Synthesis of Porphyrin-2,3,12,13- and -2,3,7,8-tetraones: Building Blocks for the Synthesis of Extended Porphyrin Arrays

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The first synthesis of a porphyrin-2,3,12,13-tetraone and porphyrin-2,3,7,8-tetraones is reported; these compounds are useful compounds for the construction of laterally-extended porphyrin systems as is illustrated by the synthesis of linear and bent tris-porphyrins, **10** and **11**, respectively, and the tetrakis-porphyrin **12**.

The porphyrin periphery with its four pyrrolic rings arranged on a square matrix has an attractive geometry for construction of molecular arrays based on a square grid motif. Annulation of each pyrrolic ring would offer an entry into such arrays. While simple tetrabenzoporphyrins are known, the methodology for their construction is not amenable for the synthesis of more elaborate structures.[1] Other molecular arrangements involving poly-porphyrin components are accessible through ring annulation of opposite pyrrolic rings on the porphyrin periphery, leading to linear extended arrays, and through annulation of adjacent pyrrolic rings, leading to bent, stepped, kinked, and square arrays. To minimize the steps involved, such elaboration of the porphyrin system requires the synthesis of appropriately functionalized porphyrin 'building blocks'. We now report the first synthesis of porphyrin-2,3,12,13- and 2,3,7,8-tetraones and demonstrate their use for the construction of porphyrin-based nanomolecular structures with syntheses of the linear and bent tris-porphyrins **10** and **11**, respectively, and the tetrakis-porphyrin **12**.

Titration of [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]copper(II) **1** in CH_2Cl_2 with a solution of nitrogen dioxide in light petroleum over several hours initially gave the mononitrated adduct[2] which upon further treatment yielded the dinitrated porphyrin **2** as a mixture of five isomers in 85% yield after chromatography over silica (Scheme 1). This is another example of copper(II) chelation directing subsequent nitration regioselectively to β-pyrrolic positions of 5,10,15,20-tetraarylporphyrins.[2] The mixture **2** was demetalated in a two-phase conc. H_2SO_4–CH_2Cl_2 system and the resultant free-base dinitro compounds were reduced with $SnCl_2{\cdot}2H_2O$/HCl to give the diamino compounds **3** in 86% overall yield. Photo-oxidation[3] of **3** afforded a mixture of the free-base 2,3,12,13-tetraone **4** and the free-base 7- and 8-aminodiones **5**. The purification of compounds **4** and **5** required a very difficult separation by chromatography but this was readily overcome by selective metalation with zinc(II) acetate.

The tetraone **4** has a bacteriochlorin π-electron delocalization pathway while compounds **5** are chlorins. As the electronic properties of the substituents are very different in the two systems, we reasoned that there should be a difference in the inner N–H acidity and hence an exploitable difference in the kinetics of metal ion complexation. Indeed treatment of the photolysis product with zinc(II) acetate resulted in complete metalation of **5** to afford **6** while the tetraone **4** remained unmetalated. This facilitated an extremely easy separation by chromatography over silica and afforded the porphyrin-2,3,12,13-tetraone **4**[†] (non-polar green band) in 24% yield from the two steps and the zinc aminoporphyrin-2,3-diones **6** (polar orange band) in 63% yield.

The zinc(II) aminoporphyrin-2,3-diones **6** readily undergo photo-oxidation in the presence of Rose Bengal to afford the zinc(II) porphyrin 2,3,7,8-tetraone **7** in 90% yield, unlike the free-base compound **5** which is completely inert under the same conditions. Demetalation of **7** by treatment with a conc. HCl–CH_2Cl_2 mixture gave the free-base porphyrin-2,3,7,8-tetraone **8** in 98% yield (Scheme 1).

The difference in reactivity of **5** and **6** towards singlet oxygen can be readily explained. There is a low bond-order associated with the β,β′-pyrrolic bond[4] across which singlet oxygen has to add in compound **5**. In the metalated derivative **6**, the bond order of the appropriate bond is higher.[4] In contrast tetraone **4**, which arises from 2,12- and 2,13-diaminoporphyrins, is readily produced *via* the intermediacy of a free-base 12-aminoporphyrin-2,3-dione in which the amino group resides on a double bond.

In order to illustrate the usefulness of these tetraones for the construction of laterally-extended oligo-porphyrin systems we now report straight-forward synthesis of the linear and bent tris-porphyrins **10** and **11**, respectively. The 1:1 adduct, 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-24,25-diamino-quinoxalino[2,3-*b*]porphyrin **9**, was prepared in high yield by condensation of 1,2,4,5-benzenetetramine with the free-base porphyrin-2,3-dione and then used in reactions with each of the free-base tetraones. Reaction of excess **9** with the 2,3,12,13-tetraone **4** in refluxing toluene for 48 h gave the linear tris-porphyrin **10** in 84% yield. Reaction of excess **9** with the 2,3,7,8-tetraone **8** in refluxing toluene for 72 h gave the bent tris-porphyrin **11** in 93% yield.

In each of these syntheses of tris-porphyrin we have deliberately reacted excess diamine **9** with the tetraones under forcing conditions to take the reaction through to the 2:1 adduct. When milder reaction conditions were used for reaction with the linear 2,3,12,13-tetraone we were able to isolate the 1:1 adduct, the corresponding bis-porphyrin-dione, in 75% yield and convert it by reaction with 0.5 equiv. of 1,2,4,5-benzenetetramine into the linear tetrakis-porphyrin **12** in 68% yield (Scheme 1). Previously we have described the synthesis of a bis-porphyrin[5] and its elaboration in many steps into a tetrakis-porphyrin **12**;[6] the route described herein results in a substantial improvement in overall yield and efficiency.

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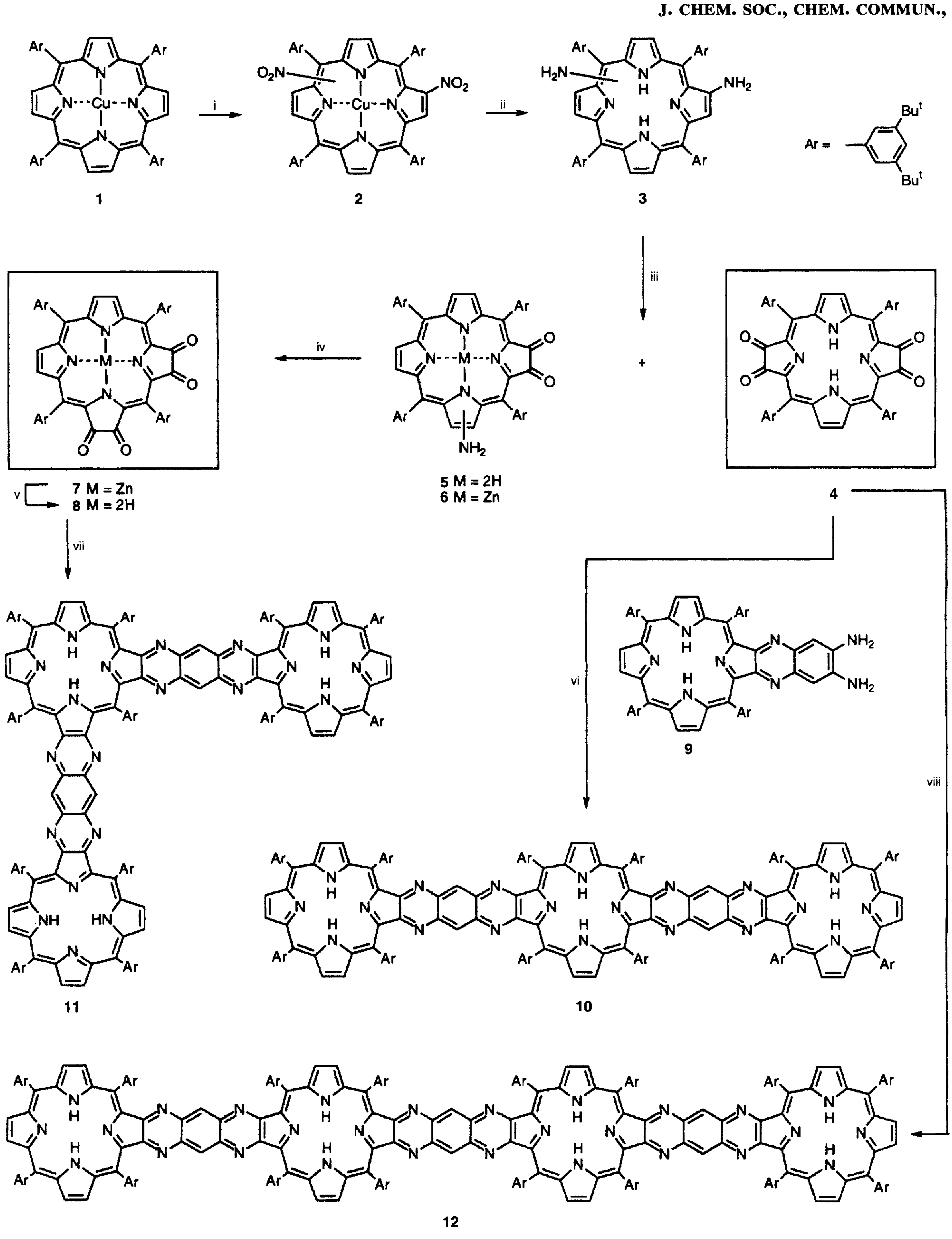
Footnotes

[†] All new compounds have been fully characterized by elemental analysis, MS, NMR and IR spectroscopy. *Selected spectroscopic data* for compound **4**: IR ($CHCl_3$) ν_{max}/cm^{-1} 3400w (NH) and 1724 (CO); UV–VIS ($CHCl_3$) λ_{max} (log ε)/nm 386 (5.09), 419 (4.88), 636 (3.81), 705 (3.80), 744 (3.82) and 772 (3.84); ^{1}H NMR (400 MHz, $CDCl_3$) δ −1.32 (2 H, br s, NH), 1.44 (72 H, s, *tert*-butyl H), 7.65 (8 H, d, J = 1.7 Hz, H_o), 7.74 (4 H, t, J = 1.7 Hz, H_p) and 8.50 (4 H, d, ^4J = 1.8 Hz, β-pyrrolic H). MS *m/z* 1123 (100%). For **8**: IR ($CHCl_3$) ν_{max}/cm^{-1} 1726 (CO); UV–VIS ($CHCl_3$) λ_{max} (log ε)/nm 391 (4.89), 515 (4.14), 555sh (4.05) and 646sh (3.84); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (18 H, s, *tert*-butyl H), 1.42 (36 H, s, *tert*-butyl H), 1.45 (18 H, s, *tert*-butyl H), 7.33 (2 H, d, J = 1.7 Hz, H_o), 7.52 (4 H, d, J = 1.7 Hz, H_o), 7.62 (1 H, t, J = 1.7 Hz, H_p), 7.67 (2 H, t, J = 1.7 Hz, H_p), 7.73 (1 H, t, J = 1.7 Hz, H_p), 7.76 (2 H, d, J = 1.7 Hz, H_o), 7.94 and 8.13 (4 H, ABq, J_{AB} = 4.7 Hz, β-pyrrolic H). In the $CDCl_3$ spectrum the inner NH's are not visible, in the C_6D_6 spectrum a 2 H broad singlet appears at δ 3.07. MS *m/z* 1123 (100%).



Scheme 1 *Reagents and conditions*: i, NO_2 in light petroleum, 25 °C; ii, conc. H_2SO_4–CH_2Cl_2, 10 min., neutralization; then $SnCl_2$/HCl, CH_2Cl_2, 25 °C, 66 h, neutralization; iii, O_2 in CH_2Cl_2, *hν*, then $Zn(OAc)_2 \cdot 2H_2O$ in CH_2Cl_2–MeOH, heat, 1.5 h, chromatography over silica; iv, O_2, *hν*, Rose Bengal, 2–4 h, chromatography over silica; v, conc. HCl–CH_2Cl_2, neutralization; vi, **9** (2 equiv.) in deoxygenated toluene, heat under N_2, 48 h; vii, **9** (2.5 equiv.) in deoxygenated toluene, heat under N_2, 72 h; viii, **9** (1 equiv.) in pyridine under N_2, 7 d, isolation of 1 : 1 adduct by chromatography and then reaction of it with 1,2,4,5-benzenetetramine tetrahydrochloride (0.5 equiv.) in boiling pyridine under N_2, 7 d

References

1 A. H. Jackson, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol. 1, ch. 9, pp. 365–389; E. A. Luk'yanets, V. N. Kopranenkov and E. A. Makarova, *J. Gen. Chem. USSR(Engl. Transl.)*, 1981, **51**, 2353; M. Hannack and T. Zipplies, *J. Am. Chem. Soc.*, 1985, **107**, 6127.

2 M. M. Catalano, M. J. Crossley, M. M. Harding and L. G. King, *J. Chem. Soc., Chem. Commun.*, 1984, 1535.

3 M. J. Crossley and L. G. King, *J. Chem. Soc., Chem. Commun.*, 1984, 920.

4 M. J. Crossley, M. M. Harding and S. Sternhell, *J. Am. Chem. Soc.*, 1992, **114**, 3266.

5 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1987, 39.

6 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1991, 1569.