Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
www.zaac.wiley-vch.de
ARTICLE

DOI: 10.1002/zaac.201500695

Functionalized Paddle Wheel Complexes from BODIPY Carboxylic Acids

Sebastian Höfler,[a] Anne Scheja,[a] Benedikt Wolfram,[a] and Martin Bröring*[a]

Keywords: BODIPY dyes; Paddle wheel structures; Carboxylate complexes; Copper; Rhodium

Abstract. A series of BODIPY carboxylic acids carrying aromatic linking units between the luminophor and the carboxylate functional group was prepared using Sonogashira and Stille type coupling protocols. Ferrocene and hydroquinone units could be introduced by either of these methods. Metal complex formation of the BODIPY carboxylic acid ligands was investigated with the divalent metal ions of copper and rhodium. Copper forms insoluble material, which crystallized in one case. The X-ray crystallographic analysis shows the presence of a BODIPY-appended paddle wheel complex with typical Cu···Cu and Cu–O distances and four BODIPY units in a distance of 9.681 Å and 9.747 Å from the dinuclear center. Treatment with donor solvents results in the decomposition/monomerization of the compound, which could be shown crystallographically for pyridine. Rhodium(II) ions form soluble paddle wheel complexes with four different BODIPY carboxylates. The crystallographic analysis of one example shows the isostructural nature of the dirhodium and the dicopper derivatives. Optical spectroscopy and cyclic voltammetry provide first insights into efficient intramolecular energy- and electron transfer pathways for the rhodium complexes.

Introduction

All metal ions form carboxylate complexes with carboxylic acids and some of their derivatives. Such complexes are known to exist as mono-, di-, or oligonuclear molecules, or as polymeric coordination networks nowadays called MOFs (metal-organic framework). One particularly intriguing subclass is that of the dinuclear paddle wheel or Chinese lantern type structure of the general formula $[M_2(RCO_2)_4L_2]$, which is realized in molecular complexes of many divalent metal ions like Cu^{II}, Rh^{II}, Ru^{II}, Co^{II}, Cr^{II}, Mo^{II}, and others.[1] In the paddle wheel structures each carboxylate ligand coordinates to both metal ions thus bridging the two metals and keeping them at a very close distance. Therefore metal–metal bonds or strong antiferromagnetic interactions are typically found in these species. In many reports, the introduction of such dinuclear metal cores as nodes into larger molecular architectures and polymers was achieved using carboxylate ligands with an additional function. Figure 1 shows a recent, typical example with the general motif of such paddle wheel structures.[2]

BODIPYs (*bo*ron *dipy*rrines; Figure 2) are potent luminescent dyes.[3] They are easily prepared in large amounts from readily available chemicals, show very high fluorescence quantum yields, are thermally and photochemically very robust and were found to show almost no cytotoxicity.[4] In addition, the outstanding synthetic addressability of BODIPYs[5] and the ease, by which the photophysical properties can be altered through chemical means[6] has triggered much interest in the chemical society. A large body of work has thus been devoted

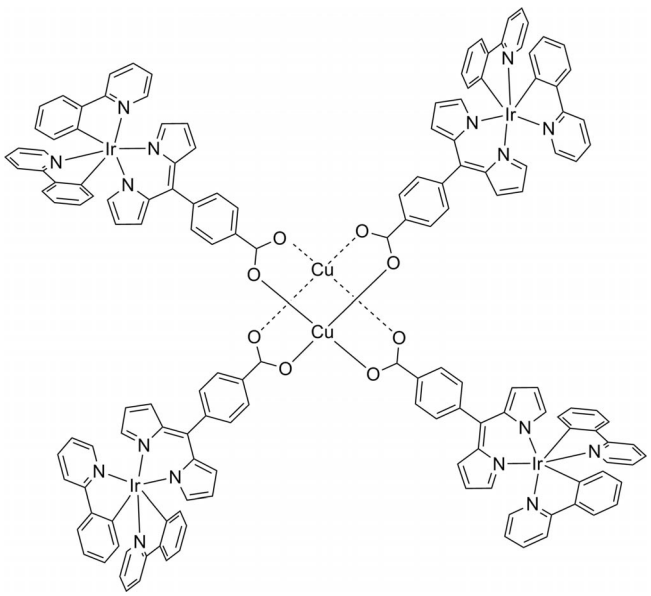


Figure 1. Heterometallic Cu_2 paddle wheel complex with peripherally bound iridium complex fragments.[2]

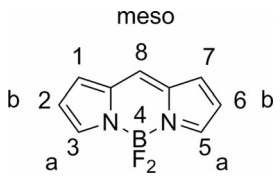


Figure 2. BODIPY general formula and numbering scheme.

* Prof. Dr. M. Bröring
E-Mail: m.broering@tu-bs.de
[a] Institut für Anorganische und Analytische Chemie
Technische Universität Braunschweig
Hagenring 30
38106 Braunschweig, Germany
Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201500695** or from the author.

to investigate this scaffold for applications as, for example, electroluminescent dye,[7] chemosensor,[8] luminescence marker,[9] singlet oxygen sensitizer,[3f,10] photocatalyst,[11] and many more, including commercialization in the biomedical sector. Another prominent use of BODIPYs is that of an antenna chromophore for artificial light harvesting systems[12] and in solar cells. For these applications the photochemical robustness of BODIPYs is of great importance.

There is an actual trend to combine BODIPY dyes with metal complex fragments and/or nanoparticles in order to prepare functional (supra)molecular materials for applications in, for example, energy research and pharmaceutical science.[13] Within this context we attempted to use BODIPY ligands with peripheral carboxylate functions for the preparation of dinuclear paddle wheel complexes, and to study their properties. The approach was successful, and first results are reported in this contribution.

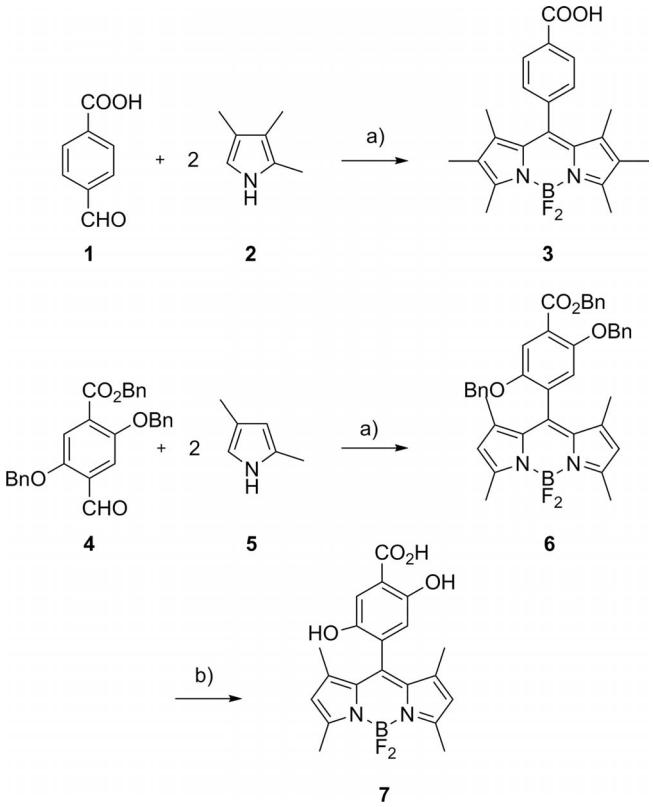
Results and Discussion

Preparation and Characterization of BODIPY Carboxylic Acids

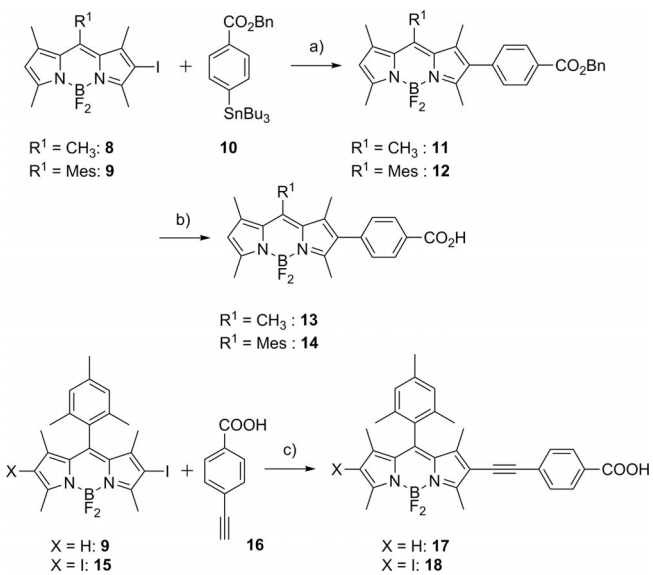
For this project, the use of BODIPY carboxylic acids with the carboxylate function connected to either the *meso* or the β position and with additional electron relay units (ferrocenyl or hydroquinonyl subunits) was anticipated. Several new structures had thus to be established. Scheme 1 shows the syntheses of the new BODIPY carboxylates **3** and **7**, where the carboxylic acid groups are connected to the BODIPY through the *meso* position. In both cases the BODIPY luminophor was formed in a one-pot reaction by condensation of the respective benzaldehyde with the appropriate alkylpyrrole, followed by dehydrogenation and difluoroboration, in 13 % and 35 % yield, respectively. In the case of **6** the benzylic protection groups can be removed hydrogenolytically in one step using 10 % palladium on charcoal as the catalyst. This deprotection yields quantitative amounts of the hydroquinone **7**. Oxidation to the quinone was unsuccessful.

β-Carboxylated BODIPYs have been prepared in the past but show photo- and thermolabile behavior.[14] Therefore different linking units with and without additional functionalities were introduced. Stille coupling of the organo tin reagent **10** with the β-iodoBODIPYs **8** and **9** gave the benzyl esters **11** and **12** in 73 % and 93 % yield, respectively. As before, the hydrogenolysis of these benzyl esters using 10 % palladium on charcoal proceeds smoothly and results in the almost quantitative formation of the desired carboxylic acids **13** and **14**. An elongated phenylacetylene linker was introduced by Sonogashira coupling of the mono- and diiodo-BODIPYs **9** and **15** with 4-carboxyphenylacetylene **16**. In both cases only the monosubstituted products **17** and **18** were obtained in 69 % and 79 % yield, respectively. In these cases the carboxy group is compatible with the reaction conditions and no protection group strategy needs to be applied (Scheme 2).

As depicted in Scheme 3 the functional group compatibility of the Sonogashira reaction allows the exchange of the C_6H_4

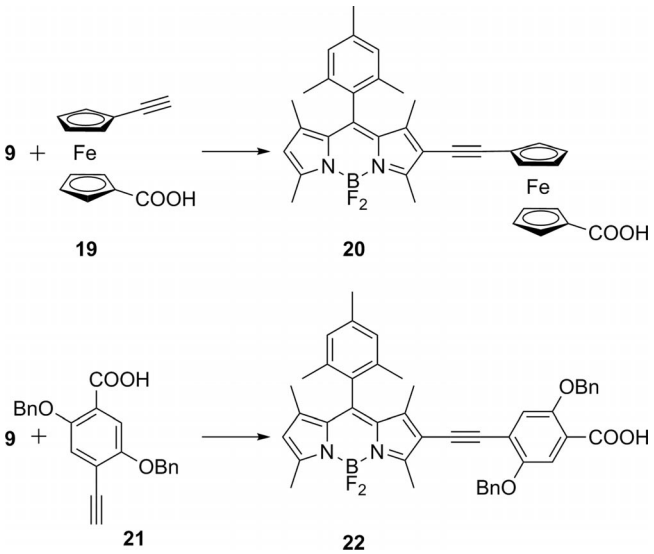


Scheme 1. Preparation of **3** and **7**: (a) 1. TFA, CH_2Cl_2; 2. DDQ; 3. $BF_3{\cdot}Et_2O$, NEt_3. (b) Pd/C, H_2, EtOH.



Scheme 2. Preparation of **13**, **14**, **17** and **18**: (a) $Pd(PPh_3)_4$, toluene; (b) Pd/C, H_2, EtOH; (c) Pd^0, Cu^I, THF, NEt_3.

precursor **16** with the functional ferrocenyl alkyne **19** and with the protected hydroquinone alkyne **21**. Coupling with iodo-BODIPY **9** results directly in the bifunctional carboxylic acids **20** and **22** in 87 % and 79 % isolated yields, respectively.



Scheme 3. Preparation of functionalized **20** and **22**: Pd^0, Cu^I, THF, NEt_3.

All new carboxylic acids were identified by mass spectrometry and characterized by ^1H, ^{13}C, ^{19}F, and ^{11}B NMR methods. In three cases single crystals formed which were suitable for X-ray diffraction analyses. Crystallographic data for these analyses is given in Table 3. The *meso* substituted BODIPY carboxylic acid **3** forms blocks from dichloromethane and crystallizes in the space group $P\bar{1}$ with $Z = 2$. The molecular structure and the packing scheme of **3** are shown in Figure 3 and Figure 4.

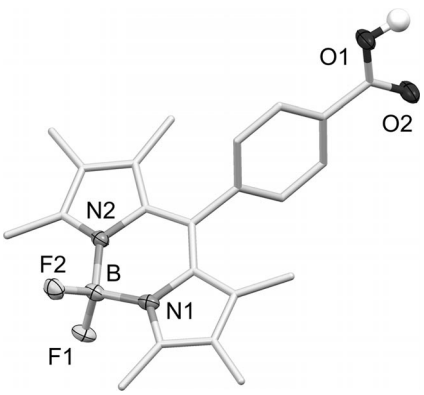


Figure 3. Molecular structure of BODIPY carboxylic acid **3** (ellipsoids set to 50 % probability; carbon-bound hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: B–N1 1.550(2), B–N2 1.551(2), B–F1 1.400(2), B–F2 1.393(2), C–O1 1.314(2), C–O2 1.227(2); N1–B–N2 106.9(1), N1–B–F1 109.8(1), N1–B–F2 110.6(1), N2–B–F1 110.1(1), N2–B–F2 110.1(1), F1–B–F2 109.3(1), O1–C–O2 123.57(13).

Compound **3** constitutes a typical BODIPY with a coplanar core of two five-membered and one six-membered ring. The boron atom is bound to two nitrogen atoms [1.550(2) Å and 1.551(2) Å] and two F atoms [1.400(2) and 1.393(2) Å] in a distorted tetrahedron with bond angles at the boron atom in the range of 106.9(1)–110.6(1)°. All C–C and C–N bond lengths of the C_9N_2 unit are aligned from 1.384(2)–1.430(2) Å (C–C), and from 1.347(2)–1.399(2) Å (C–N), supporting the delocalized nature of the π system within the chromophore. The 4-carboxyphenyl substituent at the *meso* position is planar in itself (max. deviation from the C_7O_2 plane of 0.043 Å) and rotated by 76.94° from the mean squares C_9N_2B plane of the BODIPY. The quasi orthogonal arrangement of the π systems is enforced by the two methyl groups located at the β′ positions so that no free rotation of the *meso* aryl group is expected.

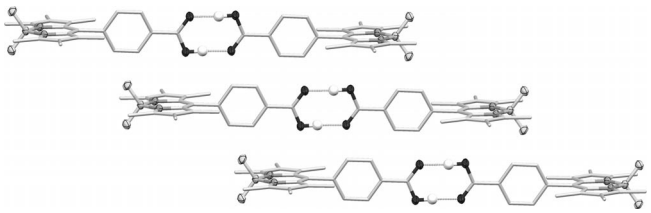


Figure 4. Hydrogen bonding and packing scheme representation of **3** (ellipsoids set to 50 % probability; carbon-bound hydrogen atoms are omitted for clarity). Selected bond lengths /Å and distances /Å: O–H 0.964, O···H 1.664, O···O 2.626, {center C_2O_4}–{center C_3N_2B} 9.080.

The metrics of the carboxylate group clearly show two different types of C–O bonds with bond lengths of 1.314(2) Å and 1.227(2) Å. A proton was found during refinement at the more distantly bound oxygen atom O1. The carboxylates of two neighboring molecules form hydrogen bonds leading to dimeric structures as shown in Figure 4. The crystal lattice forms by coplanar packing of such hydrogen bonded dimers.

The *meso*-methyl derivative **13** formed a single crystal from a dichloromethane/pentane mixture. The structure was solved in space group $P\bar{1}$ with two crystallographically distinct, but very similar molecules in the unit cell. Only molecule A is shown in Figure 5.

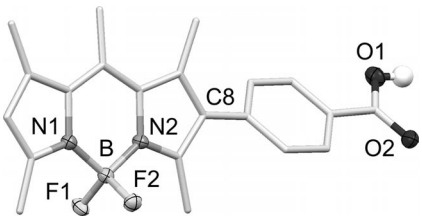


Figure 5. Molecular structure of BODIPY carboxylic acid **13** (molecule A; ellipsoids set to 50 % probability; carbon-bound hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: B–N1 1.542(2), B–N2 1.549(2), B–F1 1.389(2), B–F2 1.390(2), C–O1 1.273(2), C–O2 1.260(2), C8–C_{phenyl} 1.479(2); N1–B–N2 107.01(11), N1–B–F1 108.96(12), N1–B–F2 110.42(12), N2–B–F1 110.99(12), N2–B–F2 109.67(12), F1–B–F2 109.76(12), O1–C–O2 124.21(13).

The almost planar C_9N_2B and distorted tetrahedral BF_2N_2 subunits of **13** are characterized by bond lengths and angles as expected. For example, the data of the coordination unit around the boron atom is found at the following values: B–N: 1.542(2) and 1.549(2) Å; B–F: 1.389(2) and 1.390(2) Å; *X*–B–*Y* angles: 107.01(11)–110.99(12)°. Other than for **3**, however, the 4-carboxyphenyl substituent of 13 is not found in an almost perpendicular orientation but largely rotated in direc-

tion of a coplanar arrangement with the BODIPY core. The interplane angle of these planar subunits of only 39.65° accounts for a significant degree of conjugation between the luminophor and the designated metal binding site. Typical for carboxylic acids, and similar to the behavior or **3**, identical molecules of **13** form hydrogen bridged dimers, from which the crystal forms by π stacking (Figure 6).

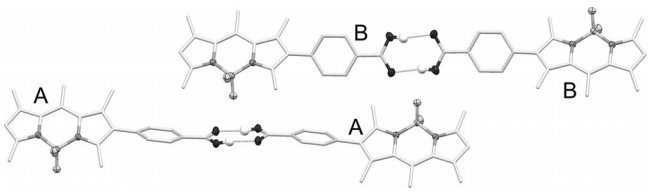


Figure 6. Hydrogen bonding and packing scheme representation of **18** (ellipsoids set to 50 % probability; carbon-bound hydrogen atoms are omitted for clarity). A and B denominate the crystallographically different molecules of **13**. Selected bond lengths /Å and distances /Å: O–H 0.84, O···H 1.771/1.895, O···O 2.598/2.720, {center C_2O_4}-{center C_3N_2B} 10.991/11.120.

BODIPY carboxylic acid **18** carrying the acetylene-elongated 4-carboxyphenyl group at the β position crystallized from chloroform in the triclinic system, space group $P\bar{1}$, with $Z = 2$. Figure 7 and Figure 8 illustrate the molecular structure of **18** and the arrangement of the molecules in the crystal packing.

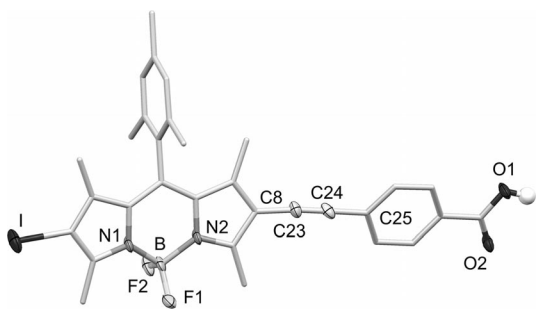


Figure 7. Molecular structure of BODIPY carboxylic acid **18** (ellipsoids set to 50 % probability; carbon-bound hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: B–N1 1.560(12), B–N2 1.553(11), B–F1 1.378(12), B–F2 1.395(12), C–O1 1.294(1), C–O2 1.235(1), C–I 2.080(9), C8–C23 1.426(12), C23–C24 1.192(12), C24–C25 1.440(12); N1–B–N2 105.5(7), N1–B–F1 111.2(8), N1–B–F2 109.1(8), N2–B–F1 111.2(8), N2–B–F2 109.4(8), F1–B–F2 110.3(8), O1–C–O2 125.1(8), C8–C23–C24 175.1(10), C23–C24–C25 177.2(10).

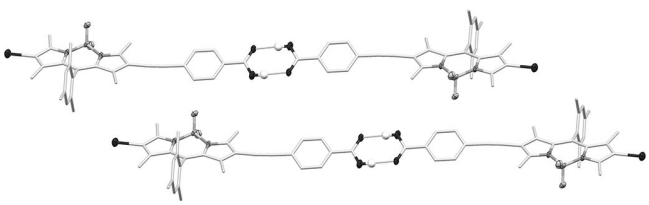


Figure 8. Hydrogen bonding and packing scheme representation of **18** (ellipsoids set to 50 % probability; carbon-bound hydrogen atoms are omitted for clarity). Selected bond lengths /Å and distances /Å: O–H 0.84, O···H 1.79, O···O 2.616, {center C_2O_4}-{center C_3N_2B} 13.542.

As for **3** and **13**, the C_9N_2B luminophor of **18** and the metrics of the BF_2N_2 subunit account for a typical BODIPY with aligned bond lengths and a distorted tetrahedral coordination of the boron atom [B–N: 1.560(12) and 1.553(11) Å; B–F: 1.378(12) and 1.395(12) Å; *X*–B–*Y* angles: 105.5(7)–111.2(8)°]. The mesityl substituent at the *meso* position is found in an almost perpendicular orientation with a torsion angle of 89.00° while the bridging acetylene linker leads to a basically coplanar arrangement of the carboxyphenyl group with the BODIPY chromophore. As before, the carboxylic acid groups of two molecules form a hydrogen-bridged system leading to the dimerization of two molecules, and the crystal is again formed by π stacking interactions of these dimers.

The new BODIPY carboxylic acids are characterized by an intense absorption in the optical spectrum at about 500–550 nm and by fluorescence from the excited singlet state. The fluorescence band appears close to the absorption maximum with a small Stokes shift of 17–31 nm and with high quantum yields for most of the compounds (Table 1). For the ferrocene and hydroquinone derivatives **20** and **7**, however, the quantum yields drop dramatically, indicating an efficient electron or energy transfer process in the excited state. The same holds true for the iodinated **18**, where spin orbit coupling of the heavy atom results in efficient quenching of the singlet excited state. Further dependencies on the quantum yields like substitution pattern or donor strengths of the substituents are not obvious.[15]

Table 1. Photophysical data of BODIPY carboxylic acids (CH_2Cl_2).

Compound	Absorption λ_{max} /nm	ε[a)]	Emission λ_{max} /nm	Φ_F[b)]
3	528	65500	550	0.50
7	502 [c)]	n.d.	519 [c)]	0.03
13	509 [c)]	91000	536 [c)]	0.88
14	516	77700	534	0.94
17	532	42100	559	0.53
18	553	64900	580	0.08
20	533	21700	552	< 0.01
22	538	34400	569	0.48

a) Given in $L \cdot mol^{-1} \cdot cm^{-1}$. b) Excitation with λ_{max}. c) In THF.

BODIPY-appended Paddle Wheel Complexes

When the new BODIPY carboxylic acids are treated with copper(II) salts a solid forms immediately in all cases. This solid could not be redissolved without decomposition of the material. Therefore a careful cocrystallization procedure was sought for the preparation of the desired copper complexes. If dilute solutions of $Cu(OTf)_2$ and of one of the BODIPY carboxylic acids in THF are layered, a solid deposits at the liquid-liquid interface. In the case of **3** crystals are formed, which can be used for a crystallographic analysis. The new compound **23** crystallizes in the triclinic system in space group $P\bar{1}$. Cocrystallized solvent (THF) is present in the crystal lattice, which had to be treated with the SQUEEZE command in one position due to massive disorder. Crystallographic data is given in Table 3. Figure 9 illustrates the molecular structure of **23** and provides selected bond lengths and angles.

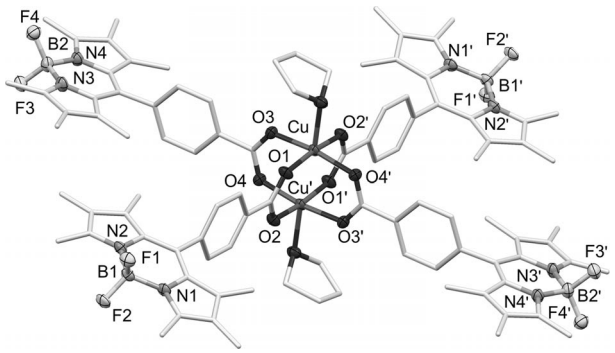


Figure 9. Molecular structure of the bis-copper(II) paddle wheel complex **23** (ellipsoids set to 50 % probability; carbon-bound hydrogen atoms and cocrystallized solvent molecules are omitted for clarity). Selected bond lengths /Å and angles /°: Cu···Cu 2.6007(9), Cu–O1 1.967(2), Cu–O2 1.974(2), Cu–O3 1.968(2), Cu–O4 1.962(2), Cu–O5 2.205(2), B1–N1 1.536(4), B1–N2 1.544(4), B1–F1 1.401(4), B1–F2 1.397(4), C–O1 1.269(4), C–O2 1.266(4), B2–N3 1.541(4), B2–N4 1.551(4), B2–F3 1.404(4), B2–F4 1.383(5), C–O3 1.264(4), C–O4 1.264(4); O1–C–O2 125.8(3), O3–C–O4 126.7(3).

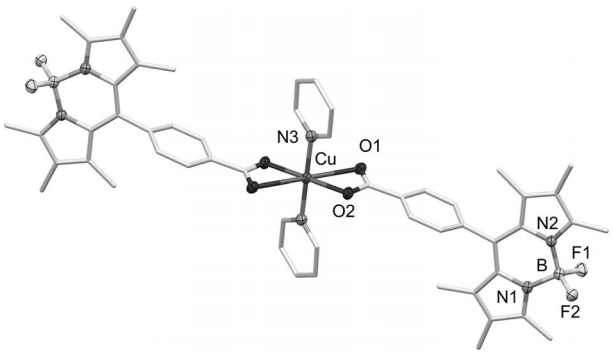


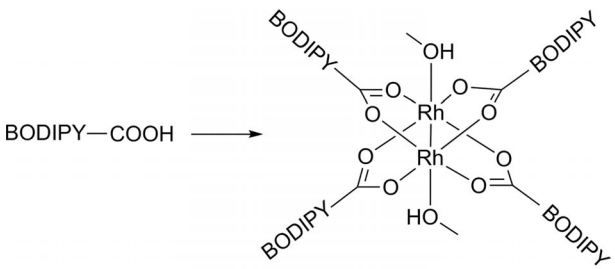
Figure 10. Molecular structure of the copper(II) carboxylate complex **24** (ellipsoids set to 50 % probability; carbon-bound hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: Cu–O1 2.595(1), Cu–O2 1.9562(10), Cu–N3 2.0376(12), B–N1 1.5503(18), B–N2 1.5436(18), B1–F1 1.3933(16), B1–F2 1.3936(17), C–O1 1.2357(16), C–O2 1.2894(15); O1–Cu–O2 56.36(9), O1–C–O2 123.23(12).

Compound **23** constitutes a typical copper paddle wheel structure with two THF molecules as ligands in the axial positions at a distance of 2.205(2) Å and a Cu–Cu distance of 2.6007(9) Å. The BODIPY carboxylate ligands show bond lengths and angles very similar to the non-bonded acid **3**. The phenyl group is rotated away from the BODIPY mean squares C_9N_2B plane by 76.29° and almost coplanar with the carboxy group. The boron atoms are bound by two nitrogen and two fluorine donors in a distorted tetrahedral way. The only significant difference is the enhanced bite angle of the O–C–O moiety for **23**, which is 2.2–3.1° larger due to the bridging binding mode. In this arrangement the centers of four BODIPY luminophors are located at distances of 9.682 Å and 9.747 Å from the central Cu···Cu unit.

Further characterization of **23** was hindered by the extremely low solubility of the compound. Instead an exchange of the THF ligands with pyridine or 4,4′-bipyridine during the cocrystallization procedure was attempted. Despite many attempts these approaches were unsuccessful. In the case of pyridine, however, a mononuclear complex **24** carrying two BODIPY carboxylate ligands formed and could be analysed crystallographically. **24** crystallizes in space group $P2_1/c$ with $Z = 2$. Crystallographic data is given in Table 3. Figure 10 illustrates the molecular structure of **24** and provides selected bond lengths and angles.

As for the dinuclear **23** the BODIPY carboxylate ligand does not undergo significant structural changes upon coordination, and the distance of the BODIPY luminophor center to the copper(II) ion of 9.672 Å is also similar as in **23**. The copper(II) ion of **24** is coordinated in a distorted octahedral environment typical for a $3d^9$ system. Within the polyhedron the stronger N donor ligand pyridine occupies two opposite equatorial positions at a distance of 2.0376(12) Å and pushes one of the weaker O donor atoms of each BODIPY carboxylate ligand into the Jahn-Teller axis. This results in a highly unsymmetric binding of the carboxylate group with Cu–O bond lengths of 1.9562(10) Å at the equatorial positions and 2.595(1) Å in the axis, with a O–Cu–O angle of only 56.36(9)°. Thus, the breaking-up of the dinuclear paddle wheel structure in the presence of donor solvents appears to be a simple consequence of the reorientation of the Jahn-Teller axis towards the carboxylate ligand donors.

The introduction of a BODIPY-containing periphery to dinuclear Rh(II) complexes was more successful and led to four soluble paddle wheel systems **25**–**28** (Scheme 4). In all cases the BODIPY carboxylic acid and rhodium(II)acetate were heated in 1,2-dichlorobenzene with 1 % methanol to 150 °C for 5 h. Chromatographic purification and recrystallization from dichloromethane/*n*-hexane yielded 71–73 % of dark green-metallic solids. For the other BODIPY carboxylic acids, in particular for those carrying addition hydroquinone or ferrocene bridges, only decomposed material was obtained.



3 **25**
13 **26**
14 **27**
17 **28**

Scheme 4. Preparation of BODIPY-appended Rh_2-paddle wheel complexes **25**–**28**. $Rh_2(OAc)_4(H_2O)_2$, 1,2-dichlorobenzene, methanol, reflux 5 h.

The molecular structure of Rh^{II} paddle wheel complexes with BODIPY antennae could be studied in the case of **25** (Figure 11). A single crystal suitable for a X-ray diffraction study grew from the reaction mixture. The compound crystallizes in space group $P2_1/c$, with $Z = 2$ as a mixed dichlorobenzene/methanol solvate. Crystallographic details are given in Table 3.

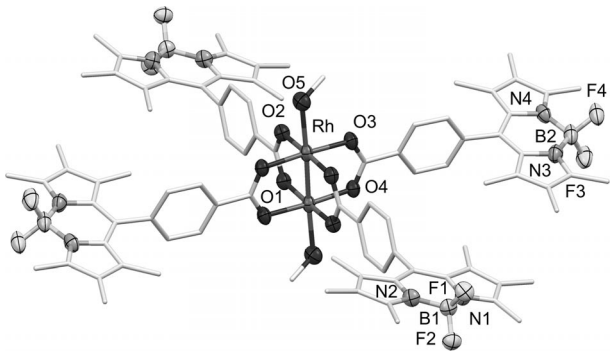


Figure 11. Molecular structure of the dirhodium(II) paddle wheel complex **25** (ellipsoids set to 50% probability; carbon-bound hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: Rh–Rh 2.3914(8), Rh–O1 2.042(3), Rh–O2 2.026(3), Rh–O3 2.027(3), Rh–O4 2.037(3), Rh–O5 2.317(4), B1–N1 1.548(7), B1–N2 1.547(7), B1–F1 1.395(7), B1–F2 1.376(7), C–O1 1.283(6), C–O2 1.261(6), B2–N3 1.522(9), B2–N4 1.533(8), B2–F3 1.419(7), B2–F4 1.400(7), C–O3 1.272(6), C–O4 1.262(6); O1–C–O2 127.4(4), O3–C–O4 126.7(4).

The molecular structure of the dirhodium complex **25** is very similar to the isotypical structure of the copper compound **23**. Four BODIPY carboxylates are bound to the Rh–Rh bonded metal core in bridging fashions and at Rh–O distances of 2.026(3)–2.042(3) Å, and as before, the labile axial positions are occupied by weakly coordinating solvent molecules (methanol for **25**) with a Rh–O distance of 2.317(4) Å. The Rh–Rh distance is found at 2.3914(8) Å which is a typical value for such single bonded species (for comparison: Rh–Rh distance in $[Rh_2(OAc)_4(H_2O)_2]$: 2.378 Å)[16]. As for **23** this arrangement results in four BODIPY luminorphor units located in distances of 9.712 Å and 9.763 Å of the dinuclear core. In contrast to the copper chelate **23**, however, **25** is soluble in organic solvents without decomposition of the dinuclear structure. Donor solvent do not monomerize **25** as they do for **23**, presumably due to the strong, additional rhodium(II)–rhodium(II) single bond.

The solubility of the dirhodium paddle wheel complexes **25**–**28** allows a more detailed spectroscopic investigation. Of particular interest with respect to the possibility of an antenna function of the BODIPY units are the optical spectra and the electrochemical behavior of the species. UV/Vis spectra were measured from ca. 10^{-5} mol·L^{-1} solutions of **25**–**28** in dichloromethane. The results for absorption and emission behavior are given in Figure 12 and in Table 2. The absorption spectra are very similar to those of the respective BODIPY carboxylates, so that an electronic or excitonic influence of the dirhodium subunit or of an adjacent BODIPY chromophore can be excluded. Fluorescence of **25**–**28** is observed with similar Stokes shifts as for the free BODIPY ligands **3**, **13**, **14**, and **17**, however, the quantum yields are at very small values < 1 %. This indicates a very efficient energy- or electron transfer from the excited singlet state, presumably due to the presence of the nearby Rh_2 core. An alternative interpretation comes from an aggregation caused quenching process (ACQ), which is typically observed for low-solubility chromophores. The phenomenon of aggregation induced emission has been proposed for propeller shaped donor-acceptor type fluorophors,[17] but does not seem to be in action here.

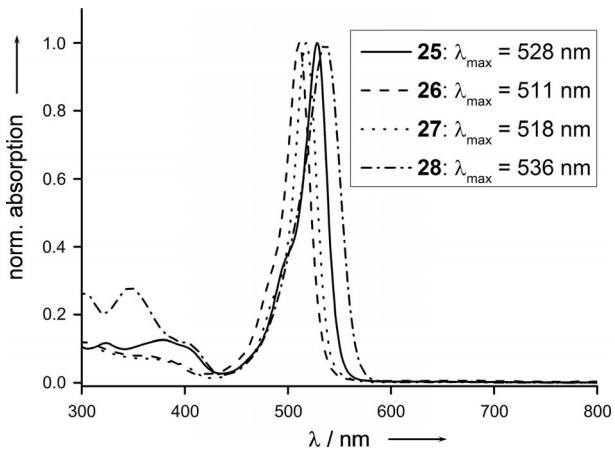


Figure 12. Normalized UV/Vis absorption spectra of dirhodium(II) paddle wheel complexes **25**–**28** (ca. 10^{-5} mol·L^{-1}, dichloromethane).

Table 2. Photophysical data of dirhodium complexes **25**–**28** (CH_2Cl_2).

Compound	Absorption λ_{max} /nm	ε[a)]	Emission λ_{max} /nm	Φ_F[b)]
25	528	190600	555	<0.01
26	511	–[c)]	536	<0.01
27	518	358600	537	<0.01
28	536	234200	562	<0.01

a) Given in L·mol^{-1}·cm^{-1}. b) Excitation with λ_{max}. c) Unreliable data due to low solubility.

Finally, cyclic voltammetry was applied to the BODIPY carboxylic acid **3** and the dirhodium complex **25** (Figure 13). Both compounds show oxidation and reduction steps at similar potentials, indicating a basically BODIPY centered redox behavior of the dinuclear **25** without visible interaction between the four redox sites. There is, however, a significant difference in the electrochemical reversibility of the processes. While the oxidation process is reversible for both compounds, the reduction of the paddle wheel complex **25** becomes irreversible.

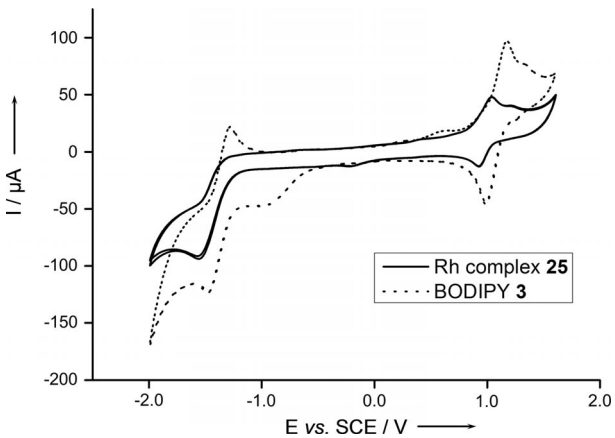


Figure 13. Cyclic voltammetry of BODIPY carboxylic acid **3** and dirhodium paddle wheel complex **25** (CH_2Cl_2, 0.5 mol·L^{-1} $TBAPF_6$, 200 mV·s^{-1}).

Such a difference may be interpreted as a fast and efficient electron transfer from the BODIPY radical anion to the dirhodium core. However, further spectroelectrochemical and photophysical studies are necessary here to support this point.

Conclusions

The study has shown that BODIPY carboxylate ligands are readily prepared if aromatic or unsaturated linkers are placed between the luminophor and the CO_2H group. Even functionalized systems are available by Palladium catalyzed Sonogashira- and Stille coupling protocols. However, the latter reaction requires the use of benzyl protection groups for carboxy and hydroxyl substituents. Depending on the site and type of the carboxylic acid group attachement different relative orientations of the BODIPY plane and the CO_2 plane are accessible. Paddle wheel type dinuclear complexes form with divalent copper and rhodium ions in good yields. While research on the copper derivatives is hampered by an extremely low solubility, rhodium carboxylates with appended BODIPY units can be dissolved undecomposed in many solvents. First investigations suggest the antenna function of the BODIPY units with respect to energy and electron transfer processes. This functionality offers much potential for future studies on BODIPY-appended paddle wheel complexes.

Experimental Section

General: Solvents were dried according to standard procedures in an inert gas atmosphere of argon or nitrogen. All reagents were purchased from commercial sources in reagent grade and used as received. NMR spectra were obtained with a Bruker DPX 200, a Bruker Avance II 300, a Bruker DRX 400, a Bruker Avance III 400, and a Bruker Avance II 600 spectrometer with room temperature as measuring temperature. Chemical shifts (δ) are given in ppm relative to residual protio solvent resonances (^{1}H, ^{13}C NMR spectra) or to external standards ($BF_3{\cdot}Et_2O$ for ^{11}B and $CFCl_3$ for ^{19}F NMR spectra). Mass spectra were recorded with a Finnigan MAT95 (HR-EI) or a Finnigan LCQ Deca (ESI). Values *m/z* are given for the most abundant isotopes only. CHN analyses were measured with an Elementar Vario Micro Cube or an Elementar Vario EL. A Shimadzu UV-1601 PC spectrophotometer and a Varian Cary Eclipse spectrofluorometer were used to acquire absorption and emission spectra. Absolute fluorescence quantum yields were determined in aerated solvents by a PTI QuantaMaster 40 UV/VIS spectrofluorometer equipped with an integrating sphere. The provided corrections for excitation and emission were applied. Cyclic voltammetry was performed with a Princeton Applied Research VersaSTAT 3 potentiostat under inert conditions at room temperature in absolute CH_2Cl_2 containing nBu$_4$NPF$_6$. A self-made 3-electrode set-up with two platinum wires as working and counter electrodes and a silver wire as quasi-reference electrode was used and ferrocene as internal standard had been added. Single crystal X-ray diffraction studies were performed with an Oxford Diffraction Xcalibur E (**18**), or an Oxford Diffraction Xcalibur (**3**, **13**, **23**, **24**, **25**). All structures were solved with SIR-92[18] or SHELXS,[19] and refined with SHELXL.[20] WinGX[21] and Mercury[22] were used during refinement and analysis of the crystallographic data. A summary of the crystallographic data and structure refinement results are listed in Table 3

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1418580, CCDC-1418581, CCDC-1418582, CCDC-1418583, CCDC-1418584, and CCDC-1424950 (for **3**, **18**, **23**, **24**, **25**, and **13**, respectively) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

1,2,3,5,6,7-Hexamethyl-8-(4-carboxyphenyl)-BODIPY (3): 2,3,4-Trimethylpyrrole (2.29 g, 21 mmol) and 4-formylbenzoic acid (1.50 g, 10 mmol) in dichloromethane (650 mL) were treated with trifluoroacetic acid (20 µL) and stirred for 4 h under inert conditions. DDQ (2.21 g, 9.8 mmol) was added, and the mixture was stirred for an additional 15 min before triethylamin (12 mL, 86 mmol), followed by

Table 3. Selected crystallographic data for **3**, **13**, **18**, **23**–**25**.

	3	**13**	**18**	**23**·4THF	**24**	**25**·2C$_6$H$_4$Cl$_2$·4CH$_3$OH
Formula	$C_{22}H_{23}BF_2N_2O_2$	$C_{21}H_{21}BF_2N_2O_2$	$C_{31}H_{28}BF_2IN_2O_2$	$C_{112}H_{136}B_4Cu_2F_8N_8O_{14}$	$C_{54}H_{54}B_2CuF_4N_6O_4$	$C_{106}H_{118}B_4Cl_4F_8N_8O_{14}Rh_2$
M_r /g·mol^{-1}	396.23	382.20	636.26	2140.60	1012.20	2270.94
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a /Å	6.7449(6)	7.7593(4)	8.7562(16)	13.2863(7)	7.8961(2)	10.6057(8)
b /Å	9.0266(6)	14.2596(6)	9.047(2)	14.0673(8)	15.7848(2)	35.2660(14)
c /Å	17.3846(16)	16.6737(6)	18.562(5)	17.5167(8)	20.5179(5)	14.9508(16)
α /°	84.132(6)	93.617(4)	84.48(2)	95.231(4)	90	90
β /°	81.279(8)	95.738(4)	82.79(2)	95.681(4)	106.648(2)	111.689(7)
γ /°	89.325(8)	104.261(4)	75.477(16)	118.117(6)	90	90
V /Å^3	1040.71(15)	1771.67(14)	1409.0(6)	2837.7(3)	2450.12(9)	5196.0(7)
Z	2	4	2	1	2	2
$d_{calcd.}$ /g·cm^{-3}	1.264	1.433	1.500	1.253	1.372	1.451
μ /mm^{-1}	0.766	0.879	1.181	1.088	1.199	4.194
2θ limits /°	4.93–75.78	3.21–76.17	4.44–50.0	3.61–78.32	3.58–75.46	3.42–75.78
Measured	12980	38137	13552	46026	10994	46812
Independent	4279	7374	4963	11735	10994	9830
Observed[a)]	3704	6333	3809	8691	9943	7975
Parameters/ restraints	272/0	517/0	361/6	695/56	326/0	677/0
R_1[b)] all data	0.0466	0.0516	0.1246	0.0978	0.0554	0.0776
wR_2[c)]	0.1076	0.1149	0.1730	0.2146	0.1480	0.1727

a) Observation criterion: $I > 2\sigma(I)$. b) $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. c) $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

BF_3·OEt_2 (16 mL, 170 mmol) were added. After 2 h the fluorescent mixture was treated with $NaHCO_3$ solution, extracted with dichloromethane, and the organic layer was dried with Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography on silica with CH_2Cl_2/MeOH 99/1 to yield the title compound (1.85 g, 4.66 mmol, 13 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.25 (d, 2 H, J = 8.4 Hz, Ar–*H*), 7.44 (d, 2 H, J = 8.4 Hz, Ar–*H*), 2.53 (s, 6 H, CH_3), 1.85 (s, 6 H, CH_3), 1.27 (s, 6 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 171.1, 154.7, 141.7, 138.5, 138.3, 130.9, 130.1, 129.7, 128.9, 126.8, 12.7, 12.1, 9.0. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.2 ppm (q, J_{BF} = 33 Hz, 2F; 2×BF_2). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.99 ppm (t, J_{BF} = 33 Hz, 1B; BF_2). **MS** (ESI): m/z = 395 ([M]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε[rel]) = 380 (8600), 528 (65500); λ_{em} (λ_{ex} = 528 nm) = 550 nm. $C_{22}H_{23}BF_2N_2O_2$: calcd. C 66.69, H 5.85, N 7.07 %; found: C 66.58, H 6.01, N 7.21 %.

8-(4-(2,5-Bisbenzyloxy)benzoic Acid Benzylate)-1,3,5,7-tetramethyl-BODIPY (6): Benzaldehyde **4** (453 mg, 1.00 mmol) and pyrrole **5**[23] (215 mg, 2.25 mmol) in dry dichloromethane (250 mL) were treated with trifluoroacetic acid (15 µL) and stirred for 8 h. DDQ (227 mg, 1.00 mmol) was added and stirring was continued for 30 min bevor triethylamine (0.85 mL, 6.00 mmol) and boron trifluoride etherate (1.35 mL, 13.0 mmol) were added. After 3 h sodium hydrogen carbonate solution was added, the organic layer was separated, dried with $MgSO_4$ and purified by silica chromatography with dichloromethane. Recrystallization from ethyl ether at –20 °C yields 234 mg (0.35 mmol, 35 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.57 (s, 1 H, Ar–*H*), 7.44 – 7.15 (m, 15 H, Bn–*H*), 6.89 (s, 1 H, Ar–*H*), 5.95 (s, 2 H, *β-H*), 5.37 (s, 2 H, CH_2Ph), 5.09 (s, 2 H, CH_2Ph), 5.06 (s, 2 H, CH_2Ph), 2.56 (s, 6 H, CH_3), 1.33 (s, 6 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 165.5, 155.6, 153.1, 149.0, 142.5, 136.8, 136.5, 136.1, 135.8, 130.9, 129.7, 128.6, 128.6, 128.5, 128.4, 128.3, 127.9, 127.2, 127.1, 121.6, 121.1, 116.8, 116.2, 71.4, 70.7, 67.1, 14.6, 14.0. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 1.00 (t, J_{BF} = 33.0 Hz, 1B, BF_2). **^{19}F NMR** (376 MHz $CDCl_3$): δ = –146.2 (dq, J_{FF} = 110, J_{BF} = 32.8 Hz, 1F, BF_1F$_2$), 145.3 (dq, J_{FF} = 110, J_{BF} = 32.9 Hz, 1F, BF$_1$$F_2$). **MS** (ESI+): m/z = 671 ([M + H]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε) = 309 (9900), 506 (68400) nm; λ_{em} (λ_{ex} = 506 nm) = 528 nm. $C_{41}H_{37}BF_2N_2O_4$·0.5Et_2O: calcd. C 72.99, H 5.98, N 3.96 %; found: C 73.21, H 6.31, N 3.72 %.

8-(4-(2,5-Bishydroxy)benzoic acid)-1,3,5,7-tetramethyl-BODIPY (7): BODIPY **6** (25 mg, 37 µmol) and Pd/C were treated with hydrogen gas in ethanol (15 mL) for 30 min. The mixture was filtered with ethanol and the eluate taken to dryness whereupon the product remained as a red solid (yield: 13.6 mg, 34 µmol, 92 %). Attempts to purify the compound led to decomposition. **^{1}H NMR** (300 MHz, [D_6]DMSO): δ = 9.65 (br. s, 1 H, COO*H*), 7.40 (s, 1 H,Ar–*H*), 6.78 (s, 1 H, Ar–*H*), 6.17 (s, 2 H, β-*H*), 3.17 (s, 2 H, O*H*), 2.44 (s, 6 H, 2×CH_3), 1.54 (s, 6 H, 2×CH_3). **^{11}B NMR** (96 MHz, [D_6]DMSO): δ = 1.33 (t, J_{BF} = 32.2 Hz, 1B, BF_2). **UV/Vis** (THF): λ_{abs} (ε[rel]) = 308 (0.2), 335 (0.17), 502 (1); λ_{em} (λ_{ex} = 502 nm) = 519 nm.

2-(4-Benzyloxycarbonylphenyl)-1,3,5,7,8-pentamethyl-BODIPY (11): 2-IodoBODIPY **8**[24] (141 mg, 0.41 mmol), stannylbenzoic acid benzylester **10**[25] (250 mg, 0.50 mmol), and $Pd(PPh_3)_4$ (10 mg, 8 µmol) in dry toluene were heated to 100 °C for 24 h. After removal of the solvent the mixture was subjected to silica chromatography with dichloromethane/pentane 1:1 to yield the title compound (140 mg, 0.30 mmol, 72 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.14 (d, 2 H, J = 8.5 Hz, Ar–*H*), 7.47 (m, 2 H, Bn–*H*), 7.40 (m, 3 H, Bn–*H*), 7.29 (d, 2 H, J = 8.5 Hz, Ar–*H*), 6.11 (s, 1 H, β-*H*), 5.40 (s, 2 H, CH_2Ph), 2.65 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.3, 154.9, 151.0, 141.9, 139.1, 136.6, 136.1, 132.8, 131.8, 130.4, 129.8, 128.7, 128.6, 128.3, 128.2, 121.9, 66.7, 17.5, 16.9, 15.3, 14.5, 13.1. **^{11}B NMR** (96 MHz, $CDCl_3$): δ = 0.92 (t, J_{BF} = 32.7 Hz, 1B, BF_2). **^{19}F NMR** (188 MHz, $CDCl_3$): δ = –146.9 (q, J_{BF} = 32.6 Hz, 2F, BF_2). **MS** (ESI): m/z = 473 ([M + H]$^+$). **UV/Vis** λ_{abs} (ε[rel]) = 364 (0.07), 508 (1); λ_{em} (λ_{exc}: 508 nm) = 536 nm.

2-(4-Benzyloxycarbonylphenyl)-1,3,5,7-tetramethyl-8-mesityl-BODIPY (12): 2-IodoBODIPY **9**[26] (200 mg, 0.41 mmol), 4-stannylbenzoic acid benzylester **10**[25] (250 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (10 mg, 8 µmol) in dry toluene were heated to 100 °C for 24 h. After removal of the solvent the mixture was subjected to silica chromatography with dichloromethane/pentane 1:1 to yield the title compound (216 mg, 0.38 mmol, 93 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.19 (d, 2H, J = 8.6 Hz, Ar–*H*), 7.35–7.31 (m, 2H, Bn–*H*), 7.23–7.13 (m, 2H, Bn–*H*), 6.97 (d, 2H, J = 8.6 Hz, Ar–*H*), 6.79 (s, 2H, Mesityl-*H*), 5.77 (s, 1H, β-*H*), 5.29 (s, 2H, CH_2Ph), 2.75 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.11 (s, 6H, CH_3), 1.50 (s, 3H, CH_3), 1.46 (s, 3H, CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = 1.74 (t, J = 32.5 Hz, 1B, BF_2). **^{19}F NMR** (188 MHz, $CDCl_3$): δ = –146.7 (q, J_{BF} = 31.9 Hz, 2F, BF_2). **MS** (ESI): m/z = 599 ([M + H]$^+$). **UV/Vis** λ_{abs} (ε[rel]): 278 (0.30), 368 (0.07), 515 (1.0) nm; λ_{em} (λ_{exc}: 515 nm) = 536 nm.

2-(4-Carboxyphenyl)-1,3,5,7,8-pentamethyl-BODIPY (13): Benzyl protected BODIPY **11** (100 mg, 0.21 mmol) in ethanol and Pd/C (10 mg) was stirred for 2 h under a blanket of hydrogen. The solvent was removed and the residue purified by silica chromatography with dichloromethane/methanol 99:1 (yield: 79 mg, 0.206 mmol, 98 %). **^{1}H NMR** (200 MHz, [D_6]DMSO): δ = 8.04 (d, J = 8.1 Hz, 2H, Ar-*H*), 7.40 (d, J = 8.1 Hz, 2H), 6.30 (s, 1H, β-*H*), 2.69 (s, 3H, CH_3), 2.45 (s, 6H, CH_3), 2.38 (s, 3H, CH_3), 2.34 (s, 3H, CH_3). **^{11}B NMR** (96 MHz, [D_6]DMSO): δ = 0.90 (t, J = 34.1 Hz, 1B, BF_2). **^{19}F NMR** (188 MHz, [D_6]DMSO): δ = –143.1 (m, 2F, BF_2). **MS** (ESI): m/z = 381 ([M – H]$^+$). **UV/Vis** λ_{abs} (CH_2Cl_2, ε[L mol^{-1} cm^{-1}]) = 303 (8300), 365 (6200), 508 (91000) nm; λ_{em} (λ_{exc}: 509 nm) = 536 nm. $C_{21}H_{21}BF_2N_2O_2$·0.5H_2O: calcd. C 64.47, H 5.67, N 7.16 %; found: C 63.77, H 5.57, N 7.09 %.

2-(4-Carboxyphenyl)-1,3,5,7-tetramethyl-8-mesityl-BODIPY (14): Benzyl protected BODIPY **11** (200 mg, 0.35 mmol) in ethanol and Pd/C (10 mg) was stirred for 2 h under a blanket of hydrogen. The solvent was removed and the residue purified by silica chromatography with dichloromethane/methanol 99:1 (yield: 162 mg, 0.33 mmol, 94 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (d, 2H, J = 8.4 Hz, Ar-*H*), 7.29 (d, 2H, J = 8.4 Hz, Ar-*H*), 6.96 (s, 2H, Mes-*H*), 6.02 (s, 1H, β-*H*), 2.59 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.14 (s, 6H, CH_3), 1.41 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 171.4, 156.5, 152.4, 143.4, 142.3, 139.9, 138.8, 137.8, 134.8, 131.6, 131.3, 131.1, 130.3, 130.2, 130.0, 129.1, 127.6, 121.5, 21.2, 19.6, 14.7, 13.5, 13.3, 11.5. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 1.10 (t, J_{BF} = 32.4 Hz, 1B, BF_2). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.6 (q, J_{BF} = 31.3 Hz, 2F, BF_2). **MS** (ESI): m/z = 485 ([M – H]$^+$). **UV/Vis** λ_{abs} (ε[L mol^{-1} cm^{-1}]) = 311 (7000), 515 (77700) nm; λ_{em} (λ_{exc}: 515 nm) = 534 nm. $C_{29}H_{29}BF_2N_2O_2$·H_2O: calcd. C 69.06, H 6.20, N 5.55 %; found: C 68.88, H 6.59, N 5.84 %.

1,3,5,7-Tetramethyl-8-mesityl-2-((4-carboxyphenyl)-ethinyl)-BODIPY (17): 2-Iodo-BODIPY **9**[26] (168 mg, 0.34 mmol), 4-ethinylbenzoic acid **16**[27] (50 mg, 0.34 mmol), $Pd(PPh_3)_4$ (15 mg, 13 µmol), and copper(I)iodide (10 mg, 52 µmol) in dry THF (8 mL) and Hünig base (2 mL) were stirred at 55 °C for 24 h. After cooling the solvent was removed in vacuo and the residue was subjected to silica chromatography with ethyl ether/*n*-hexane 2:1 + 1 % acetic acid.

Recrystallization from ethyl acetate/*n*-hexane yields the title compound (120 mg, 0.23 mmol, 69 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.04 (d, 2 H, *J* = 8.5 Hz, Ar-*H*), 7.52 (d, 2 H, *J* = 8.5 Hz, Ar-*H*), 6.98 (s, 2 H, Mes-*H*), 6.04 (s, 1 H, β-*H*), 2.71 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.10 (s, 6 H, CH_3), 1.53 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.6, 158.1, 156.0, 144.5, 142.3, 141.9, 138.9, 132.1, 131.1, 130.7, 130.1, 129.4, 129.3, 129.1, 127.9, 122.1, 113.9, 95.1, 86.2, 21.2, 19.5, 14.8, 13.6, 13.5, 12.1. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 31.8 Hz, 1B, *B*F$_2$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.8 (q, *J* = 32.8 Hz, 2F, BF$_2$). **MS** (ESI+): *m*/*z* = 509 ([M – H]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε[L·mol^{-1}·cm^{-1}]) = 343 (9700), 533 (42100) nm. λ_{em} (λ_{exc}: 533 nm) = 559 nm. $C_{31}H_{29}BF_2N_2O_2$·0.75$C_4H_8O_2$: calcd. C 70.84, H 6.12, N 4.86 %; found: C 71.19, H 5.79, N 4.52 %.

2-Iod-6-(ethinyl(4-carboxyphenyl))-1,3,5,7-tetramethyl-8-mesityl-BODIPY (18): 2,6-Diiodo-BODIPY **15**[28] (85 mg, 0.14 mmol), 4-ethinylbenzoic acid **16**[27] (50 mg, 0.34 mmol), Pd(PPh_3)$_4$ (10 mg, 8 µmol), and CuI (4 mg, 21 µmol) were heated in dry THF (5 mL) and Hünig base (1.5 mL) to 60 °C for 24 h. After cooling the solvent was removed in vacuo and the residue was subjected to silica chromatography with dichloromethane/pentane 1:1 and recrystallized from ethyl acetate/*n*-hexane to yield the title compound (70 mg, 0.11 mmol, 79 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.05 (d, 2 H, *J* = 8.6 Hz, Ar-*H*), 7.53 (d, 2 H, *J* = 8.6 Hz, Ar-*H*), 6.99 (s, 2 H, Mes-*H*), 2.72 (s, 3 H, CH_3), 2.67 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.09 (s, 6 H, CH_3), 1.53 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.9, 154.1, 152.5, 144.7, 142.5, 139.3, 134.8, 131.4, 131.2, 130.6, 129.3, 129.1, 128.2, 127.8, 127.8, 127.7, 121.7, 95.7, 85.5, 21.2, 19.5, 16.1, 15.8, 13.7, 12.4. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.81 (t, 1B, J_{BF} = 32.0 Hz, 1B, *B*F$_2$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.5 (q, J_{BF} = 31.9 Hz, 2F, BF$_2$). **MS** (ESI+): *m*/*z* = 617 ([M-F]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε[L·mol^{-1}·cm^{-1}]) = 298 (14200), 339 (12900), 393 (9800), 553 (64900) nm. λ_{em} (λ_{exc} = 553 nm) = 580 nm. $C_{45}H_{41}BF_2N_2O_4$·$C_4H_8O_2$·C_6H_{14}: calcd. C 60.75, H 6.22, N 3.46 %; found: C 60.92, H 6.32, N 3.27 %.

2-(1-Ethinyl-1′-ferrocenyl carboxylic acid)-1,3,5,7-tetramethyl-8-mesityl-BODIPY (20): 2-Iodo-BODIPY **9**[26] (100 mg, 0.20 mmol), ethinylferrocenyl carboxylic acid **19**[29] (64 mg, 0.25 mmol), Pd(PPh_3)$_4$ (20 mg, 18 µmol), and copper(I)iodide (10 mg, 52 µmol) were heated in dry THF. (12 mL) and Hünig base (3 mL) to 55 °C for 24 h. After cooling the solvent was removed in vacuo and the residue was subjected to silica chromatography with ethyl ether/*n*-hexane 2:1 + 2 % methanol to yield the title compound (107 mg, 0.17 mmol, 87 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 6.97 (s, 2 H, Mes-*H*,), 6.01 (s, 1 H, β-*H*), 4.85 (m, 2 H, Cp-*H*), 4.48(m, 4 H, Cp-*H*), 4.30 (m, 2 H, Cp-*H*), 2.68 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 2.35 (s, 3 H, Mes-*para*-CH_3), 2.10 (s, 6 H, Mes-*ortho*-CH_3), 1.51 (s, 3 H, CH_3), 1.40 (s, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 176.5, 143.6, 142.0, 138.8, 134.8, 132.2, 132.0, 131.6, 130.8, 130.7, 129.3, 129.1, 128.6, 128.5, 121.5, 77.7, 72.9, 71.8, 71.6, 70.5, 67.7, 21.2, 19.5, 14.7, 14.1, 13.5, 12.3. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 31.8 Hz, 1B, *B*F$_2$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = - 146.8 (q, *J* = 31.2 Hz, 2F, BF$_2$). **MS** (ESI-) *m*/*z* = 617 ([M – H]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε[L·mol^{-1}·cm^{-1}]) = 289 (6400), 375 (4000), 533 (21700) nm. λ_{em} (λ_{exc}: 533 nm) = 552 nm. $C_{35}H_{33}BF_2FeN_2O_2$·2CH_3OH: calcd. C 65.12, H 6.06, N 4.11 %; found: C 64.85, H 6.32, N 4.32 %.

2-(4-Ethinyl-(2,5-(bisbenzyloxy)carboxyphenyl))-1,3,5,7-tetramethyl-8-mesityl-BODIPY (22): 2-Iodo-BODIPY **9**[26] (270 mg, 0.55 mmol), 4-ethinylbenzoic acid derivative **21** (140 mg, 0.39 mmol), Pd(PPh_3)$_4$ (10 mg, 8 µmol) and CuI (4 mg, 21 µmol) in dry THF (10 mL) and Hünig base (3 mL) were stirred at 60 °C for 24 h. After cooling the solvent was removed in vacuo and the residue was subjected to silica chromatography with dichloromethane/pentane 1:1 to yield the title compound (313 mg, 0.43 mmol, 79 %). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.75 (s, 1 H, Ar-*H*), 7.43 (m, 8 H, Bn-*H*), 7.30 (m, 2 H, Bn-*H*), 7.17 (s, 1 H, Ar-*H*), 6.98 (s, 2 H, Mes-*H*), 6.04 (s, 1 H, β-*H*), 5.24 (s, 2 H, CH_2Ph), 5.18 (s, 2 H, CH_2Ph), 2.58 (s, 6 H, CH_3), 2.38 (s, 3 H, CH_3), 2.07 (s, 6 H, CH_3), 1.42 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 164.8, 158.2, 153.7, 151.1, 142.3, 138.9, 136.0, 134.8, 134.1, 130.7, 129.3, 129.2, 129.2, 129.1, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 120.3, 116.9, 115.6, 91.3, 91.1, 73.2, 71.1, 21.2, 19.5, 15.8, 14.8, 13.6, 13.4, 12.0. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.88 (t, J_{BF} = 33.2 Hz, 1B, *B*F$_2$, *B*F$_2$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.8 (q, J_{BF} = 33.1 Hz, 2F, BF$_2$). **MS** (ESI+): *m*/*z* = 703 ([M-F]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε [rel]) = 300 (11700), 372 (14200), 538 (34400) nm. λ_{em} (λ_{exc} = 538 nm) = 569 nm. $C_{45}H_{41}BF_2N_2O_4$·H_2O: calcd. C 72.98, H 5.85, N 3.78 %; found: C 73.40, H 5.58, N 3.89 %.

Copper Paddlewheel Complex 23: BODIPY carboxylic acid **3** (44.8 mg, 0.11 mmol) in THF (6 mL) and triethylamine (100 µL) was carefully layered with a solution of copper(II)triflate (7.5 mg, 0.02 mmol) in THF (1.5 mL) and left for 3 d. At the interphase small crystals formed, which were collected, washed with hexane, and dried to yield the title compound as a THF solvate (25 mg, 13.5 µmol, 67 %). $C_{88}H_{88}B_4Cu_2F_8N_8O_8$: calcd. C 61.88, H 5.19, N 6.56 %; found: C 61.28, H 5.38, N 6.34 %.

Bispyridin Copper Complex 24: Copper(II)triflate (5 mg, 13.8 µmol) and BODIPY carboxylic acid **3** (12 mg, 30 µmol) were dissolved in THF (2 mL) and triethylamine (20 µL) and left in a pyridine saturated atmosphere for one week. The title compound forms red-brownish crystals which were collected, washed with *n*-hexane, and dried to yield 6 mg (6 µmol, 43 %) of **24**.

Rhodium Paddlewheel Complex 25: BODIPY carboxylic acid **3** (224 mg, 0.57 mmol) and rhodium acetate (50 mg, 0.11 mmol) were heated in 1,2-dichlorobenzene (20 mL) and methanol (20 µL) to 150 °C for 4 h. After removal of the solvents in vacuo the residue was purified by silica chromatography with dichloromethane + 0.5 % methanol to yield the title compound (139 mg, 77.8 µmol, 71 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (d, 8 H, *J* = 8.3 Hz, Ar-*H*), 7.23 (d, 8 H, *J* = 8.3 Hz, Ar-*H*), 2.49 (s, 24 H, CH_3), 1.80 (s, 24 H, CH_3), 1.12 (s, 24 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 184.8, 154.4, 139.9, 138.8, 138.5, 131.3, 130.1, 129.9, 127.9, 126.5, 12.7, 12.2, 8.9. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 32.6 Hz, 4B, *B*F$_2$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.2 (m, 8F, BF$_2$). **MS** (ESI): *m*/*z* = 1767 ([M-F]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε[L·mol^{-1}·cm^{-1}]) = 323 (23300), 380 (24700), 528 (190600) nm. λ_{em} (λ_{exc}: 500 nm) = 513 nm; λ_{em} (λ_{exc}: 528 nm) = 555. $C_{90}H_{96}B_4F_8N_8O_{10}$·2$H_2O$: calcd. C 57.29, H 5.34, N 5.94 %; found: C 57.08, H 5.18, N 6.17 %.

Rhodium Paddlewheel Complex 26: BODIPY carboxylic acid **13** (75 mg, 0.20 mmol) and rhodium acetate (20 mg, 0.05 mmol) were heated in 1,2-dichlorobenzene (15 mL) and methanol (20 µL) to 150 °C for 4 h. After removal of the solvents in vacuo the residue was purified by silica chromatography with dichloromethane + 0.5 % methanol to yield the title compound (62 mg, 35.8 µmol, 72 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.39 (d, 4 H, *J* = 3.6 Hz, Ar-*H*), 7.37 (d, 4 H, *J* = 3.6 Hz, Ar-*H*), 7.14 (d, 4 H, *J* = 3.6 Hz, Ar-*H*), 7.12 (d, 4 H, *J* = 3.6 Hz, Ar-*H*), 6.00 (s, 4 H, *β*-*H*), 2.50 (s, 6 H, CH_3), 2.45 (s, 12 H, CH_3), 2.32 (s, 12 H, CH_3), 2.29 (s, 6 H, CH_3), 2.14 (s, 12 H, CH_3). ^{13}C NMR was not measured due to the insufficient solubility of **26**. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.83 (m, 4B, *B*F$_2$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.7 (m, 8F, BF$_2$). **MS** (ESI): *m*/*z* = 1753

([M + Na]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε[L·mol^{-1}·cm^{-1}]) = 308 (36600), 366 (23900), 511 (269600) nm. λ_{em} (λ_{exc}: 511 nm) = 536 nm. $C_{84}H_{80}B_4F_8N_8O_8$·2MeOH: calcd. C 57.55, H 4.94, N 6.24 %; found: C 57.76, H 5.12, N 6.34 %.

Rhodium Paddlewheel Complex 27: BODIPY carboxylic acid **14** (96 mg, 0.20 mmol) and rhodium acetate (20 mg, 0.05 mmol) were heated in 1,2-dichlorobenzene (10 mL) and methanol (20 µL) to 150 °C for 4 h. After removal of the solvents in vacuo the residue was purified by silica chromatography with dichloromethane + 0.5 % methanol to yield the title compound (70 mg, 32.6 µmol, 72 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.96 (d, 8 H, J = 8.4 Hz, Ar-*H*), 7.05 (d, 8 H, J = 8.4 Hz, Ar-*H*), 6.91 (s, 8 H, Mes-*H*), 6.01 (s, 4 H, *β*-*H*), 2.56 (s, 12 H, CH_3), 2.41 (s, 12 H, CH_3), 2.30 (s, 12 H, Mes-CH_3), 2.08 (s, 24 H, Mes-CH_3), 1.38 (s, 12 H, CH_3), 1.21 (s, 12 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 185.0, 156.1, 152.8, 143.1 142.1, 138.7, 138.1, 138.0, 137.9, 134.8, 132.0, 131.1, 130.0, 129.8, 129.4, 129.1, 129.0, 121.0, 31.1, 21.2, 19.5, 14.7, 13.5, 11.4. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 1.03 (m, 4B, BF_2). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.6 (m, 8F, BF_2). **MS** (ESI): m/z = 2146 ([M]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε[L·mol^{-1}·cm^{-1}]) = 269 (61700), 368 (26000), 517 (358600) nm. λ_{em} (λ_{exc}: 517 nm) = 537 nm. $C_{116}H_{112}B_4F_8N_8O_8$·2$CH_3OH$: calcd. C 64.09, H 5.47, N 5.07 %; found: C 64.27, H 5.24, N 5.10 %.

Rhodium Paddlewheel Complex 28: BODIPY carboxylic acid **17** (80 mg, 157 µmol) and rhodium acetate (15 mg, 34 µmol) were heated in 1,2-dichlorobenzene (10 mL) and methanol (20 µL) to 150 °C for 4 h. After removal of the solvents in vacuo the residue was purified by silica chromatography with dichloromethane + 0.5 % methanol to yield the title compound (54 mg, 24 µmol, 73 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 (d, 6H, J = 8.4 Hz, Ar-*H*), 7.45 (dd, 2H, J_1 = 3.5, J_2 = 6.0 Hz, Ar-*H*), 7.30 (d, 6H, J = 8.4 Hz, Ar-*H*), 7.21 (dd, 2H, J_1 = 3.5, J_2 = 6.0 Hz, Ar-*H*), 6.94 (s, 8H, Mes-*H*), 6.02 (s, 4H, *β*-*H*), 2.65 (s, 12H, CH_3), 2.57 (s, 12H, CH_3), 2.33 (s, 12H, Mes-CH_3), 2.06 (s, 24H, Mes-CH_3), 1.46 (s, 12H, CH_3), 1.39 (s, 12H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 184.7, 157.8, 156.1, 144.2, 142.3, 141.9, 138.9, 134.8, 132.6, 131.9, 130.7, 130.5, 130.3, 130.0, 129.3, 129.1, 129.0, 127.7, 127.6, 121.9, 114.1, 95.4, 85.2, 21.2, 19.5, 14.8, 13.6, 13.5, 12.1. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.89 (t, J = 30.4 Hz, 4B, BF_2). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –146.9 (m, 8F, BF_2). **MS** (ESI): m/z = 2306 ([M + 2 MeOH]$^+$). **UV/Vis** (CH_2Cl_2): λ_{abs} (ε[L·mol^{-1}·cm^{-1}]) = 298 (64000), 346 (67100), 405 (27600), 537 (234200) nm. λ_{em} (λ_{exc}: 537 nm) = 562 nm. **HRMS** (ESI): m/z calcd. for $C_{124}H_{112}B_4F_8N_8O_8Rh_2$ ([M]$^{2+}$): 1121.35117; found.: 1121.35072.

Supporting Information (see footnote on the first page of this article): Preparation and analysis of precursors **2**, **4**, and **21**.

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Received: September 28, 2015
Published Online: November 26, 2015

