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Asymmetric synthesis and electrochemical behaviour of a C_2 chiral bisferrocenyl orthoquinone

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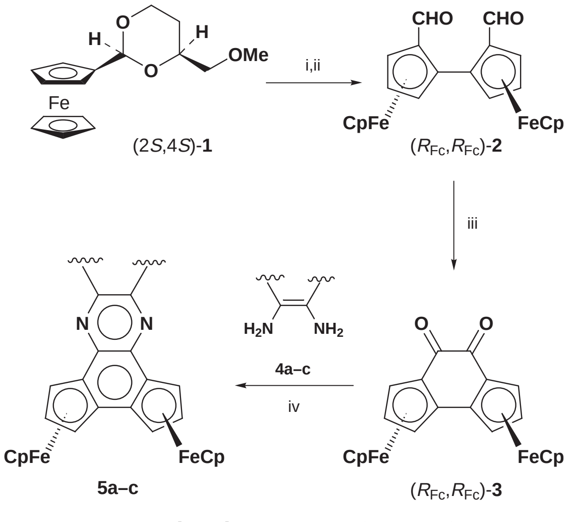
A new chiral bisferrocenyl quinone with C_2 symmetry was prepared by asymmetric synthesis; further condensation with 1,2-diamines led to enantiopure polyaromatic heterocycles into which two ferrocene units are fused.

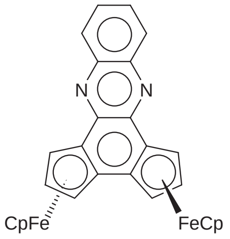
Due to their unique structural and electronic properties, *o*-benzoquinones[1] and their diimine derivatives have received a great deal of attention as transition metal ligands in coordination chemistry and catalysis.[2] Their 1,2-diketone structure allows the construction of polyaromatic systems *via* various types of condensation reactions. This has led to numerous applications in material sciences[3] and supramolecular chemistry.[4]

We report here the asymmetric synthesis of a new chiral orthoquinone in which two electron-rich ferrocene units are fused. Diastereoselective ortholithiation of enantiopure ferrocenyl acetal (2*S*,4*S*)-**1** by the reported method[5] and further oxidation of the lithio intermediate by iron(III) acetylacetonate led, after removal of the acetal protecting groups, to the chiral bisferrocene bisaldehyde (R_{Fc},R_{Fc})-**2**† in a 70% yield (Scheme 1). Due to the high diastereoselectivity of the deprotonation (98%), only the C_2 symmetric isomer was formed and no *meso* isomer was detected. Pinacolisation of (R_{Fc},R_{Fc})-**2** was efficiently realised by reaction of an excess of SmI_2 in THF and gave a mixture of air sensitive diols which were directly oxidised by MnO_2 in dry $CHCl_3$. After chromatographic purification, the new C_2 symmetric *o*-quinone (R_{Fc},R_{Fc})-**3**‡ was isolated in 55% yield (starting from **2**) and was fully characterised. This deep blue complex proved to be air stable and could be easily prepared on a multigram scale using this procedure.

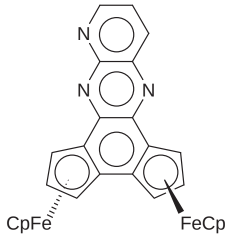
As a first application, we turned to the condensation of (R_{Fc},R_{Fc})-**3** with various aromatic 1,2-diamines. After optimisation, it was found that condensation of quinone **3** with an excess of 1,2-diaminobenzene in refluxing toluene gave a quantitative yield of the quinoxaline derivative **5a** when freshly activated 4 Å molecular sieves or alumina[6] were used as a dehydrating agent. In the case of adducts **5b**,**c**, longer reaction time were required and optimised yields reached 70% after purification. We found as well that *N*-alkylation of the pyridine nitrogen of adduct **5b** by iodomethane gave a quantitative yield of the stable green pyridinium salt **6**. The structure of the quinoxaline adducts as well as the starting quinone could be unambiguously confirmed by standard ^1H and ^{13}C NMR methods as well as HRMS. The electrochemical behaviour of bisferrocene (Fe^{II}, Fe^{II}) complexes such as **3** and **5a** was studied by cyclic voltammetry[7] (Fig. 1). This allowed us to study the stability in solution of the higher oxidation states (Fe^{II}, Fe^{III}) and (Fe^{III}, Fe^{III}). Recording the CV at low sweep rate for **5a** gave two reversible one electron oxidation waves at low potential. In the time scale of the analysis, the mixed valence complex (Fe^{II}, Fe^{III}) is completely stable as well as the corresponding bisferricinium (Fe^{III}, Fe^{III}). As expected, quinone **3** proved to be more difficult to oxidize, showing an increase of +0.34 V for the first oxidation compared to **5a**. The first oxidation wave giving the mixed valence state is reversible at all sweep rates, but the second oxidation wave remains irreversible for sweep rates up to 1000 V s^{-1}, thus showing chemical evolution of the bisferricinium complex. Increasing the sweep rate up to 2000–3000 V s^{-1} shows that this evolution is slow and a life time for the bisferricinum (Fe^{III},Fe^{III}) was evaluated at 3×10^{-2} s. It was also noted that **3** didn't display any reduction wave, in agreement with the electron-rich nature of the carbonyl groups.



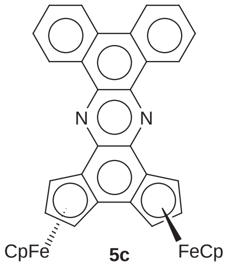
Scheme 1 *Reagents and conditions*: i, Bu^{t}Li (1.1 equiv.), Et_2O, −78 to 25 °C, 1 h, then $Fe(acac)_3$ (1.4 equiv.), 25 °C, 15 h; ii, TsOH, CH_2Cl_2, H_2O, 25 °C, 3 h (70% from **1**); iii, SmI_2 (2.4 equiv.), THF, 25 °C, 15 min, then MnO_2, $CHCl_3$, 25 °C, 30 min (55–60% from **2**); iv, 1,2-diamine (2–3 equiv.), PhMe, 4 Å MS or Al_2O_3, reflux.

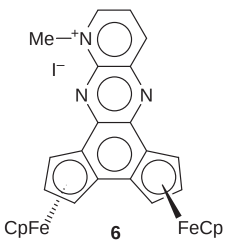


5a



5b





We are currently studying the chemistry and the electrochemical behaviour of those enantiopure bimetallic complexes as well as the isolation of the mixed valence complexes.

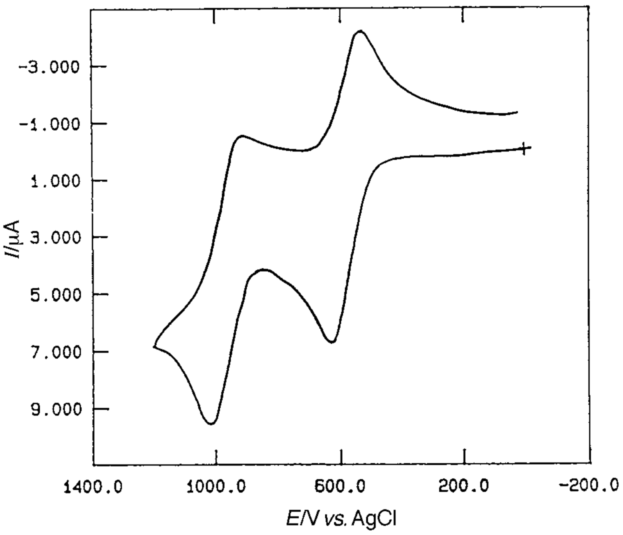


Fig. 1 Cyclic voltammogram of **5a** (2 mM) in 0.1 M Bu_4NBF_4–CH_2Cl_2 at a Pt electrode with a sweep rate of 0.1 V s^{-1}.

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Notes and references

† A multistep synthesis of bisaldehyde **2** was first reported using a resolution step: K. Schlögl and M. Walser, *Monatsh. Chem.*, 1969, **100**, 97.

‡ *Synthesis of quinone* **3**: A solution of bisaldehyde **2** (3.33 g, 7.8 mmol) in 30 ml of dry THF was treated under argon with 180 ml of a 0.1 M THF solution of SmI_2 dropwise. After 10 min, the reaction mixture was quenched with aq. NH_4Cl and extracted with Et_2O. After work up, the crude reaction mixture was taken up in 300 ml of $CHCl_3$ and stirred with 30 g of activated MnO_2 for 20 min. Filtration of the reaction mixture on Celite followed by flash chromatography on silica gel (cyclohexane–Et_2O 20:80 to CH_2Cl_2–Et_2O 20:80) delivered the pure quinone **3** as a deep blue solid (1.92 g, 58% yield from **2**).

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