Aluminium(III) porphyrins as supramolecular building blocks†

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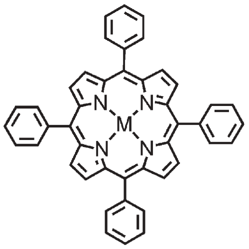
Aluminium(III) porphyrin–carboxylate complexes, including a porphyrin pentamer, have been characterised by NMR spectroscopy, MALDI spectrometry and single crystal X-ray diffraction; these complexes can also be coordinated by a sixth, nitrogenous, ligand to the aluminium(III) centre.

The design of multiporphyrin arrays has been an area of intense research. Their use in areas such as molecular recognition, sensing, molecular-level electronics and natural system mimics has been the major driving force. These arrays have been assembled by covalent bond formation or through non-covalent interactions such as hydrogen bonding.[1] However, designing and building arrays utilising axial coordination has proven to be a useful approach to the development of these assemblies with well defined geometries.[2] Knowledge of the preferred coordination number, geometry and ligand preference of a metalloporphyrin allows for the rational design of such arrays. To date, much of the attention has been paid to metalloporphyrins containing zinc(II), ruthenium(II), tin(IV), platinum(II) and rhodium(III) metal centres.[3] For many years the use of aluminium(III) porphyrins has mostly been limited to polymerisation reactions and activation of organic substrates.[4] There currently exist only a few examples in which an aluminium(III) porphyrin has been used for the construction of arrays which employ phenolates as the axial ligand.[5] Surprisingly, the use of benzoates as the axial ligand, for the development of arrays, has never been investigated. There have been isolated reports of aluminium(III)–benzoate complexes, but no systematic studies.[6] Herein, we present a systematic study of axially bound benzoates to aluminium(III) porphyrins and their potential use as supramolecular building blocks.

The synthesis of **3** proceeded smoothly upon the addition of benzoic acid to a solution of the reactive intermediate **2**, generated by the addition of trimethylaluminium to tetraphenylporphyrin (TPP), **1**. The ^{1}H NMR spectrum confirmed the coordination of the axially bound benzoate by the upfield shift of the benzoate proton resonances due to the shielding effect of the porphyrin. The magnitude of the upfield shifts for the *o*-, *m*- and *p*-protons of the benzoate are 2.96 ppm, 1.07 ppm and 0.90 ppm, respectively. Single crystal X-ray diffraction also confirmed the structure (see ESI†).‡ An ethanol molecule is coordinated to the sixth coordination site of the aluminium(III) centre in the solid state.



1 M = H_2
2 M = AlMe
3 M = Al(benzoate)
4 M = AlOH

The axially bound benzoate ligand is not displaced by water but exchange does occur with excess competitive carboxylic acids. This is slow on the chemical shift timescale, but rapid on the relaxation timescale, giving intense EXSY cross peaks between free and coordinated acids. A Hammett plot was constructed to gain some insight into the thermodynamics of the exchange process by making a series of 1:1 solutions containing **3** and a 4-substituted benzoic acid (R = $-NO_2$, –F, –Me, –*tert*-butyl and –OMe). In all cases, the exchange was slow on the chemical shift timescale and the ratio of association constants, K/K_H, was determined from the integration values of the two bound species at equilibrium. The absolute association constants could not be determined since the aluminium(III) centre is always carboxylate-bound even at low concentrations. Fig. 1 shows the resulting linear Hammett plot. The +0.76 ρ value is consistent with the development of a negative charge during the exchange process, the equilibrium being shifted to the right by electron-withdrawing groups. While the exact mechanism of exchange is unknown, we speculate that it is similar to that previously described for the tin(IV)–acetate exchange.[7] During these studies a six-coordinate aluminium(III) porphyrin complex was never detected: the complexes always maintained

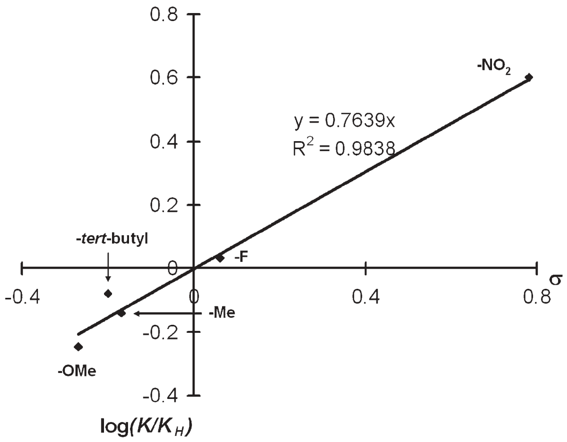


Fig. 1 Hammett plot.

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† Electronic supplementary information (ESI) available: X-Ray data, spectroscopic data, experimental procedures, Hammett plot data and competition data. See DOI: 10.1039/b605435h

their 1:1 stoichiometry. This is confirmed by the fact that there are no significant shifts in the proton resonances of any excess 'free' acid.

It has been shown previously that neutral nitrogen donor ligands can be used to fill the vacant sixth coordination site.[8] Using UV-vis spectroscopy the binding of 4-*tert*-butylpyridine or *N*-methylimidazole to **3** was confirmed by a bathochromic shift of the Soret band from 414 nm to 426 nm. Comparable shifts have been reported for the addition of pyridines to zinc(II) porphyrin.[3a] The UV-vis titrations show an isosbestic point confirming the presence of only two species in solution: the association constants were determined to be 3×10^3 M^{-1} for the 4-*tert*-butylpyridine and 4×10^5 M^{-1} for the *N*-methylimidazole.[9] In a competition experiment for *N*-methylimidazole between complex **3** and the *para*-nitro substituted version, there was a preference for the *para*-nitro complex by a factor of 4, due to the more electron deficient aluminium(III) metal centre (see ESI†).

Single crystal X-ray analysis (Fig. 2) confirms the coordination of 4-*tert*-butylpyridine to the vacant site of **3**.‡ The aluminium is bound to the four nitrogens of the porphyrin, with bond lengths ranging from 1.995(4) Å to 2.017(4) Å. The bond lengths of the benzoate oxygen, O(2), and the nitrogen of the 4-*tert*-butylpyridine, N(5), to the aluminium(III) metal centre, Al(1), are 1.843(3) and 2.215(4) Å, respectively. It has been suggested that five-coordinate aluminium(III) porphyrin in solution bearing an axial oxygen donor exists with the metal centre pulled up out of the plane of the porphyrin, although very little convincing evidence has been shown.[10] To date, there is no known X-ray structure of a five-coordinate aluminium(III)–benzoate porphyrin complex. The benzoate bound to complex **3** will be an effective reporter if the aluminium(III) centre is pulled back into the plane, since this should result in an additional upfield shift of the benzoate proton resonances. The ^{1}H NMR spectrum, see Fig. 3, shows the effect of the addition of 2 equivalents of 4-*tert*-butylpyridine to **3** on the proton resonances of the benzoate. As expected, an additional upfield shift of the coordinated benzoate is seen, consistent with the benzoate being pulled towards the porphyrin plane. These new chemical shifts correspond nicely with those of the benzoates bound to a six-coordinate tin(IV) centre.[7]

In order for these aluminium(III) porphyrins to be useful for the construction of large arrays, a more suitable starting material, other than the very reactive complex **2**, is required. Fortunately, complex **4**, a hydrolysed version of **2**, can also be used to generate **3** quantitatively by the addition of one equivalent of benzoic acid. This reaction also generates one equivalent of water which has no effect on the highly stable complex **3**.

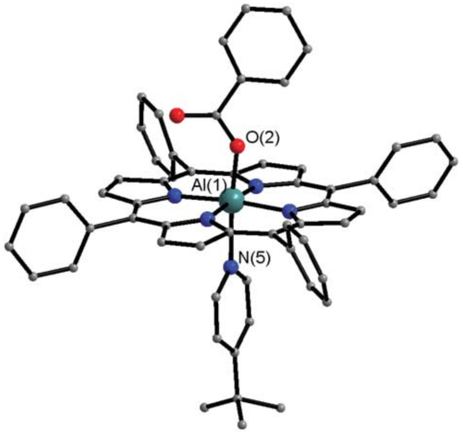


Fig. 2 Ball and stick representation of 4-*tert*-butylpyridine coordinated to complex **3**.

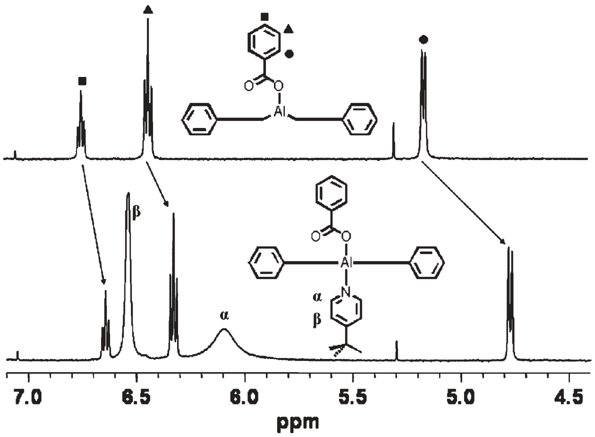
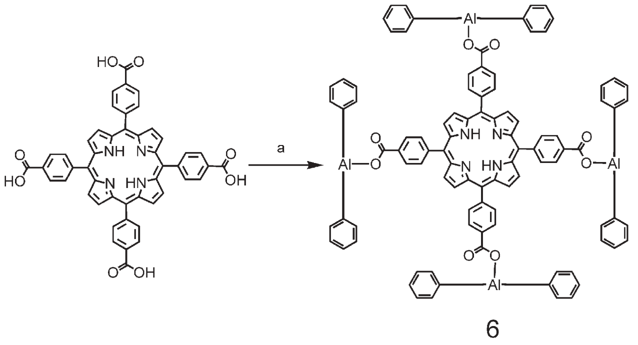


Fig. 3 ^{1}H NMR comparison of complex **3** (top) and the coordination of 4-*tert*-butylpyridine to complex **3** (bottom), emphasising the upfield shift of the benzoate resonances. Scale in ppm.

As a first test a porphyrin pentamer was sought. Scheme 1 details the approach used for the construction of a pentamer consisting of a central tetra(4-carboxyphenyl) porphyrin, **5**, surrounded by four tetraphenylaluminium(III) porphyrins. The synthesis was carried by the addition of **5** to six equivalents of **4** in chloroform.[11] The formation of the desired structure, **6**, was confirmed by ^{1}H NMR spectroscopy and MALDI mass spectrometry. The MALDI spectrum displays the $[\mathbf{6}]^{\cdot+}$ peak at *m*/*z* 3343.01, close to the calculated value of 3343.03, with a matching isotopic pattern. The stepwise formation of **6** can be studied by ^{1}H NMR spectroscopy as shown in Fig. 4, where the effect of the addition of two and four equivalents of **4** upon the central NH protons of the tetra(4-carboxyphenyl) porphyrin core can be seen. The addition of two equivalents shows the presence of mono-, di- (both *cis* and *trans*), tri- and tetrasubstituted complexes. The addition of two more equivalents yielded the expected tetrasubstituted complex, pentamer **6**, indicated by the presence of only one signal for the central NH protons. This additive upfield shift of the central protons has been seen previously.[12]



Scheme 1 The synthesis of the porphyrin pentamer. (a) 6 equiv. AlTPP(OH), $CHCl_3$.

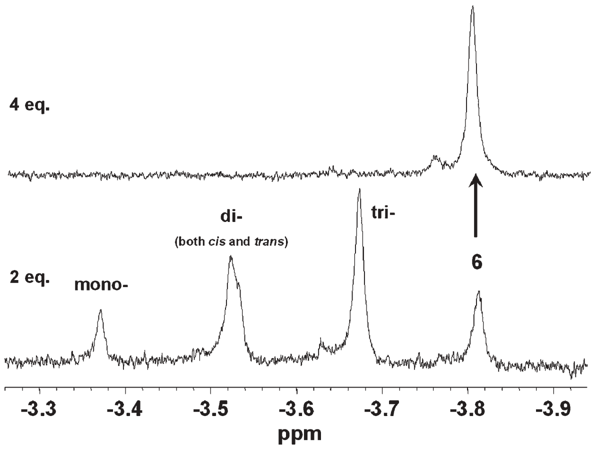


Fig. 4 ^{1}H NMR comparison showing the effects of adding 2 equiv. (bottom) and 4 equiv. (top) of **4** on the central NH proton resonances in the core of the pentamer, **6**.

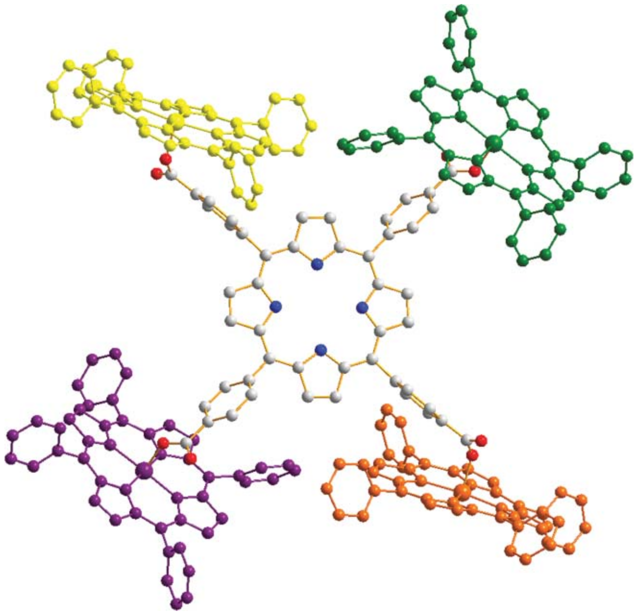


Fig. 5 Ball and stick representation of **6**. The four peripheral aluminium porphyrins are displayed as separate colours (purple, orange, yellow and green). Hydrogens, solvent and coordinated DMSO solvent molecules have been omitted for clarity.

Single crystal X-ray analysis also revealed the desired structure, **6**, as shown in Fig. 5.‡ The molecule sits on a crystallographic centre of symmetry positioned at the centre of the central porphyrin ring. The four aluminium centres form a rectangle with sides measuring approximately 16.3 and 15.0 Å. Each aluminium(III) porphyrin has a coordinated DMSO bound through the oxygen.

In conclusion, we have shown that aluminium(III) porphyrin–benzoate complexes are robust and the relative stabilities can be predicted through a Hammett plot. These complexes are stable in the presence of water and do not require an inert atmosphere. Aluminium(III) porphyrins effectively have two independent faces capable of binding both an oxygen donor and nitrogen donor, simultaneously, in the axial positions. This robustness and ability to coordinatively differentiate the two sides of the porphyrin make them an attractive alternative to tin(IV) porphyrins. The usefulness of complex **4** as a starting material for large arrays has been demonstrated through quantitative formation of the stable porphyrin pentamer, **6**. Currently, we are taking advantage of the coordinative properties of the outer faces, using imidazole-based ligands, of complex **6** to generate mixed metal arrays.

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Notes and references

‡ CCDC 604449 (**3**), 604450 (**6**) and 604451 (**3**·4-*tert*-butylpyridine). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605435h. Crystal data for **3**: $C_{55}H_{45}AlN_4O_4$, M = 852.93, monoclinic, $P2_1/n$ (No. 14), a = 13.326(2), b = 16.495(3), c = 21.114(4) Å, β = 108.394(2)°, V = 4404.2(13) Å^3, Z = 4, μ(Mo-Kα) = 0.100 mm^{-1}, T = 150(2) K, dark red plates; 6652 independent measured reflections (R_{int} = 0.0895), F^2 refinement, R_1 = 0.0501, wR_2 = 0.112 on 4236 observed data [$I > 2\sigma(I)$], and R_1 = 0.0951, wR_2 = 0.134 on all data. Crystal data for **3**·4-*tert*-butylpyridine: $C_{60.5}H_{46.5}AlN_5O_2Cl_{1.5}$, M = 955.68, monoclinic, $P2_1/n$ (No. 14), a = 11.8780(1), b = 10.4528(1), c = 42.0274(4) Å, β = 94.962(1)°, V = 5198.5(1) Å^3, Z = 4, μ(Mo-Kα) = 0.164 mm^{-1}, T = 220(2) K, 7369 independent measured reflections (R_{int} = 0.027), F^2 refinement, R_1 = 0.114, wR_2 = 0.380 on 6355 observed data [$I > 2\sigma(I)$], and R_1 = 0.124, wR_2 = 0.394 on all data. Crystal data for **6**: $C_{242}H_{198}Al_4Cl_4N_{20}O_{16}S_8$, M = 4140.34, triclinic, $P\bar{1}$ (No. 2), a = 17.0248(14), b = 18.7182(16), c = 19.0603(16) Å, α = 104.949(1), β = 105.955(1), γ = 94.339(1)°, V = 5571.7(8) Å^3, Z = 1, μ(Mo-Kα) = 0.21 mm^{-1}, T = 150(2) K, 15881 independent measured reflections (R_{int} = 0.028), F^2 refinement, R_1 = 0.160, wR_2 = 0.471 on 12262 observed data [$I > 2\sigma(I)$], and R_1 = 0.186, wR_2 = 0.497 on all data.

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