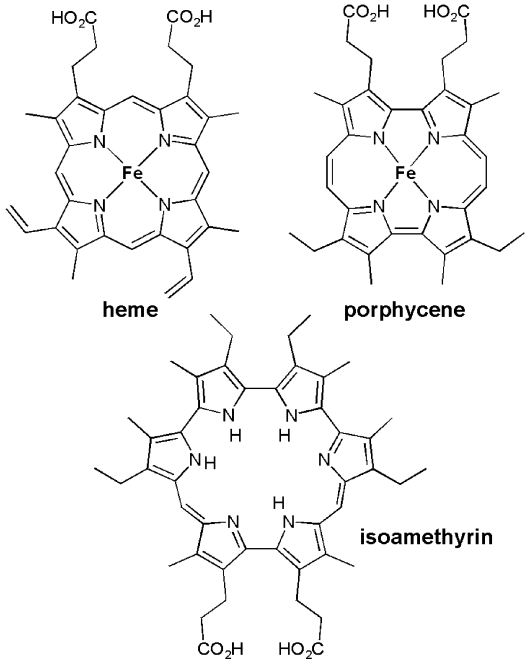
The known 5,5′-diformyl-3,3′-bis(methoxycarbonylethyl)-4,4′-dimethyl-2,2′-bipyrrole was employed in the preparation of biomimetic functional porphyrinoids. Tetrapyrrolic 2,2′-bidipyrrins could be obtained from condensations with two equivalents of 3,4-dialkyl-2-methylpyrroles. From these compounds, a manganese(III) corrole as well as a boron-containing bis(bodipy) fluorophor are accessible as functional species in one-step reactions. Both products were investigated by means of X-ray crystallography. Attempts to hydrolyze the methyl ester moieties were successful only for the manganese corrole and yielded a buffer–soluble, heme-analogous corrole complex. The dinuclear BF_2 chelate [bis(bodipy)], on the other hand, decomposes unselectively under the applied conditions. A rationale for this decomposition was derived from crystallographic work on a related hydrolysis product with a F–B–O–B–F moiety.

Introduction

Nature prepares simple porphyrins by highly conserved routes via the ubiquitous uroporphyrinogene III.[1] The original periphery of uroporphyrinogene III is composed of four acetate and four propionate side chains only. Later transformations usually remove CO_2 from some of these substituents, but leave others untouched.[2] The best-known example for this biosynthetic pathway is arguably the heme moiety, in which all acetate and two of the four propionate groups have been transformed into methyl and vinyl groups, respectively.[3] In nature, the remaining propionate groups enhance the water solubility of the chromophore. More importantly, they are responsible for the proper orientation of the heme (or other porphyrinoid) cofactor in biological matrices, e.g. in heme enzymes, B_{12} enzymes (as the respective amides) to name a few.[4]

Most porphyrin isomers[5] and many contracted[6] and expanded analogues[7] contain a 2,2′-bipyrrole as an integral subunit. Therefore, the preparation of a dipropionate or diacetate bipyrrole as a functional precursor would be the most general entry to a broad variety of water-soluble and biomimetically substituted porphyrinoids.[8] Such a bipyrrole can be found in the patent literature[9] as part of the preparation of the functionalized porphycene in Scheme 1, and very recently the details of an eight-step synthesis of this bipyrrole have been published.[10] However, the functionalized bipyrrole has so far been used almost exclusively as a precursor to metalloporphycenes,[11] and only two examples of expanded porphyrinoids derived from this building block are present in the literature (Scheme 1).[10,12] In the field of non-natural porphyrinoids, the objective of water-solubility is usually tackled by the use of charge, by employing peripheral ammonium, carboxylate or sulfonate groups either on *meso*-aryl positions or directly attached to the pyrrolic β positions.[13] We have now investigated this valuable bipyrrolic precursor and employed it for the preparation of new functional dyes with biomimetic decorations. In this contribution, we present the synthesis of 2,2′-bidipyrrin dipropionates and the use of these tetrapyrrolic compounds as building blocks for two non-natural porphyrinoids, a manganese corrole and a bis(bodipy) fluorophor.



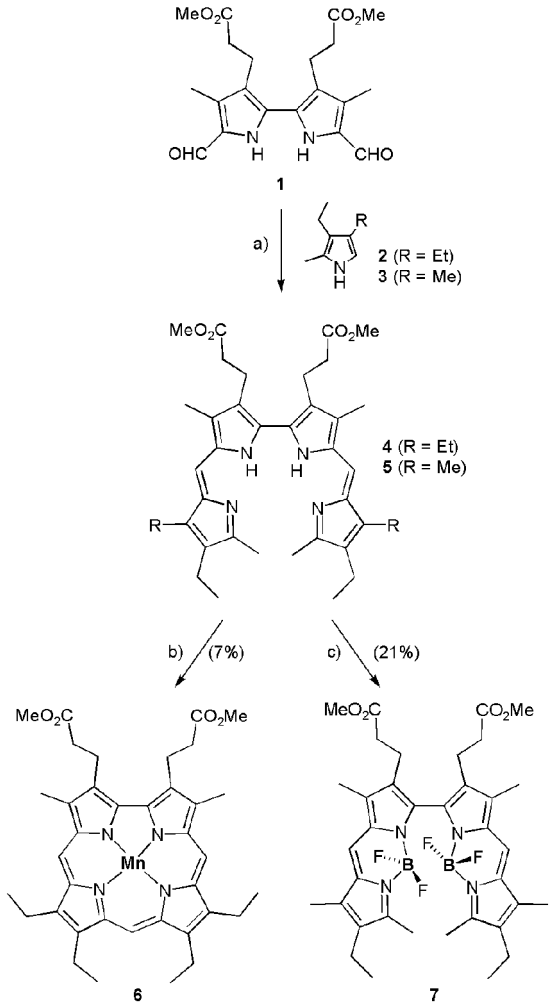
Scheme 1. Functional propionate substituted porphyrinoids.

[a] Fachbereich Chemie, Philipps-Universität,
Hans-Meerwein-Straße, 35032 Marburg, Germany
Fax: +49-6421-2825356
E-mail: broering@staff.uni-marburg.de

Results and Discussion

Use of Bipyrrole 1 in 2,2′-Bidipyrrin Synthesis

Two new 2,2′-bidipyrrins **4** and **5** have been prepared from the bipyrrolic precursor **1** as entries to new functional tetrapyrroles with biomimetic decorations (Scheme 2). 2,2′-Bidipyrrins are versatile open-chain tetrapyrroles.[14] They have been employed in the preparation of novel fluorophors,[15] as ligands in helical transition-metal complexes,[16] in helicates,[17] and in polynuclear complexes,[18] and can be used as precursors in the template-assisted oxidative macrocyclization to corroles[19] and other macrocyclic non-natural porphyrinoids.[20] The methyl propionate substituted bidipyrrins **4** and **5** were prepared by an application of a well-established method from **1** and the trialkylpyrroles **2**[21] and **3**[22] through HBr-induced double condensation, and are separated from the reaction mixture simply and efficiently by precipitation with aqueous $HClO_4$ as the bis(hydroperchlorate). From these the neutral free-base tetrapyrroles are available by twofold deprotonation, by using triethylamine in methanol as the reagent system. The methyl propionate side chains do not interfere or hydrolyze under these conditions, such that excellent yields for pure **4** and **5** of 89% and 75%, respectively, have been observed. The presence of the new bidipyrrins **4** and **5** is indicated by resonances for the *meso*-methine groups at 6.74 and 6.75 ppm in the ^{1}H NMR spectra, and at 115.47 and 115.44 ppm in the ^{13}C NMR spectra, respectively, and the expected stretched conformation of the ligands is clearly apparent from the characteristic broad absorption band at 583 nm in the optical spectra of their deep blue solutions.[14]



Scheme 2. Preparation of functional dyes **6** and **7**. (a) (i) HBr, methanol, then $HClO_4$, (ii) NEt_3, methanol; (b) $Mn(OAc)_2$, NMP, Δ; (c) $BF_3 \times Et_2O$, 2,6-lutidine, dichloromethane.

Preparation and Analysis of Manganese Corrole 6

Since manganese corroles show much promise in catalysis[23] and in biohybrid systems,[24] the tetraethyl derivative **4** was further converted into the manganese corrole **6** by the action of manganese(II) acetate and molecular oxygen in *N*-methylpyrrolidone at 160 °C.[19a] After aqueous workup and purification by chromatography with diethyl ether/*n*-hexane on neutral alumina, the desired compound could be obtained as a dark green powder in 7% yield (Scheme 2). Combustion analysis confirms the presence of the paramagnetic manganese species, and the molecular ion $[M + 1]^+$ could be detected and confirmed by high resolution APCI-MS. The ^{1}H NMR spectrum of **6** gives broad and unstructured lines in the range 0–130 ppm, which could be assigned, in part, to specific groups on the basis of the signal intensity and number. The optical spectrum is characteristic for a manganese(III) corrole and displays a strong Soret-type absorption band at 391 nm with shoulders in the hypsochromic and the hypochromic regions, in addition to a complex pattern of less intense Q-band-like absorption bands between 450 and 850 nm.[25]

As known for other manganese corroles, **6** undergoes a clean one-electron oxidation upon prolonged exposure to halogenated solvents and to air to form the respective chloromanganese(IV) complex **6′**.[26] This compound was obtained in a single crystal from a crystallization attempt on **6** in dichloromethane/acetonitrile/*n*-hexane and could be analyzed by X-ray diffraction in more detail. Complex **6′** crystallizes as the tris(acetonitrile) solvate at –20 °C. The molecular structure of the macrocyclic compound and selected bond lengths and angles are presented in Figure 1. Crystallographic data for the structure determination is summarized in Table 1. Complex **6′** is only the third chloromanganese corrole structurally characterized by means of X-ray crystallography. The manganese atom is seated in a distorted square-pyramidal environment with Mn–N distances between 1.915 and 1.943 Å, a doming of 0.407 Å from the N_4 mean squares plane, and a Mn–Cl bond length of 2.338 Å. The corrole ring itself shows a very slightly domed structure with effectively coplanar pyrrole rings in the bipyrrolic subunit. All these data are similar to those observed before.[26,27] Interestingly, the methyl propionate side chains are found in parallel stretched conformations and tilted away from the plane of the macrocycle to the

same side. This behaviour can be understood from the crystal packing. An investigation of the crystal structure reveals the presence of slipped π-stacked manganese corrole interactions with an interplanar distance of 3.711 Å. The observed conformation of the propionate groups therefore appears as a simple steric necessity in order to allow these stacking interactions.

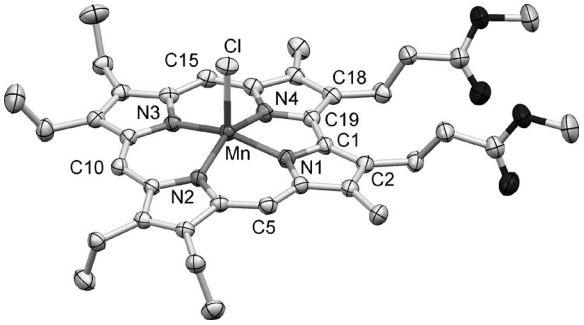


Figure 1. Molecular structure of chloromanganese corrole **6′** (ellipsoids set at 50% probability; hydrogen atoms removed for clarity). Selected bond lengths [Å] and angles [°]: Mn–N1 1.915(2), Mn–N2 1.943(2), Mn–N3 1.940(2), Mn–N4 1.921(2), Mn–Cl 2.338(2), N1–Mn–N2 89.03(9), N1–Mn–N3 154.85(7), N1–Mn–N4 78.18(9), N1–Mn–Cl 101.80(9), N2–Mn–N3 93.52(8), N2–Mn–N4 153.90(7), N2–Mn–Cl 102.18(7), N3–Mn–N4 89.03(8), N3–Mn–Cl 102.09(8), N4–Mn–Cl 102.65(8).

Preparation and Analysis of bis(bodipy) 7

The hexamethylsubstituted bidipyrrin **5** was used to prepare the functionalized bis(bodipy) derivative **7**. Bis(bodipy)s[15] are novel covalent dimers of the well-known bodipy fluorophors[28] with advantageous photophysical properties.[29] Compound **7** was prepared from **5** and BF_3/etherate by the optimized procedure described earlier,[15] as a dark green powder in 21% yield (Scheme 2). Compound **7** is highly fluorescent in solution even upon excitation by ambient light, and solutions of the new compound always appear red because of the emitted photons. Figure 2 provides an overview of the optical absorption and emission spectra of **7** in dichloromethane. With the exception of the pronounced exciton coupling of 68 nm in the absorption spectra,[30] the intense and broad emission at 640 nm with a Stokes shift of 86 nm appears as the most prominent optical feature of the fluorophor. In the ^{19}F NMR spectrum of **7**, another peculiarity is found in the complex pattern of the signal for F2. While for F1 the expected doublet of quartets with coupling constants $^2J_{F1,F2}$ = 138 Hz and $^1J_{F1,B}$ = 34 Hz is observed, the signal for F2 is more complex and indicates the presence of additional coupling partners. The overall shape of this signal can be fitted in some detail if one more coupling constant $J_{F2,F2'}$ of about 25 Hz is taken into consideration. Such a "through-space" coupling (as opposed to "through-bond" couplings) may occur if the two fluorine atoms are bound in a very close and rigid relationship and has been considered for related cases earlier.[31] A closer look to the spectrum, however, reveals an even higher degree of complexity of the signal for F2. A detailed analysis to address this point is currently being undertaken.

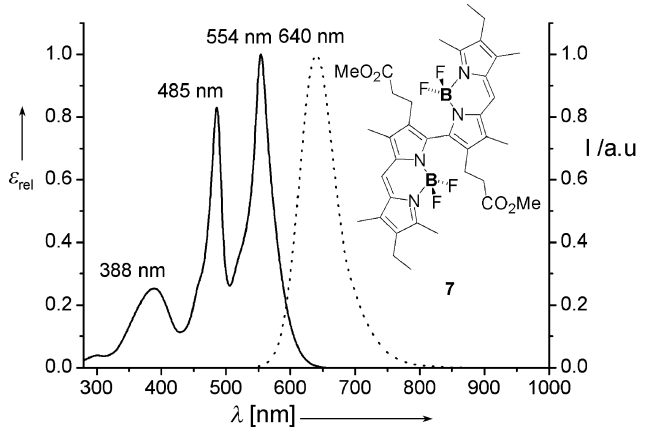


Figure 2. Absorption (–) and emission spectra (···) of bis(bodipy) **7** (CH_2Cl_2).

Compound **7** is the first bis(bodipy) derivative without the *meso*-aryl substituent that could be investigated by single-crystal X-ray diffraction. A suitable crystal of **7** was grown from a dichloromethane/*n*-hexane solution upon slow evaporation at ambient temperature. The molecular structure of the compound is presented in Figure 3. Table 1 provides details for the crystallographic determination.

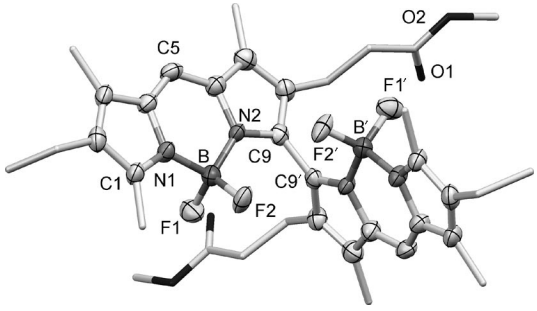


Figure 3. Molecular structure of bis(bodipy) **7** (ellipsoids set at 50% probability; hydrogen atoms removed for clarity). Selected bond lengths [Å] and angles [°]: B–N1 1.563(6), B–N2 1.507(6), B–F1 1.377(5), B–F2 1.387(6), C9–C9′ 1.477(8), N1–B–N2 107.2(4), N1–B–F1 107.7(4), N1–B–F2 108.5(4), N2–B–F1 111.4(4), N2–B–F2 112.7(4), F1–B–F2 109.1(4).

Bis(bodipy) **7** is composed of two crystallographically identical and almost planar, boron-coordinated dipyrrin halves that are connected to each other through the C9–C9′ bond with a distance of 1.477 Å and with a dihedral angle of 79.86°. The B–N and B–F bond lengths appear to be normal with the expected bond lengths of 1.507/1.563 and 1.377/1.387 Å, respectively, but the distance between F2 and F2′ of only 2.871 Å is significantly below the van der Waals limit and explains the NMR spectroscopic finding of a large "through-space" coupling on a qualitative basis. Because of this congestion at the centre of the molecule, the BF_2 subunits are tilted out of the mean plane of the bodipy luminophor by as much as 0.228 Å. Compared

to the literature precedent, which shows a dihedral angle of 96.52°, a F2–F2′ distance of 2.968 Å and an *out-of-plane* displacement of the boron centres of only 0.049–0.145 Å, these data clearly prove differences in the conformations of *meso*-aryl and *meso*-H derivatives. The propionate side chains are again found in a stretched-out conformation, which obviously supports and stabilizes the crystal lattice in this form.

Attempted Hydrolyses of the Methyl Propionate Groups of 6 and 7

The final step towards biomimetically decorated functional dyes derived from the bipyrrolic precursor **1** is the hydrolysis of the methyl ester moieties of **6** and **7**. This step is known for other macrocyclic porphyrinoids with less reactive tetrapyrrole ligands and is usually performed by the action of tfa/HCl/H_2O[10] or by alkaline hydrolysis with KOH, methanol and thf.[9] In the case of **6** and **7**, however, both protocols result in a rapid and complete decomposition of the material, even if performed under the exclusion of air and light. After some screening we found that the ester side chains of the manganese complex **6** can be hydrolyzed in excellent yield by the use of LiOH in a thf/water mixture.[32] In order to avoid the demetallation and concomitant ring oxygenation of the corrole,[33] the neutralization step requires particular care and has to be carried out only after extractive workup by using glacial acetic acid. Diacid **8** is obtained in >90% yield as a black powder and was analyzed by high resolution mass spectrometry.

The ^{1}H NMR spectrum of **8**, obtained in [D_6]dmso solution, consists of several broad and unstructured resonance bands between 0 and 100 ppm. The number and intensity of these bands do not allow a simple interpretation of the spectrum, and because of the unfavourable relaxation dynamics, no 2D spectra could be obtained. Therefore, the assignment of the observed signals remains open. On the basis of a comparison with the spectra of the methyl ester **6** and the intensity data, three of the signals at δ = 12.4, 34.3 and 98.9 ppm can be assigned to methyl group protons with some certainty. In addition, the presence of manganese ions in the oxidation state 3+ is proposed on the basis of the large downfield shift of some of the methyl proton resonances.

As anticipated, the diacid **8** can easily be dissolved in buffered aqueous solutions at neutral pH. The optical spectrum of the manganese corrole recorded in tris-HCl buffer at pH 7.0 is shown in Figure 4, together with the spectra of the dimethyl ester **6** in dichloromethane (Mn^{IV} form) and in dmso (Mn^{III} form). The spectrum of **8** in aqueous buffer is very broad and unstructured and consists mainly of a single Soret-type band at 362 nm, accompanied by a less intense absorption band at 995 nm. The fine structure present in the spectra of manganese corroles **6** and **6′** in organic solvents is entirely lost. The reason for the unique spectral pattern of **8** in aqueous solution is not clear; however, a dynamic aggregation through the carboxylic acid/carboxylate functionalities and the manganese ion seems to be a plausible explanation for the observed spectral change. A similar behaviour was observed earlier for corresponding manganese protoporphyrin IX derivatives[13b] and on carboxylated *meso*-arylcorroles.[13c]

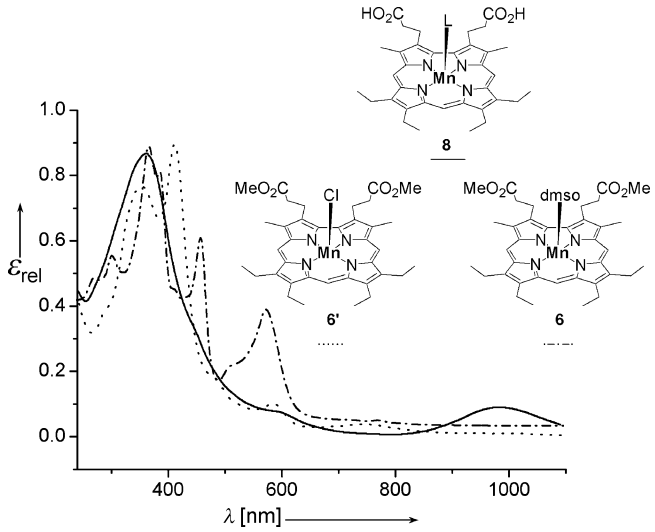


Figure 4. UV/Vis spectra of diacid **8** (–) in Tris-HCl buffer (pH 7.0) and of diester **6** (· – ·) in dmso and **6′** (···) in dichloromethane.

All attempts to hydrolyze the ester side chains of the bis(bodipy) derivative **7** remained unsuccessful. In acidic as well as in alkaline media, a rapid decomposition of the compound and the appearance of many different coloured and, in part, fluorescent spots on the thin layer chromatogram is observed. Mass spectrometric analyses of several of these spots suggest that the BF_2 groups compete against the ester groups with regard to the hydrolytic activity. This behaviour is unknown for the inert bodipys but is somewhat reminiscent of the enhanced reactivity of other porphyrinoid dinuclear boron species in which the boron atoms are in close proximity.[34] In one case, a single crystal formed during a long-term crystallization attempt of a related decasubstituted bis(bodipy). This crystal was not composed of the original material, but contained a single decomposition product. The crystallographic analysis of the material identified this compound as the hydrolysis product **9**, the acetonitrile adduct. Figure 5 presents the molecular structure of this serendipitously discovered compound. Crystallographic details are given in Table 1.

The investigation reveals that the sites of partial hydrolysis are in fact the BF_2 units. Two fluorine atoms, one from each BF_2 group, are exchanged for a bridging oxygen atom. The boron atoms reside in a nearly tetrahedral environment, and the so-formed F–B–O–B–F chain is characterized by bond lengths of 1.417 Å (B–F) and 1.408 Å (B–O), angles of 112.1° (F–B–O) and 125.8° (B–O–B′), and a torsion angle of 88.9° (F–B–O–B′). The mean-square planes of the two crystallographically identical dipyrrin backbones form an angle of only 41.6°. Other than for bis(bodipy)s, the planarity of these dipyrrin subunits is almost unaffected by the complexation of boron, and the

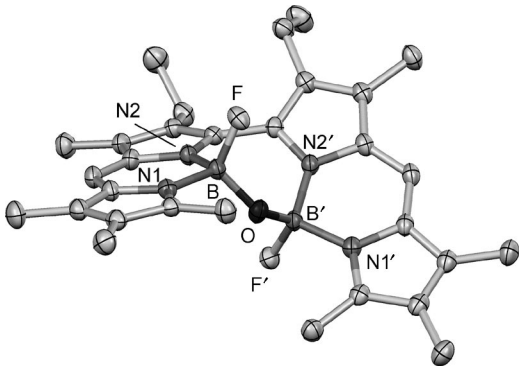


Figure 5. Molecular structure of the hydrolysis product **9** of a bis(bodipy) (ellipsoids set at 50% probability; hydrogen atoms removed for clarity). Selected bond lengths [Å] and angles [°]: B–N1 1.585(2), B–N2 1.576(2), B–F 1.417(2), B–O 1.408(2), N1–B–N2 105.38(11), N1–B–F 107.51(12), N1–B–O 110.57(12), N2–B–F 107.59(11), N2–B–O 113.35(13), F–B–O 112.06(11), B–O–B′ 125.8(2).

boron atoms are almost undisplaced from this mean-square plane (by only 0.015 Å). A largely unstrained and relaxed molecular geometry is therefore observed for the isolated hydrolysis product. The specific tendency of bis(bodipy)s to undergo hydrolytic decay through nucleophilic attack at the BF_2 moieties is obviously a consequence of the presence of two boron centres in a close spatial relationship.

Conclusions

Propionate-decorated 2,2′-bidipyrrins can be prepared from the corresponding bipyrrole **1** by using the conventional pathways. These tetrapyrroles can successfully be employed as precursors for the synthesis of manganese corroles and bis(bodipy) fluorophors with biomimetic functionalization. The study of the hydrolytic cleavage of the ester groups of these functional chromophores has revealed a gentle method for the preparation of heme-analogous manganese corroles. In addition, an unexpected hydrolytic lability has been observed for bis(bodipy) **9**, which is unknown for the parent bodipy derivatives. Presumably, this sensitivity against nucleophiles is caused by the presence of two BF_2 groups in close contact and results in the ready (although not selective) hydrolysis of the usually very robust B–F bonds. The new derivatives are of potential importance in future studies towards biohybrid systems containing non-natural porphyrinoids. First attempts in this emerging field are currently under way.

Experimental Section

General: All reagents were purchased from commercial sources and used as received. Solvents were dried prior to use by standard procedures and stored under argon in the dark. 5,5′-Diformyl-3,3′-bis(methoxycarbonylethyl)-4,4′-dimethyl-2,2′-bipyrrole (**1**),[15] 3,4-diethyl-2-methylpyrrole (**2**)[21] and 3-ethyl-2,4-dimethylpyrrole (**3**)[22] were prepared as described previously. NMR spectra were obtained with a Bruker ARX-300 or a Bruker DRX 400 spectrometer. Chemical shifts (δ) are given in ppm relative to residual protio solvent resonances (^{1}H, ^{13}C NMR spectra) or to external standards ($BF_3 \times Et_2O$ for ^{11}B and $CFCl_3$ for ^{19}F NMR spectra). High resolution ESI and APCI mass spectra were recorded with an IonSpec Ultima or a QStarPulsar i. Combustion analyses (C, H, N) were performed on an Elementar Vario EL instrument. UV/Vis spectra were measured with a Shimadzu UV-1601 spectrophotometer with concentrations of $\approx 10^{-5}$ mol/L. Emission spectra were obtained on a Varian Cary Eclipse spectrophotometer.

3,3′-Bis(2-methoxycarbonylethyl)-2,2′-bidipyrrins 4 and 5. General Procedure: Diformyl bipyrrole **1** (658.2 mg, 1.69 mmol) and alkylpyrrole **2** or **3** (4.30 mmol) were dissolved in methanol. To this solution hydrobromic acid (3.5 mL of a 48% solution in water) was added at once while stirring intensely, and the mixture was heated to reflux for 1 h. After cooling, the stirred, dark green mixture was treated with perchloric acid (3.5 mL of a 69% solution in water), whereupon the product precipitated. After an additional hour, with stirring, in an ice bath, the solid product was filtered and washed once with an ice-cold mixture of methanol and hydrobromic acid (10:1). The solid was then redissolved in methanol (35 mL), immediately treated with triethylamine (3.5 mL) and stirred for 1 h. The blue–purple solid was filtered, washed repeatedly with ice-cold methanol and recrystallized from a minimum amount of dichloromethane/methanol to yield the title product.

8,8′,9,9′-Tetraethyl-4,4′,10,10′-tetramethyl-3,3′-bis(methoxycarbonylethyl)-2,2′-bi-dipyrrin (4): Obtained (945 mg, 89%) as green needles. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.10 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_{3Et} $H^{9b,9b'}$), 1.18 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_{3Et} $H^{8b,8b'}$), 2.24 (s, 6 H, CH_{3Me} $H^{4a,4a'}$), 2.29 (s, 6 H, CH_{3Me} $H^{11,11'}$), 2.40 (q, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_{2Et} $H^{9a,9a'}$), 2.58 (q, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_{2Et} $H^{8a,8a'}$), 2.60 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_2CH_2COOMe), 3.21 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_2CH_2), 3.53 (s, 6 H, CO_2CH_3), 6.74 (s, 2 H, $H^{6,6'}$) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 9.32, 14.41, 15.13, 16.96, 17.70, 17.86, 21.13, 34.41, 51.27, 115.47, 128.05, 131.26, 134.19, 138.15, 138.47, 141.60, 143.05, 155.05, 173.49 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε, M^{-1} cm^{-1}) = 262 (18900), 335 (12200), 444 (7600), 583 (52600) nm. HRMS (ESI+): calcd. for $C_{38}H_{51}N_4O_4$ [M + 1]$^+$ 627.3905; found 627.3895. $C_{38}H_{50}N_4O_4$ (626.83): calcd. C 70.78, H 8.13, N 8.69; found C 70.78, H 7.80, N 8.77.

9,9′-Diethyl-4,4′,8,8′,10,10′-hexamethyl-3,3′-bis(methoxycarbonylethyl)-2,2′-bidipyrrin (5): Obtained (748 mg, 75%) as shiny green needles. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.07 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_2CH_3), 2.15 (s, 6 H, CH_{3Me} $H^{8,8'}$), 2.23 (s, 6 H, CH_{3Me} $H^{4,4'}$), 2.29 (s, 6 H, CH_{3Me} $H^{11,11'}$), 2.40 (q, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_2CH_3), 2.60 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_2CH_2COOMe), 3.21 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_2CH_2), 3.53 (s, 6 H, CO_2CH_3), 6.75 (s, 2 H, $H^{6,6'}$) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 9.28, 14.36, 14.58, 17.17, 21.13, 34.38, 51.26, 115.44, 128.00, 131.92, 134.16, 134.93, 138.10, 139.47, 143.03, 154.95, 173.48 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε, M^{-1} cm^{-1}) = 263 (19400), 335 (12500), 444 (7900), 583 (54500) nm. HRMS (ESI+): calcd. for $C_{36}H_{47}N_4O_4$ [M + 1]$^+$ 599.3592; found 599.3587. $C_{36}H_{46}N_4O_4 \cdot 0.5H_2O$ (607.78): calcd. C 71.14, H 7.79, N 9.22; found C 70.95, H 7.62, N 9.27.

[7,8,12,13-Tetraethyl-2,18-bis(methoxycarbonylethyl)-3,17-dimethylcorrolato]manganese(III) (6): Bidipyrrin **4** (251 mg, 0.4 mmol) and manganese acetate tetrahydrate (489 mg, 2.0 mmol) in NMP (15 mL) were heated to 160 °C for 10 min while dioxygen was bubbled through the solution. After cooling, the mixture was poured onto water (200 mL) and extracted with ethyl ether (3 × 20 mL). The ethereal extracts were dried with sodium sulfate, filtered, and the solvent was entirely removed in vacuo. The dark residue was subjected to column chromatography on neutral alu-

mina (grade III) with diethyl ether/*n*-hexane (1:1) as the eluent and was obtained as the olive green band. Recrystallization from diethyl ether/*n*-hexane (1:1) at –28 °C yielded the title compound as a dark green solid (19.5 mg, 7%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.0–4.0 (26 H), 21.0 (br. s, 4 H, CH_2), 36.3 (br. s, 4 H, CH_2), 54.1 (br. s, 1 H, 10-H), 81.0 (br. s, 2 H, 5,15-H), 126.2 (br. s, 6 H, 3,17-H) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε, M^{-1} cm^{-1}) = 324 (26400), 365 (39500), 391 (47500), 448 (11700), 479 (11900), 588 (14900), 726 (1300), 834 (1600) nm. HRMS (APCI): calcd. for $C_{37}H_{44}MnN_4O_4$ [M + 1]$^+$ 663.2738; found 663.2735. $C_{37}H_{43}MnN_4O_4 \cdot 0.5H_2O$ (671.71): calcd. C 66.16, H 6.60, N 8.34; found C 66.35, H 6.61, N 8.15.

Bis(*N*,*N*-difluoroboryl)-9,9′-diethyl-4,4′,8,8′,10,10′-hexamethyl-3,3′-bis(methoxycarbonylethyl)-2,2′-bidipyrrin (7): Bidipyrrin **5** (71.8 mg, 0.12 mmol) was dissolved in thf (100 mL) and cooled to 0 °C. At this temperature, 2,6-lutidine (5 mL) and BF_3-etherate (12 mL) were added dropwise while stirring, whereupon the mixture turned from blue–purple to wine red. Stirring was continued for 10 min before the reaction was quenched by the addition of a saturated solution of sodium hydrogen carbonate in water (100 mL). After 5 min (additional) of stirring, the layers were separated by the help of additional water and ethyl ether, and the organic layer was washed once with water (50 mL) and dried with sodium sulfate. All volatiles were removed in vacuo, and the residue was chromatographically purified on silica with dichloromethane. After removal of the solvent, the title compound remained (17.3 mg, 21%), as a green powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.08 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, CH_2CH_3), 2.24 (s, 6 H, CH_{3Me} $H^{8,8'}$), 2.33 (s, 6 H, CH_{3Me} $H^{4,4'}$), 2.42 (q, $^3J_{H,H}$ = 7.5 Hz, 4 H, CH_2CH_3), 2.43 (s, 6 H, CH_{3Me} $H^{11,11'}$), 2.53–2.67 (m, 8 H, CH_2CH_2COOMe), 3.62 (s, 6 H, CO_2CH_3), 7.22 (s, 2 H, $H^{6,6'}$) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 9.31, 9.92, 13.01, 14.10, 17.27, 20.31, 33.30, 51.38, 120.40, 129.72, 132.53, 134.54, 134.83, 135.25, 140.16, 141.81, 161.68, 173.49 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –139.5 (dq, $^2J_{F,F}$ = 138, $^1J_{B,F}$ = 34 Hz, 2 F, *F1*BF2), –146.6 to –147.3 (m, 2 F, F1B*F2*) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2): δ = –0.01 (dd, $^1J_{B\text{-}F}$ = 34 Hz, 2 B) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε, M^{-1} cm^{-1}) = 388 (1600), 486 (66400), 554 (76200) nm. HRMS (ESI+): calcd. for $C_{36}H_{44}N_4B_2F_4O_4Na$ [M + Na]$^+$ 717.3377; found 717.3383.

(7,8,12,13-Tetraethyl-2,18-dipropionyl-3,17-dimethylcorrolato)-manganese(III) (8): Under a blanket of nitrogen, manganese corrole **6** (48.5 mg, 73 μmol) was dissolved in thf (7.5 mL) and treated at ambient temperature with a degassed solution of $LiOH \times H_2O$ (30.7 mg, 0.73 mmol) in water (1.5 mL). The mixture was stirred for 25 h before ethyl ether (30 mL) and water (10 mL) were added. The layers were separated, and the aqueous layer was washed with additional ethyl ether (30 mL), before glacial acetic acid (1 mL) was added dropwise to the aqueous extracts to precipitate the title compound. After centrifugation and washing with water, the diacid **8** was isolated as a black powder (42.7 mg, 92%). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 0.7 (br. s), 12.4 (br. s, 6 H, CH_3), 20.4 (br. s), 23.8 (br. s), 34.3 (br. s, 6 H, CH_3), 98.9 (br. s, 6 H, CH_3) ppm. UV/Vis (50 mM tris-HCl buffer, pH 7.0): λ_{max} (ε_{rel}, M^{-1} cm^{-1}) = 362 (1), 596 (0.17), 995 (0.12) nm. HRMS (APCI): calcd. for $C_{35}H_{40}MnN_4O_4$ [M + 1]$^+$ 635.2425; found 635.2416.

X-ray Crystallography: Diffraction data for compounds **7** and **9** were collected on a STOE IPDS-1, data for **6** on a STOE IPDS-2, by using monochromated Mo-K_α radiation. The structures were solved by direct methods with SIR 92[35] and refined on all F^2 with SHELXL 97.[36] Graphics were prepared by using Mercury 1.4.2.[37] Further details are given in Table 1. CCDC-669710, -669711, -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.

Table 1. Crystallographic data and refinement parameters of **6**, **7** and **9**.

Compound	**6**·3CH$_3$CN	**7**	**9**·CH$_3$CN
Empirical formula	$C_{43}H_{52}ClMnN_7O_4$	$C_{36}H_{44}B_2F_4N_4O_4$	$C_{32}H_{39}B_2F_2N_5O$
M_r	821.31	694.37	572.50
T [K]	173(2)	193(2)	193(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2/c$	$C2/c$
a [Å]	11.544(11)	10.713(2)	19.752(2)
b [Å]	11.682(6)	11.1929(13)	11.9931(10)
c [Å]	17.286(12)	15.613(3)	14.6024(11)
α [°]	78.45(3)	90	90
β [°]	71.99(4)	99.88(2)	118.001(9)
γ [°]	72.97(4)	90	90
V [Å^3]	2104(3)	1844.4(6)	3054.2(5)
Z	2	2	4
D_c [Mg m^{-3}]	1.296	1.250	1.245
μ [mm^{-1}]	0.427	0.094	0.083
θ range [°]	1.84–25.86	1.82–25.00	2.24–25.87
h	–14 to 14	–12 to 12	–24 to 24
k	–14 to 13	–11 to 13	–14 to 14
l	–21 to 21	–17 to 18	–17 to 17
reflections collected	29222	10664	17651
independent	12284	3265	8111
observed [$I > 2\sigma(I)$]	5070	1109	6290
Final $R1$ [$I > 2\sigma(I)$]	0.0342	0.0612	0.0379
Final $wR2$ [$I > 2\sigma(I)$]	0.0854	0.1162	0.0936

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