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Preliminary communication

The synthesis and electrochemistry of a novel ferrocene bis-porphyrin molecule

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Abstract

The synthesis and electrochemistry of a new ferrocene bis-porphyrin molecule (**3**) derived from 1,1′-bis(chlorocarbonyl)ferrocene and 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin are reported. High field ^{1}H NMR data indicate the respective porphyrin macrocyclic rings of **3** are in a *gauche* type conformation.

Porphyrin macrocycles currently attract considerable attention as synthetic systems for investigations into solar energy conversion [1–3] and artificial photosynthesis [4–6]. This is because of their unique photophysical properties and favourable redox characteristics. We report here the synthesis and electrochemistry of a dimeric porphyrin molecule that contains a bridging ferrocene subunit.

The condensation of 1,1′-bis(chlorocarbonyl)ferrocene (**1**) [7] with two moles of 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin (**2**) [3] in the presence of triethylamine gave the new ferrocene bis-porphyrin (**3**) as a purple crystalline solid in reasonable yields (see Scheme 1). Its structure was verified by elemental analysis *, mass spectrometry, and ^{1}H NMR (Table 1) and UV-visible spectroscopy (Table 2).

The unusual ^{1}H NMR absorption pattern for the pyrrole proton signals of **3** (Table 1) is noteworthy. The expected ^{1}H NMR absorption pattern of pyrrole protons in *p*-monosubstituted *meso*-tetraphenylporphyrins usually consists of two doublets for H^1,H^2 and a singlet for H^3,H^4 pyrrole protons [8], Fig. 1. With **3** however four doublets are observed for the pyrrole protons, suggesting that either π-conjugation electronic effects of the substituted phenyl group are being transmitted to the porphyrin ring or the respective porphyrin rings are not, as would have been expected for steric reasons, *trans* to one another but are in a *gauche* type conformation (Fig. 2). The former explanation is unlikely in view of the fact that to our knowledge no π-delocalisation of these electronic effects has ever been observed

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* Found: C, 80.4; H, 4.5; N, 7.3%. **3**: calcd.: C, 80.1; H, 4.4; N, 7.5%.

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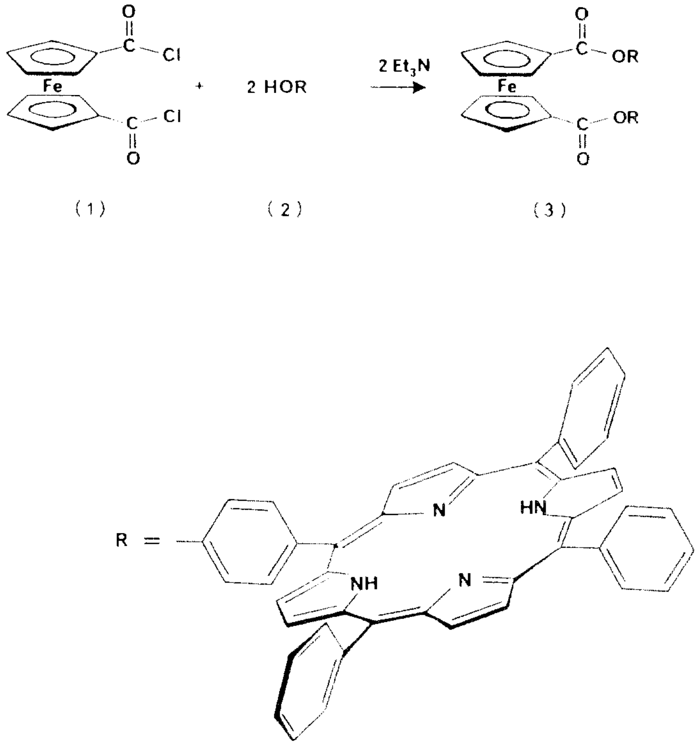


Scheme 1.

for *p*-monosubstituted meso-tetraphenylporphyrins [8], and no evidence for these effects can be found from UV-visible spectroscopic and electrochemical (see later) data for **3**.

Table 1

^{1}H NMR data for **3** in $CDCl_3$ [a]

Assignment		δ (ppm)
Pyrrole protons	8.85	(4H, d, *J* 4.8 Hz)
	8.82	(4H, d, *J* 4.8 Hz)
	8.74	(4H, d, *J* 4.8 Hz)
	8.59	(4H, d, *J* 4.8 Hz)
Substituted phenyl ring	8.29	(4H, d, *J* 8.4 Hz)
	7.71	(4H, d, *J* 8.4 Hz)
Unsubstituted phenyl rings	8.22	(4H, d of d, *J* 7.3, 2.2 Hz)
	7.70–7.80	(6H, m)
	7.89–7.42	(20H, m)
Ferrocenyl	5.36	(4H, t, *J* 1.8 Hz)
	4.83	(4H, t, *J* 1.8 Hz)
N–H	−2.80	(4H, s)

[a] Recorded at 270 MHz ambient temperature with Me_4Si as internal reference.

Table 2

UV-visible spectral data for **3** in CH_2Cl_2

λ_{max} (nm)	ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)
417 (Soret)	886
481	8.7
514	42
549	18
590	12
647	11

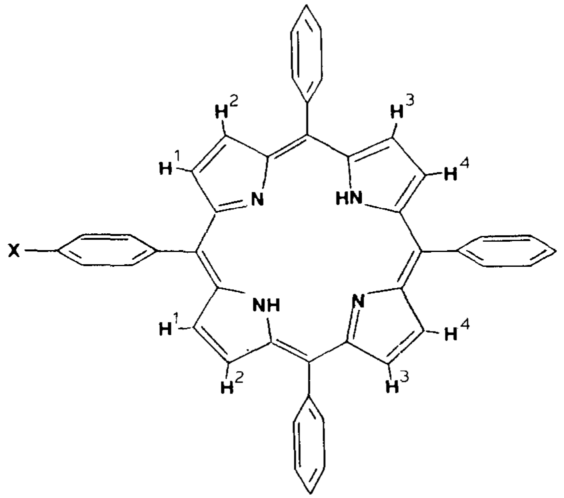


Fig. 1. *p*-Monosubstituted tetraphenylporphyrin.

Table 3

Electrochemical data for **3**

Porphyrin ring reduction		Porphyrin ring oxidation		Ferrocene oxidation	
$E_{1/2}$ (V) [a]	ΔE_p (mV) [b]	$E_{1/2}$ (V) [a]	ΔE_p (mV) [b]	$E_{1/2}$ (V) [a]	ΔE_p (mV) [b]
-1.20 [c]	70	$+0.97$ [c]	130	$+1.22$	60
-1.56 [c]	100	$+1.44$ [d]	–		

[a] Obtained from cyclic voltammetry studies in dichloromethane solvent containing 0.2 *M* $[Bu^n_4N]BF_4$ as supporting electrolyte. Solutions were ca. 2×10^{-3} *M* and measurements were made at 21 ± 1° C at 0.2 V s^{-1} scan rate using a Pt bead working electrode with $Fc^{0/+}$ internal reference. Values are quoted relative to the saturated calomel reference electrode. [b] Separation between anodic and cathodic peak potentials, values for ferrocene under the same conditions ranged from 90–110 mV. [c] Two electron process for two one electron transfers at similar potentials on the basis of the current function for 5-methoxyphenyl-10,15,20-triphenylporphyrin in the same cell. [d] Obtained using differential pulse voltammetry. See Fig. 3(b).

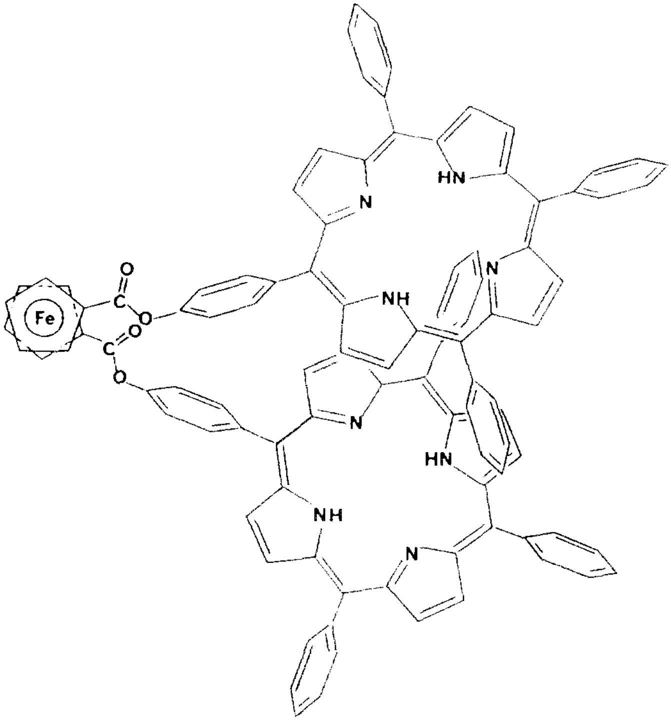


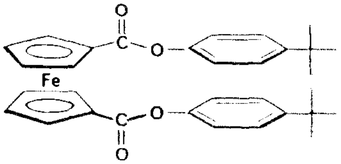
Fig. 2. Proposed gauche conformation of porphyrin rings for **3**.

Also of note are the proton signals for the unsubstituted phenyl rings of **3**; two show normal signal patterns, whereas the remaining four exhibit complicated spectral patterns supporting the proposed gauche conformation for **3**, Fig. 2.

Subsequent variable temperature NMR studies ($CDCl_3$ and DMSO) showed the ^1H NMR spectrum of **3** to be invariant over the temperature range 20–110 °C.

The UV-visible absorption spectrum of **3** in CH_2Cl_2 (Table 2) does not show any detectable interaction between the porphyrin–porphyrin [9] or ferrocene–porphyrin chromophores.

The electrochemical techniques, cyclic voltammetry and differential pulse voltammetry, were used to study the redox chemistry of **3** and the results are presented in Table 3 and Fig. 3. The cyclic voltammogram of the model ferrocene derivative **4** [10], recorded for comparison purposes, showed a reversible oxidation wave at +1.20 V, indicating that the oxidation wave at +1.22 V for **3** pertains to the ferrocenyl moiety. Furthermore the separations between the first porphyrin oxidation and first porphyrin reduction potential agree well with the "theoretical" difference of 2.25 ± 0.15 V observed for radical-anion and radical-cation formation [11].



(4)

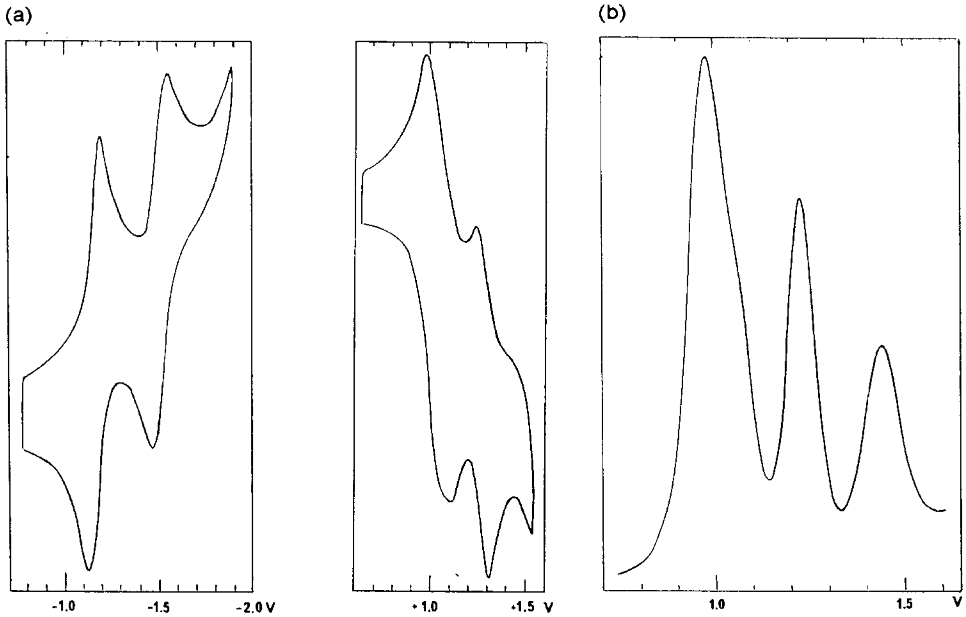


Fig. 3. (a) Cyclic voltammogram of 3; (b) differential pulse voltammogram of 3 ((CH_2Cl_2), scan rate 2 mV/s, modulation amplitude 25 mV and drop time 0.5 s).

The coordination chemistry of **3** towards a variety of transition metals is currently under investigation.

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