

Push-Pull Quinoidal Porphyrins

Martin J. Smith,^a Iain M. Blake,^a William Clegg^b and Harry L. Anderson^{*a}Received 00th January 20xx,
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A family of push-pull quinoidal porphyrin monomers has been prepared from a *meso*-formyl porphyrin by bromination, thioacetal formation, palladium-catalyzed coupling with malononitrile and oxidation with DDQ. Attempts at extending this synthesis to a push-pull quinoidal/cumulenic porphyrin dimer were not successful. The crystal structures of the quinoidal porphyrins indicate that there is no significant contribution from singlet biradical or zwitterionic resonance forms. The crystal structure of an ethyne-linked porphyrin dimer shows that the torsion angle between the porphyrin units is only about 3°, in keeping with crystallographic results on related compounds, but contrasting with the torsion angle of about 35° predicted by computational studies. The free-base quinoidal porphyrin monomers form tightly π -stacked layer structures, despite their curved geometries and bulky aryl substituents.

Introduction

Organic π -systems with small HOMO-LUMO energy gaps have many potential applications as organic semiconductors and nonlinear-optical dyes because they are easily oxidized and/or reduced, and easily polarized by electric fields.¹ Quinoidal molecules have particularly small π - π^* gaps due to resonance with the aromatic singlet biradical form.^{2,3} If the structure has a 'push-pull' pattern of electron donor and acceptor groups then a zwitterionic resonance form can also contribute (Fig. 1), which can further reduce the energy gap between the frontier orbitals, shifting the absorption to longer wavelengths.⁴⁻⁹ The energy cost of breaking a double bond to form the biradical, and separating charge to form the zwitterion, are compensated by the gain in aromaticity in the core. The effects of quinoidalization are well illustrated by the UV-vis-NIR absorption spectrum of the cumulene-linked quinoidal porphyrin dimer **Zn₂1** (Fig. 2), which exhibits a strong absorption band at 1080 nm ($\epsilon = 1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), compared to a Q band at 724 nm ($\epsilon = 5.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) for the corresponding alkyne-linked aromatic porphyrin dimer.¹⁰ The original aim of the work presented here was to synthesize a push-pull quinoidal porphyrin dimer **M₂2**. Unfortunately, we were unable to isolate this target compound; however the project provided some fascinating insights into porphyrin chemistry. We synthesized a family of push-pull quinoidal porphyrin monomers, as models for the elusive push-pull dimers. The crystal structures of these quinoidal porphyrins

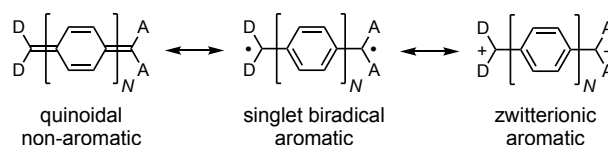


Fig. 1. Possible resonance structures of a quinoidal push-pull system (D and A are electron donor and acceptor, respectively).

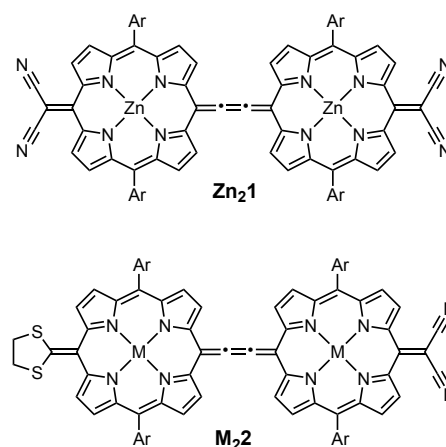


Fig. 2. Structures of the quinoidal dimer **Zn₂1** (reported in ref 10) and the elusive target of this study, **M₂2**. (Ar = 3,5 di-*tert*-butyl phenyl.)

show that they are extremely curved π -systems, yet, surprisingly, this curvature does not prevent them from packing into π -stacked assemblies. The crystal structure of an ethyne-linked porphyrin dimer shows that it forms a bimolecular aggregate in the solid state in which there is essentially no torsional twist between the two covalently linked porphyrin units, in contrast to the geometries of ethyne-linked porphyrin dimers predicted by DFT calculations, which have a torsion angle of about 35°.

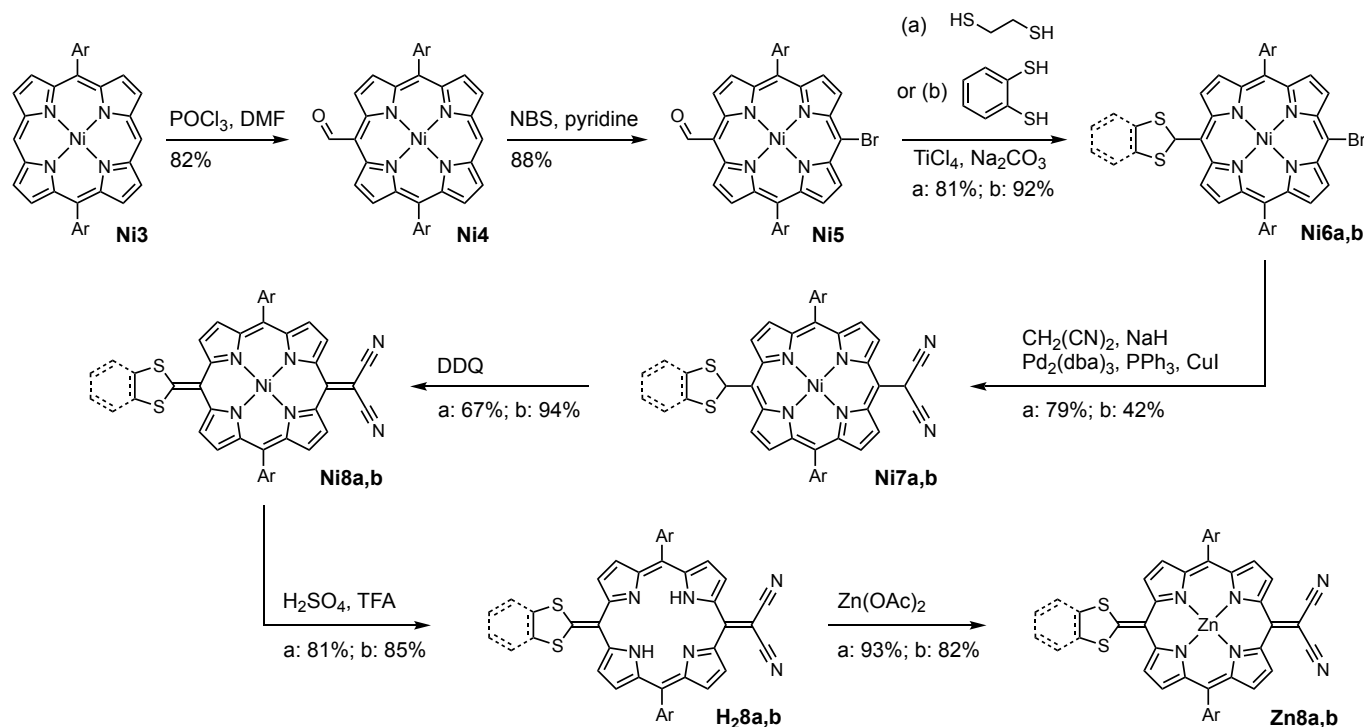
^a Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Oxford OX1 3TA, UK. E-mail: harry.anderson@chem.ox.ac.uk.

^b Chemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK. E-mail: bill.clegg@ncl.ac.uk.

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Scheme 1. Synthesis of the quinoidal porphyrin monomers **Ni8a**, **Ni8b**, **H₂8a**, **H₂8b**, **Zn8a** and **Zn8b**. (Ar = 3,5 di-*tert*-butyl phenyl.)

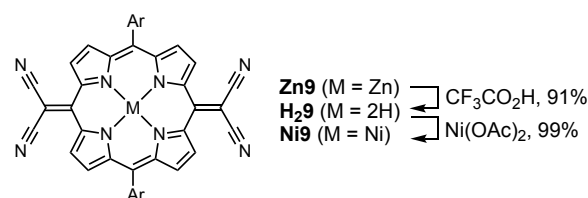
Several studies of quinoidal porphyrins have been published recently, motivated by the unusual redox activity and near-IR absorption spectra of these compounds, and by the possibility of forming stable singlet biradical ground states.¹¹ However, to the best of our knowledge, the work presented here is the first investigation of push-pull quinoidal porphyrins.^{†,12}

Results and Discussion

Synthesis and Characterization of Push-Pull Quinoidal Monomers

The chemistry of push-pull quinoidal porphyrin monomers was explored by synthesizing compounds with two types of electron donor: a) 1,3-dithiolane **M8a** and b) 1,3-benzodithiolane **M8b**, where M = Ni, Zn or H₂ (Scheme 1).^{†(12)} Vilsmeier formylation of nickel(II) porphyrin **Ni3** gave **Ni4** in excellent yield, as reported previously.¹³ Nickel porphyrins were used here to avoid demetalation. Bromination with NBS yielded **Ni5**. The plan was to condense this aldehyde with 1,2-ethanedithiol or benzene-1,2-dithiol to generate **Ni6a** or **Ni6b**, respectively. Initially, we attempted this reaction using Brønsted acid catalysis (TsOH) but these conditions failed to produce the desired products. Surprisingly, treatment of **Ni5**

with benzene-1,2-dithiol in the presence of TsOH under Otsubo's conditions (refluxing toluene)⁵ led to clean debromination and deformylation, regenerating **Ni3** in 90% yield. Formation of the thioacetals proceeded smoothly when using TiCl₄ as a Lewis acid in combination with solid Na₂CO₃ as a Brønsted base. Palladium-catalyzed Takahashi coupling^{14–16} converted **Ni6a,b** to **Ni7a,b**, then oxidation with DDQ gave the quinoidal porphyrins **Ni8a,b**. Nickel(II) was removed using sulfuric acid to give the free-bases **H₂8a,b**, which were treated with zinc(II) acetate to prepare **Zn8a,b**. The 'pull-pull' quinoidal monomers **Zn9**, **H₂9** and **Ni9** were also prepared for comparison (Scheme 2).¹⁵



Scheme 2. Synthesis of free-base and nickel(II) pull-pull porphyrins from the zinc complex **Zn9** (which was reported in ref 15).

The non-aromatic quinoidal nature of compounds **Ni8a**, **Ni8b**, **H₂8a**, **H₂8b**, **Zn8a** and **Zn8b** is obvious from their ¹H NMR spectra. For example, the NH protons of **H₂8a**, **H₂8b** and **H₂9** resonate at 12.23, 11.94 and 13.86 ppm, respectively (in CDCl₃, 298 K), whereas a typical free-base porphyrin exhibits an NH resonance at around −3 ppm. Similarly, the β-pyrrole protons of these quinoidal porphyrins appear at 6.5–7.5 ppm, whereas an aromatic porphyrin gives β-signals at 9–10 ppm. The UV-vis-NIR absorption spectra of **Zn8a** and **Zn8b** are slightly more red-shifted than that of the pull-pull analogue **Zn9** (Fig. 3). The slightly smaller HOMO-LUMO gaps of **Zn8b**, **Ni8b** and **H₂8b** are confirmed by the redox potentials (Table 1).

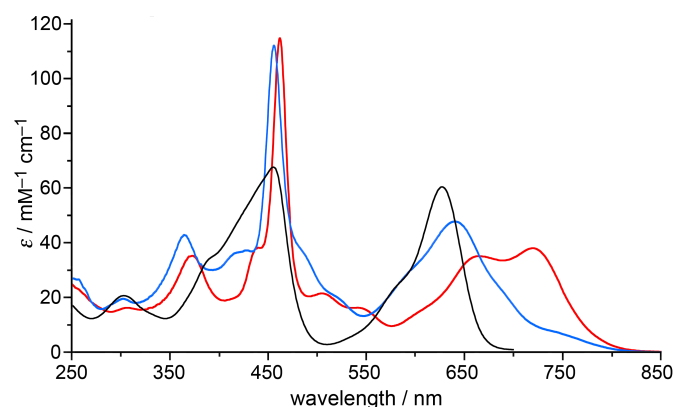


Fig. 3. The UV-visible absorption spectra of the ‘push-pull’ compounds **Zn8a** (blue) and **Zn8b** (red) and the ‘pull-pull’ compound **Zn9** (black), recorded in dichloromethane.

Table 1. Redox potentials.^a

Compound	E^1_{ox} (V)	E^1_{red} (V)	ΔE (V)
Zn8a	0.36	−1.19	1.55
Ni8a	0.56	−1.04	1.60
H₂8a	0.55	−1.02	1.57
Zn8b	0.28	−1.15	1.43
Ni8b	0.46	−0.99	1.45
H₂8b	0.45	−1.02	1.47
Zn9	0.87	−0.71	1.58
Ni9	1.12	−0.45	1.57
H₂9	[1.15] ^b	−0.55	[1.70] ^b

^a Potentials were measured by square wave voltammetry relative to internal ferrocene (Fc/Fc⁺ 0.00 V) in CH₂Cl₂ containing 0.1 M Bu₄NBF₄. ^b The oxidation potential for **H₂9** is approximate because the process is poorly reversible and occurs close to the limit of the potential window.

Attempted Synthesis of a Push-Pull Quinoidal Dimer

We attempted to prepare a push-pull quinoidal cumulenyl porphyrin dimer from **Ni6a** as shown in Scheme 3.^{17,18} Sonogashira coupling with trimethylsilylacetylene, deprotection of the alkyne and Sonogashira coupling with dibromoporphyrin **Zn12** proceeded smoothly to give the alkyne-linked dimer **NiZn13**. However, Takahashi coupling of this bromoporphyrin dimer gave an unexpected product: the *meso*-cyano porphyrin **NiZn14** instead of the desired intermediate **NiZn17**. Nitrile formation has previously been reported as a side reaction during Takahashi coupling,¹⁹ but it is not clear why it predominates here. Fortunately, changing the halogen from bromine to iodine solved the problem and **NiZn16** was converted to **NiZn17** in good yield. Oxidation of **NiZn17** with DDQ in chloroform at room temperature resulted in a rapid color change and the appearance of an intense absorption band in the near-IR (λ_{max} 1034 nm, Fig. 4), suggesting formation of **NiZn2**, but all attempts at isolating this compound gave only complex mixtures of products. Other oxidizing agents were also tested for conversion of **NiZn17** to **NiZn2** (such as chloranil, tris(4-bromophenyl)aminium hexachloroantimonate and trityl tetrafluoroborate) but none of them gave more promising results than DDQ.

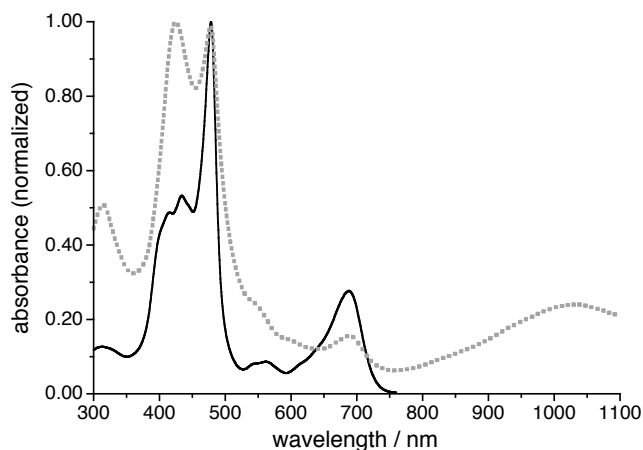
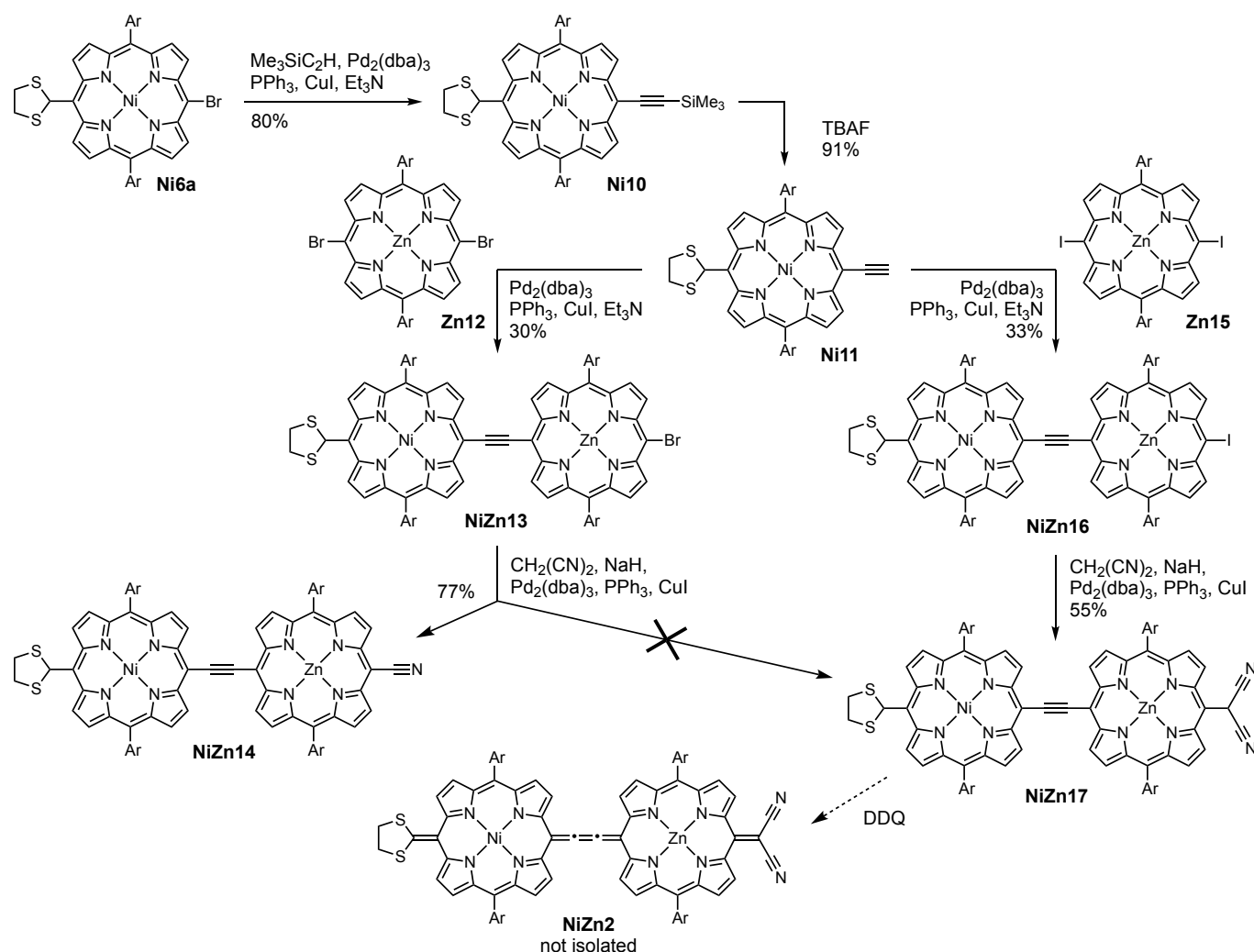


Fig. 4. UV-vis-NIR absorption spectrum of **NiZn17** before (black line) and after (grey dashed line) treatment with DDQ in chloroform (concentration ca. 5 μ M).

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Scheme 3. Attempted synthesis of the push-pull quinoidal cumulenyl dimer **NiZn2**. (Ar = 3,5 di-*tert*-butyl phenyl. For the synthesis of **Zn12** and **Zn15**, see references 17 and 18, respectively.)

X-Ray Crystallography

Here we compare the crystal structures of compounds **Ni8a**, **Zn8b**, **H28b**, **Zn9**, **H29**, **Ni10** and **NiZn14**. The structures of **Zn8b** and **Zn9** have been published previously.^{12,15} Crystals were grown by vapor diffusion of *n*-hexane into 1,2-dichloroethane (**H28b**), methanol into 1,2-dichloroethane (**Ni8a**, **Ni10**) and methanol into chloroform (**Zn8b** and **NiZn14**). All these compounds gave only very small crystals with weak diffraction, requiring use of synchrotron radiation. The structure determinations were hampered by twinning and disorder, including extensive disorder of solvent molecules, and required the application of similarity restraints on geometry

and displacement parameters. Despite the relative high *R* factors, the principal features of the molecular structures are clear, and there are no unaccountable validation alerts. Crystallographic details are given in the Electronic Supplementary Information.

The aromatic nickel(II) porphyrin **Ni10** crystallizes with four molecules in the asymmetric unit; the four molecules have essentially the same geometry (Fig. 5). The angles between the mean planes of the 1,3-dithiolane ring and the C₂₀N₄ porphyrin cores are in the range 64–67°. Apart from the 1,3-dithiolane substituent, this structure is very similar to that of a *meso*-ethynyl nickel porphyrin reported by Arnold and coworkers.²⁰

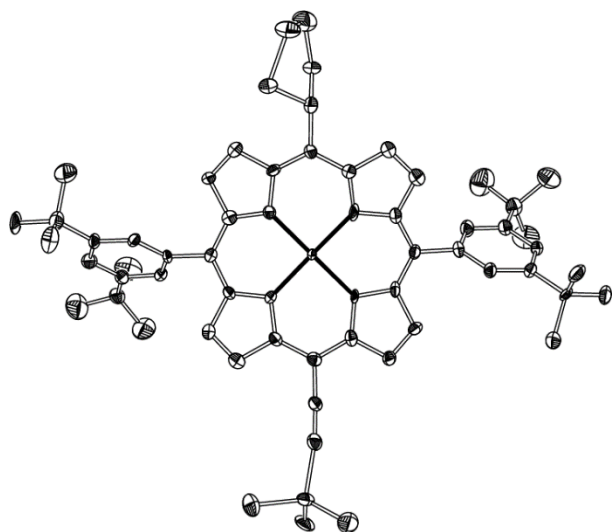


Fig. 5. The conformation of one molecule of **Ni10** (50% probability ellipsoids, no H atoms). Note the twist between the thioacetal group and the tetrapyrrolic core.

The push-pull quinoidal porphyrins **Ni8a**, **Zn8b** and **H₂8b** are all extremely curved π -systems, as seen from the comparison of **Ni8a** and **Ni10** (Fig. 6). Adoption of a saddle-shaped conformation is attributed to intramolecular steric repulsion between the β -pyrrole H atoms and the sulfur atoms or nitrile groups. In **Ni8a**, the angle between the mean planes of the thioacetal C_2S_2C ring and the $C(CN)_2$ unit is 72.5° (where 180° would correspond to a planar geometry). Similar conformations have been reported for other quinoidal porphyrins.^{11a,f}



Fig. 6. Comparison of (top) **Ni8a** (20% probability ellipsoids) and (bottom) **Ni10** (50% probability ellipsoids), both viewed without the *meso*-aryl substituents and H atoms.

The free-base quinoidal porphyrins, **H₂8b** and **H₂9**, stack into unusual extended assemblies (Fig. 7). Many $C\equiv N\cdots C(C\equiv N)_2$ and $C\equiv N\cdots C=C(C\equiv N)_2$ contacts are observed with $N\cdots C$ distances of 3.0–3.4 Å. Most of these distances are shorter than the sum of the van der Waals radii (3.41 Å). These short contacts (marked as red and green dashed lines in Fig. 7) indicate incipient nucleophilic attack of the nitrile lone pair

onto an electron deficient carbon (Fig. 7a), although there is no significant pyramidalization at the carbon centers. The structures of **H₂8b** and **H₂9** both feature columnar stacks which interlock to generate dense ‘brick walls’ of closely stacked chromophores. The closest π -stacking distances between rings are 3.13 Å in **H₂8b** (nitrogen to carbon), and 3.38 Å in **H₂9** (carbon to carbon), pyrrole rings being the partners in both cases. Both structures exhibit many short π - π contacts suggesting that they might have potential as organic semiconductors.¹

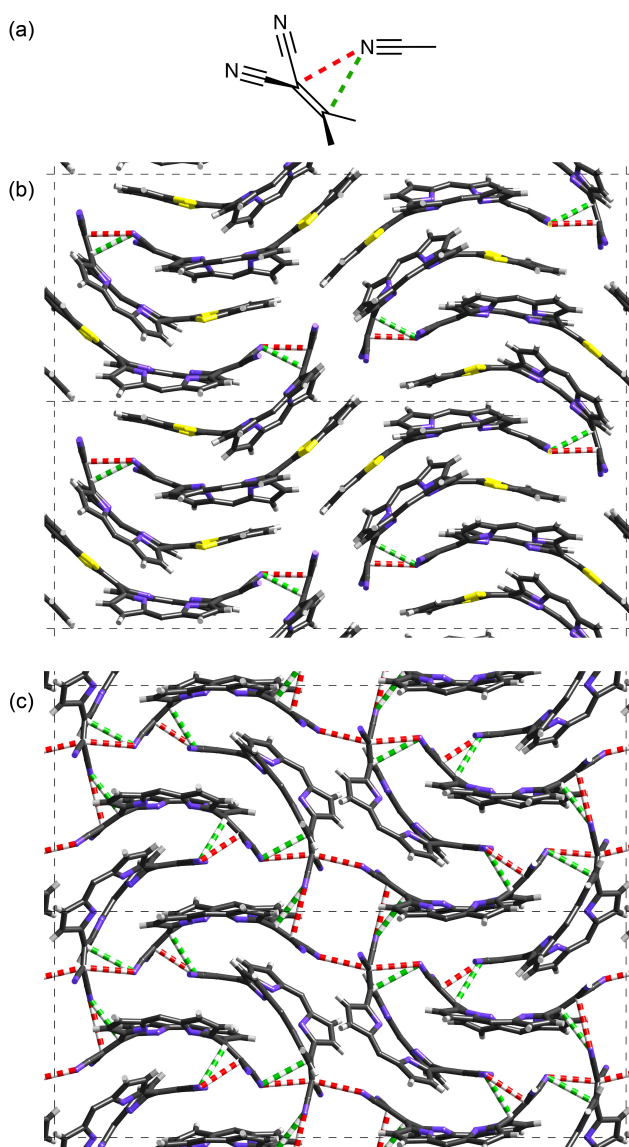


Fig. 7. Crystal packing in free-base quinoidal porphyrins **H₂8b** and **H₂9** (a) $N\cdots C$ interactions. Packing diagrams for (b) **H₂8b** and (c) **H₂9**. In both these crystals, the macrocyclic cores form tightly packed layers and the aryl substituents (not shown) form closely packed layers above and below these layers of cores. Red dashed bonds indicate $C\equiv N\cdots C(C\equiv N)_2$ interactions, with shortest lengths of (b) 3.22 and 3.24 Å; (c) 3.12, 3.19, 3.30 and 3.40 Å. Green dashed bonds indicate $C\equiv N\cdots C=C(C\equiv N)_2$ interactions, with shortest lengths of (b) 3.19 and 3.14; (c) 3.06, 3.14 and 3.13 Å. Thin grey dashed lines show the unit cells.

The bond lengths in the quinoidal porphyrins are consistent with the expected pattern of bond orders. The

differences in bond lengths between the push-pull and pull-pull systems provide no evidence for a greater aromatic contribution in the push-pull compounds (Fig. 8).

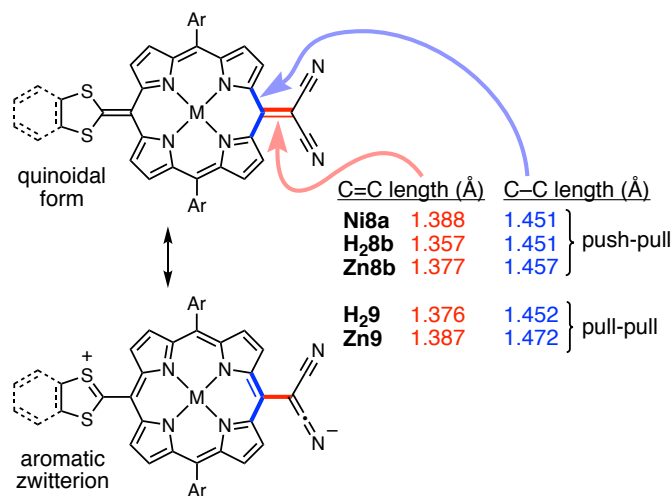


Fig. 8. Charge-transfer resonance in the push-pull quinoidal porphyrins. Comparison of the average carbon-carbon bond lengths shown here indicates that there is no significant increased zwitterionic contribution in the push-pull systems.

The aromatic porphyrin dimer **NiZn14** crystallizes as an off-set centrosymmetric anti-parallel bimolecular aggregate (Fig. 9), with one molecule of methanol coordinated to each zinc center. Disordered solvent also separates these bimolecular units. The distance between the mean planes of the two C₂₀N₄ zinc porphyrin cores is 3.29 Å, and the closest intermolecular contact (3.34 Å) occurs between the central β -pyrrole carbons of the zinc porphyrins (c.f. 3.54 Å for twice the van der Waals radius of carbon). The *meso*-aryl groups are interdigitated and they do not hinder this close π - π stacking of the porphyrin cores. The structure of this aggregate resembles that of a butadiyne-linked porphyrin tetramer.²¹ The zinc porphyrin unit in **NiZn14** is essentially planar whereas the nickel porphyrin unit is noticeably ruffled; the root-mean-square deviations of the C₂₀N₄ cores are 0.12 Å and 0.19 Å, respectively (major disorder component only). This type of distortion is common in nickel porphyrin complexes due to the short Ni-N bond length.²²

There has been some debate concerning the torsion angles in alkyne-linked porphyrin dimers because the twist between the two porphyrin units limits the extent of electronic coupling through the alkyne bridge.^{23–25} Many computational studies have predicted that steric repulsions between the β -pyrrole protons in ethyne-linked dimers result in a ground-state geometry with a torsion angle of $\theta \approx 35^\circ$ in the gas phase, with a barrier to planarity of about 6 kJ/mol.^{25–26} In contrast to these computational results, Therien and coworkers reported the crystal structures of two ethyne-linked porphyrin dimers (with palladium and platinum metal centers) in which the mean planes of the porphyrin units are exactly parallel (inversion center, torsion angle $\theta = 0^\circ$).²⁷

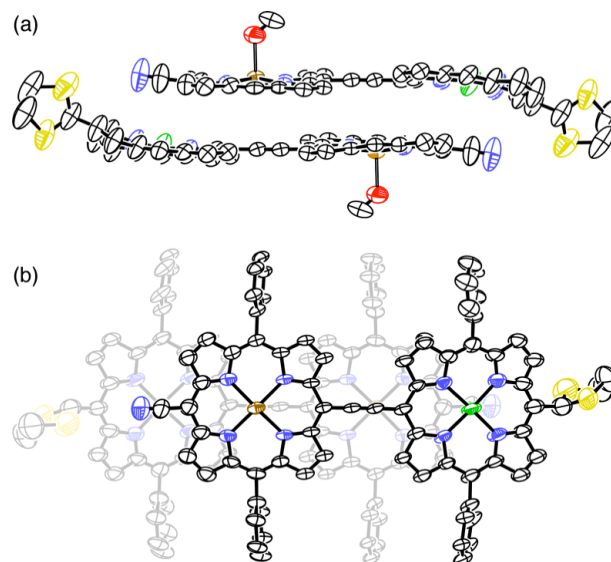


Fig. 9. Two orthogonal views of the **NiZn14** aggregate. (a) Side view, omitting *meso*-aryl substituents. (b) Plan view omitting coordinated methanol and *tert*-butyl substituents (40% probability ellipsoids).

The angle between the mean planes of the two C₂₀N₄ porphyrin cores of **NiZn14** is 10.2° but this should not be interpreted purely as a torsion angle; it is really a folding dihedral angle because the axis of rotation between these two planes is almost perpendicular to the line connecting the centers of the two porphyrins. A better measure of the torsional twist in **NiZn14** is obtained by connecting the two aryl-substituted *meso*-carbon atoms within each porphyrin core and measuring the angle between these two vectors when viewed along a line joining their midpoints; this approach gives a torsion angle of only 3.3°. Thus the barrier to planarization appears to be small enough to be overcome by crystal packing effects, as in *ortho*-unsubstituted biphenyls.²⁸ A study of conformational bias in crystal structures²⁹ concluded that higher-energy planar conformers can be favored by packing effects when the energy barrier is less than about 8–10 kJ/mol, which is consistent with the calculated barrier height in these porphyrin dimers.^{25–26}

Conclusions

This work shows that push-pull quinoidal porphyrins can be synthesized in high yield, and that they are stable under normal laboratory conditions. They are even stable enough for nickel(II) to be removed with sulfuric acid, to prepare the free-base macrocycles. The absorption spectra and redox potentials of these push-pull systems indicate that their HOMO-LUMO gaps are not significantly smaller than those of the corresponding pull-pull or push-push analogues.^{11,15} It is surprising that the quinoidal free-base porphyrins **H28b** and **H29** form infinite closely π -stacked layer structures (Fig. 7), despite the molecular curvature and bulky *meso*-aryl substituents, both of which would have been expected to prevent π -stacking. This observation suggests that these

compounds deserve investigation as possible organic semiconductor charge-transport materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

‡ The synthesis and crystal structure of compound **Zn8b** has been reported previously.¹²

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