A self-assembled aluminium(III) porphyrin cyclic trimer†‡

Gerald A. Metselaar,[a] Jeremy K. M. Sanders[b] and Javier de Mendoza*[a]

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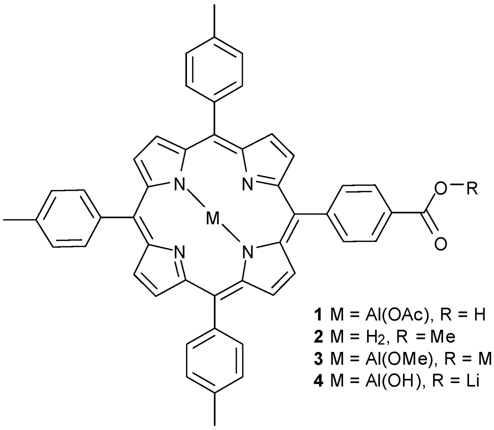
A self-assembled trimeric ring-shaped aggregate of an aluminium(III) porphyrin bearing a benzoic acid in one *meso*-position has been characterized by NMR-spectroscopy and MALDI-TOF spectrometry.

Cyclic multiporphyrin systems are interesting assemblies because of their resemblance to the natural light-harvesting system.[1] Both covalent[2] as well as supramolecular approaches[3] have been used to construct such cyclic porphyrin arrays. Many examples are reported in the literature in which metal porphyrins endowed with nitrogenous bases self-assemble to form either polymeric structures or well-defined oligomeric aggregates.[4] Inducing self-assembly of metal porphyrins bearing *O*-containing substituents like alcohols or carboxylic acids, however, has rarely been reported. Wojaczyński and coworkers found that Fe(III)-, Mn(III)-, and Ga(III) tetraphenylporphyrins bearing an OH-group in the β-pyrrolic 2-position self-assemble to form homometallic cyclic trimeric structures.[5a,c] In the case of the Fe(III)-porphyrin, the structure was confirmed by X-ray crystallography.[5d] In addition, using mixtures of the three metal porphyrins, also heterometallic cyclic trimeric aggregates could be obtained.[5d]



1 M = Al(OAc), R = H
2 M = H_2, R = Me
3 M = Al(OMe), R = Me
4 M = Al(OH), R = Li

Recently, the use of diamagnetic aluminium(III) porphyrins as supramolecular building blocks able to strongly bind axially to a carboxylate ligand has been described.[6] A pyridine can then be coordinated as a second axial ligand. Crystal structures of Al(III) porphyrins with simultaneous axial binding to a carboxylate and a pyridine reveal that the C–O–Al angle is typically ~150°.[6] This means that compound **1**, an Al(III)porphyrin with a *para*-benzoate in one *meso*-position, should self-assemble after removal of the axial acetate ligand into an almost perfect triangle $\mathbf{1}_3$ in the presence of a pyridine derivative (Fig. 1).

Porphyrin **1** was readily obtained from the free base methyl ester **2**,[7] which by addition of excess trimethylaluminium and subsequent quenching with methanol afforded **3** in 90% yield. Treatment of **3** with LiOH in a methanol–water mixture promoted formation of the lithium salt **4** by simultaneous ester hydrolysis and replacement of the OMe axial ligand by OH. Then, addition of an excess acetic acid and evaporation *in vacuo* overnight resulted in formation of the desired aggregate.

It is likely that formation of the Al-carboxylate aggregate proceeds by a similar mechanism as that proposed for the coordination of carboxylates to Sn(IV) porphyrins.[8] The first step is the formation of a hydrogen bond between the Sn–OH and the carboxylic acid in its protonated form. The Sn-carboxylate complex is subsequently formed by release of water (Fig. 2). Hence, it is necessary to have the benzoic acid of the aluminium porphyrin in its protonated form for self-assembly to take place.

As no suitable crystals for X-ray diffraction were available, the aggregation of $\mathbf{1}_n$[9] was studied in solution by NMR spectroscopy, as well as by MALDI-TOF mass spectrometry. A solution of $\mathbf{1}_n$ in deuterated chloroform gave rise to a broad and complicated ^{1}H NMR-spectrum, while a purple solid developed and precipitated from solution. Presumably this material was an oligomeric or polymeric undefined assembly. However, if an excess of *tert*-butylpyridine or 1-methylimidazole was added to the $CDCl_3$ solution of $\mathbf{1}_n$, or when the spectrum was recorded in pyridine-d_5, a well-defined ^{1}H-NMR spectrum was obtained (Fig. 3). This difference in aggregation behaviour with or without a nitrogenous base could be rationalised by looking at the crystal structures of aluminium(III) porphyrins bearing benzoate as axial ligand.[6] In the absence of *tert*-butylpyridine, the plane of the benzene ring of the benzoate is not perpendicular to the plane of the porphyrin but it is twisted by ~135° instead. On the contrary, when pyridine is coordinated as a second axial ligand, the benzoate is nicely oriented perpendicular to the porphyrin plane (Fig. 1a).

Most remarkably, the ^{1}H-NMR spectrum of $\mathbf{1}_n$ in the presence of nitrogenous bases was characterised by the presence of four well separated signals for the protons of the benzoate ring. For other aromatic acids axially bound to metallated porphyrins only two sets of signals are typically observed, for the two *ortho*- and two *meta*-protons, respectively. The observed differences in chemical shifts between the four protons are due to differences in shielding as a result of their distance to the porphyrin plane. Although these four different environments and distances are clearly seen in the crystal structure of a benzoate axially coordinated to an Al(III)

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[a] *Institute of Chemical Research of Catalonia (ICIQ), Avgd. Països Catalans 16, 43007, Tarragona, Spain. E-mail: jdemendoza@iciq.es; Fax: +34 977 920226; Tel: +34 977 920220*
[b] *University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW, England. E-mail: jkms@cam.ac.uk; Fax: +44 1223 336411; Tel: +44 1223 336017*

† The HTML version of this article has been enhanced with colour images.
‡ Electronic supplementary information (ESI) available: Experimental procedures, DOSY-NMR, MALDI-TOF-MS, calculation hydrodynamic radii. See DOI: 10.1039/b717017n

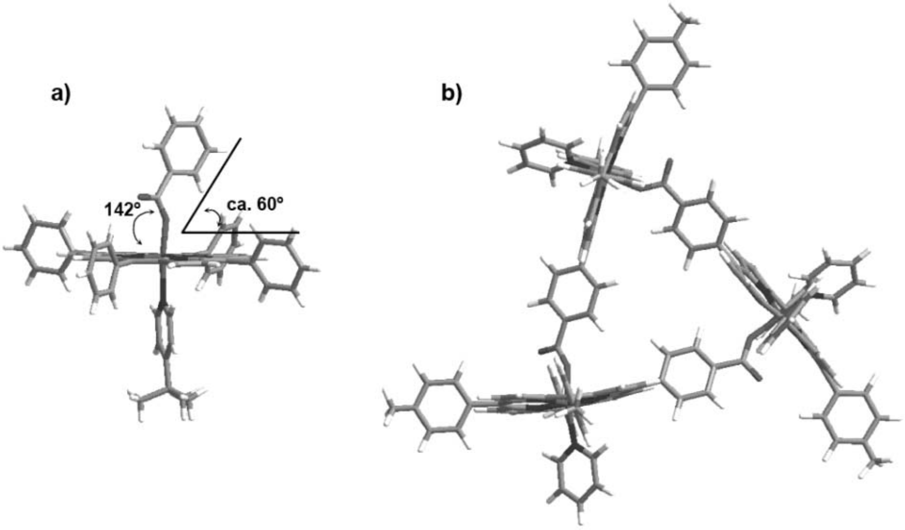

Fig. 1 a) The crystal structure of a meso-tetraphenyl aluminium(III) porphyrin bearing benzoic acid and *tert*-butylpyridine as axial ligands.[6] b) Optimized structure of trimer $\mathbf{1}_3$ bearing pyridine as additional axial ligand.[11]

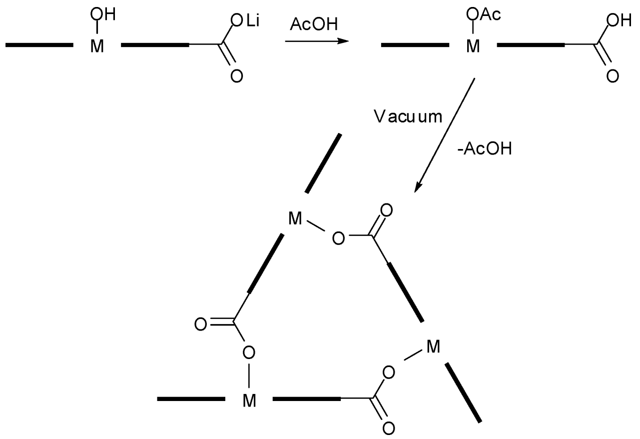

Fig. 2 Protonation of Li-carboxylate and subsequent self-assembly of metal porphyrins bearing a carboxylic acid by removal of acetic acid.

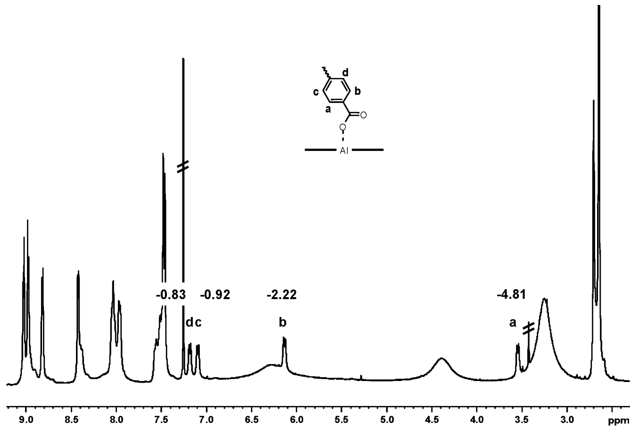

Fig. 3 ^{1}H NMR spectrum of $\mathbf{1}_3$ in $CDCl_3$ with 3 equivalents of 1-methylimidazole with the Δ*δ*-values relative to **3** (with OMe as axial ligand) indicated above the corresponding signals.

porphyrin (Fig. 1a), the rotational freedom of the benzoate in solution results in the observation of only the three typical signals for the carboxylate *ortho*-, *meta*- and *para*-protons in the ^{1}H-NMR spectrum.[10] Therefore, the frozen conformation in the case of $\mathbf{1}_n$ constitutes strong evidence for a well-organised, cyclic structure.[4e] The optimised trimer structure shown in Fig. 1b,[11] based on the coordinates of the X-ray structure of Fig. 1a, fully agrees with the angles and distances found in the latter, without any substantial distortion of the three porphyrin rings.

Further evidence for the formation of a well-defined aggregate came from ^{1}H DOSY NMR experiments (Table 1). For 0.02 M solutions of $\mathbf{1}_n$ and of its methyl ester **3** in pyridine-d$_5$, D = (2.06 ± 0.10) $\times 10^{-10}$ m^2 s^{-1} and D = (3.84 ± 0.10) $\times$ 10^{-10} m^2 s^{-1} values were found, respectively. In both cases, the diffusion coefficient found for pyridine itself was $D \sim 1.38 \times 10^{-9}$ m^2 s^{-1}, suggesting that the viscosities of the solutions were similar, so comparison of the obtained hydrodynamic radii was justified.[12] The hydrodynamic radii (r_{exp}) could be estimated by the Stokes–Einstein equation, assuming the species in solution to be spherical. Comparison of the calculated average radius (r_{calc} = average of x, y and z values of the corresponding gas phase-minimised structures)[13] with the experimental value suggests that monomer **3** is significantly smaller than expected: r_{exp} (5.9 ± 0.2 Å) *vs.* r_{calc} (6.9 Å). This difference could be ascribed to the non-spherical, disk-shaped structure of the monomeric porphyrin **3**. The trimer $\mathbf{1}_3$, on the other hand, has a more globular shape and the calculated radius (r_{calc} = 11.3 Å) corresponds remarkably well with that found experimentally (r_{exp} = 11.0 ± 0.2 Å).[14]

Table 1 Diffusion coefficients determined by DOSY and effective experimental (r_{exp}) and calculated (r_{calc}) hydrodynamic radii for **3** and $\mathbf{1}_3$

	$D/1\times 10^{-10}$ m^2 s^{-1}	r_{exp}/Å^a	r_{calc}/Å
Monomer **3**	3.84 ± 0.10	5.9 ± 0.2	6.9
Trimer $\mathbf{1}_3$	2.06 ± 0.10	11.0 ± 0.2	11.3

[a] Calculated using the Stokes–Einstein equation: $R = K_bT/6\pi\eta D$ where K_b is the Boltzmann constant and T is the absolute temperature. The viscosity of pyridine η(20 °C) = 0.95 cp was used.

Finally, additional support for the formation of self-assembled trimers was obtained by MALDI-TOF mass spectrometry. When **1** was deposited on the MALDI-plate from a pyridine solution, a relatively large signal for a trimeric assembly $\mathbf{1}_3$ was found, with only a small signal for the dimer $\mathbf{1}_2$ and a signal for monomeric **1** as additional peaks. When deposition on the MALDI-plate from a chloroform solution containing only five equivalents of *tert*-butylpyridine, small peaks were also observed for tetrameric $\mathbf{1}_4$ and larger oligomeric assemblies in addition to **1** and $\mathbf{1}_2$ or $\mathbf{1}_3$ aggregates. As mentioned already for the ^{1}H-NMR spectra, (excess) pyridine is needed to prevent linear aggregation.

In conclusion, introduction of a *para*-benzoate moiety at one *meso*-position of an Al(III) porphyrin results in a self-assembled cyclic trimer in the presence of nitrogenous bases. It is likely that playing with angles (such as *meta*-benzoates) or spacers would yield a diversity of self-assembled structures based on the Al(III) porphyrin scaffold. Additionally, use of diverse pyridyl or bipyridyl axial ligands would expand the supramolecular assemblies into more complex, hierarchically assembled three-dimensional networks. These strategies are currently being developed in our laboratories.

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14 For hypothetical $\mathbf{1}_4$ and $\mathbf{1}_2$ species: r_{cal} = 12.1 Å and r_{calc} = 9.8 Å, respectively. See ESI‡.