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Phenanthroline–dipyrromethene conjugates: synthesis, characterization, and spectroscopic investigations

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ABSTRACT

Mono- and tri-topic ligands, based on dipyrromethenes and the 1,10-phenanthroline nucleus, as well as BF_2 complexes derived thereof are described. While BODIPY 12 has been X-ray crystallographically characterized, the structural features of the free ligands 9 and 10 may render them useful as precursors for the elaboration of novel supramolecular architectures.

1. Introduction

The self-assembly of suitable tectons using the coordination motif is now recognized as a highly efficient strategy for the construction of supramolecular architectures.[1] The incorporation of transition metal centers into such species offers access to potential host molecules with electron transfer, magnetic, and/or optical properties.[2] From the many molecular polygons described thus far, triangular structures were scarce and little studied,[3] at the time we initiated our work. More recently, however, the synthesis of multimetallic supramolecular triangles, including those derived from directional-bonding rather than the template approach, has met more success.[4] Our efforts in this field are aimed toward the design and synthesis of such metal-based macrocycles and, initially, we first reported the synthesis of novel C_{2v}-symmetrical boron-complexes derived from dipyrromethene-2,10-dicarboxylates.[5] Subsequently, in addition to a new family of N_2O_2-tetradentate Schiff base ligands and complexes derived thereof,[6] we reported the synthesis of novel rigid angular building blocks with a pre-programmed 60° angle based on the dipyrromethene-(dipyrrin) and 1,10-phenanthroline-ligands.[7] Since then, template directed multimetallic supramolecular triangles incorporating the 1,10-phenanthroline nucleus have been described.[8] Herein, we now report full experimental details on the synthesis, characterization, and spectroscopic evaluation of dipyrromethene, phenanthroline–dipyrromethene conjugates, and their respective boron-complexes.

2. Results and discussion

meso-Aryl-dipyrrins can be prepared through oxidation of the corresponding dipyrromethanes, which in turn are accessible via the acid catalyzed condensation of arylaldehydes and pyrrole,[9] or directly from the latter and arylacyl chlorides.[10] However, when excess pyrrole was reacted with phenanthrolinedicarboxaldehyde **1**[11] or its diacyl chloride derivative **2**,[11] under a variety of conditions (vide infra), multicomponent mixtures, from which the expected bis-adducts could not be isolated, were obtained. We therefore turned our attention to less reactive pyrrole derivatives with improved organic solubility.[5] Thus, while no reaction between acyl chloride **2** with **3**[12] or **4**[13] occurred, treatment of trisubstituted pyrrole **3** with dialdehyde **1** in a 4:1 molar ratio in TFA gave the desired bis(dipyrromethane) **5** in 65% yield (Scheme 1). Similarly, reaction of **1** with an excess of ethyl pyrrole ester **4** in TFA at room temperature gave the bis-adduct **6** in an analogous manner (66%). However, with a co-solvent (MeOH or CH_2Cl_2) or other acid catalysts (*p*-TsOH or $BF_3 \cdot OEt_2$) lower yields or no reaction was observed.

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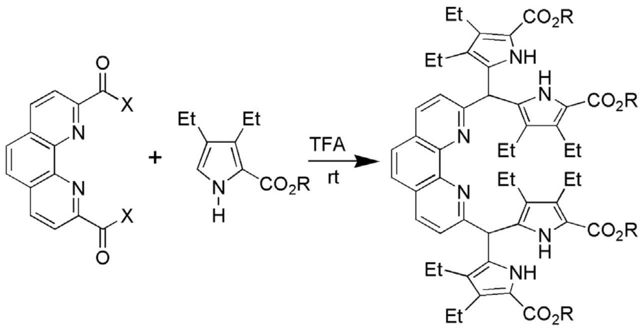


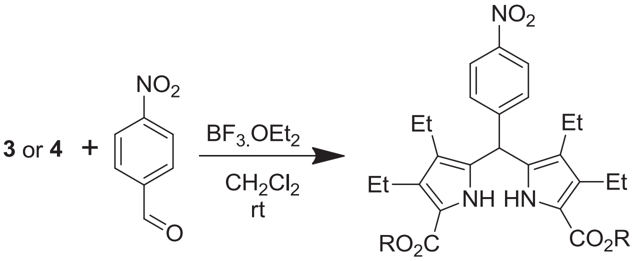
1 X = H
2 X = Cl

3 R = Bn
4 R = Et

5 R = Bn (65%)
6 R = Et (66%)

Scheme 1.

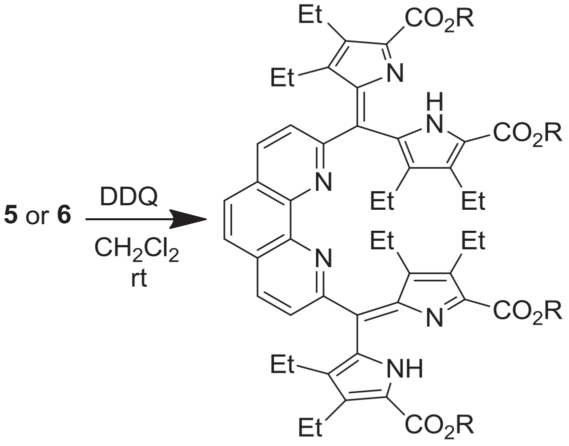
In comparison, dipyrromethanes **7** (85%) and **8** (65%) were best obtained via treatment of **3** and **4** with *p*-nitrobenzaldehyde (2:1 molar ratio) in CH_2Cl_2 in the presence of 0.5 equiv of $BF_3\cdot OEt_2$, respectively (Scheme 2).



7 R = Bn (85%)
8 R = Et (65%)

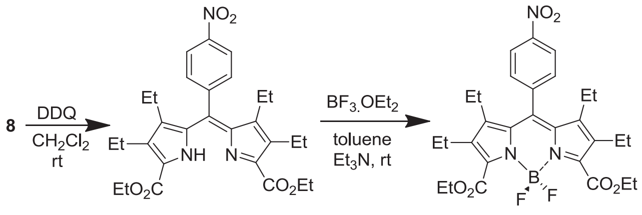
Scheme 2.

Oxidation of **5**, **6** (Scheme 3), and **8** (Scheme 4) to their corresponding dipyrromethene derivatives **9** (98%), **10** (92%), and **11** (90%) occurred readily with DDQ in dry CH_2Cl_2. In contrast to their precursors, **9**–**11** appear to be hydrogen bonded to a molecule of water as indicated from their proton NMR- and mass-spectra.



9 R = Bn (98%)
10 R = Et (92%)

Scheme 3.



11 (90%)

12 (95%)

Scheme 4.

In order to probe the coordination properties of our novel ligands **9**, **10**, and **11**, we decided to synthesize BF_2 complexes (BODIPY dyes) since they are known to exhibit rich electro- and photo-chemical properties.[14] Thus, treatment of **11** with an excess of $BF_3\cdot OEt_2$ in dry toluene in the presence of Et_3N at ambient temperature gave the corresponding boron complex **12** in high yield (95%, Scheme 4).

The solid state structure of **12** is illustrated in Fig. 1. The two pyrrole rings and their linking carbon atom are co-planar to within 0.09 Å, the boron atom lying 0.18 Å out of this plane. Thus, the central C_3N_2B ring has a slightly folded conformation, there being a ca. 8° fold about the N···N vector (the C_3N_2 portion being planar to within 0.008 Å), and this results in a pseudo axial/equatorial disposition of the two fluorine substituents. The *para*-nitrophenyl unit is oriented orthogonally (88°) to the plane of the central six-membered heterocyclic ring.

On the other hand, reaction of the tri-topic ligands **9** and **10** with an excess of $BF_3\cdot OEt_2$ in dry toluene in the presence of Et_3N at ambient temperature, resulted in formation of both, the mono- and dinuclear complexes **13** (18%), **14** (24%) and **15** (52%), **16** (65%), respectively (Scheme 5). While the C_{2v}-symmetric boron-complex **12** exhibits first order NMR characteristics, complexes **13**–**16** display diastereotopic methylene signals in their proton- as well as two distinct resonances (dq) in their ^{19}F NMR spectra, consistent with restricted rotation along the σ-bonds connecting the dipyrrin and

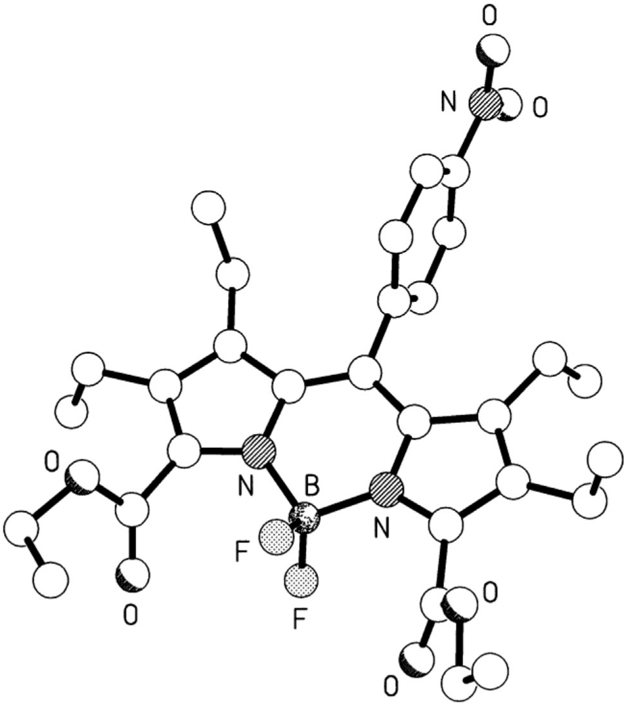


Fig. 1. X-ray crystal structure of **12**.

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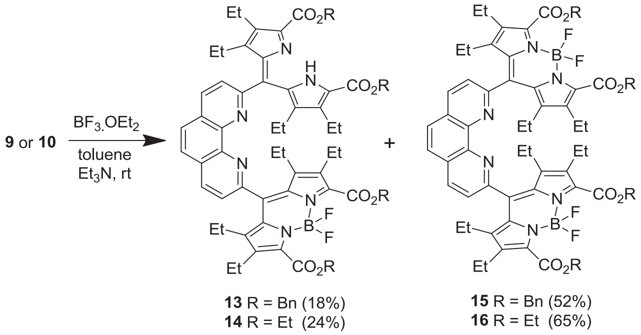
phenanthroline fragments. In addition, **13** and **14** appear also to complex a molecule of water (vide supra).



Scheme 5.

Preliminary results show the red colored complexes **13** (λ_{max}=577 nm), **14** (λ_{max}=575 nm), **15** (λ_{max}=580 nm), and **16** (λ_{max}=579 nm) to be distinctively fluorescent (Fig. 2) and as such are expected to have rich and diverse physicochemical properties.

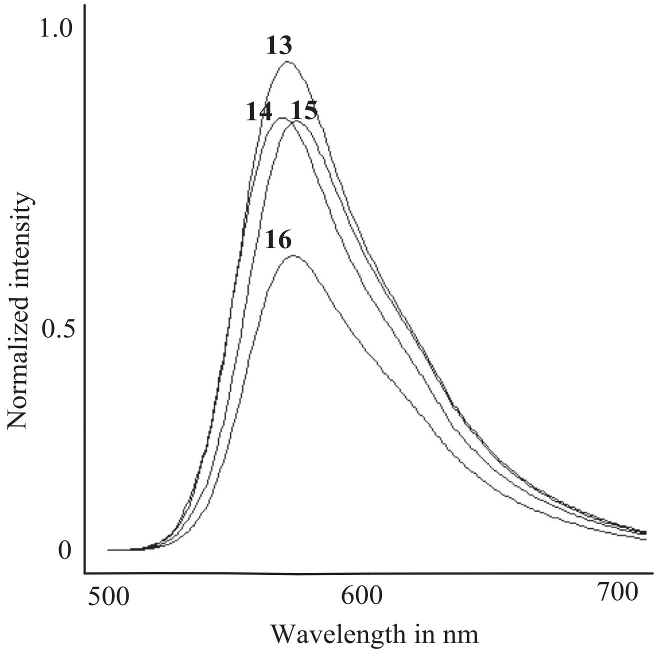


Fig. 2. Fluorescence spectra of complexes **13**–**16**.

3. Conclusion

In summary, the synthesis and initial complexation studies of novel angular building blocks, based on the dipyrrin- and 1,10-phenanthroline-nuclei, have been carried out successfully. These rigid multidentate ligands may prove useful for the elaboration of coordinatively-linked supramolecular triangles. As our preliminary photophysical investigations indicate, complexes derived thereof should have rich and diverse physicochemical properties. Such studies will be the subject of future work.

4. Experimental section

4.1. General procedures

All reactions were conducted in oven- or flame-dried glassware. Hexanes refer to the petroleum fraction bp 40–60 °C. Solvents used for reactions were distilled prior to use: toluene (from sodium); dichloromethane (from CaH_2). All other reagents were used as commercially supplied. TLC was carried out on E. Merck precoated silica gel $60F_{254}$ plates. Chromatography refers to flash chromatography on E. Merck silica gel 60, 40–60 μm (eluants are given in parentheses). Phenanthrolinedicarboxaldehyde **1**,[11] benzyl 3,4-diethylpyrrole-2-carboxylate (**3**),[12] and ethyl 3,4-diethylpyrrole-2-carboxylate (**4**)[13] were prepared according to literature procedures.

4.2. Bis(dipyrromethane) (5)

To a solution of dialdehyde **1** (0.48 g, 2.0 mmol) in TFA (20 mL), benzyl pyrrole ester **3** (2.1 g, 8.2 mmol) was added and the mixture stirred at 20 °C for 20 min under N_2. The reaction mixture was poured onto ice and water (100 mL), neutralized with 2.5 M NaOH, and extracted with $CHCl_3$ (3×20 mL). The combined organics were dried (Na_2SO_4), rotary evaporated and the crude residue redissolved in the minimum amount of $CHCl_3$. Precipitation upon the addition of EtOAc followed by filtration and drying under vacuum gave bis(dipyrromethane) **5** (1.6 g, 65%) as a pale yellow solid: R_f 0.15 (hexanes/Et_2O 1:1); mp 193 °C; IR (film) ν_{max} 3303, 1677, 1436, 1249 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.98 (t, J=7.4 Hz, 12H), 1.06 (t, J=7.3 Hz, 12H), 2.51 (q, J=7.4 Hz, 8H), 2.66 (q, J=7.3 Hz, 8H), 4.93 (s, 8H), 6.13 (s, 2H), 7.08 (m, 20H), 7.63 (d, J=8.3 Hz, 2H), 7.72 (s, 2H), 8.19 (d, J=8.3 Hz, 2H), 10.69 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.4, 17.9, 18.9, 42.6, 65.7, 118.0, 123.5, 124.0, 126.6, 127.9, 128.1, 128.2, 128.5, 131.6, 134.0, 137.0, 138.3, 144.9, 160.2, 161.3; MS (FAB) m/z 1228 $[M-H]^+$; HRMS (FAB) calcd for $C_{78}H_{81}N_6O_8$: $[M+H]^+$ 1229.6116, found $[M+H]^+$ 1229.6148. Anal. Calcd for $C_{78}H_{80}N_6O_8$: C, 76.20; H, 6.56; N, 6.84. Found: C, 76.42; H, 6.31; N, 6.68.

4.3. Bis(dipyrromethane) (6)

The same reaction as above with ethyl pyrrole ester **4** (1.6 g, 8.2 mmol), gave bis(dipyrromethane) **6** (1.3 g, 66%) as a white solid: R_f 0.25 (hexanes/Et_2O 1:1); mp 243 °C; IR (film) ν_{max} 3300, 1681, 1438, 1254 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02 (t, J=7.4 Hz, 12H), 1.09 (t, J=7.1 Hz, 12H), 1.15 (t, J=7.4 Hz, 12H), 2.56 (q, J=7.4 Hz, 8H), 2.73 (q, J=7.4 Hz, 8H), 4.04 (m, 8H), 6.16 (s, 2H), 7.65 (d, J=8.3 Hz, 2H), 7.70 (s, 2H), 8.19 (d, J=8.3 Hz, 2H), 10.75 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.5, 16.2, 16.3, 17.9, 18.8, 42.4, 59.8, 118.0, 123.1, 124.0, 126.4, 127.9, 131.6, 133.6, 137.9, 144.9, 160.3, 161.6; MS (FAB) m/z 980 $[M-H]^+$; HRMS (FAB) calcd for $C_{58}H_{72}N_6O_8$: $[M^{+\cdot}]$ 980.5412, found $[M^{+\cdot}]$ 980.5374. Anal. Calcd for $C_{58}H_{72}N_6O_8$: C, 70.99; H, 7.40; N, 8.56. Found: C, 70.62; H, 7.59; N, 8.61.

4.4. Dipyrromethane (7)

To a solution of p-nitrobenzaldehyde (0.30 g, 2.0 mmol) and benzyl pyrrole ester **3** (1.0 g, 4.0 mmol) in dry CH_2Cl_2 (50 mL), $BF_3 \cdot OEt_2$ (0.13 mL, 1.0 mmol) was added dropwise at 0 °C under N_2. The mixture was allowed to warm up to 20 °C and stirred for a further 16 h. The dark red mixture was extracted with CH_2Cl_2 (3×30 mL), washed with aq (5%) $NaHCO_3$ (3×25 mL), dried (Na_2SO_4), rotary evaporated, and chromatographed (CH_2Cl_2/hexanes 7:1) to give dipyrromethane **7** (1.1 g, 85%) as a yellow/green solid: R_f 0.13 (CH_2Cl_2/hexanes 7:1); mp 83 °C; IR (film) 3345, 1702, 1643, 1445, 1348, 1255 ν_{max} cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, J=7.5 Hz, 6H), 1.09 (t, J=7.5 Hz, 6H), 2.30 (q, J=7.5 Hz, 4H), 2.68 (q, J=7.5 Hz, 4H), 5.21 (s, 4H), 5.63 (s, 1H), 7.20 (d, J=8.9 Hz, 2H), 7.33 (m, 10H), 8.10 (d, J=8.9 Hz, 2H), 8.62 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.2, 16.3, 17.6, 18.8, 40.2, 66.3, 118.5, 124.3, 125.0, 128.4, 128.5, 128.9, 129.3, 130.8, 134.6, 136.4, 147.0, 148.0, 161.7; MS (FAB) m/z 647 $[M^{+\cdot}]$; HRMS (FAB) calcd for $C_{39}H_{41}N_3O_6$: $[M^{+\cdot}]$ 647.2995, found $[M^{+\cdot}]$ 647.2974.

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4.5. Dipyrromethane (8)

The same reaction as above with ethyl pyrrole ester **4** (0.39 g, 2.0 mmol), gave after chromatography (CH_2Cl_2/hexanes 7:1) dipyrromethane **8** (0.34 g, 65%) as a yellow solid: R_f 0.10 (CH_2Cl_2/hexanes 7:1); mp 139 °C; IR (film) 3347, 1689, 1644, 1460, 1348, 1252 ν_{max} cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (t, J=7.5 Hz, 6H), 1.16 (t, J=7.4 Hz, 6H), 1.30 (t, J=7.1 Hz, 6H), 2.35 (q, J=7.5 Hz, 4H), 2.72 (q, J=7.4 Hz, 4H), 4.23 (m, 4H), 5.68 (s, 1H), 7.24 (d, J=8.6 Hz, 2H), 8.16 (d, J=8.6 Hz, 2H), 8.70 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.7, 16.1, 16.3, 17.6, 18.8, 40.1, 60.4, 118.8, 124.2, 124.9, 129.4, 130.5, 134.2, 147.4, 148.4, 162.1; MS (FAB) m/z 523 $[M^{+\cdot}]$; HRMS (FAB) calcd for $C_{29}H_{37}N_3O_6$: $[M^{+\cdot}]$ 523.2682, found $[M^{+\cdot}]$ 523.2664. Anal. Calcd for $C_{29}H_{37}N_3O_6$: C, 66.52; H, 7.12; N, 8.02. Found: C, 66.78; H, 7.25; N, 8.09.

4.6. Bis(dipyrromethene) (9)

To a solution of bis(dipyrromethane) **5** (79 mg, 64 μmol) in dry CH_2Cl_2 (4 mL), DDQ (44 mg, 0.19 mmol) was added and the mixture stirred at 20 °C for 10 min under N_2. The dark brown mixture was diluted with CH_2Cl_2 (20 mL), washed with brine (3×15 mL), dried ($MgSO_4$), rotary evaporated, and chromatographed (hexanes/EtOAc 9:1–4:1) to give bis(dipyrromethene) **9** (77 mg, 98%) as an orange/brown solid: R_f 0.40 (hexanes/EtOAc 2.3:1); mp 103 °C; IR (film) ν_{max} 3289, 1668, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.46 (br m, 12H), 1.10 (m, 12H), 1.90 (br m, 8H), 2.67 (br m, 8H), 5.37 (br m, 8H), 6.53 (s, 2H), 7.28 (d, J=8.5 Hz, 2H), 7.34–7.60 (m, 20H), 7.88 (s, 2H), 8.27 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 16.0, 17.4, 18.3, 66.1, 71.7, 115.8, 123.1, 126.6, 127.8, 128.0, 128.5, 135.1, 136.4, 137.8, 143.9, 162.2, 164.1; MS (FAB) m/z 1225 $[M^{+\cdot}]$; HRMS (FAB) calcd for $C_{78}H_{77}N_6O_8$: $[M+H]^+$ 1225.5803, found $[M+H]^+$ 1125.5834. Anal. Calcd for $C_{78}H_{76}N_6O_8$: C, 76.45; H, 6.25; N, 6.86. Found: C, 76.40; H, 6.35; N, 6.62.

4.7. Bis(dipyrromethene) (10)

The same reaction as above with bis(dipyrromethane) **6** (92 mg, 94 μmol), gave after chromatography (hexanes/EtOAc 9:1–4:1) bis(dipyrromethene) **10** (84 mg, 92%) as a pale pink solid: R_f 0.43 (hexanes/EtOAc 2.3:1); mp 170 °C; IR (film) ν_{max} 3288, 1666, 1243 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.45 (br m, 12H), 1.12 (t, J=7.1 Hz, 12H), 1.20 (m, 12H), 1.89 (br m, 8H), 2.65 (m, 8H), 4.32 (br m, 8H), 6.49 (s, 2H), 7.24 (d, J=8.5 Hz, 2H), 7.85 (s, 2H), 8.23 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 14.3, 15.8, 17.3, 18.2, 60.0, 71.7, 116.0, 123.0, 126.5, 127.7, 134.3, 134.7, 137.6, 143.9, 162.4, 164.2; MS (FAB) m/z 977 $[M^{+\cdot}]$; HRMS (FAB) calcd for $C_{58}H_{69}N_6O_8$: $[M+H]^+$ 977.5177, found $[M+H]^+$ 977.5185. Anal. Calcd for $C_{58}H_{68}N_6O_8$: C, 71.29; H, 7.01; N, 8.60. Found: C, 71.35; H, 7.13; N, 8.75.

4.8. Dipyrromethene (11)

Following the same procedure as for the preparation of **9**, dipyrromethane **8** (84 mg, 0.16 mmol) and DDQ (73 mg, 0.32 mmol) gave after 16 h and chromatography (hexanes/EtOAc 9:1–4:1) dipyrromethene **11** (75 mg, 90%) as a pale yellow solid: R_f 0.45 (hexanes/EtOAc 2.3:1); mp 174 °C; IR (film) ν_{max} 3431, 1685, 1524, 1444, 1351, 1241 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78 (t, J=7.5 Hz, 6H), 1.18 (t, J=7.4 Hz, 6H), 1.34 (t, J=7.1 Hz, 6H), 2.07–2.29 (m, 4H), 2.73 (q, J=7.5 Hz, 4H), 4.28 (q, J=7.1 Hz, 4H), 7.59 (d, J=8.8 Hz, 2H), 8.22 (d, J=8.8 Hz, 2H), 8.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.3, 15.2, 15.7, 17.6, 18.3, 60.2, 74.9, 117.6, 123.5, 123.9, 128.5, 132.3, 135.2, 147.6, 150.2, 161.6; MS (FAB) m/z 522 $[M^{+\cdot}]$; HRMS (FAB) calcd for $C_{29}H_{36}N_3O_6$: $[M+H]^+$ 522.2604, found $[M+H]^+$ 522.2587. Anal. Calcd for $C_{29}H_{35}N_3O_6$: C, 66.78; H, 6.76; N, 8.06. Found: C, 66.76; H, 6.64; N, 7.84.

4.9. BODIPY (12)

To a solution of dipyrromethene **11** (60 mg, 0.12 mmol) in dry toluene (5 mL), $BF_3 \cdot OEt_2$ (0.72 mL, 5.7 mmol) was added dropwise at 20 °C under N_2. The mixture was allowed to stir at 20 °C for 10 min, after which Et_3N (0.43 mL, 3.1 mmol) was added dropwise, whereby the solution turned from dark purple to red. After stirring for a further 30 min at 20 °C, the reaction mixture was neutralized with 2 M HCl, extracted with EtOAc (3×10 mL), dried ($MgSO_4$), rotary evaporated, and chromatographed (hexanes/EtOAc 4:1–2.3:1) to give complex **12** (62 mg, 95%) as an orange/red solid: R_f 0.40 (hexanes/EtOAc 2.3:1); mp 235–240 °C; IR (film) ν_{max} 1734, 1528, 1350, 1231, 1168 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.71 (t, J=7.5 Hz, 6H), 1.09 (t, J=7.5 Hz, 6H), 1.45 (t, J=7.1 Hz, 6H), 1.60 (q, J=7.5 Hz, 4H), 2.44 (q, J=7.5 Hz, 4H), 4.49 (q, J=7.1 Hz, 4H), 7.68 (d, J=8.7 Hz, 2H), 8.41 (d, J=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 15.1, 16.2, 17.3, 18.9, 62.2, 77.2, 123.5, 130.0, 131.5, 135.5, 140.7, 146.7, 147.6, 148.8, 162.1; ^{11}B NMR ($CDCl_3$, 125 MHz) δ 0.04 (t, J=27.7 Hz); ^{19}F NMR ($CDCl_3$, 235 MHz) δ −145.8 (q, J=27.7 Hz); MS (FAB) m/z 569 $[M^{+\cdot}]$; HRMS (FAB) calcd for $C_{29}H_{34}BF_2N_3O_6$: $[M^{+\cdot}]$ 569.2509, found $[M^{+\cdot}]$ 569.2507. *Crystal data for* **12**: $C_{29}H_{34}BF_2N_3O_6$, M=569.4, monoclinic, $P2_1/c$ (no. 14), a=20.478(3), b=17.580(2), c=8.131(3) Å, β=100.99(2)°, V=2873(1) Å^3, Z=4, D_c=1.316 g cm^{-3}, μ(Cu Kα)=8.37 cm^{-1}, T=193 K, orange platy needles; 4238 independent measured reflections, F^2 refinement, R_1=0.107, wR_2=0.267, 3112 independent observed reflections [$|F_o|>4\sigma(|F_o|)$, 2θ=120°], 386 parameters. The high final value for R_1 is a consequence of the very poor quality of the crystalline sample, which suffered from multiple twinning effects; the constitution and structure of the compound is, however, unambiguous.

4.10. Complexes 13 and 15

The same reaction as above with bis(dipyrromethene) **9** (16 mg, 13 μmol) and $BF_3 \cdot OEt_2$ (0.17 mL, 1.3 mmol), gave after chromatography (hexanes/EtOAc 4:1–2.3:1) complex **13** (3 mg, 18%) as a red solid: R_f 0.69 (hexanes/EtOAc 1:1); mp 103 °C; IR ($CHCl_3$) ν_{max} 3440, 1702, 1536, 1231, 1167, 1126 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.53 (t, J=7.4 Hz, 6H), 0.68 (t, J=7.4 Hz, 6H), 0.96 (t, J=7.4 Hz, 6H), 1.10 (t, J=7.4 Hz, 6H), 1.31 (m, 2H), 1.61 (m, 2H), 2.12 (m, 4H), 2.37 (m, 4H), 2.70 (m, 4H), 5.21 and 5.27 (ABq, J=12.5 Hz, 4H), 5.47 (s, 4H), 7.25–7.44 (m, 16H), 7.50–7.60 (m, 4H), 7.62 (d, J=8.4 Hz, 1H), 7.80 (d, J=8.2 Hz, 1H), 7.99 (s, 2H), 8.32 (d, J=8.4 Hz, 1H), 8.43 (d, J=8.2 Hz, 1H), 9.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.2, 15.4, 15.5, 17.3, 17.5, 18.3, 19.0, 65.7, 67.9, 74.6, 77.3, 117.0, 122.0, 124.1, 124.3, 127.0, 127.6, 128.0, 128.1, 128.3, 128.5, 128.6, 128.8, 132.8, 133.1, 135.3, 136.4, 136.5, 137.5, 143.9, 144.3, 145.2, 145.8, 147.9, 152.9, 160.8, 160.9, 162.1; ^{11}B NMR ($CDCl_3$, 125 MHz) δ 0.23 (t, J=28.0 Hz); ^{19}F NMR ($CDCl_3$, 235 MHz) δ −142.7 (dq, J=28.0 and 96.6 Hz), −148.7 (dq, J=28.0 and 96.6 Hz); MS (FAB) m/z 1271 $[M-2H]^+$; HRMS (FAB) calcd for $C_{78}H_{75}BF_2N_6O_8$: $[M^{+\cdot}]$ 1272.5708, found $[M^{+\cdot}]$ 1272.5736, followed by **15** (9 mg, 52%) as a dark red solid: R_f 0.56 (hexanes/EtOAc 1:1); mp 240 °C; IR ($CHCl_3$) ν_{max} 1731, 1536, 1226, 1170, 1128 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.48 (t, J=7.4 Hz, 12H), 0.89 (t, J=7.5 Hz, 12H), 1.25 (m, 4H), 1.39 (m, 4H), 2.29 (m, 8H), 5.42 (s, 8H), 7.29–7.40 (m, 12H), 7.47–7.57 (m, 8H), 7.88 (d, J=8.2 Hz, 2H), 8.09 (s, 2H), 8.48 (d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.5, 16.0, 17.6, 19.1, 68.2, 77.6, 125.0, 128.3, 128.6, 128.8, 129.1, 129.4, 133.1, 135.6, 136.8, 145.3, 145.4, 146.2, 147.8, 153.9, 162.3; ^{11}B NMR ($CDCl_3$, 125 MHz) δ 0.09 (t, J=27.8 Hz); ^{19}F NMR ($CDCl_3$, 235 MHz) δ −141.6 (dq, J=27.8 and 95.6 Hz), −150.1 (dq, J=27.8 and 95.6 Hz); MS (FAB) m/z 1321 $[M^{+\cdot}]$, 1243 $[M-Ph]^+$;

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HRMS (FAB) calcd for $C_{78}H_{74}B_2F_4NaN_6O_8$: $[M+Na]^+$ 1343.5588, found $[M+Na]^+$ 1343.5611.

4.11. Complexes 14 and 16

Following the same procedure as for the preparation of **12**, bis(dipyrromethane) **10** (81 mg, 83 μmol) and $BF_3 \cdot OEt_2$ (0.52 mL, 4.1 mmol) gave after chromatography (hexanes/EtOAc 4:1–2.3:1) complex **14** (20 mg, 24%) as a red solid: R_f 0.40 (hexanes/EtOAc 2.3:1); mp 185–190 °C; IR (film) ν_{max} 3457, 1697, 1538, 1236, 1168, 1128 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.55 (t, J=7.4 Hz, 6H), 0.70 (t, J=7.4 Hz, 6H), 1.06 (t, J=7.5 Hz, 6H), 1.15 (t, J=7.3 Hz, 6H), 1.31 (t, J=7.1 Hz, 6H), 1.46 (t, J=7.1 Hz, 8H), 1.79 (m, 2H), 2.13 (m, 4H), 2.41 (m, 4H), 2.70 (q, J=7.3 Hz, 4H), 4.25 (dq, J=1.6 and 7.1 Hz, 4H), 4.49 (q, J=7.1 Hz, 4H), 7.63 (d, J=8.4 Hz, 1H), 7.82 (d, J=8.2 Hz, 1H), 8.00 (s, 2H), 8.33 (d, J=8.4 Hz, 1H), 8.44 (d, J=8.2 Hz, 1H), 8.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 14.4, 15.2, 15.4, 15.7, 17.3, 17.5, 18.2, 19.0, 59.8, 62.0, 74.7, 117.3, 122.0, 124.0, 126.9, 127.6, 128.6, 128.9, 132.7, 134.8, 135.1, 136.5, 137.4, 143.9, 144.3, 145.0, 146.2, 147.8, 152.9, 161.1, 162.3; ^{11}B NMR ($CDCl_3$, 125 MHz) δ 0.14 (t, J=27.8 Hz); ^{19}F NMR ($CDCl_3$, 235 MHz) δ −143.2 (dq, J=27.8 and 97.5 Hz), −148.6 (dq, J=27.8 and 97.5 Hz); MS (FAB) m/z 1023 $[M-2H]^+$; HRMS (FAB) calcd for $C_{58}H_{67}BF_2N_6O_8$: $[M^{+\cdot}$, monoisotopic] 1023.5120, found: $[M^{+\cdot}$, monoisotopic] 1023.5319, followed by **16** (58 mg, 65%) as a dark red solid: R_f 0.24 (hexanes/EtOAc 2.3:1); mp 235–240 °C; IR (film) ν_{max} 1722, 1540, 1226, 1170, 1137, 1099 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.51 (t, J=7.4 Hz, 12H), 1.01 (t, J=7.5 Hz, 12H), 1.31 (m, 4H), 1.42 (t, J=7.1 Hz, 16H), 2.36 (m, 8H), 4.44 (m, 8H), 7.91 (d, J=8.2 Hz, 2H), 8.13 (s, 2H), 8.51 (d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 15.1, 15.7, 17.3, 18.8, 61.9, 77.4, 124.6, 128.0, 129.2, 132.6, 135.1, 136.5, 144.9, 145.1, 146.2, 147.3, 153.6, 162.2; ^{11}B NMR ($CDCl_3$, 125 MHz) δ 0.02 (t, J=27.7 Hz); ^{19}F NMR ($CDCl_3$, 235 MHz) δ −142.2 (dq, J=27.7 and 96.4 Hz), −149.7 (dq, J=27.7 and 96.4 Hz); MS (FAB) m/z 1073 $[M^{+\cdot}]$; HRMS (FAB) calcd for $C_{58}H_{67}B_2F_4N_6O_8$: $[M+H]^+$ 1073.5142, found: $[M+H]^+$ 1073.5167.

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