



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



Antonio Garrido Montalban*, Antonio J. Herrera, Jes Johannsen, Andrew J.P. White, David J. Williams

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

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ABSTRACT

Mono- and tri-topic ligands, based on dipyrrromethenes 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.

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1. Introduction

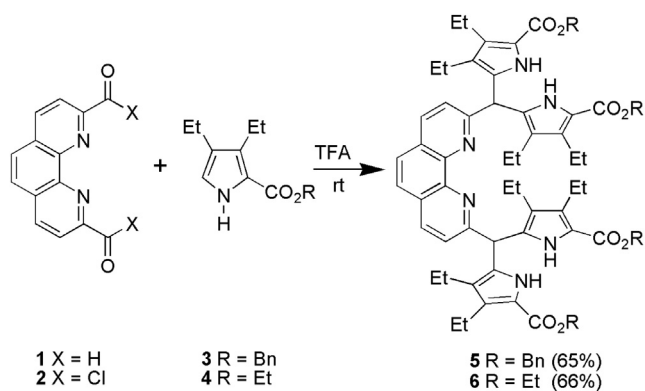
The self-assembly of suitable tectons using the coordination motif is now recognized as a highly efficient strategy for the construction of supramolecular architectures.¹ The incorporation of transition metal centers into such species offers access to potential host molecules with electron transfer, 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 dipyrrromethene-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 dipyrrromethene-(dipyrroin) 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 dipyrrromethene, phenanthroline–dipyrrromethene conjugates, and their respective boron-complexes.

2. Results and discussion

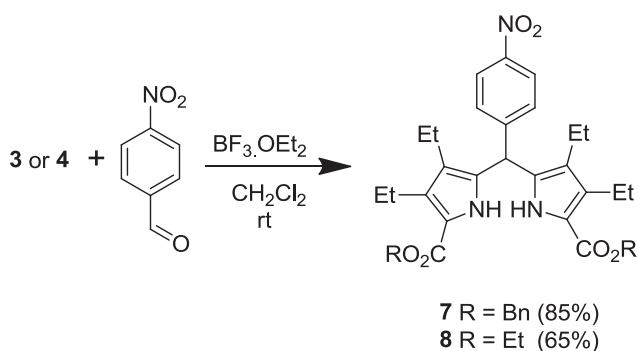
meso-Aryl-dipyrroins can be prepared through oxidation of the corresponding dipyrrromethanes, which in turn are accessible via the acid catalyzed condensation of arylaldehydes and pyrrole,⁹ or directly from the latter and arylacyl chlorides.¹⁰ However, when excess pyrrole was reacted with phenanthrolinecarboxaldehyde **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(dipyrrromethane) **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 $\text{BF}_3 \cdot \text{OEt}_2$) lower yields or no reaction was observed.

* Corresponding author. Tel.: +1 858 453 7200; fax: +1 858 453 7210; e-mail addresses: amontalban@arenapharm.com, catalaba@hotmail.com (A. Garrido Montalban).



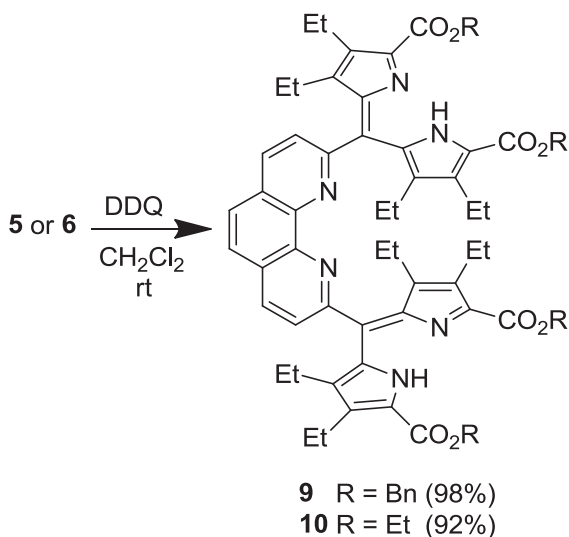
Scheme 1.

In comparison, dipyrrmethanes **7** (85%) and **8** (65%) were best obtained via treatment of **3** and **4** with *p*-nitrobenzaldehyde (2:1 molar ratio) in CH₂Cl₂ in the presence of 0.5 equiv of BF₃·OEt₂, respectively (Scheme 2).

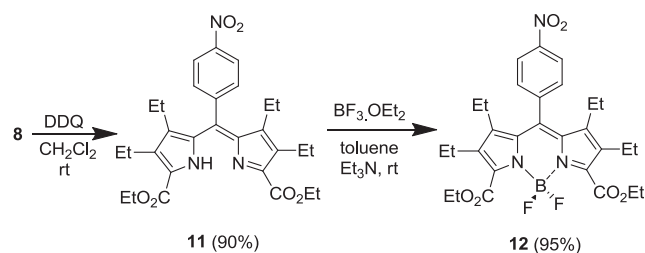


Scheme 2.

Oxidation of **5**, **6** (Scheme 3), and **8** (Scheme 4) to their corresponding dipyrrmethene derivatives **9** (98%), **10** (92%), and **11** (90%) occurred readily with DDQ in dry CH₂Cl₂. 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.



Scheme 3.

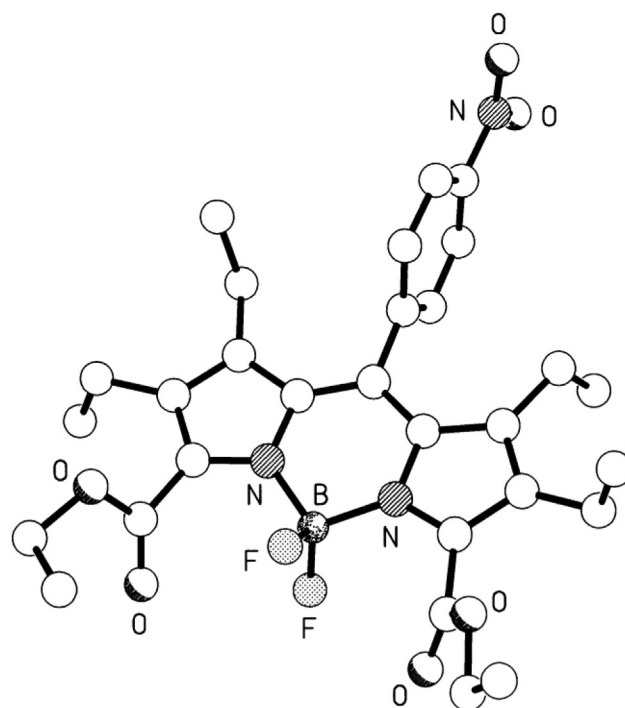


Scheme 4.

In order to probe the coordination properties of our novel ligands **9**, **10**, and **11**, we decided to synthesize BF₂ complexes (BODIPY dyes) since they are known to exhibit rich electro- and photo-chemical properties.¹⁴ Thus, treatment of **11** with an excess of BF₃·OEt₂ in dry toluene in the presence of Et₃N 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 C₃N₂B ring has a slightly folded conformation, there being a ca. 8° fold about the N...N vector (the C₃N₂ 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 BF₃·OEt₂ in dry toluene in the presence of Et₃N 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 ¹⁹F NMR spectra, consistent with restricted rotation along the σ-bonds connecting the dipyrin and

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

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