

Synthesis and crystal structure of a push–pull quinoidal porphyrin: a nanoporous framework assembled from cyclic trimer aggregates†

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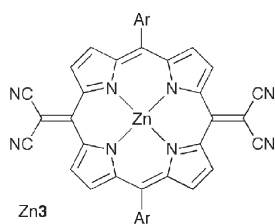
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A quinoidal porphyrin has been synthesised with such a curved π -system that π - π stacking leads to the formation of cyclic trimer aggregates in the crystal, which pack to generate cylindrical channels with an internal diameter of 1.0 nm.

Push–pull quinoidal chromophores generally exist in resonance with aromatic-zwitterionic canonical forms, often resulting in strong second-order nonlinear optical behaviour,¹ and leading to charge-transfer absorption bands at visible to near infrared wavelengths.^{2,3} For example, Otsubo's diphenoquinoid **1** (Fig. 1) shows a strong absorption band at 1045 nm, a remarkably long wavelength for a π -system of this size.² These results motivated us to explore the behaviour of push–pull quinoidal systems with porphyrinoid cores, as a strategy for distorting the electronic structure of the porphyrin, shifting the absorption further into the infrared and enhancing nonlinear optical effects.⁴ Here we report the first synthesis of a push–pull quinoidal porphyrin (**M2** where $M = 2H$, Ni and Zn , Scheme 1). In contrast to Otsubo's diphenoquinoid **1**, the aromatic-zwitterionic canonical form makes little contribution in these quinoidal porphyrins, and the HOMO–LUMO gaps of the push–pull systems **M2** are only slightly smaller than those of the pull–pull analogues **M3**.⁵ The crystal structure of **Zn2** has several extraordinary features: the chromophore is so highly curved that π - π stacking generates cyclic trimer aggregates, which pack to create a honeycomb of 10 Å diameter channels. Zinc porphyrin macrocycles line the walls of each channel, with chains of H-bonded methanol molecules, some with partial occupancy, streaming into the channel from each Lewis-acidic zinc site.



The push–pull quinoidal porphyrin **Ni2** was synthesised from the 5-bromo-15-formyl porphyrin **Ni4**⁶ as shown in Scheme 1, by thioacetal formation, Takahashi coupling^{5,7} and DDQ oxidation. This chemistry proceeds most cleanly with the nickel(II) complexes, and the product **Ni2** is readily demetallated with acid to afford the

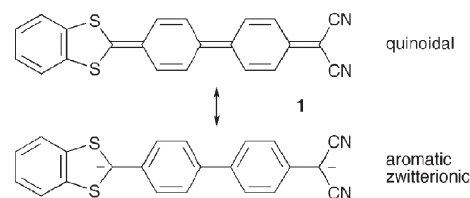
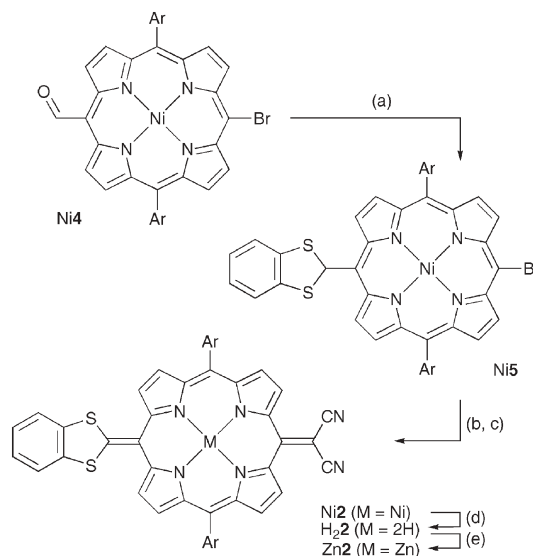


Fig. 1 Otsubo's push–pull diphenoquinoid **1**.



Scheme 1 Synthesis of the quinoidal push–pull porphyrins (Ar = 3,5-Bu₂C₆H₃). *Reagents and conditions:* (a) 1,2-benzenedithiol, TiCl₄, Na₂CO₃, 92%; (b) NaCH(CN)₂, [Pd₂(dba)₃], CuI, PPh₃, 42%; (c) DDQ, 94%; (d) H₂SO₄, TFA, 85%; (e) Zn(OAc)₂, 90% yield.

free-base **H22**, providing access to other metal complexes such as **Zn2**. The quinoidal characters of **Ni2**, **H22** and **Zn2** are immediately apparent from the lack of porphyrin aromatic ring current effects in their ¹H NMR spectra; the β -protons resonate at 6.8–7.6 ppm (*cf.* 8.2–9.5 ppm in a simple porphyrin) and the NH protons of **H22** appear at 11.9 ppm (*cf.* –3.0 ppm in a typical free-base porphyrin).

The absorption and emission spectra reveal several interesting differences in electronic structure between the push–pull **M2** and pull–pull **M3** systems. For example, the spectra of the zinc complexes are compared in Fig. 2. All of the observed absorption bands correlate well with those predicted by DFT calculations⁸ (see calculated transitions in Fig. 2 and MOs in Fig. 3). The longest

† Electronic supplementary information (ESI) available: details of spectroscopic data and DFT calculations. See <http://www.rsc.org/suppdata/cc/b5/b502776d/>

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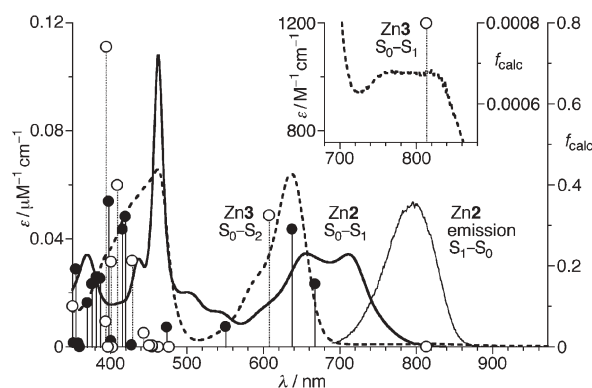


Fig. 2 Experimental and calculated absorption spectra of Zn2 (plain) and Zn3 (dashed), and the fluorescence spectrum of Zn2, in benzene containing 1% pyridine; calculated DFT excitation wavelengths and oscillator strengths (f_{calc}) are denoted by black and white circles respectively. The emission spectrum of Zn2 (excitation at 655 nm) is plotted on an arbitrary vertical scale. The insert shows an expansion of the absorption spectrum of Zn3.

wavelength (S_0-S_1) absorption of Zn3 is virtually forbidden (f_{calc} 0.0008; λ_{calc} 813 nm), and indeed this band is so weak that at first we overlooked it,⁵ but it appears reproducibly at 770–820 nm (ϵ 1000 M⁻¹ cm⁻¹, see insert in Fig. 2). The low oscillator strength of this transition explains why Zn3 is non-fluorescent. In contrast, Zn2 gives a clear fluorescence band (λ_{max} 795 nm) because its S_0-S_1 transition is allowed (f_{calc} 0.16), due to its lower symmetry. The HOMO and LUMO of both molecules are delocalised over the donor and acceptor groups, so these orbitals show the greatest change in energy, comparing Zn2 and Zn3. The calculated increase in HOMO and LUMO energy, and reduction in HOMO–LUMO gap, in Zn2 are consistent with the first oxidation and reduction potentials (Zn3: $E_1^{\text{Red}} = -0.71$ V, $E_1^{\text{Ox}} = 0.87$ V; Zn2: $E_1^{\text{Red}} = -1.15$ V, $E_1^{\text{Ox}} = 0.28$ V, all data recorded in CH₂Cl₂ with 0.1 M Bu₄NBF₄ relative to ferrocene; scan rate 0.1 V/s).

Crystals of the push-pull porphyrinoid Zn2 were grown by vapour diffusion of methanol into a chloroform solution.[†] The asymmetric unit contains three molecules of Zn2, and 21 molecules of methanol. Each zinc atom is ligated by a chain of hydrogen-bonded methanol molecules, with the O–H···O hydrogen bonds

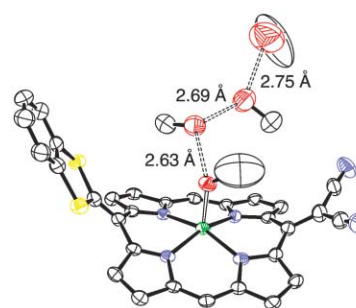


Fig. 4 Structure of Zn2, showing the O···O distances in a chain of H-bonded MeOH (omitting aryl substituents; 40% probability ellipsoids). The other two molecules of Zn2 in the asymmetric unit have similar geometries, although in these cases the methanol is more disordered.

becoming progressively longer on moving away from the Lewis-acidic zinc site, as illustrated in Fig. 4. The three crystallographically distinct molecules of Zn2 adopt the same conformation, and the bond lengths in the porphyrinoid core are very similar to those in Zn3,⁵ showing that Zn2 is quinoidal rather than aromatic. A contribution from the aromatic-zwitterionic canonical of Zn2 would result in an elongation of the C=C(CN)₂ and C≡N bonds,^{3,9} but comparison of the crystal structures of Zn2 and Zn3 gives no indication of an effect of this type. Evidently the aromatic stabilisation in the zwitterionic canonical form of Zn2 is insufficient to compensate for the energy of charge separation.

The conjugated π -system of Zn2 is severely nonplanar due to steric clashes between the β -hydrogens and sulfur atoms (mean H···S distance: 2.67 Å *cf.* 2.91 Å for sum of van der Waals radii) at one side, and between the β -hydrogens and nitrile carbons (mean H···C distance: 2.57 Å *cf.* 2.87 Å for sum of van der Waals radii) at the other. Similar distortions characterise the solid-state conformations of other quinoidal porphyrins such as Zn3,^{5,10} and of closely related push-pull anthraquinoids.³ The angle between the mean plane of the thioacetal benzene ring and that of the porphyrin core is about 120° (129.1°, 123.6° and 122.8° for the three molecules), so π - π stacking between these planes leads to the formation of a cyclic trimeric aggregate, as shown in Fig. 5. The aggregate has virtual C_{3h} symmetry, with each benzene ring stacking directly over the Zn–N–C–C–N ring of an adjacent porphyrin core, as illustrated in Fig. 5B. The shortest contact in

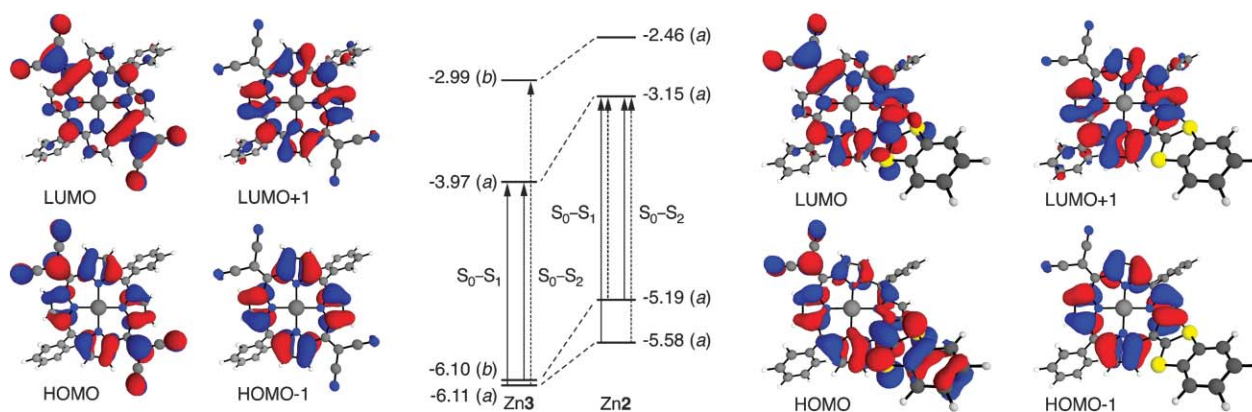


Fig. 3 Frontier orbitals of Zn3 (left) and Zn2 (right) from time-dependent DFT calculations (using Becke's three-parameter hybrid functional, B3LYP/6-31G(d)).⁸ Solid and dotted arrows denote the major and minor contributions of one-electron excitations respectively.

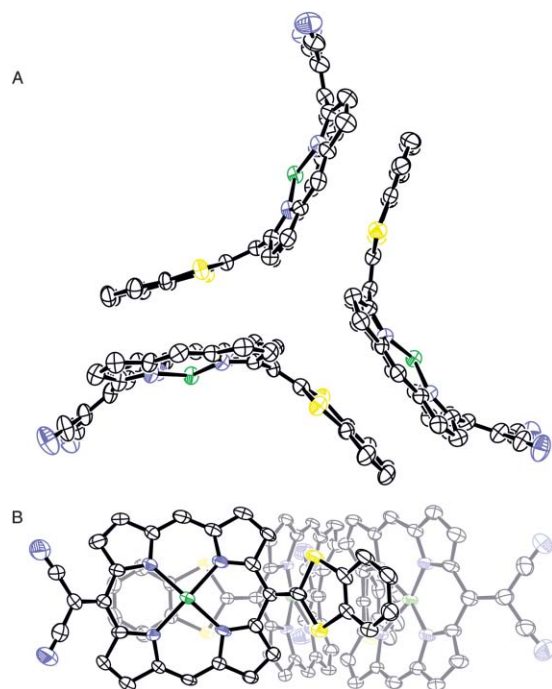


Fig. 5 Two views of the $(\text{Zn}2)_3$ aggregate, omitting coordinated methanol and aryl substituents; 50% probability ellipsoids.

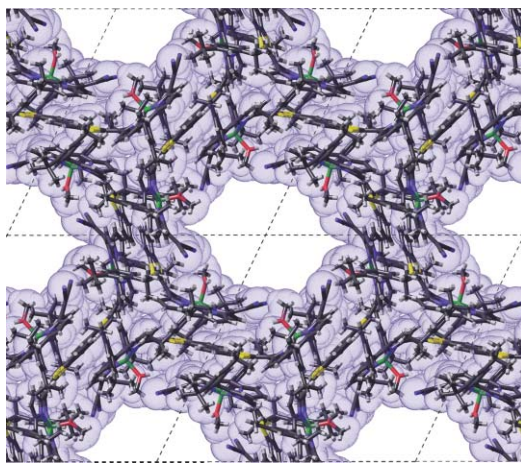


Fig. 6 Packing diagram for $\text{Zn}2$ showing the van der Waals surface, omitting methanol except where coordinated to zinc; an infinite projection along the a -axis.

each case is between a pyrrole nitrogen and a carbon atom of the benzene ring ($\text{C}\cdots\text{N}$ distances: 3.36, 3.43 and 3.44 Å, cf. 3.41 Å for the sum of the van der Waals radii). These aggregates pack to generate infinite methanol-filled channels (Fig. 6). The channels are large enough to accommodate a continuous cylinder of 10 Å diameter within the van der Waals surface. The planes of the porphyrin and the thioacetal benzene ring are parallel to the walls of the channels (Figs. 5A and 6 have the same orientation), and contacts between cyclic trimer aggregates are confined to the *meso*-3,5-di-*tert*-butylphenyl substituents. Although many other zeolite-like nanoporous organic frameworks have been reported, very few exhibit such large continuous channels.¹¹

In summary, we report the first synthesis of a quinoidal push–pull porphyrin. The NMR spectra, electronic absorption spectra, DFT calculations and crystal structure of this macrocycle show no significant contribution from the aromatic-zwitterionic canonical. The curved structure of the chromophore results in the formation of unusual cyclic trimer aggregates in the solid state, which pack into a remarkable honeycomb structure. The channels in this framework appear to be just large enough to accommodate a string of C_{60} molecules (van der Waals radius 10.5 Å).

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Notes and references

‡ Crystal data for $\text{Zn}2$: crystals were grown from $\text{CHCl}_3/\text{CH}_3\text{OH}$ and the structure was solved using synchrotron X-rays at Daresbury Station 9.8. $\text{C}_{58}\text{H}_{54}\text{N}_6\text{S}_2\text{Zn}\cdot 6.5\text{CH}_3\text{O}$, $M = 1172.8$, triclinic, space group $P\bar{1}$, $a = 20.792(3)$, $b = 24.707(3)$, $c = 25.188(3)$ Å, $\alpha = 63.913(2)$, $\beta = 84.532(2)$, $\gamma = 81.473(2)^\circ$; $V = 11486(3)$ Å³, $Z = 6$, $\lambda = 0.6932$ Å, $\mu = 0.42$ mm⁻¹, $T = 150$ K, $R = 0.0807$ for 18810 observed reflections [$I > 2\sigma(I)$] and $R_w = 0.2381$ for all 32471 unique reflections. CCDC 264994. See <http://www.rsc.org/suppdata/cc/b5/b502776d/> for crystallographic data in CIF or other electronic format.

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