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Fusion and planarization of a quinoidal porphyrin dimer[†]

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The crystal structure, near-infrared spectrum and electrochemistry of a quinoidal triply-linked porphyrin dimer are compared with those of its singly-linked precursor; fusing the two porphyrins planarizes the π -system and reduces the optical HOMO–LUMO gap while increasing the gap between the first oxidation and reduction potentials.

Near infrared (NIR) radiation has many important technological applications,¹ and there is a need for new optoelectronic materials operating in this wavelength region (800–2000 nm). Conjugated porphyrin oligomers^{2–5} are promising materials in this context, and recently two strategies have been developed for shifting their absorption spectra far into the NIR: we have synthesized strongly conjugated quinoidal porphyrin dimers,³ while Osuka and coworkers have created directly fused porphyrin tapes with *meso–meso-*, β – β - and β – β -links.^{4,5} Here we discuss the synthesis, electronic structure and crystal structure of a porphyrin dimer **1** which simultaneously exemplifies both these design strategies.

Previously we reported the synthesis of quinoidal porphyrin dimer **2** from dibromo dimer **3** as shown in Scheme 1.³ Steric repulsion between the inner β -hydrogens forces this molecule into a non-planar conformation. The ¹H and ¹³C NMR spectra of **2** show that the two porphyrin macrocycles are not coplanar, but do not allow one to distinguish between the two possible non-planar geometries (D_2 twist or C_{2h} double fold). Molecular mechanics calculations predicted a twisted D_2 conformation, however single crystal X-ray diffraction has now revealed that the molecule has the alternative C_{2h} conformation in the solid state, as shown in Fig. 1.‡ This is the structure of the pyridine complex, with one molecule of pyridine coordinated to each zinc atom. The molecule has a crystallographic inversion centre

 \dagger Electronic supplementary information (ESI) available: synthetic procedures. See http://www.rsc.org/suppdata/cc/b2/b204265g/

and there is almost a plane of symmetry through both zinc atoms, perpendicular to both macrocycles, giving the molecule virtual C_{2h} symmetry. The central $C_{meso}=C_{meso}$ bond length is 1.38 Å, and the tetra-substituted alkene unit is planar (maximum deviation ± 0.03 Å for six carbon atoms). The mean planes of the two macrocycles are parallel, with a separation of 2.79 Å, and the two π -systems almost overlap, with a β -C··· β -C intermacrocycle distance of 3.05 Å. The ends of the molecule are distorted to minimize steric interaction between the nitrile groups and the outer β -hydrogens, as observed in related structures.^{3,6}

The non-planar conformation of **2** probably disrupts the conjugation, so we sought to fuse and planarize the molecule by removing the four central hydrogens, to give compound **1**. We explored both routes shown in Scheme 1. Oxidation of dibromodimer **3** under Osuka's scandium(III) triflate/DDQ conditions⁵ gave the fused dibromo-dimer **4**, but in low yield (9%) due to incomplete reaction (45% of **3** was reisolated). Quinoidalization of **4** using Takahashi coupling conditions^{3,6} proceeded smoothly to give the target compound **1** in 84% yield. Surprisingly, oxidation of the quinoidal dimer **2** worked much better than oxidation of **3**, giving **1** in 83% yield. The strain in



Fig. 1 Side view of the structure of $2 \cdot (\text{pyridine})_2$ omitting aryl substituents (50% probability ellipsoids).



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Scheme 1 Reagents: (a) NaCH(CN)₂, [Pd₂(dba)₃], CuI, PPh₃ then NIS, (b) Sc(OTf)₃, DDQ. (Ar = 3,5-Bu²₂C₆H₃).



Fig. 2 Two views of the structure of $1 \cdot (MeOH)_2$, (A) omitting methanol and (B) omitting aryl substituents (50% probability ellipsoids).



Fig. 3 Absorption spectra of 1, 2 and 4 in 1% C₅H₅N-CH₂Cl₂.

2 apparently facilitates its oxidation, making this the best route to **1**.

The crystal structure of the methanol complex of **1** is shown in Fig. 2.‡ This compound crystallizes as a tight bimolecular aggregate; the two molecules in each aggregate are related *via* an inversion centre. The 'naphthalene' core of the dimer is planar to within ± 0.04 Å. The central C_{meso}=C_{meso} bond length is 1.43 Å, and although this is formally a double bond it is not significantly shorter than the formally single C_{meso}-C_{meso} bonds in Osuka's triply linked dimers (analogs of **4** with aryl instead of bromine substituents).⁴ The plane-plane separation at the centre of the aggregate is 3.4 Å and the closest intermolecular contact is between a nitrile nitrogen and the central carbon of the dicyanomethylene unit (N···C distance = 3.13 Å).

The electronic absorption spectra of dimers 1, 2 and 4 are compared in Fig. 3. As expected, the absorption of 1 (λ_{max} = 958 nm; ε = 9.4 × 10⁴ M⁻¹cm⁻¹) is sharper and more redshifted than that of 2 (λ_{max} = 780 nm; ε = 6.9 × 10⁴ M⁻¹cm⁻¹), but it is surprising that dimer 4 exhibits the longest



Fig. 4 Cyclic voltammogram of 1.§

wavelength absorption ($\lambda_{max} = 1139$ nm; $\varepsilon = 1.1 \times 10^4$ M⁻¹cm⁻¹). The unexpected blue shift on quinoidalization of **4** to **1** might be due to the greater bond-length alternation in quinoidalized porphyrins.

While planarization of 2 to 1 results in a dramatic decrease in the optical HOMO–LUMO gap, the electrochemical gap between the first oxidation and reduction potentials $(E_1^{\text{Ox}} - E_1^{\text{Red}})$ increases from 0.53 to 1.00 V on conversion of 2 to 1. Compound 1 displays reversible oxidation $(E_1^{\text{Ox}} = 0.35 \text{ V})$ and reduction $(E_1^{\text{Red}} = -0.65 \text{ V})$ waves, whereas the redox processes of 2 are poorly reversible, but can be measured by square wave voltammetry $(E_1^{\text{Ox}} = 0.10 \text{ V}; E_1^{\text{Red}} = -0.43 \text{ V}).$ The easier oxidation and reduction of 2 probably reflects the strain in the neutral form which would be released if oxidation or reduction converts the central C=C link to a single bond, allowing the macrocycles to twist to orthogonal orientations. The first and second one-electron oxidations of 1 are separated by 0.25 V, whereas the first and second one-electron reductions almost coincide as seen in Fig. 4.

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Notes and references

‡ *Crystal data* for 1: crystals grown from CHCl₃–CH₃OH, C₁₀₂H₉₆N₁₂Zn₂·8CH₄O·3H₂O, *M* = 1931.13, triclinic, space group *P*1, *a* = 14.6863(2), *b* = 17.3636(2), *c* = 22.3909(3) Å, *α* = 110.2640(4), *β* = 98.4021(4), *γ* = 96.5091(9)°; *V* = 5215.6 Å³, *Z* = 2, *μ* = 0.524 mm⁻¹, *R* = 0.0648, *R*_w = 0.0676, *I*₀ = 13933 observed [*I* > 3.0*σ*(*I*)] reflections out of *N* = 19263 unique, GOF = 1.0537.

Crystal data for **2**: crystals grown from CHCl₃–pyridine–pentane, $C_{102}H_{100}N_{12}Zn_2 \cdot 2C_5H_5N \cdot 4CHCl_3$, M = 2260.49, triclinic, space group $P\bar{1}$, a = 14.4288(3), b = 15.0483(3), c = 15.3810(4) Å, $\alpha = 82.9828(7)$, $\beta = 73.3295(7)$, $\gamma = 63.312(1)^\circ$; V = 2858.4 Å³, Z = 1, $\mu = 0.753$ mm⁻¹, R = 0.0534, $R_w = 0.0645$, $I_o = 6723$ observed $[I > 3.0\sigma(I)]$ reflections out of N = 10015 unique, GOF = 1.0480.

Both data sets were collected on an Enraf Nonius Kappa CCD diffractometer; T = 150 K, λ (Mo-K α) = 0.71073 Å. CCDC reference numbers 185524 and 185525. See http://www.rsc.org/suppdata/cc/b2/b204265g/ for crystallographic data in CIF or other electronic format.

§ Redox potentials were measured by square wave and cyclic voltammetry (0.1 V s^{-1}) in CH₂Cl₂ with 0.1 M Bu₄NPF₆ and a carbon working electrode, and are quoted relative to E_1^{Ox} of internal ferrocene.

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