Redox-Induced *cis* → *trans* Isomerisation of Bis(porphyrinyl)ethenes: A Possible Basis for a Molecular Memory Element?

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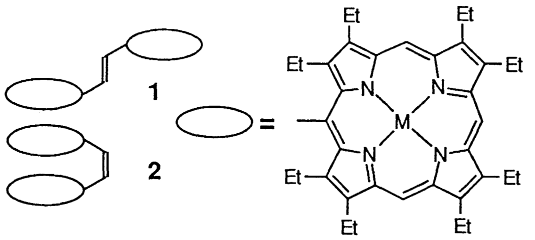
trans-1,2-Bis(octaethylporphyrin-5-yl)ethene free base and its dinickel(II) complex exhibit narrow electrochemical band gaps (1.44 and 1.49 eV, respectively) and broad, solvent-dependent absorption bands at low energy, whilst the corresponding *cis* isomers undergo rapid redox-induced *cis* →*trans* isomerisation.

Studies of porphyrin dimers with defined geometries enforced by various bridging units have been driven by attempts to mimic the photosynthetic reaction centers,[1] and have generated numerous structures in which the macrocycles are held in face-to-face, oblique, or linear dispositions by various covalent linkers.[2] Lately, there has been added interest in structures of this type in "molecular electronics", e.g. structures such as planar fused dimers,[3] "molecular photonic wires",[4] and conjugated alkyne-bridged arrays.[5-9] The *ethene*-linked octaethylporphyrin (OEP) dimers H_4**1** (*trans*) and H_4**2** (*cis*),[10-12] have been structurally characterised as the dinickel(II) complexes Ni_2**1** and Ni_2**2** respectively.[2,11] The data presented below suggest that the *trans* isomer has features in common with "strongly-coupled" porphyrin dimers, and also reveal a novel and potentially useful feature of the *cis* isomer.



The cyclic voltammogram of H_4**1** [Figure 1(a)] shows two overlapping one-electron reductions ($red_{1/2}$) and a pair of one-electron oxidations (ox_1 and ox_2), the shape of the curves being independent of the initial scan direction.[13] The superimposed square wave scan defines the ox_1/ox_2 splitting to be 100±5 mV. Any splitting of red_1 and red_2 is below the resolution of our experiments. In other potentially mixed-valence linearly-disposed porphyrin dimers, the ox_1/ox_2 splitting is also larger than the red_1/red_2 splitting.[6,8,9] The HOMO-LUMO gap ΔE [= $E(ox_1) - E(red_1)$], is only 1.44 eV.[14] This is very narrow compared with monomeric porphyrins or alkyne-conjugated dimers.[6,8,9] The voltammetry of the dinickel complex Ni_2**1** (ΔE = 1.49 eV) closely resembles that of H_4**1**.[13] The redox gaps have contracted on both sides, i.e. **1** is both easier to oxidize (high HOMO) and easier to reduce (low LUMO) than other OEP dimers, including {[Ni(OEP)]C_2H_4[Ni(OEP)]}, Ni_2**3** and {[M(OEP)](μ-C_4)-[M(OEP)]}, **4**.[8,9,16] The small ΔE predicts the existence of a low energy band in the visible spectrum. Both H_4**1** and Ni_2**1** possess such absorption bands, shown for Ni_2**1** in Figure 2.

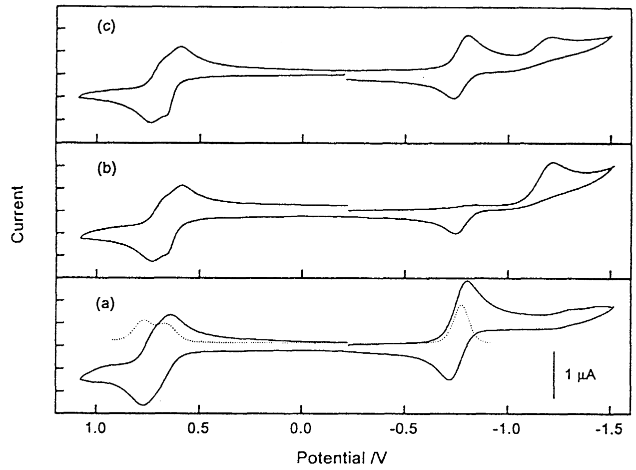


Figure 1. Voltammograms: (a) H_4**1**, initial direction cathodic (dotted line = square wave scan, positive to negative); (b) H_4**2**, initial direction cathodic; (c) H_4**2**, initial direction anodic.[13]

While we were preparing our work for publication, we discovered that another group had independently noticed this feature.[17] Published spectra of **1** had previously shown only two of its three distinguishing features, namely, the slight splitting of the Soret band and the additional intense "Q band" at *ca.* 500 nm. No importance was attached to the low energy "tail" on the Q bands of the neutral species.[2,12,18] Comparisons of **1** with either the *cis* isomer **2** or the *ethane*-bridged dimer **3** reveal that the last two features are unique to **1**.[19] The dependence of their energy and shape on the nature of the medium (Figure 2) suggests that these bands have significant intramolecular charge-transfer character.

We have also studied the electrochemistry of the *cis* isomer H_4**2**. Figure 1(b) shows a cyclic voltammogram with initial scan direction cathodic, in which there is a very weak peak at *ca.* -0.8 V (due to traces of H_4**1**), then a broad reduction wave peaking at *ca.* -1.2 V. On the return anodic sweep, the reverse wave appears at the same potential as that for the *trans* isomer H_4**1**. On continuation of the scan to positive potentials, the oxidations are almost coincident with those of H_4**1**. Figure 1(c) shows the result of a scan initially in the anodic direction, and a marked relative increase in the height of the inner reduction wave is revealed. The dinickel complex Ni_2**2** displays similar voltammograms. These data and other confirmatory cyclic voltammetric experiments suggested a very facile *cis* →*trans* isomerisation induced at the electrode by the addition or abstraction of (presumably) two electrons.[22] To confirm this conclusion, micro-scale bulk oxidation and reduction cycles at potentials

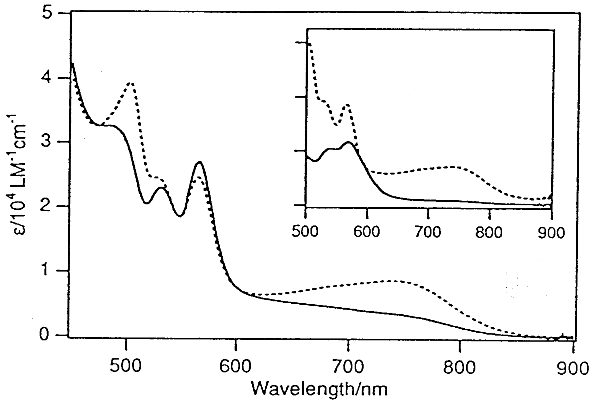


Figure 2. Visible absorption spectra: Ni$_2$**1**, (—) in CHCl$_3$, (····) in 0.2 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$. Inset: Electrochemical (oxidative) conversion of Ni$_2$**2** (—) to Ni$_2$**1** (····) in 0.2 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$.

suggested by the voltammetry were performed on solutions of H$_4$**2** and Ni$_2$**2**. In each case, visible spectra recorded before and after showed that isomerisation had indeed occurred, irrespective of the initial direction of polarisation. The inset spectra in Figure 2 show, as an example, the results of an oxidation cycle for Ni$_2$**2**. This diagram also emphasises the dramatic difference in the spectra of **1** and **2**. The oxidations of the two isomers apparently occur at about the same potentials, but the *cis* isomer is much harder to reduce, indicating a higher LUMO energy.

Thus **1** appears to represent a novel class of porphyrin dimer, in which both conjugation and proximity strongly perturb the frontier orbitals. Redox-induced *cis* →*trans* switching could be used as a concept for an optically-readable (780 nm) permanent molecular memory. We will soon be pursuing spectroelectrochemical examination of these systems to characterise the novel behaviour of both isomers more fully.

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13 Conditions: 293±1 K, porphyrin concentrations *ca.* 4 x 10^{-4} M in CH$_2$Cl$_2$ containing 0.5 M Bu$_4$NPF$_6$, Pt working and counter electrodes, Ag/AgCl/CH$_2$Cl$_2$ reference electrode; potentials internally standardised using Fc/Fc$^+$ at + 0.55 V. Scan rates for cyclic and square wave voltammetry, 100 and 10 mVs^{-1}, respectively. Redox potentials (V): H$_4$**1**: E(red$_{1/2}$) –0.78; E(ox$_1$) +0.66; E(ox$_2$) +0.76; E(ox$_3$) +1.5; ΔE 1.44; Ni$_2$**1**: E(red$_{1/2}$) –0.87; E(ox$_1$) +0.62; E(ox$_2$) +0.72; E(ox$_3$) +1.4; ΔE 1.49.
14 The unusual *reduction* potential of H$_4$**1** has previously been reported in connection with the mechanism of its formation by aerial oxidation of the ethane-bridged analogue {[H$_2$(OEP)]C$_2$H$_4$[H$_2$(OEP)]}, H$_4$**3**.[10] Our results are consistent with those of Higuchi *et al.*, who recently reported the *oxidation* potential of Ni$_2$**1**.[15]
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16 Redox potentials (V): Ni$_2$**3**: E(red$_{1/2}$) –1.41 (irreversible); E(ox$_1$) +0.72; ΔE 2.13; Ni$_2$**4** (at 293 K): E(red$_{1/2}$) –1.01; E(ox$_1$) +0.92; ΔE 1.93.[8,9] The substituent effect of a *meso*-vinyl substituent in the *monomer* is small, i.e. *meso*-vinylNiOEP: E(red) –1.27 (irrev.); E(ox) +0.86; ΔE 2.13; NiOEP: E(red) –1.30 (irrev.); E(ox) +0.90; ΔE 2.20.
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18 A strong broad band (λ_{max} 775 nm) was reported for *tetraprotonated* **1**.[10] This was confirmed in the present work.
19 This is despite the shorter centre-to-centre distance in the *cis*-isomer. As also noted in ref. 17, the spectra of Ni$_2$**1** recall those of the "strongly-coupled" MP$_2$ sandwich complexes of M(IV) (M = Zr, Hf, U, Th), which exhibit strong interporphyrin communication mediated by the metal ion orbitals.[20] An alternative suggestion from Chirvony and Gurinovich assigns the additional bands to a particular conformational isomer about the *meso*-C–CH=CH–*meso*-C unit.[21]
20 For example, see O. Bilsel, J. Rodriguez, S. N. Milam, P. A. Gorlin, G. S. Girolami, K. S. Suslick, and D. Holten, *J. Am. Chem. Soc.*, **114**, 6528 (1992).
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22 Senge *et al.* reported the slow (overnight at 120 °C) thermal isomerisation of Ni$_2$**2** to Ni$_2$**1**,[2] whilst the equilibration of the free bases H$_4$**1** and H$_4$**2** has also been studied.[12] These processes are much less facile than the electrochemical isomerisation.