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

Maxwell J. Crossley * and James A. McDonald

School of Chemistry, The University of Sydney, NSW 2006, Australia

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Reaction of porphyrin-2,3-diones with aromatic aldehydes and NH4OAc in AcOH-CHCl3 affords 2-aryl-1H-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 multiporphyrin 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-dione¹ 1 with the corresponding arylaldehyde in the presence of excess

Bu

Bu

M = 2 H1 2 Μ = Zn(II)

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Bu

Bu

Bu^t

OHC

κ Βυ

Bu

Bu

Bu

NH₄OAc in a refluxing 1:1 mixture of AcOH-CHCl₃ 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 NH₄OAc with porphyrin-2,3,12,13-tetraone⁴ 10. Linear extended bis(2-aryl-1H-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-

Ĥ

3

N H

Bu

Βu

Bu^t

Ru

Βu

Βu

BL

Bu



 $\begin{array}{l} \textbf{4} \ \ \textbf{M} = 2 \ \textbf{H}, \ \textbf{R} = \textbf{H} \\ \textbf{5} \ \ \textbf{M} = 2 \ \textbf{H}, \ \textbf{R} = \textbf{NO}_2 \\ \textbf{6} \ \ \textbf{M} = 2 \ \textbf{H}, \ \textbf{R} = \textbf{C} \\ \textbf{E} \\ \textbf{CSIMe}_3 \\ \textbf{ii} \ \textbf{\Box} \quad \textbf{7} \ \ \textbf{M} = 2 \ \textbf{H}, \ \textbf{R} = \textbf{CHO} \\ \textbf{8} \ \ \textbf{M} = 2 \ \textbf{I}, \ \textbf{R} = \textbf{CHO} \\ \textbf{8} \ \ \textbf{M} = 2 \ \textbf{I}, \ \textbf{R} = \textbf{CHO} \end{array}$

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Bu 9







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 CH_2Cl_2 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

 $CHCl_3$) 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) butadiynelinked 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, CH_2Cl_2 , stir for 30 min in air; ii, HCl (7 M), CH_2Cl_2 , stir for 2 min; iii, $Zn(OAc)_2 \cdot 2H_2O$, CH_2Cl_2 -MeOH, Δ , 1 h; iv, CuCl, TMEDA, CH_2Cl_2 , stir for 3 h in air.



Scheme 4 Reagents and conditions: i, NH_4OAc , $AcOH-CHCl_3$, Δ , 72 h.

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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 calculated ¹² 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.

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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 (4.30), 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**

- $\begin{array}{l} \mathsf{R} = \mathsf{C} \equiv \mathsf{C} \mathsf{SiMe}_3 ; \ 382 \ (3.86), \ 438 \ (5.33), \ 476 \ (3.41), \ 526 \ (3.36), \ 563 \ (3.70), \\ 597 \ (3.99), \ 653 \ (3.40), \ 692 \ (3.20); \ \mathbf{12} ; \ 326 \ (4.65), \ 420 \ (5.48), \ 517 \ (4.45), \\ 552 \ (4.15), \ 587 \ (4.09), \ 640 \ (3.69); \ \mathbf{15} ; \ 310 \ (4.41), \ 427 \ (5.43), \ 480 \ (3.39), \\ 492 \ (4.31), \ 514 \ (3.68), \ 586 \ (4.03); \ \mathbf{16} ; \ 348 \ (4.74), \ 426 \ (5.70), \ 513 \ (4.16), \\ 550 \ (4.71), \ 587 \ (4.45); \ \mathbf{17} : \ 242 \ (4.66), \ 427 \ (5.85), \ 519 \ (4.75), \ 556 \ (4.38), \\ 589 \ (4.29), \ 649 \ (3.91); \ \mathbf{18} : \ 241 \ (4.60), \ 429 \ (5.39), \ 519 \ (4.50), \ 552 \ (4.56), \\ 588 \ (4.36), \ 649 \ (3.56); \ \mathbf{19} : \ 250 \ (4.82), \ 352 \ (5.01), \ 369 \ (5.00), \ 429 \ (5.87), \\ 454 \ (5.83), \ 519 \ (4.50), \ 554 \ (4.87), \ 556 \ (4.80); \ \mathbf{20} : \ (10unen) \ 321 \ (4.60), \\ 431 \ (5.68), \ 458 \ (5.43), \ 516 \ (4.15), \ 554 \ (4.69), \ 589 \ (4.42). \end{array}$
- 1 M. J. Crossley and P. L. Burn, J. Chem. Soc., Chem. Commun., 1987, 39.
- 2 M. J. Crossley and P. L. Burn, J. Chem. Soc., Chem. Commun., 1991, 1569.
- 3 B. Radziszewski, Ber., 1882, 15, 1493.
- 4 M. J. Crossley, L. J. Govenlock and J. K. Prashar, J. Chem. Soc., Chem. Commun., 1995, 2379.
- 5 D. P. Arnold, A. W. Johnson and M. Mahendran, J. Chem. Soc., Perkin Trans. 1, 1978, 366.
- 6 D. P. Arnold and L. J. Nitschinsk, Tetrahedron, 1992, 48, 8781.
- 7 D. P. Arnold, D. A. James, C. H. L. Kennard and G. Smith, J. Chem. Soc., Chem. Commun., 1994, 2131.
- 8 D. P. Arnold and D. A. James, J. Org. Chem., 1997, 62, 3460.
- 9 H. L. Anderson, Inorg. Chem., 1994, 33, 972.
- 10 R. W. Wagner, T. E. Johnson, F. Li and J. S. Lindsey, J. Org. Chem., 1995, 60, 5266.
- 11 T. Förster, Faraday Discuss. Chem. Soc., 1959, 27, 7.
- 12 SPARTAN version 4.0, Wavefunction Inc., Irvine, CA, USA, 1995.

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