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Fully π-Conjugated Helices from Oxidative Cleavage of *meso*-Aryl-Substituted Expanded Porphyrins

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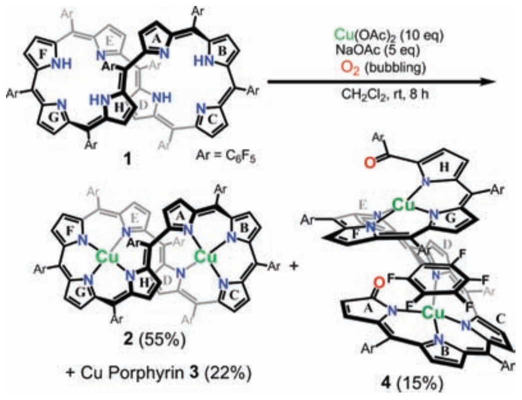
Helical molecules possess a unique position in current chemistry as a result of their intriguing structural and electronic properties as well as their prevalent occurrence as a structural motif in nature. Various helical molecules have thus been extensively studied to date, including helicene,[1] helicates,[2] foldamers,[3] artificial DNA,[4] $(C_2S)_n$ helices,[5] salt-bridged strands,[6] and so on. However, to the best of our knowledge, fully π-conjugated helices have remained unexplored, despite their potential importance in basic and applied chemistry. A promising possibility may be molecular solenoids working on a conducting property.[7] Ineffective π delocalization in helical molecules is mainly the result of interruption of π conjugation by cross-conjugation[8] and/or π-electron localization on aromatic segments,[9] which can be seen in their absorption spectra that display absorption maxima at <450 nm.

Here we report that fully π-conjugated octa- and heptapyrrolic helices were obtained as bis-Cu(II) complexes from oxidative cleavage of octaphyrin and heptaphyrin, respectively. Although similar oxidative cleavages are known for cyclic tetrapyrrolic pigments,[10,11] such long coiling oligopyrromethene helices are unknown.

Scheme 1. Copper Metalation of **1** under O_2 Bubbling Conditions



Recently, we reported that Cu(II) metalation of the figure-eight macrocycle [36]octaphyrin(1.1.1.1.1.1.1.1) (**1**) gave bis-Cu(II) complex **2**, which underwent an unprecedented splitting reaction to give two Cu(II) porphyrins **3**.[12] Here we found that the new reddish-brown product **4** was obtained in 15% yield along with **2** (55%) and **3** (22%) when the Cu(II) metalation of **1** was conducted under continuous O_2 bubbling at room temperature for 8 h (Scheme 1). X-ray diffraction (XRD) analysis revealed that the structure of **4** is an octapyrrolic helix winding around two copper ions (Figure 1a)[13] in which one of the *meso*-pentafluorophenyl substituents is inserted between the two turns of the helical backbone, causing a long Cu−Cu distance of 6.28 Å and an irregular helix pitch of 5−8 Å. Cu(1) is bound to the four nitrogen atoms of the pyrrole rings **A**, **B**, **C**, and **D**, while Cu(2) is bound to the four nitrogen atoms of the pyrrole rings **E**, **F**, **G**, and **H**. This structure indicated that the oxidative cleavage proceeded at the *meso*-α bond of the octaphyrin macrocycle.[10] The oxygen source for **4** was assigned to be molecular oxygen, since **4** was not formed under anaerobic conditions even in the presence of water. In addition, the experimental facts that **1** was not cleaved without $Cu(OAc)_2$ and that **4** was not formed upon treatment of isolated **2** with $Cu(OAc)_2$ have led us to consider that the oxidative ring opening may occur during the Cu(II) metalation of **1**. The importance of Cu(II) ion in the oxidation process can be seen in other related examples.[10h,14]

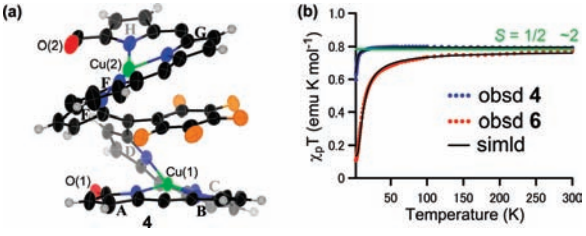


Figure 1. (a) X-ray crystal structure of **4** (50% probability thermal ellipsoid plot; only the inserted *meso*-C_6F_5 substituent is shown). (b) Temperature-dependent magnetic susceptibilities of **4** and **6**.

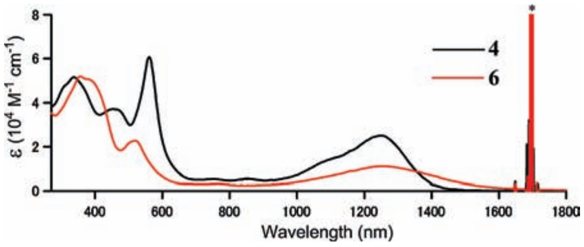


Figure 2. UV−vis−NIR absorption spectra of **4** and **6** in CH_2Cl_2. The * marks vibrational overtones of the solvent.

The UV−vis−near-IR (NIR) absorption spectrum of **4** in CH_2Cl_2 (Figure 2) displays a broad band at $\lambda_{max} = 1248$ nm with $\varepsilon = 25\,000$ M^{-1} cm^{-1} that serves as evidence of the effective delocalization of the 38 π electrons over the whole helical structure. The structure of **4** is conformationally rigid, as shown by the fact that variable-temperature ^{19}F NMR measurements recorded the presence of a single conformer from 213 to 383 K in toluene-d_8 [see the Supporting Information (SI)]. Variable-temperature magnetic susceptibility measurements indicated that the oxidation state of both copper ions is +2 and that these Cu(II) ions interact through a very weak antiferromagnetic coupling with $J/k_B = -0.88$ K (Figure 1b). Electron spin resonance (ESR) measurements at 5 K showed a small half-field resonance signal (see the SI). The observed spin−spin

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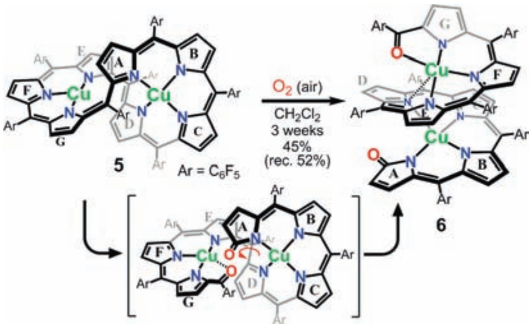
interaction probably operates through effective spin delocalization over the helical π conjugation.[15]

Scheme 2. Oxidative Cleavage of Biscopper Heptaphyrin **5**



We also found that figure-eight bis-Cu(II) heptaphyrin **5** with unique T-shaped coordination[16] gradually changed in air over 3 weeks to give brown product **6** in 45% yield with the recovery of **5** (52%) (Scheme 2). Here again, the oxygen source for **6** was determined to be molecular oxygen, since **5** was stable under inert gas. The structure of **6** was determined by XRD analysis to be a genuine helix with a constant helix pitch of ~4.0 Å and a Cu−Cu distance of 3.25 Å (Figure 3).[13] Cu(1) is bound to the four nitrogen atoms of pyrrole rings **A**, **B**, **C**, and **D** with distances of 1.95, 1.92, 1.95, and 2.02 Å, respectively, while Cu(2) is bound to the three nitrogen atoms of pyrrole ring **E**, **F**, and **G** with distances of 1.92, 1.94, and 1.88 Å, respectively, and to the terminal benzoyl oxygen atom with a distance of 2.20 Å. In addition, a Cu(1)−N(4)−Cu(2) network with distances of 2.02 and 2.61 Å for Cu(1)−N(4) and Cu(2)−N(4), respectively, and an angle of 88.4° for Cu(1)−N(4)−Cu(2) was observed. Importantly, the helical 34 π electron network is preserved smoothly, with small dihedral angles (<20.3°) to allow the full conjugation. It is considered that the formation of **6** is triggered by regioselective cleavage at the *meso*-α bond next to pyrrole ring **A** and subsequent bond rotation between pyrrole rings **D** and **E** (Scheme 2).

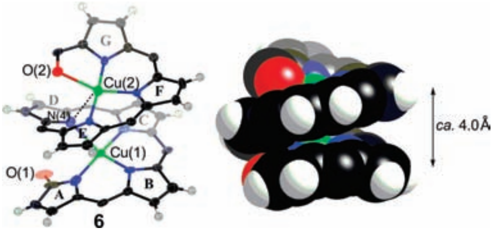


Figure 3. X-ray crystal structure of **6**: (left) 50% probability thermal ellipsoid plot; (right) space-filling plot. The *meso*-C$_6$F$_5$ substituents have been omitted for clarity.

The UV−vis−NIR absorption spectrum of **6** in CH$_2$Cl$_2$ (Figure 2) shows a low-energy broad band at 1262 nm with $\varepsilon = 11\,000$ M^{-1} cm^{-1}. The temperature-dependent magnetic susceptibility measurements revealed the presence in **6** of two Cu(II) ions and their antiferromagnetic interaction with $J/k_B = -6.75$ K (Figure 1b). The larger antiferromagnetic interaction in **6** than in **4** may be ascribed to the superexchange interaction mediated by N(4). ESR measurements at 5 K again showed a clear half-field resonance signal (see the SI). The delocalized spin density distribution also supports the full conjugation.[15] Finally, the conformational flexibility of **6** is noteworthy, since **6** gradually reaches an equilibrium between two conformers in solution, as revealed by TLC analysis, UV−vis−NIR absorption, and ^{19}F NMR spectra. According to the ^{19}F NMR analysis, the ratio of the helical conformer to the other conformer is ~2:1 (see the SI).

In summary, oxidative cleavage of *meso*-aryl-substituted [36]octaphyrin and [32]heptaphyrin provided fully π-conjugated helices as bis-Cu(II) complexes with smoothly π-conjugated networks. These helical molecules exhibited NIR absorption bands with large absorbance as evidence of full π conjugation, hence showing that linear oligopyrromethenes are particularly suitable for the formation of fully π-conjugated helices upon appropriate metal coordination. These transformations constitute a new synthetic route to linear oligopyrromethenes via a topological change from a figure-eight macrocycle to a coiling helix. Chiral resolution and further elongation of such π-conjugated helices are actively being pursued in our laboratory.

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Supporting Information Available: Sample preparation, characterization, DFT single-point calculations, and X-ray crystallographic details for **4** (CCDC-751202) and **6** (CCDC-751203). This material is available free of charge via the Internet at http://pubs.acs.org.

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