

Voltammetric and UV to Near-IR Spectroelectrochemical Characterization of the *meso,meso'*-Buta-1,3-diyne-Bridged Octaethylporphyrin Dimers $\{[M(OEP)](\mu-C_4)[M(OEP)]\}$ ($M_2 = H_4, Co_2, Ni_2, Cu_2, Zn_2, Pd_2, Pt_2, Co/Ni,$ and Ni/Zn), in their Neutral, Mononegative, and Dinegative Oxidation States

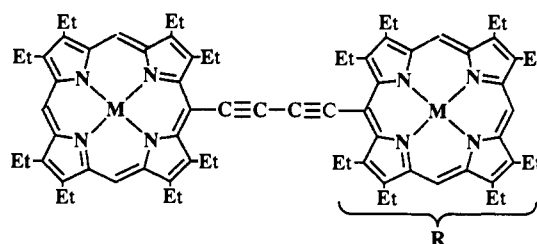
Dennis P. Arnold^{*,†} and Graham A. Heath[‡]

Centre for Instrumental and Developmental Chemistry
Queensland University of Technology
G.P.O. Box 2434, Brisbane, Australia 4001
Research School of Chemistry
Australian National University
Canberra, Australia 0200

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The binuclear pigments $\{[M(OEP)](\mu-C_4)[M(OEP)]\}$ (I) were first prepared by Arnold *et al.*,¹ who recently announced an improved synthesis of the original Ni₂ complex and its conversion to the free base, M₂ = H₄.² Porphyrin dimers of various structures are under close study through their relevance to the mechanism of photosynthesis,³ their potential applications in "molecular electronics",⁴ and the intrinsic interest of such proximally paired chromophores.⁵ To achieve bridge-mediated communication between porphyrin centers, Crossley^{4a,b} and others⁶ have designed coplanar dimers linked by fused aromatic rings. Alternatively, one or more disubstituted aromatic rings may be used as rigid spacers, but conjugation in such systems is obstructed by mutual crowding between atoms of the bridge and those around the porphyrin periphery.^{3c,7} In contrast, the butadiyne bridge is strictly linear yet sterically nondemanding and rotationally flexible with respect to conjugation between the porphyrin π -systems. Structure I therefore embodies a quite distinct and complementary principle for porphyrin oligomerization. Furthermore, substituted diacetylenes are important in their own right because of their solid-state polymerization, electrical conductivity, and nonlinear optical properties,⁸ and the present derivatives I are exceptional in bearing redox-active porphyrin termini.

To probe the degree of interporphyrin communication in I, we have incorporated a range of metal ions of varying electronegativity: M₂ = (Ni₂), Pd₂, Pt₂, Co₂, Cu₂, Zn₂, Ni/Zn, and Ni/Co (Table I)^{9,10} and determined their stepwise electrode potentials (a classical index of interaction in binuclear systems¹¹). We have



I: R as shown; II: R = -C₆H₅ and M = Ni

also characterized the electrogenerated reduced species I^{•-} and I²⁻ by their absorption spectra¹² (300–3200 nm).

In dichloromethane, the dimers show two closely-spaced reversible reductions whose resolution improves upon cooling, typified by the voltammetry of I, M₂ = Ni₂, in Figure 1. The dimer reductions are clearly porphyrin-centred (excepting M = Co) but *ca.* 400 mV easier than reduction of the corresponding monomeric [M(OEP)] complexes, due partly to the electronic influence of the diyne substituent. Two corresponding oxidations are observed at 20 °C, although the electrode response becomes complex at -40 °C through aggregation of the electrogenerated cations. The overall HOMO–LUMO gap (estimated by $\Delta E = E_{ox}^0 - E_{red}^0$) is 1.79 eV for the binuclear Ni₂ complex, i.e., ΔE has contracted by only 0.22 V compared to the appropriate model monomer $\{[M(OEP)](\mu-C_4)[C_6H_5]\}$ (II).¹³ Moreover, the separation of successive reductions in I, typically 60–100 mV, contrasts with the *ca.* 300 mV observed in fused coplanar diporphyrins.^{4a,14} Finally, the metal-dependent variation in reduction potentials for M₂ = Ni, Pd, Pt, etc. (Table I) follows the pattern for unperturbed [M(OEP)] complexes measured under comparable conditions.¹⁵

The electronic absorption spectra of complex I, M₂ = Ni₂, and its radical anion I^{•-} and dianion I²⁻ are shown in the Figure. The reduced states were selectively characterized *in situ* using a cryostatic optically transparent thin-layer electrogenerative (OTTLE^{12b}) cell. Very similar spectral progressions are seen for the Ni₂, Cu₂, Pd₂, Pt₂, and Ni/Zn complexes. The reduction products are indefinitely stable under these conditions, and I is recovered completely when the potential is adjusted to -0.6 V. The spectra of I^{•-} contain a strong band near 11 000 cm⁻¹ (ϵ *ca.* 6 × 10⁴ M⁻¹ cm⁻¹). Familiar porphyrin radical anions also absorb in this general region though less intensely,¹⁶ and so does

(9) Homobimetallic derivatives were prepared by standard methods applicable for monoporphyryns;¹⁰ the heterobimetallic complexes were obtained using Zn(OAc)₂ or Co(OAc)₂ treatment of the species I, M₂ = Ni, H₂, itself prepared from I, M₂ = H₄, by treatment with Ni(acac)₂ in CHCl₃. Complexes were purified by column chromatography on silica gel and recrystallization from CHCl₃/CH₃OH and were characterized by NMR and FAB mass spectroscopy, elemental analysis (C, H, N), and by the voltammetric and spectroelectrochemical studies. Synthesis of the new derivatives was announced at the RACI 9th National Convention, Monash University, Melbourne, December 1992 (Inorganic Division Abstracts TI-23).

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(13) Compound II was prepared by coupling (bromoethynyl)benzene with *meso*-ethynylNi(OEP), using palladium(0) catalysis; see similar examples in Arnold, D. P.; Nitschinsk, L. *J. Tetrahedron Lett.* 1993, 34, 693–696. The bathochromic effects of multiple *meso*-ethynyl substituents have also been reported, see Anderson, H. L. *Tetrahedron Lett.* 1992, 33, 1101–1104.

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[†] Queensland University of Technology.

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Table I. Selected Electrochemical and Spectroscopic Data (E° in V, ν_{\max} in cm^{-1})^a

compound	$E^\circ(\text{ox}_1)$	$E^\circ(\text{red}_1)$	$E^\circ(\text{red}_2)$	$\Delta E(\text{ox}_1 - \text{red}_1)$	$\nu_{\max}/\text{neutral}^b$	$\nu_{\max}/\text{radical anion}$	$\nu_{\max}/\text{dianion}$
I, $M_2 = H_4$	+0.92	-0.89	-0.96	1.81	21 050	10 740, 4140	9430
Ni ₂	+0.86	-0.93	-1.03	1.79	20 750, 16 240	11 460, 4600	10 080
Pd ₂	+0.90	-0.98	-1.04	1.88	21 210, 17 010	11 800, 4500	9660
Pt ₂	+0.92	-1.00	-1.07	1.92	21 650, 17 290	12 210, 4500	9740
Cu ₂	+0.81	-1.04	-1.07	1.85	20 840, 16 490	11 630, 4500	9820
Zn ₂	+0.67	-1.3 ^c	-1.3 ^c	ca. 1.95	20 620, 16 320 ^d	ca. 12 000 br	9470
Ni/Zn	+0.68	-1.06	-1.33	1.74	20 710, 16 290 ^d	11 600, 6100	9770
Co/Ni	+0.96 ^{c,e}	-0.75 ^e	-1.13	1.71 ^e	20 860, 16 300	10 050 ^f	
Co ₂	ca. 0.95 ^{c,e}	-0.74 ^{c,e}	-0.74 ^{c,e}	1.65 ^e	21 060, 16 490		
II, M = Ni	+0.97 ^g	-1.04 ^g	-1.54	2.01 ^g	22 880, 16 530	11 100	

^a Conditions: spectra of neutral species, 293 ± 2 K; spectroelectrochemistry and voltammetry, CH_2Cl_2 , 0.5 M Bu_4NPF_6 , 233 ± 2 K, Pt working electrode, E° vs Ag/AgCl, Fc/Fc⁺ couple at +0.55 V. ^b For I, this refers to first component of Soret band and, where metalated, to $Q(0,0)$. ^c Unresolved. ^d Low-frequency shoulder also present. ^e Oxidation may be $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$, reduction is $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$. ^f Refers to $\text{Co}^{\text{I}}, \text{Ni}^{\text{II}}$ radical, $\text{I}^{\cdot-}$. ^g For NiOEP under comparable conditions: $E^\circ_{\text{ox}} + 0.92$, $E^\circ_{\text{red}} -1.32$; ΔE 2.24 V.

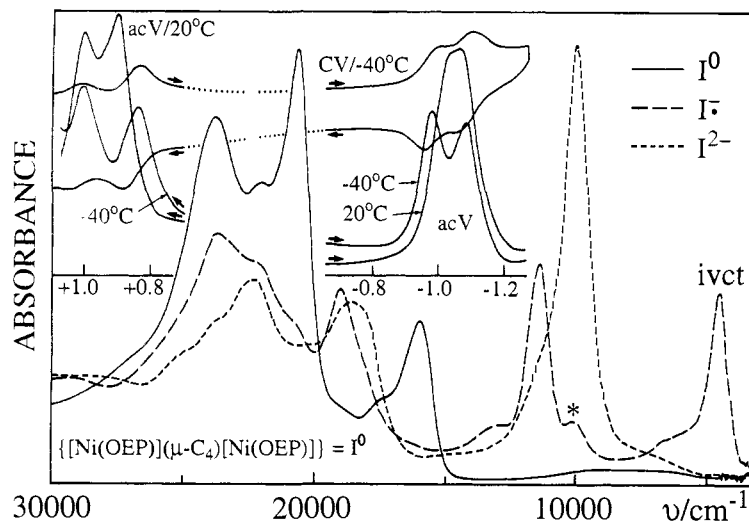


Figure 1. Optical spectra of I, $M_2 = \text{Ni}_2$, and its electrogenerated anions in CH_2Cl_2 at -40°C . I (—); $\text{I}^{\cdot-}$ (---) at -0.98 V; “ivct”, see text; * = <10% of I^{2-} ; I^{2-} (· · ·) at -1.15 V. The inset shows the voltammetry of I, $M_2 = \text{Ni}_2$, in CH_2Cl_2 (vs Ag/AgCl): acV = alternating current mode (205 Hz), scan rate 20 mV s^{-1} ; CV = cyclic dc mode, scan rate 100 mV s^{-1} .

monomeric $\text{II}^{\cdot-}$ (ϵ ca. $1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). A further striking feature of most of the $\text{I}^{\cdot-}$ spectra is the near-IR absorption band at ca. 4500 cm^{-1} (ϵ ca. $5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which we assign to electronic promotion within the π -system of the intermediate-valence diporphyrin. A similar band is seen for the $\text{H}_4 \text{I}^{\cdot-}$ species. The designated “ivct” band is absent for I^{2-} and for monomeric $\text{II}^{\cdot-}$. It moves to higher energy as required in the Ni/Zn heterometalated radical anion.¹⁷ Apart from the cobalt-containing derivatives which undergo reduction at the metal rather than the macrocycle, only $\{[\text{Zn}(\text{OEP})](\mu\text{-C}_4)[\text{Zn}(\text{OEP})]\}^{\cdot-}$, which has the most negative $E^\circ(\text{red}_1)$, is optically distinctive (Table I). Even so, $\{[\text{Zn}(\text{OEP})](\mu\text{-C}_4)[\text{Zn}(\text{OEP})]\}^{2-}$ returns to the general pattern. For I^{2-} , the most prominent feature is an exceptionally

(17) Comparing Ni_2 with Ni/Zn, the gap between red_1 and red_2 increases by 0.17 V (Table I) and the ivct band is blue-shifted by 1500 cm^{-1} (0.175 eV) and broadened ($\Delta\nu_{1/2}$ $1000 \rightarrow 2600 \text{ cm}^{-1}$). A similar band is predicted from ΔE° values for the $\text{Co}^{\text{I}}/\text{Ni}^{\text{II}}$ radical anion to appear at ca. 8000 cm^{-1} , and indeed the $10\,050\text{-cm}^{-1}$ band for this species has a broad tail in such a region.

intense band ($\epsilon > 10^5$ for the Ni_2 complex, and even more intense for the Pd_2 and Pt_2 analogues) near $10\,000 \text{ cm}^{-1}$, which probably corresponds to the nearby band in monomeric $\text{II}^{\cdot-}$ (equivalent in oxidation state to I^{2-}) and likewise to the comparable band in semireduced $\text{I}^{\cdot-}$.

We conclude that the frontier orbitals of such diacetylene-bridged diporphyrins show only weak interporphyrin bonding in the ground state. However, strong cooperative effects are evident in the optical spectra of the reduced species $\text{I}^{\cdot-}$ and I^{2-} , most notably in the emergence of unprecedented, intense absorption bands near 1000 nm , within the domain of the Nd/YAG laser. Studies aimed at establishing the relationship between electronic coupling and molecular conformation in I and in related oligomers are continuing.

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