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Phenanthroline dipyrromethene conjugates: potential building blocks for the construction of novel supramolecular architectures

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ABSTRACT

Novel tritopic ligands, based on dipyrromethenes and the 1,10-phenanthroline nucleus, as well as BF_2 complexes derived thereof are described. While BODIPY dyes **9–12** have been successfully prepared, the structural features of the free ligands **7** and **8** may render them useful as precursors for the elaboration of novel supramolecular architectures.

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 has met more success.[4] Our efforts in this field are aimed toward the design and synthesis of such metal-based macrocycles and, as a first step, we report the synthesis of novel rigid angular building blocks with a preprogrammed 60° angle based on the dipyrromethene-(dipyrrin)[5] and 1,10-phenanthroline-ligands.[6]

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,[7] or directly from the latter and arylacyl chlorides.[8] However, when excess pyrrole was reacted with phenanthrolinedicarboxaldehyde **1**[9] or its diacyl chloride derivative **2**,[9] 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. This approach was successfully applied by us earlier for the synthesis of novel C_{2v}-symmetrical boron-complexes derived from dipyrromethene-2,10-dicarboxylates which were in turn prepared from the corresponding dipyrromethane derivatives (Fig. 1).[10] Thus, while no reaction between acyl chloride **2** with **3**[11] or **4**[12] 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%).[13] 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.

Oxidation of **5** and **6** (Scheme 2) to their corresponding dipyrromethene derivatives **7** (98%) and **8** (92%) occurred readily with DDQ in dry CH_2Cl_2. In contrast to their precursors, **7** and **8** appear to be hydrogen bonded to a molecule of water as indicated from their proton NMR and mass spectra.

In order to probe the coordination properties of our novel ligands **7** and **8**, we decided to synthesize BF_2 complexes (BODIPY dyes) since they are known to exhibit rich electro- and photochemical properties.[14] Thus, reaction of the tritopic ligands **7** and **8** with an excess of $BF_3{\cdot}OEt_2$ in dry toluene in the presence of Et_3N at ambient temperature resulted in the formation of both, the mono- and di-nuclear complexes **9**[15] (18%), **10** (24%), and **11** (52%), **12**[16] (65%), respectively (Scheme 3). As expected, complexes **9–12** 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 phenanthroline fragments. In addition, **9** and **10** appear also to complex a molecule of water (vide supra).

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. In addition, it is expected that complexes derived thereof should have rich and diverse physicochemical properties. In fact, preliminary results show the red colored complexes **9** (λ_{max} = 577 nm), **10** (λ_{max} = 575 nm), **11** (λ_{max} = 580 nm), and **12** (λ_{max} = 579 nm) to be distinctively fluorescent (Fig. 2) and such work will be reported in due course.

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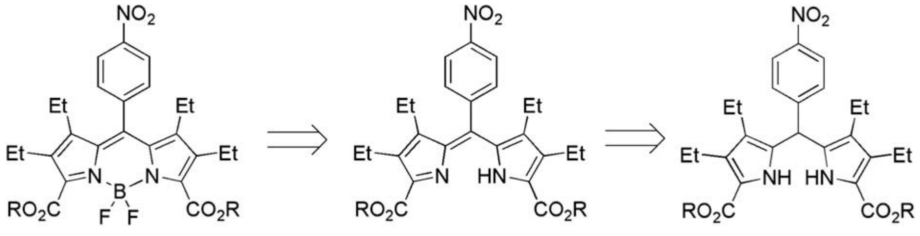
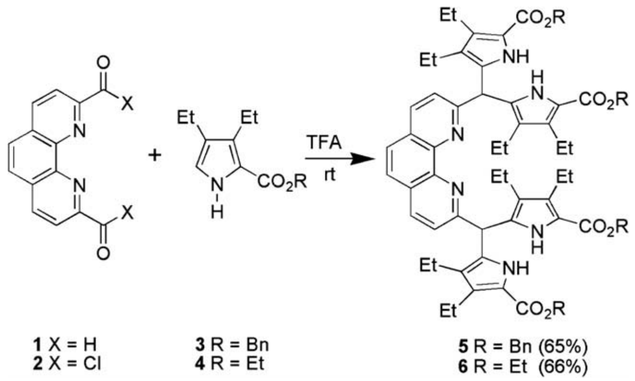
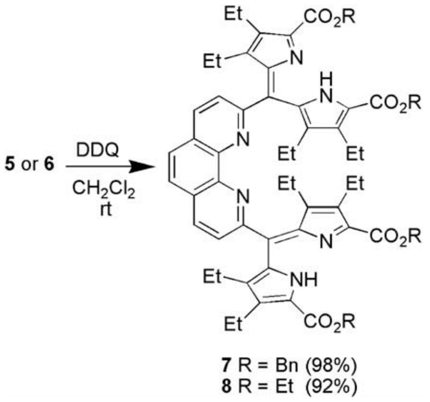


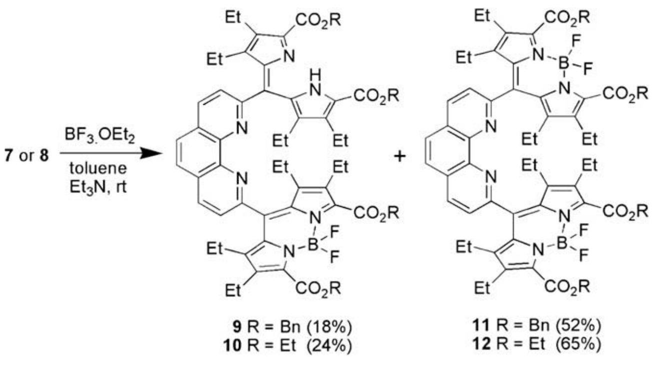
Figure 1.



Scheme 1.



Scheme 2.



Scheme 3.

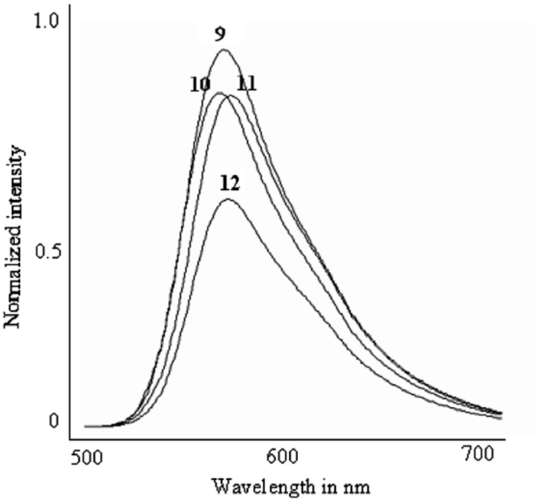


Figure 2. Fluorescence spectra of complexes **9**–**12**.

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13. *Synthetic procedure for the preparation of bis-dipyrromethanes* **5** and **6**: 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 was 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 was 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. The same reaction as mentioned above with ethyl pyrrole ester **4** (1.6 g, 8.2 mmol) gave bis(dipyrromethane) **6** (1.3 g, 66%) as a white solid.
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15. *Selected data for* **9**: ^{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), 6.54 (s, 1H), 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, 2H); ^{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); HRMS (FAB) calcd for $C_{78}H_{75}BF_2N_6O_8$: [M$^+$] 1272.5708, found [M$^+$] 1272.5736.
16. *Selected data for* **12**: ^{1}H 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); ^{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); HRMS (FAB) calcd for $C_{58}H_{67}B_2F_4N_6O_8$: [M+H]$^+$ 1073.5142, found: [M+H]$^+$ 1073.5167.