Oxidation-induced control of self-assembly using a bis-dipyrromethyl substituted phenanthroline building block†‡§

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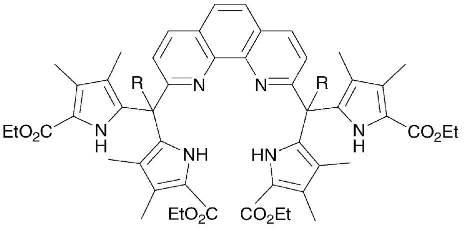
Oxygenation of the *meso*-carbon atoms of the novel building block bis-dipyrromethyl substituted phenanthroline triggers a change in the hydrogen bond interactions from intramolecular to intermolecular.

Organized assemblies and engineered frameworks with well-defined geometries are a current challenge in supramolecular science.[1–9] One attractive approach to obtaining such structures could involve the use of intra- and intermolecular hydrogen bond interactions.[6–9] The study of synthetic assemblies linked in such a way could lead both to the creation of new structures with intrinsic aesthetic appeal, while providing insights into biological processes. Within this context, assemblies wherein slight changes in structure are used to change the overall macroscopic functional properties of a particular system would be of particular appeal. Hydrogen bond interactions are, of course, a critical feature of both the protein and nucleic acid worlds, and here very slight modifications of structure can have dramatic consequences. For example, the oxygenation of methionine residues (sulfides to sulfoxides) in biosynthetic spider silk proteins acts to disrupt hydrophobic interactions and limit the formation of β-sheets in the poly-alanine regions that control crystallinity.[10] To the best of our knowledge, it has not yet proved possible to replicate anywhere near this level of control in a synthetic H-bonded assembly. In this paper we present a first step towards accomplishing this long-range goal. Specifically, we describe the synthesis and solid structural features of the new oligopyrrole phenanthroline derivatives (**1** and **2**, Fig. 1). While the *meso*-unsubstituted derivative **1** crystallizes in its monomeric form, the corresponding hydroxylated derivative **2** self assembles into a one dimensional array in the solid state.

We are unaware of any precedent for phenanthroline derivatives bearing dipyrromethane substituents attached directly to the phenanthroline C2 and C9 carbon atoms. In fact, there are only a few reports on directly linked 2,9-(*meso*-porphyrinyl) substituted phenanthrolines or bipyridines.[11,12] On the other hand, the use of α-carbonyl-functionalized pyrrole moieties as building blocks to create hydrogen bonded self-assembled aggregates has received some attention of late.[6] This led us to explore the solid state self-assembly properties of **1** and **2**. Here, the thinking was that by using a more elaborate phenanthroline dipyrromethane-bearing core, new structural motifs might be stabilized. In addition, we appreciated that the use of larger monomeric building blocks (*e.g.*, **1** and **2**) would permit small changes to be made without unduly modifying the subunit structure as a whole.

Compound **1** was prepared *via* the hydrochloric acid catalyzed condensation of phenanthroline-2,9-dicarbaldehyde[13] and 3,4-dimethyl-2-ethyloxycarbonylpyrrole[14] in acetonitrile followed by chromatographic work-up over alumina. Oxidation of **1** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in dichloromethane and a subsequent basic aqueous work-up followed by column chromatographic purification over alumina, led to the formation of the *meso*-hydroxylated product **2**. Both **1** and **2** gave ^{1}H and ^{13}C nmr spectroscopic and mass spectrometric data consistent with their proposed structures. They were also characterized by single crystal X-ray diffraction analysis as described below.

Single crystals of **1** suitable for X-ray diffraction analyses were grown by slow evaporation of a chloroform solution.¶ Compound **2** was crystallized by diffusion of *n*-pentane into a dichloromethane solution.‖ In both cases, the resulting structures reveal a helical arrangement for the monomeric subunits in the solid state with a pitch of 3.20 Å for **1** (Fig. 2) and 3.48 Å in the case of **2** (Fig. 3) stabilized by four intramolecular hydrogen bonds. As depicted in Fig. 2 and 3, two intramolecular hydrogen bonds are observed between the pyrrole nitrogen and the phenanthroline nitrogen atoms in both structures (for **1**: N4–H···N1, 2.710(3) Å, 126(3)°; N6–H···N2, 2.742(3) Å, 128(2)°; for **2**: N2–H···N3, 2.709(3) Å, 117°; N5–H···N4, 2.688(3) Å, 119°).



1 R = H
2 R = OH

Fig. 1 Schematic representation of the phenanthroline derivatives **1** and **2**.

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‡ The HTML version of this article has been enhanced with colour images.

§ Electronic supplementary information (ESI) available: Synthetic procedures and X-ray data. See DOI: 10.1039/b716796b

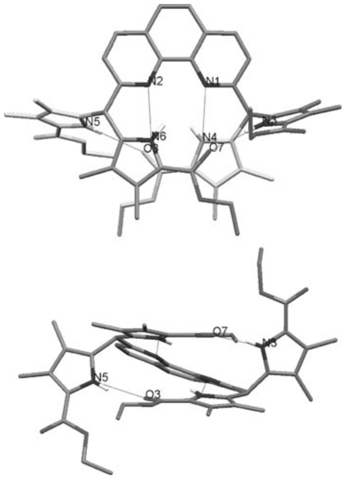

Fig. 2 Top and side views of the solid state structure of **1**. Solvent molecules of crystallization and hydrogen atoms, except those on the pyrrolic nitrogen atoms have been omitted for clarity.

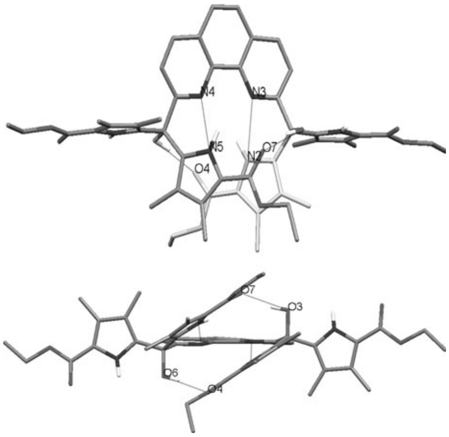

Fig. 3 Top and side views of the crystal structure of **2**. Solvent molecules of crystallization and hydrogen atoms, except those involved in hydrogen bonding have been removed for the sake of clarity.

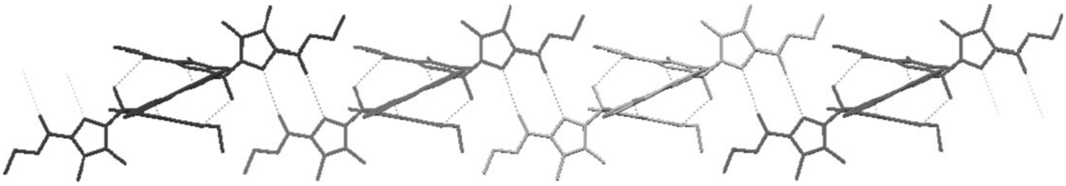

Fig. 4 Section of the crystal lattice of **2**. Solvent molecules of crystallization are omitted for clarity.

In the case of **1**, a second pair of hydrogen bonds is observed between the pyrrole nitrogen NH groups and the carbonyl oxygen atoms O3 and O7 of the ester groups (N3–H···O7, 2.813(3) Å, 172(3)°; N5–H···O3, 2.950(3) Å, 171(2)°).

A second pair of intramolecular hydrogen bonds is also seen in the structure of **2**. Here, however, and in contrast to what is seen in the solid state structure of **1**, the second pair involves the carbonyl oxygen atoms O4 and O7 as the hydrogen bond acceptors and the hydroxyl groups of each *meso*-position as the donors (Fig. 3, O3–H···O7, 2.822(2) Å, 163(3)°; O6–H···O4, 2.793(2) Å, 172(3)°). This latter pattern allows the two remaining pyrrole moieties to remain open for ancillary intermolecular interactions.

As shown in Fig. 4, compound **2** does indeed participate in intermolecular interactions in the solid state. In particular, two NH···O bonds are observed between the pyrrole nitrogen atom of one molecule and the carbonyl oxygen atom of a neighboring molecule and *vice versa* (N1–H···O9′, 3.010(3) Å, 164°; N6–H···O2′, 3.067(3) Å, 171°). The net result is a one-dimensional chain in the solid state that is stabilized *via* oriented pyrrole NH···carbonyl O hydrogen bonds.

The change in overall structure between **1** and **2** is noteworthy, particularly in light of the simple nature of the chemistry involved. While further studies of these and related systems are warranted, the present results lead us to predict that appropriately functionalized oligopyrrolic cores have a role to play in crystal engineering,[6,15,16] and that they might be particularly useful as systems with which to explore the effect that small changes in core chemistry have on the overall self-assembly process. In the specific case of **1** and **2**, these changes could include, *inter alia* metalation of the phenanthroline core, as well as anion recognition studies involving the pyrrolic NH protons. Work along these lines is currently in progress using this and related systems.[17]

Acknowledgements

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¶ For compound **1**, the data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation. Standard procedures were followed. Crystal data: $C_{50}H_{56}N_6O_8 \cdot CHCl_3$, M_r = 988.38, T = 153(2) K, triclinic, space group $P\bar{1}$, a = 17.4821(2), b = 17.7345(2), c = 17.8705(3) Å, α = 97.040(1), β = 109.612(1), γ = 102.223(1)°, V = 4986.7(2) Å^3, ρ_{calc} = 1.316 Mg m^{-3}, μ = 0.243 mm^{-1}, Z = 4, reflections collected: 36 894, independent reflections: 22 761 (R_{int} = 0.0385), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0748, w$R2$ = 0.1805, R indices (all data): $R1$ = 0.1561, w$R2$ = 0.2165. Because there are two crystallographically unique molecules in the crystal averaged values for hydrogen bonding interactions are reported. CCDC 665296. For crystallographic data in CIF format see DOI: 10.1039/b716796b

‖ The same data collection and analysis procedures were used for compound **2** as were for **1**. Crystal data: $C_{50}H_{56}N_6O_{10} \cdot C_5H_{12} \cdot CH_2Cl_2$, M_r = 1058.10, T = 153(2) K, triclinic, space group $P\bar{1}$, a = 11.0307(2), b = 15.0724(3), c = 18.4602(4) Å, α = 99.633(2), β = 99.191(2), γ = 111.289(2)°, V = 2737.0(1) Å^3, ρ_{calc} = 1.284 Mg m^{-3}, μ = 0.182 mm^{-1}, Z = 4, reflections collected: 22 637, independent reflections: 12 451 (R_{int} = 0.0383), final R indices [$I > 2\sigma(I)$]:

$R1 = 0.0633$, $wR2 = 0.1407$, R indices (all data): $R1 = 0.1164$, $wR2 = 0.1671$. CCDC 665297. For crystallographic data in CIF format see DOI: 10.1039/b716796b.

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