

Fused porphyrin-imidazole systems: new building blocks for synthesis of porphyrin arrays

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Reaction of porphyrin-2,3-diones with aromatic aldehydes and NH_4OAc in $\text{AcOH}-\text{CHCl}_3$ affords 2-aryl-1*H*-imidazo[4,5-*b*]porphyrins which, with appropriate substitution, are useful building blocks for the synthesis of multi-porphyrin arrays; porphyrin-tetraones are similarly converted into the corresponding bis-fused systems.

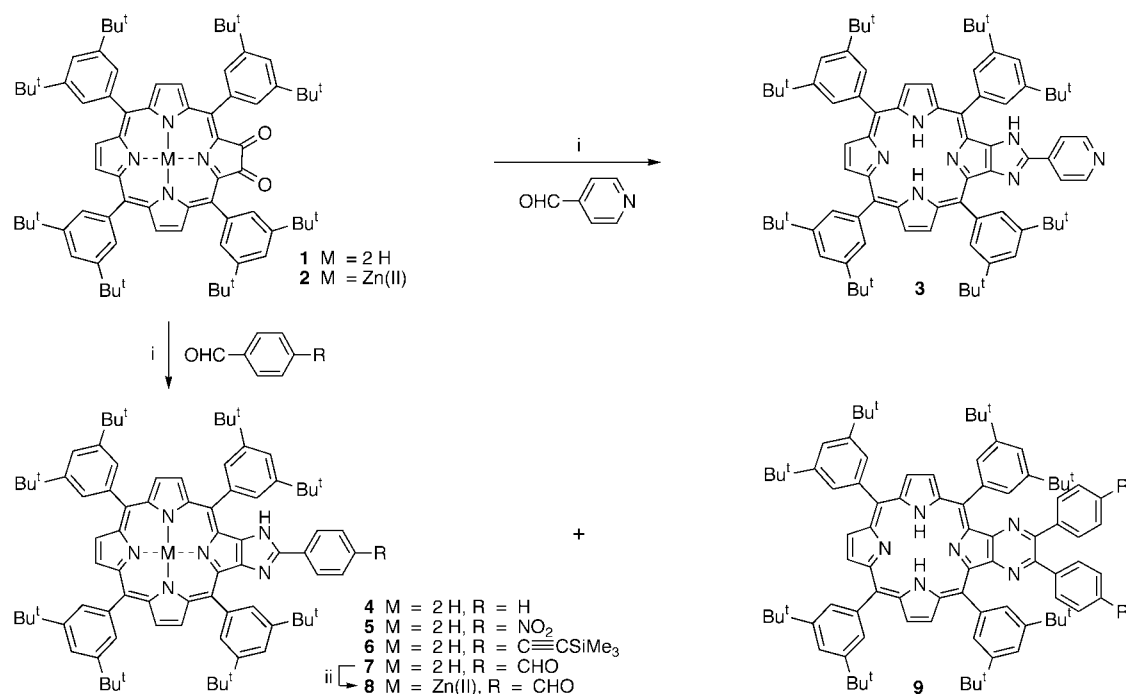
Multi-porphyrin systems that occur naturally have a variety of geometries between interacting chromophores. Most model compounds designed to mimic such porphyrin systems have relied on linkage through *meso*-positions or have used flexible chains linked through single positions. The only previous multi-porphyrin models with β -pyrrolic rings on adjacent porphyrin rings were constructed by reaction of porphyrin-2,3-diones with aromatic 1,2-diamines.^{1,2} The formation of the imidazole ring in the synthesis of 2,3,5-triphenylimidazole (lophine) by reaction of an α -dione, benzil, with benzaldehyde and ammonia has been known since last century.³ We now report that porphyrin-2,3-diones, despite the α -dione system being attached to a 5-membered heterocyclic ring, show similar reactivity towards aromatic aldehydes and ammonia. This provides a new method of functionalising the porphyrin macrocycle by introduction of a 2'-arylimidazole ring fused across a β,β -pyrrolic position of the porphyrin and allows the synthesis of more elaborated systems by bridging of porphyrin units through the new functionality.

2-Aryl-1*H*-imidazo[4,5-*b*]porphyrins **3–7**† were prepared in good yields by the condensation of porphyrin-2,3-dione **1** with the corresponding arylaldehyde in the presence of excess

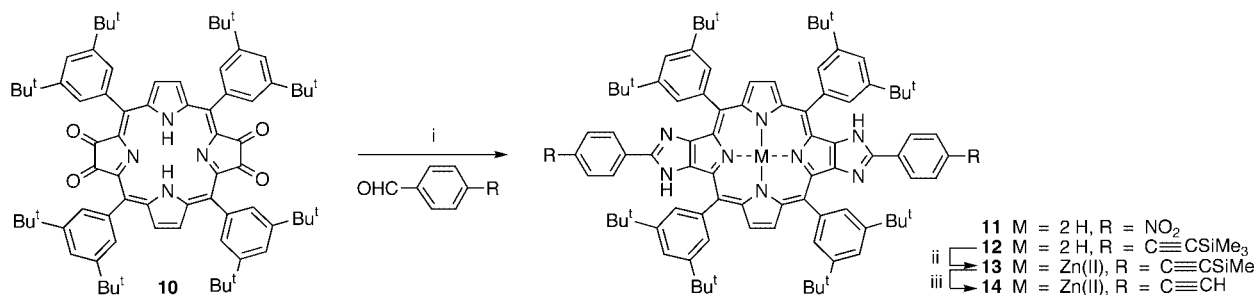
NH_4OAc in a refluxing 1:1 mixture of $\text{AcOH}-\text{CHCl}_3$ for 1 to 24 h (Scheme 1). These reactions could be carried out readily on a multi-gram scale. The products **3–7** are easily purified by column chromatography over silica and recrystallisation. The ^1H NMR spectra of imidazoporphyrins **3–7** show a broad singlet at about 8.4 ppm, indicating the presence of the imidazole NH and the lack of symmetry in the spectra show that imidazole tautomerism is slow on the ^1H NMR timescale. In each of the reactions producing compounds **3–7**, the corresponding 2,2',2,3'-diarylpyrazino[2,3-*b*]porphyrin product **9**† was formed in 10–15% yield. More-highly substituted porphyrins are available from similar reactions of aldehydes and NH_4OAc with porphyrin-2,3,12,13-tetraone **10**. Linear extended bis(2-aryl-1*H*-imidazo)porphyrins **11** and **12**† were obtained (Scheme 2), again in good yields; the corresponding pyrazino compounds were also observed as minor products. 5,10,15,20-Tetrakis-(3,5-di-*tert*-butylphenyl)porphyrin-2,3,7,8-tetraone⁴ also reacts similarly with arylaldehydes to give bis-fused L-shaped extended systems.

Compounds **14** and **15** are useful building blocks for construction of a range of linear bis- and tris-porphyrin systems with butadiyne linkages⁵ generated by CuCl -mediated coupling of the terminal acetylenes.^{6–10} Compound **14** was obtained in 98% yield by desilylation of the ethynyl unit of zinc(II) porphyrin **13** (Scheme 2). Compound **15** was obtained in two steps [metallation with zinc(II) and desilylation] from porphyrin **6** in 71% overall yield.

The dizinc(II) butadiyne-linked bis(imidazoporphyrin) **16** was prepared in 90% yield by stirring a solution of zinc(II) 2-[4-



Scheme 1 Reagents and conditions: i, NH_4OAc , $\text{AcOH}-\text{CHCl}_3$, Δ [**3**: 2 h (40%), **4**: 6 h (54%), **5**: 24 h (62%), **6**: 4 h (48%) and **7**: 2 h (66%)]; ii, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, CH_2Cl_2 -MeOH, Δ , 1 h (85%).



Scheme 2 Reagents and conditions: i, NH₄OAc, AcOH-CHCl₃, Δ [**11**: 48 h (31%) and **12**: 6.5 h (31%)]; ii, Zn(OAc)₂·2H₂O, CH₂Cl₂-MeOH, Δ, 2 h (91%); iii, K₂CO₃, CH₂Cl₂-MeOH, Δ, 15 min (98%).

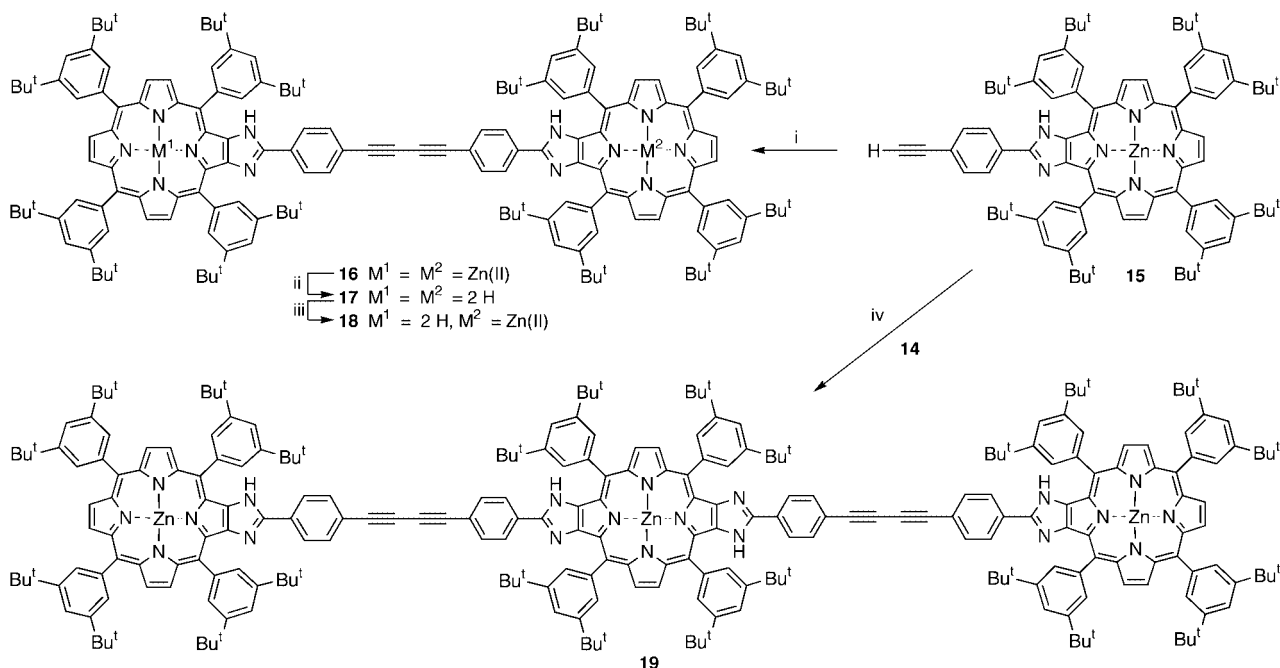
(ethynyl)phenyl]-1*H*-imidazo[4,5-*b*]porphyrin **15** in CH₂Cl₂ with an excess of freshly-prepared CuCl and TMEDA in air at room temperature for 30 min (Scheme 3). The UV-vis spectrum of bisporphyrin **16**[†] shows slight broadening of the Soret band and unaltered Q bands compared with the spectrum of the monomer **15**.[†] This indicated that there is negligible ground state electronic communication between the porphyrin rings of **16**.

Dizinc(II) bisporphyrin **16** was treated with 7 M HCl in a two-phase system to afford the free base butadiyne-linked bis(imidazoporphyrin) **17**[†] in 93% yield. Bis(imidazoporphyrin) **17** was treated with Zn(OAc)₂·2H₂O (1 equiv.) to afford a mixture of free base **17** (28%), dizinc(II) **16** (36%) and the desired monozinc(II) bis(imidazoporphyrin) **18**[†] (31%) after purification (Scheme 3). Photo-induced energy-transfer in butadiyne bis(imidazoporphyrin) system **18** (1 × 10⁻⁶ M in

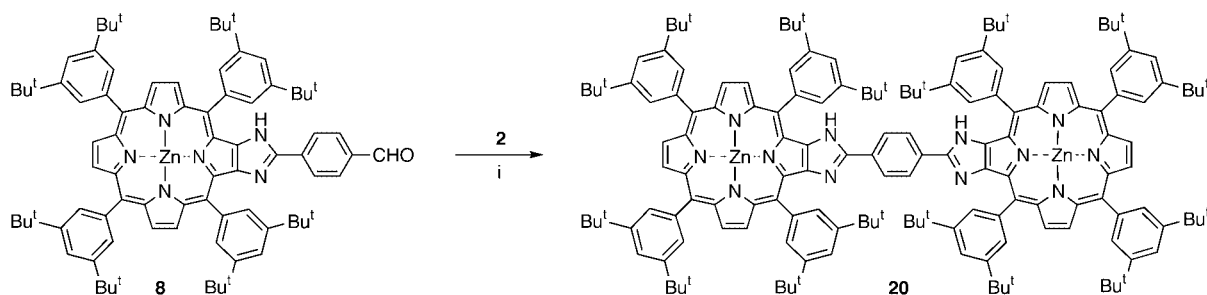
CHCl₃) from the zinc(II) porphyrin to the free base porphyrin was found to be 80% efficient which accords with a Förster-type (dipole-dipole) electronic energy-transfer mechanism.¹¹

The synthesis of linear tris(imidazoporphyrin) **19** illustrates the utility of the linear zinc(II) bis[2-[4-(ethynyl)phenyl]-1*H*-imidazo]porphyrin building block **14** to prepare larger ordered multi-porphyrin arrays. The linear trizinc(II) butadiyne-linked tris(imidazoporphyrin) **19**[†] was prepared in 29% yield by a cross-coupling reaction between **14** (1 equiv.) and zinc(II) 2-[4-(ethynyl)phenyl]-1*H*-imidazo[4,5-*b*]porphyrin **15** (2.5 equiv.) using an excess of freshly-prepared CuCl and TMEDA in air at room temperature for 3 h (Scheme 3). Dizinc(II) butadiyne-linked bis(imidazoporphyrin) **16** was obtained as a by-product in 45% yield.

The utility of the condensation is illustrated further by reaction of the [zinc(II) (imidazo)porphyrin]-appended arylaldehyde



Scheme 3 Reagents and conditions: i, CuCl, TMEDA, CH₂Cl₂, stir for 30 min in air; ii, HCl (7 M), CH₂Cl₂, stir for 2 min; iii, Zn(OAc)₂·2H₂O, CH₂Cl₂-MeOH, Δ, 1 h; iv, CuCl, TMEDA, CH₂Cl₂, stir for 3 h in air.



Scheme 4 Reagents and conditions: i, NH₄OAc, AcOH-CHCl₃, Δ, 72 h.

8 with zinc(II) porphyrin-2,3-dione **2** and NH₄OAc in AcOH–CHCl₃ at reflux for 72 h. This reaction gave the novel dizinc(II) bisporphyrin **20**† in 42% yield (Scheme 4). The zinc-to-zinc distance in arene-linked bisporphyrin **20** was calculated¹² to be 18.5 Å which is significantly shorter relative to the zinc-to-zinc distance in the dizinc(II) bis(imidazoporphyrin) **16** (ca. 28.3 Å) and between the zinc ions in the terminal porphyrins of the trizinc(II) tris(imidazoporphyrin) **19** (56.6 Å).

The use of these novel compounds and systems to probe further the influence of porphyrin orientation and alignment on interporphyrin electronic communication is under active investigation in our laboratory.

Acknowledgements

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Notes and references

† All imidazoporphyrins have been fully characterised by elemental analysis, mass spectroscopy, ¹H NMR spectrometry and spectroscopic techniques. Visible spectroscopic data of selected porphyrins: 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin: λ_{max}(CHCl₃)/nm 405sh (log ε 4.91), 422 (5.66), 487sh (3.66), 519 (4.28), 555 (4.04), 593 (3.78), 648 (3.85); **3**: 317 (4.30), 424 (5.50), 484 (3.75), 519 (4.23), 554 (4.02), 587 (3.89), 646 (3.45); **4**: 422 (5.51), 519 (4.24), 554 (4.00), 588 (3.94), 647 (3.85); **6**: 423 (5.51), 519 (4.35), 554 (4.01), 588 (3.92), 649 (3.62); **8**: 346 (4.42), 431 (5.42), 524 (3.90), 550 (4.29), 592 (4.05); **9**

R = C≡CSiMe₃: 382 (3.86), 438 (5.33), 476 (3.41), 526 (3.36), 563 (3.70), 597 (3.99), 653 (3.40), 692 (3.20); **12**: 326 (4.65), 420 (5.48), 517 (4.45), 552 (4.15), 587 (4.09), 640 (3.69); **15**: 310 (4.41), 427 (5.43), 480 (3.39), 492 (4.31), 514 (3.68), 586 (4.03); **16**: 348 (4.74), 426 (5.70), 513 (4.16), 550 (4.71), 587 (4.45); **17**: 242 (4.66), 427 (5.85), 519 (4.75), 556 (4.38), 589 (4.29), 649 (3.91); **18**: 241 (4.60), 429 (5.39), 519 (4.50), 552 (4.56), 588 (4.36), 649 (3.56); **19**: 250 (4.82), 352 (5.01), 369 (5.00), 429 (5.87), 454 (5.83), 519 (4.50), 554 (4.87), 596 (4.80); **20**: (toluene) 321 (4.60), 431 (5.68), 458 (5.43), 516 (4.15), 554 (4.69), 589 (4.42).

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