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Remarkable homology in the electronic spectra of the mixed-valence cation and anion radicals of a conjugated bis(porphyrinyl)butadiyne†

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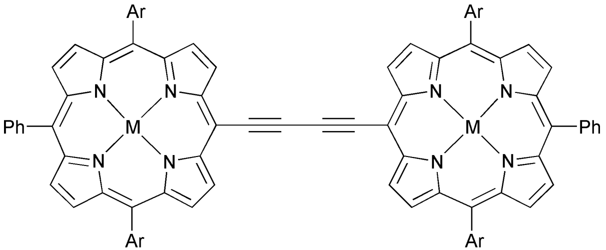
The π-radical cation and anion of the dizinc complex of a bis(triarylporphyrinyl)butadiyne, 1^+ and 1^-, respectively, display remarkably similar near-IR signatures, with intense bands near 1000 and 2500 nm, as predicted by the appropriate frontier-orbital model for inter-porphyrin coupling across the conjugated bridge.

Bis- and oligo(porphyrins) conjugated through alkyne-containing bridges linked directly to the *meso* carbons display unique spectroscopic and redox properties, making them promising candidates for applications in non-linear optics and molecular electronics. Their structural and photophysical properties have been investigated in detail by Anderson,[1] Therien[2] and others.[3]

Our work has focused on bis(octaethylporphyrin) systems of the form MOEP–C_4–MOEP.[4] We have systematically varied the metal ion M in the parent systems[4c,g] and explored the consequences of extending the conjugated bridge.[4b,e,f] A distinctive contribution is the *in situ* examination of UV to IR absorption spectra of the electrogenerated mono- and dianions of these bis(porphyrins).[4c,f,g] In both series, remarkably intense near- to mid-IR bands exist, which we assigned to transitions involving the newly-occupied π-orbitals of the reduced forms. Instability and apparent aggregation frustrated attempts to examine the corresponding cations. To address this, we designed a new series of bis(porphyrins) in which the 15,15′-*meso* carbons are protected by phenyl groups and the porphyrin faces are encumbered by *tert*-butyl groups on the lateral aryl substituents. The IR/near-IR spectra of the cation and anion radicals derived from the dizinc complex **1** display a remarkable homology (Fig. 1), fulfilling an important prediction of our earlier two-porphyrin eight-orbital model for inter-porphyrin interactions.

The conjugated bis(porphyrin) **1**‡ was prepared by *meso*-bromination of diaryl(phenyl)porphyrin free base, insertion of zinc(II), Pd/Cu catalysed coupling with trimethylsilylethyne, deprotection with fluoride, then oxidative coupling of the ethynyl porphyrin using copper(II) acetate in pyridine.[2a,3a,4e] The diaryl(phenyl)porphyrin was prepared from 5,15-bis(3′,5′-di-*tert*-butylphenyl)porphyrin by the method of Senge and Feng.[5] There are only two previous examples of bis(*triaryl*porphyrinyl) butadiynes.[6] The optical spectrum of **1** in CH_2Cl_2 or $CHCl_3$ resembles those of similar butadiyne-linked dizinc bis(porphyrins) of the 5,15-diarylporphyrin type,[2b] except that the extinction coefficients for **1** are more than double those of the diphenylporphyrin (DPP) complex.[2b] Addition of electrolyte, 0.5 M Bu_4NPF_6, causes red-shifts (400–900 cm^{-1}) and minor changes in relative band intensities of **1**.

Binuclear **1**§ displays similar voltammetric features to those reported by Therien and coworkers for the DPP analogue,[2a] and by ourselves for a range of OEP derivatives.[4c,f,g] There are two ring-centred one-electron oxidations separated by *ca.* 110 mV, representing successive formation of the monocation and dication, and a corresponding pair of reductions separated by *ca.* 100 mV.¶ The voltammetric HOMO–LUMO gap $\Delta E = E^0_{ox} - E^0_{red}$ of 1.85 V is typical of butadiyne-linked porphyrin dimers.[2a,4c,f,g]



1: M = Zn, Ar = 3,5-di-t-butylphenyl

The new oxidation states implied by voltammetry were examined *in situ* from the UV to the mid-IR (300–3200 nm) at 220 K in an optically transparent thin-layer electrogenerative (OTTLE[7]) cell. Fig. 2 illustrates the progressive oxidation of **1** to 1^+. Neutral **1** could be potentiostatically retrieved and recycled as desired. The OTTLE progressions for **1** to 1^- and for 1^- to 1^{2-} were equally well-defined and reversible at this temperature.†‖ EPR spectra measured *in situ* confirm the paramagnetism of 1^+ and 1^-. The axial signal for 1^- (*g* 2.003, 1.994) resembles that of (NiOEP–C_4–NiOEP)$^-$, also reported for the first time.† The influence of binuclearity on the EPR signal is not obvious, unlike its profound effect on the optical spectra, because monomeric porphyrin $S = \frac{1}{2}$ paramagnets are already innately axial (whether the splitting is resolved or not)

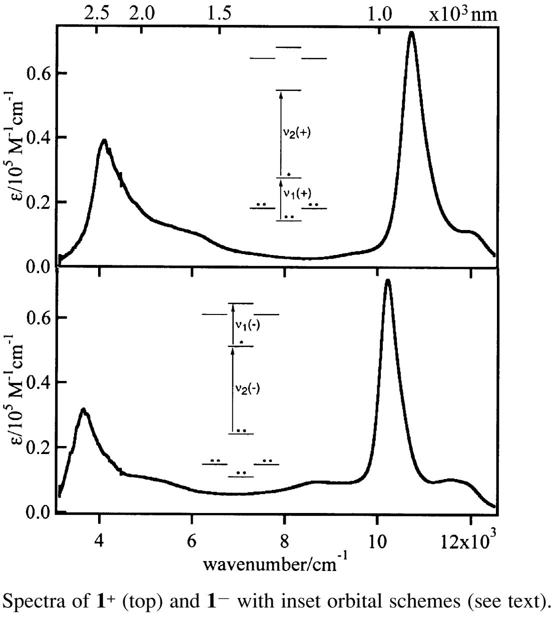


Fig. 1 Spectra of 1^+ (top) and 1^- with inset orbital schemes (see text).

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† Electronic supplementary information (ESI) available: Fig. S1: voltammetry of **1** at 233 K; Fig. S2 and S3: OTTLE-cell progressions of **1** to 1^- and 1^- to 1^{2-}, respectively; Fig. S4: EPR spectra. See http://www.rsc.org/suppdata/cc/b2/b200803n/

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and their symmetry may be reduced further by intrinsic and extrinsic factors.[8]

In the IR/near-IR region, where **1** is transparent, $\mathbf{1}^+$ has two intense bands denoted $\nu_1(+)$ (4090 cm^{-1}, ε = 40 000) and $\nu_2(+)$ (10710 cm^{-1}, 74 000), as shown in Fig. 1. The strikingly similar spectrum of $\mathbf{1}^-$ shows bands $\nu_1(-)$ (3635 cm^{-1}, 32 000) and $\nu_2(-)$ (10210 cm^{-1}, 73 000). Monomeric porphyrin radical cations and anions also have informative but much weaker near-IR bands which continue to attract close attention.[4g,9]

From our previous data on MOEP–C_4–MOEP anions, we constructed a semi-quantitative 'two-porphyrin eight-orbital' scheme based on the experimental band energies and the symmetry properties of the monoporphyrin orbitals that either interact strongly across the conjugated bridge (*x*-orbitals) or are orthogonal to this axis (*y*-orbitals).[4g] The scheme is in accord with MO calculations on these systems.[2e,4d] We designate that neutral **1** possesses eight frontier electrons (8e) and we are seeking to characterise mixed-valence $\mathbf{1}^+$ (7e) and $\mathbf{1}^-$ (9e), the former class being unprecedented. The orbital occupancies and consequent transitions are shown as insets in Fig. 1. The optical results obtained for the anions of **1** parallel the 8e/9e/10e progression gathered for our OEP series and reinforce the generic application of the scheme to the reduced states of both triaryl- and octaethylporphyrin with respect to electronic coupling and optical properties. The obvious homology between the almost superimposable (within 500 cm^{-1}) two-band IR/near-IR optical spectra for $\mathbf{1}^+$ and $\mathbf{1}^-$ is quite extraordinary.

Qualitatively, it underscores the formal analogy between the transitions demanded in 7e and 9e systems, namely the ν_2 ('Q-band') transition is available to both, and the 'basement' π/π $\nu_1(+)$ promotion in the 7e cation is replaced by the corresponding 'upper-storey' π^*/π^* $\nu_1(-)$ low-energy promotion of the 9e anion. The typical Q-band profile of a neutral porphyrin is maintained upon both oxidation and reduction (Figs. 1 and 2).

Quantitatively, the spectral match of Fig. 1 demonstrates that (i) the energy gaps are broadly insensitive to successive changes in oxidation state; (ii) ring/ring coupling through the conjugated bridge (probed directly by ν_1) is nearly identical in the π and π^* levels, as we had assumed elsewhere,[4g] and as borne out by calculations on both NiP–C_4–NiP (unsubstituted)[4d] and ZnDPP–C_2–ZnDPP[2e] neutral species. We note that electron-pair correlation terms tend to cancel systematically in transitions that connect a doubly-occupied level with a singly-occupied one, so that $\nu_2(-)$ converges on 'innocent' $\nu_2(+)$, while both $\nu_1(+)$ and $\nu_1(-)$ faithfully map the respective MO spacings.[10]

In summary, switching from β-octaethyl to *meso*-triaryl substitution does not alter the distinctive near-IR spectral signatures of the binuclear 9e and 10e anions and in addition has allowed us to access the corresponding dizinc monocation, the first representative of the class of '7e' conjugated bis(porphyrin) pigments. The remarkable 7e/9e congruency strongly reinforces the utility of a simple frontier-orbital model and the discovery of radically new IR-absorbing chromophores demonstrates the merit of pursuing such redox-altered compounds.

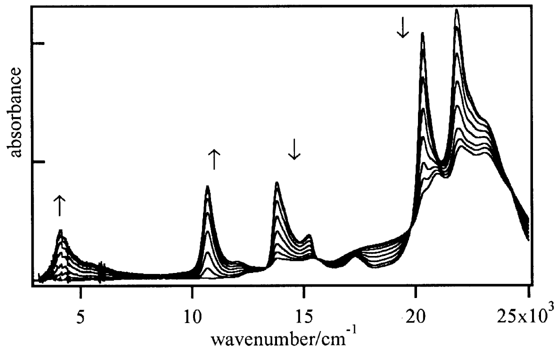

Fig. 2 Spectral progression during the one-electron oxidation of **1**.

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Notes and references

‡ *Characterisation data* for **1**: δ_H ($CDCl_3$) 10.06, 9.18, 8.96, 8.90 (all d, β-H), 8.22 (dd, *o*-H of 15,15′-Ph), 8.15 (d, *o*-H of Ar), 7.86 (t, *p*-H of Ar), 7.76 (m, *m,p*-H of Ph), 1.60 (s, Bu^t); UV/VIS (CH_2Cl_2): λ_{max}/nm (log ε) 678 (4.79), 628 (4.54), 565 (4.33), 481 (5.28), 446 (5.35), 443(sh) (5.29), 424(sh) (5.15); FAB-MS: maximum of cluster at *m*/*z* 1699 (M^+ requires 1698). Anal. Calc. for $C_{112}H_{110}N_8Zn_2\cdot0.5CH_2Cl_2$ C, 77.59; H, 6.43; N, 6.43. Found C, 77.68, H, 6.62, N, 6.33%.

§ *Voltammetric data* for **1**: E^0 (ac voltammetry at 20 mV s^{-1} on Pt, 0.5 M $TBAPF_6/CH_2Cl_2$, 233 K, *vs.* Ag/AgCl in CH_2Cl_2, Fc/Fc^+ at +0.55 V): +0.83, + 0.72, −1.13, −1.23 V.

¶ Closely-spaced redox potentials are fully compatible with strong coupling in the intermediate hemi-bonded states as long as the ring/ring conjugation is maintained in the respective two-electron-bonded dianion or dication. In such cases, the resonance energy contributions to disproportionation systematically cancel.[4g] On spectroscopic evidence, we regard these 7e and 9e mixed-valence species as strongly-coupled (Class III) systems.

‖ The OTTLE progressions confirm redox equilibration of the species concerned, with discernible disproportionation of the odd-electron states.

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