ChemComm

Bis(ferrocenyl)porphyrins. Compounds with strong long-range metal–metal coupling†

Peter D. W. Boyd,[b] Anthony K. Burrell,*[a] Wayne M. Campbell,[a] Paul A. Cocks,[c] Keith C. Gordon,[c] Geoffrey B. Jameson,[a] David L. Officer*[a] and Zhongde Zhao[b]

[a] *IFS - Chemistry, Massey University, Private Bag 11222, Palmerston North, New Zealand. E-mail: A.K.Burrell@massey.ac.nz*
[b] *Chemistry Department, The University of Auckland, Auckland, New Zealand*
[c] *Chemistry Department, University of Otago, PO Box 56, Dunedin, New Zealand*

Received (in Cambridge, UK) 26th January 1999, Accepted 4th March 1999

The condensation of a dipyrromethane with ferrocene aldehyde leads to a single atropisomer of α,α-5,15-bis(ferrocenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin 1; electrochemistry of 1 and Ni-1 reveals two consecutive ferrocene-based one-electron oxidation waves, which are separated by 0.19 and 0.41 V, respectively.

Discrete systems in which remote sites are electronically coupled have exciting possibilities for applications in molecular electronic devices.[1] However, despite much effort, particularly with compounds containing two connected ferrocene moieties,[2] useful devices have not yet been forthcoming. This is primarily because communication between the electronic (especially the redox) states at the two sites decreases rapidly with distance. Recent studies have identified a combination of factors that influence communication between connected ferrocene moieties, including the type of connection,[2] the length of the connector[3] and the orientation of the two ferrocenes.[4] Here, we report the synthesis, structure and properties of a bis(ferrocenyl)porphyrin **1** in which these factors are synergistically combined to give unprecedented strong coupling between the ferrocene moieties.

Porphyrin **1**‡ is formed in a classical condensation reaction between ferrocene aldehyde and a tetraalkyl dipyrromethane. The insertion of nickel gives Ni-**1**.§ To our surprise, compound **1** is formed as a single isomer in high yield (58%), with both ferrocenyl groups in a *syn* (or α,α-atropisomer) configuration with respect to the porphyrin macrocycle. The *anti* product, the α,β-atropisomer, is not observed. CPK-model studies indicate that the porphyrinogen conformation which leads to the α,α-isomer is the least sterically congested and thereby the most accessible to chemical oxidation to form **1**. This preference has not been observed previously and is a direct result of the unique steric requirements of the ferrocenyl moiety. Upon oxidation of the porphyrinogen, the methyl groups in the β-pyrrolic positions offer sufficient steric hindrance to prevent any isomerisation.

The geometry was confirmed by single-crystal structure determinations of **1**¶ [Fig. 1(a)] and its nickel(II)-substituted derivative Ni-**1**¶ [Fig. 1(b)]. The large steric bulk of the ferrocenyl moiety at opposite *meso* positions, clashing with the β-methyl substituents, not only prevents rotation of the ferrocenyl moiety but leads to a strongly ruffled porphyrin core. However, comparison of **1** and Ni-**1** reveals that the ferrocenyl moieties are not rigidly locked in a single conformation. Indeed the conformational disorder shown by Ni-**1** in the *solid state* provided further indication of the restricted conformational flexibility of the ferrocene groups, relevant to solution-state conformational flexibility and to the distinctive electrochemistry shown by these compounds.

The electrochemistry of **1** and Ni-**1** [Fig. 2(d)] shows two consecutive ferrocene-based one-electron oxidation waves

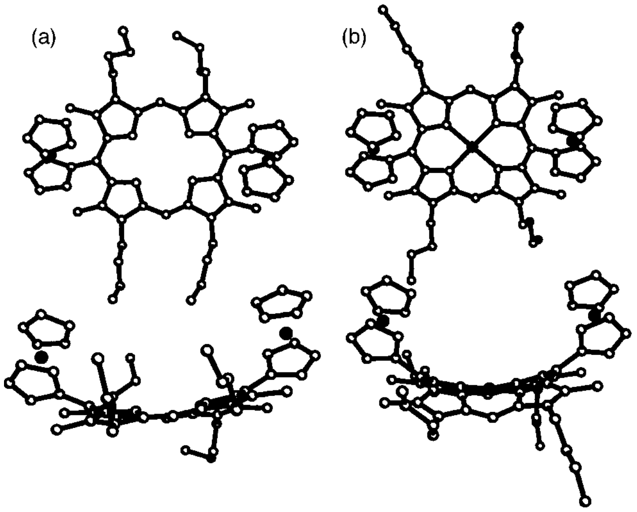

Fig. 1 Molecular structures of **1** (a) and the major conformation of Ni-**1** (b). The top view looking down on the porphyrin plane, showing the twist of the ferrocenyl moieties; the bottom view is side-on to the porphyrin plane, showing the distortions of the porphyrin ring.

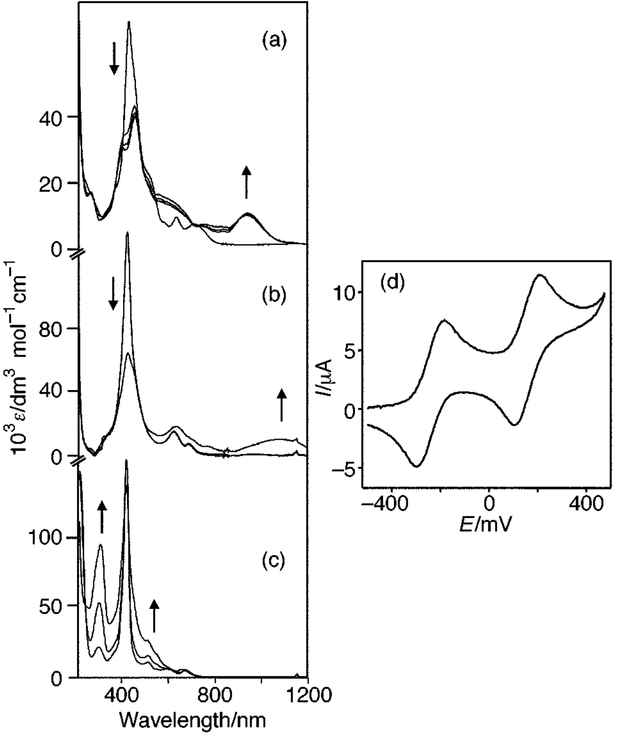

Fig. 2 Spectro-electrochemical UV–VIS spectra of Na-**1** (a), **1** (b) and **3** (c); arrows indicate direction of change in peaks during oxidation. (d) Cyclic voltammogram of Ni-**1** in CH_2Cl_2 at room temperature, *E*°/ *versus* Fc/Fc$^+$.

---

† The authors would like to dedicate this paper to Professor Warren R. Roper on the occasion of his 60th birthday.

separated by 190 and 410 mV, respectively. Spectroelectrochemical UV–VIS studies of **1** and Ni-**1** reveal that both show the growth of an absorption at 1080 and 946 nm, respectively [Fig. 2(a) and (b)], with single electron oxidation. These are assigned as intravalence charge-transfer (IVCT) bands. Further oxidation leads to depletion of these features. The behaviour of **1** and Ni-**1** may be contrasted to that of the sterically less congested reference compound **3**.‖ This compound shows a single two-electron ferrocene oxidation[7] and no near-IR absorption when oxidised [Fig. 2(c)]. From the separation of oxidation waves in **1** and Ni-**1** a conproportionation constant (K_c) of 1.6×10^3 for **1** and 8.5×10^6 for Ni-**1** is calculated,[6] indicating strong coupling of the ferrocene moieties. The small bandwidth of the IVCT band for the Ni-$\mathbf{1}^+$ complex ($\Delta\nu_{\frac{1}{2}} = 1400\ \mathrm{cm}^{-1}$) suggests that it is a class III (highly localised) mixed-valence species,[7] consistent with the large value of K_c. For **1**, $\Delta\nu_{\frac{1}{2}} = 2600\ \mathrm{cm}^{-1}$, suggesting a class II/III behaviour.[6]

For **1** and Ni-**1** the coupling between ferrocene units, at a separation of > 10 Å, is remarkably high. Biferrocene shows an oxidation-wave peak splitting of only 330 mV where the ferrocenyl irons are < 5.4 Å distant,[8] and **3**, where a ferrocene–ferrocene distance of at least 10 Å can be estimated, has no observable coupling. Such strong coupling between the two ferrocenes was largely unexpected, as the related 5,10,15,20-tetraferrocenylporphyrin **2** and 5,15-diferrocenyl-10,20-di-*p*-tolylporphyrin **3**[9] display no such coupling. These porphyrins, however, lack substituents at the β-pyrrolic positions, and the ferrocenyl moieties are free to rotate, as evidenced by ^{1}H NMR spectroscopy.

A density functional calculation,** seeking to establish a basis for the origin of differences between **2**, **3** and **1** (and Ni-**1**), was carried out on the monocation $\mathbf{1}^+$. The singly occupied HOMO in this system is delocalised over both ferrocene moieties and is composed of ferrocene (xy, $x^2 - y^2$, e_{2g}) Fe d orbitals and the porphyrin a_{2u} π molecular orbital. The separation between the positive and negative combination of these orbitals has been proposed to be related to the strength of coupling between ferrocene centres in mixed-valence systems.[3,10] In this case the difference in energy for the alpha spin orbitals is *ca.* 0.1 eV. This strong coupling appears to be the result of extensive mixing of both ferrocenyl molecular orbital systems with that of the porphyrin connector π system, as is apparent in the diminished intensity of the Soret band at 410 nm for **1** and Ni-**1** but not **3** upon oxidation.

The low symmetry of **1** and Ni-**1** (at best C_{2v}), the possibility of extensive vibronic coupling as a result of the restricted rotational flexibility of the ferrocenyl groups propagating into distortions of the porphyrin core, and the molecular dipole created by the α,α-atropisomer are all possible factors that may underpin the strong coupling. A thorough study of this system will be made in order to determine (i) the factors that lead to the very strong coupling and (ii) the extent to which this communication between two ferrocenyl moieties can be modified and exploited. For now, these results show for the first time in diferrocenylporphyrin systems that strong coupling can be created between remote centres using the porphyrin core as a connector.

We are grateful to The Public Good Science Fund (MAU602 and MAU809), the University of Auckland Research Committee and the Marsden Fund of New Zealand (UOA613) for support of this work and to Dr Cliff Rickard and The University of Auckland for X-ray data collection.

Notes and References

‡ Electrochemical data, CH_2Cl_2 solution, at room temperature, $E^{0/}$ *vs.* Fc/Fc$^+$ (peak separation/mV; I_A/I_c): −0.27 (120, 1.0), −0.08 (100; 1.0).

§ Electrochemical data, CH_2Cl_2 solution, at room temperature, $E^{0/}$ *versus* Fc/Fc$^+$ (peak separation/mV; I_A/I_c): −0.24 (110; 1.0), 0.17 (100; 1.0).

¶ *Crystal data*: $\mathbf{1}\cdot CH_2Cl_2$: $C_{61}H_{72}Cl_2Fe_2N_4$, $M_r = 1043.83$, triclinic, space group $P\bar{1}$, $a = 13.722(3)$, $b = 14.908(3)$, $c = 15.368(3)$ Å, $\alpha = 73.49(3)$, $\beta = 87.40(3)$, $\gamma = 62.68(3)°$, $V = 2664.6(9)$ Å^3, $Z = 2$, $D_c = 1.301$ Mg m^{-3}, $\mu = 0.688$ mm^{-1}, Enraf-Nonius CAD-4 diffractometer, Mo-Kα radiation ($\lambda = 0.71073$ Å), red crystal ($0.11 \times 0.11 \times 0.31$ mm), data collection range 4.0–40.0°, $0 \leqslant h \leqslant 13$, $-12 \leqslant k \leqslant 14$, $-14 \leqslant l \leqslant 14$, reflections collected 5249, unique 4967 [$R_{int} = 0.0896$]. The structure was solved by direct methods and refined by a full-matrix least-squares procedures to give final residuals of GOF = 0.987, parameters = 623, $R_1 = 0.0586$ [2219 data with $I > 2\sigma(I)$], $wR_2 = 0.1645$ (all data). The largest residual electron densities were 0.568 and −0.438 e Å^{-3}.

Ni-$\mathbf{1}\cdot 0.25H_2O$: $NiC_{60}H_{68}Fe_2N_4O_{0.25}$, $M_r = 1019.78$, tetragonal, space group $I4_1/a$, $a = 28.5339(2)$, $c = 24.6067(1)$ Å, $V = 20034.4(2)$ Å^3, $Z = 16$, $D_c = 1.352$ Mg m^{-3}, $\mu = 0.988$ mm^{-1}, Seimens Smart diffractometer, Mo-Kα radiation ($\lambda = 0.71073$ Å), red crystal ($0.10 \times 0.09 \times 0.28$ mm), data collection range 16–46.5°, $-21 \leqslant h \leqslant 22$, $-27 \leqslant k \leqslant 31$, $0 \leqslant l \leqslant 27$, unique reflections 6852. Two distinct conformations are apparent. Thus, bond distances, bond angles and planarity associated with the substituted pyrrolic and ferrocenyl moieties were restrained to common values for the chemically approximately equivalent parameters, while permitting conformational flexibility at the *meso* positions, utilising the features of SHELXL-96 (G. M. Sheldrick SHELXL-96. Institut für Anorganische Chemie der Universität Göttingen, Germany, 1997) final values conform closely to expected values (J. L. Hoard, in *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, Elsevier, Amsterdam, 1975, ch. 8) and the Ni is properly centred in the porphyrin hole for each conformation with relative occupancies of 0.684(5) and 0.316. Final values of residuals: GOF = 1.066, R_1 [4023 data with $F > 4\sigma(F)$] = 0.0805, wR_2 (all data) = 0.2036 for a model described by 1193 variable parameters and 3511 restraints on geometry and thermal motion. The largest residual electron densities were 0.356 and −0.335 e Å^{-3}.

CCDC 182/1186. See http://www.rsc.org/suppdata/cc/1999/637/ for crystallographic files in .cif format.

‖ 5,15-Diferrocenyl-10,20-ditolylporphyrin **3**, was prepared from tolyl dipyrromethane and ferrocene aldehyde using standard methods (F. Li, K. Yang, J. S. Tyhonas, K. A. MacCrum and J. S. Lindsey, *Tetrahedron*, 1997, **53**, 12339).

** A density functional calculation of the electronic structure of the singly oxidised $\mathbf{1}^+$ was performed using the Amsterdam Density Functional program (ADF 2.3.0, Theoretical Chemistry, Vrije Universiteit, Amsterdam (E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41; G. te Velde and E. J. Baerends, *J. Comput. Phys.*, 1992, **99**, 84). The molecular geometry used in the calculation was taken from the X-ray crystal structure of **1**, with butyl substituents replaced by methyl groups. Double-ξ Slater-type basis sets were used for C(2s, 2p), N(2s, 2p) and H(1s) augmented by a single 3d polarisation function. A triple-ξ basis set was used for Fe (3s, 3p, 3d, 4s). The inner electron configurations were assigned to the core and were treated using the frozen core approximation. The calculation was spin unrestricted and used the local density approximation (S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200) with non-local corrections for exchange (A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098) and with nonlocal corrections for correlation (C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785).

1 A. J. Bard, *Pure Appl. Chem.*, 1971, **25**, 379; R. M. Metzger and C. A. Panetta, *New J. Chem.*, 1991, **15**, 209.

2 L. M. Tolbert, X. Zhao, Y. Ding and L. A. Bottomley, *J. Am. Chem. Soc.*, 1995, **117**, 12 891.

3 A.-C. Ribou, J.-P. Launay, A. L. Sachtleben, H. Li and C. W. Spangler, *Inorg. Chem.*, 1996, **35**, 3755.

4 C. Patoux, C. Coudret, J.-P. Launay, C. Joachim and A. Gourdon, *Inorg. Chem.*, 1997, **36**, 5037.

5 J. L. Sessler, M. R. Johnson, S. E. Creager, J. C. Fettinger and J. A. Ibers, *J. Am. Chem. Soc.*, 1990, **112**, 9310.

6 C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1; S. Barlow and D. O'Hare, *Chem. Rev.*, 1997, **97**, 637.

7 A. R. Rezvani, C. E. B. Evans and R. J. Crutchley, *Inorg. Chem.*, 1995, **34**, 4600.

8 W. H. Morrison, S. Krogsrud and D. N. Hendrickson, *Inorg. Chem.*, 1973, **12**, 1998.

9 N. L. Loim, N. V. Abromova and V. I. Sokolov, *Mendeleev Commun.*, 1996, 46.

10 M. D. Newton, *Chem. Rev.*, 1991, **91**, 767; C. Joachim, J.-P. Launay and S. Woitellier, *Chem. Phys.*, 1990, **147**, 131; S. Larsson, *J. Am. Chem. Soc.*, 1981, **103**, 4034; P. Siddarth and R. A. Marcus *J. Phys. Chem.*, 1990, **94**, 2985; C. Patoux, J.-P. Launay, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, S. James and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1998, **120**, 3717.

Communication 9/00691E