

Supplementary Material (ESI) for Chemical Communications  
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Supporting information for Chemical Communication

## Aluminium(III) Porphyrins as Supramolecular Building Blocks

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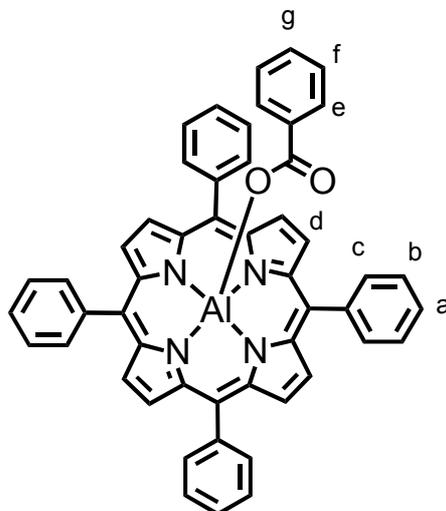
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## Experimental

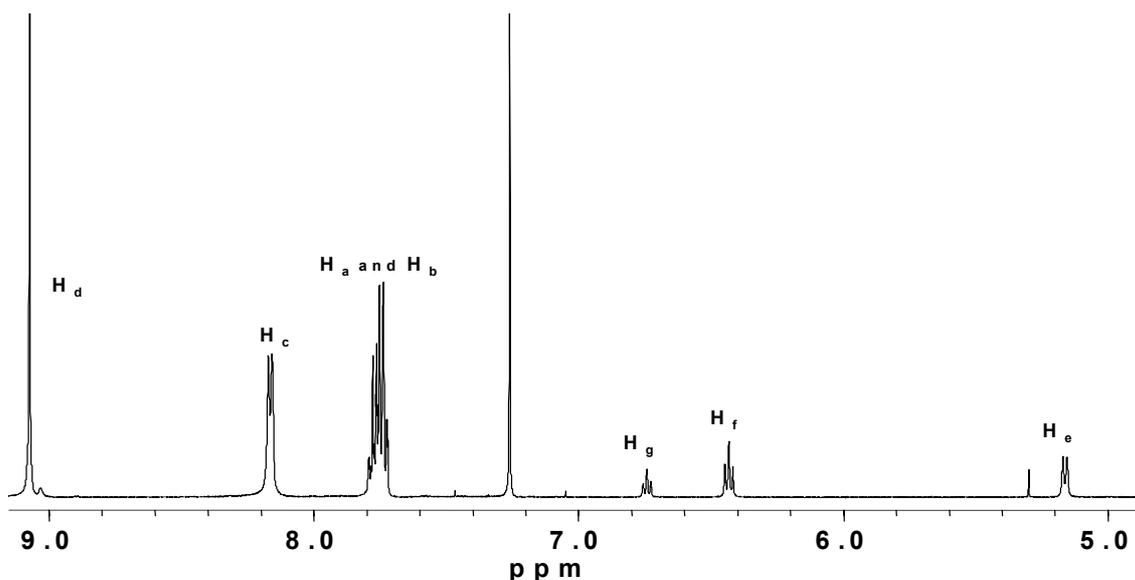
<sup>1</sup>H NMR spectra were obtained on a Bruker Avance 500 instrument operating at 500.1 MHz (using the deuterated solvent as the lock and the residual solvent or tetramethylsilane as the internal reference). Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. Matrix Assisted Laser Desorption Ionisation Time of Flight mass spectra (MALDI-TOF MS) were recorded on 4700 Proteomics Analyser (Applied Biosystems) with TOF/TOF optics. The spectra were acquired in reflector mode and 1000 laser shots were averaged together. UV/visible spectra were obtained on a Hewlett Packard 8452A diode array spectrometer using a 1 cm path quartz cell versus a pure-solvent reference. The absorption spectra were recorded in at concentrations of  $2.0 \times 10^{-6}$  M.

Data for complex **3**\* 4-tert-butylpyridine was collected at 220 K on a Nonius Kappa CCD with graphite monochromated Mo-K<sub>α</sub> radiation ( $\lambda = 0.71073$  Å). Crystallographic data for complexes **3** and **6** were collected using the synchrotron radiation source at Station 9.8, Daresbury SRS, UK, on a Bruker SMART CCD diffractometer. All structures were solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods against  $|F^2|$  data. Non-disordered and non-solvent non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated and treated as idealized contributions. In complex **3**\* 4-tert-butylpyridine the free solvent was restrained with DFIX commands. In complex **6** the 'free' DMSOs were restrained with DFIX commands using averaged bond distances and distances between atoms.

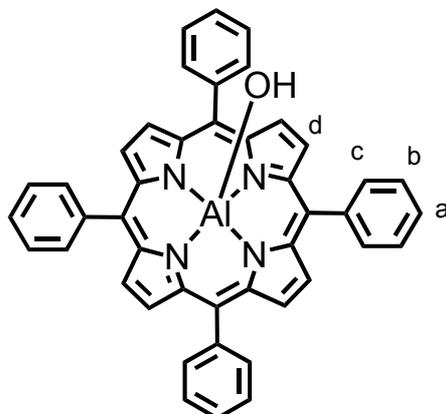
### Complex 3



To a solution of tetraphenylporphyrin (0.200 g, 0.325 mmol) in 25 mL of dry toluene was added excess trimethylaluminum (1.2 mL, 2.0M in hexane) under an atmosphere of N<sub>2</sub>. The resulting solution was stirred at room temperature for 4 hr, at which time the excess trimethylaluminum and toluene were removed under dynamic vacuum. The purple solid was placed under a N<sub>2</sub> atmosphere and 10 mL of dry toluene was added. Benzoic acid (0.050 g, 0.410 mmol) was added, as the solid, against a gentle stream of N<sub>2</sub>, stirring was continued overnight. The toluene was removed and the purple solid redissolved in DCM. The solution was filtered, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated yield the desired product **1** (0.172 g, 70 %). Note: If excess benzoic acid is present it can be removed by washing the purple solid with several portions of hot 30-40 pet ether. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 9.07 (s, 8H, H<sub>d</sub>), 8.16 (d, 8H, 6.7 Hz, H<sub>c</sub>), 7.79-7.72 (m, 12H, H<sub>a</sub> and H<sub>b</sub>), 6.74, (t, 1H, 7.4 Hz, H<sub>g</sub>), 6.43 (dd, 2H, 7.4 Hz and 7.4Hz, H<sub>f</sub>), 5.16 (d, 2H, 7.4 Hz, H<sub>e</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>/nm (ε/dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>) 414 (4.3 x 10<sup>5</sup>), 546 (1.7 x 10<sup>4</sup>). MALDI-MS (calc) for C<sub>51</sub>H<sub>33</sub>AlN<sub>4</sub>O<sub>2</sub> [M]<sup>+</sup> m/z 760.24 found m/z 760.19.

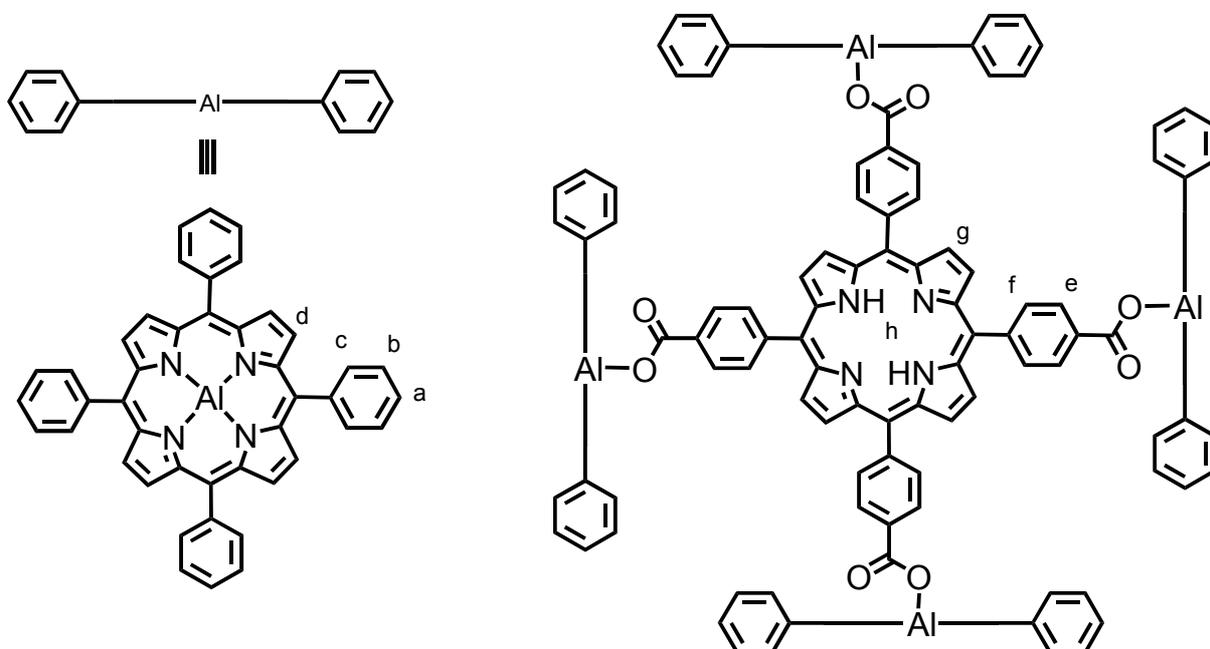


## Complex 4



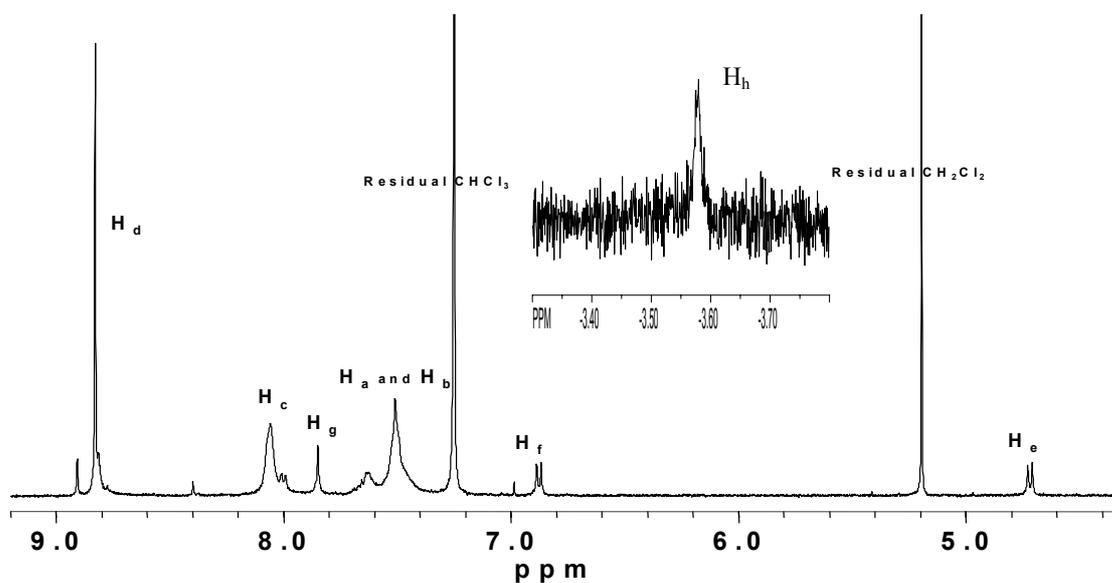
To a solution of tetraphenylporphyrin (0.500 g, 0.813 mmol) in 30 mL of dry toluene was added 1.2 equivalents trimethylaluminum (0.5 mL, 2.0M in hexane) under an atmosphere of  $N_2$ . The resulting solution was stirred at room temperature for 4 hr, at which time 5ml of water was added and stirring was continued overnight. The toluene was removed and the purple solid was redissolved in DCM. The solution was filtered, dried with  $Na_2SO_4$  and evaporated yield the desired product **2** (0.407 g, 76 %).  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 9.07 (s, 8H,  $H_d$ ), 8.24 (d, 8H, 6.4 Hz,  $H_c$ ), 7.76-7.80 (m, 12H,  $H_a$  and  $H_b$ ). UV-vis ( $CH_2Cl_2$ ):  $\lambda_{max}/nm$  ( $\epsilon/dm^3mol^{-1}cm^{-1}$ ) 414 ( $6.0 \times 10^5$ ), 546 ( $2.1 \times 10^4$ ). MALDI-MS (calc) for  $C_{44}H_{29}AlN_4O$   $[M]^+$  m/z 656.22 found m/z 656.18.

## Complex 6



To a solution of tetra(4-carboxy-phenyl) porphyrin (0.029 g, 0.037 mmol) in 50 mL of chloroform, containing a few drops of DMSO, was added 6 equivalents of **4** (0.144 g, 0.220

mmol). The resulting solution was stirred at room temperature for 1 hr, at which time the solvent was removed under dynamic vacuum. Alternately, DMSO can be omitted from the preparation and the chloroform solution can be refluxed for 4 hrs. The resulting purple solid was redissolved in a minimal amount of chloroform and 3 ml of toluene was added. The solution was allowed to stand a room temperature overnight at which time a purple solid develop. The solid was collected by vacuum filtration yielding the desired product **6** (0.084 g, 68 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$  + a few drops of  $d^6$ -DMSO) 8.83 (s, 32H,  $\text{H}_d$ ), 8.07 (m, 32H,  $\text{H}_c$ ), 7.86 (s, 8H,  $\text{H}_g$ ), 7.52 (m, 48H,  $\text{H}_a$  and  $\text{H}_b$ ), 6.88 (d, 8H, 8.2 Hz,  $\text{H}_f$ ), 4.72 (d, 8H, 8.2 Hz,  $\text{H}_e$ ), -3.56 (s, 2H, ). UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ) 414 ( $11.8 \times 10^5$ ), 548 ( $3.7 \times 10^4$ ), 516 ( $7.8 \times 10^4$ ). MALDI-MS (calc) for  $\text{C}_{224}\text{H}_{138}\text{Al}_4\text{N}_{20}\text{O}_8$   $[\text{M}]^+$  m/z 3343.03 found m/z 3343.01.



### Hammet Plot

Solutions containing equal molar amounts of **3** and a *para*-substituted benzoic acid were prepared. The concentration was  $5 \times 10^{-3}M$ . Plots were constructed using Hammett substituent constants,  $\sigma$ , and  $K/K_H$ .  $K/K_H$  was obtained from integration of the two bound species at equilibrium. The following equation was employed.

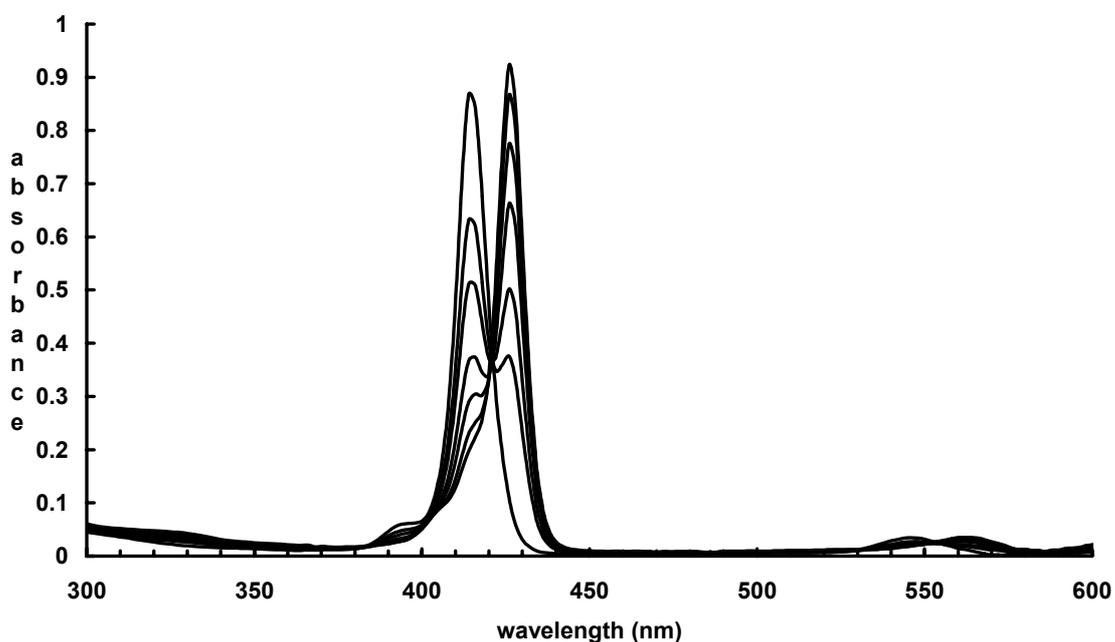
$$\frac{K}{K_H} = \frac{[\text{PorBC}][\text{BA}]_{\text{free}}}{[\text{PorBA}][\text{BC}]_{\text{free}}}$$

Where  $[\text{PorBC}]$  is the concentration of the porphyrin complex containing the *para*-substituted benzoic acid,  $[\text{BA}]_{\text{free}}$  is the concentration of the free benzoic acid,  $[\text{PorpBA}]$  is concentration of complex **3** and  $[\text{BC}]$  is concentration of the *para*-substituted benzoic acid at equilibrium.

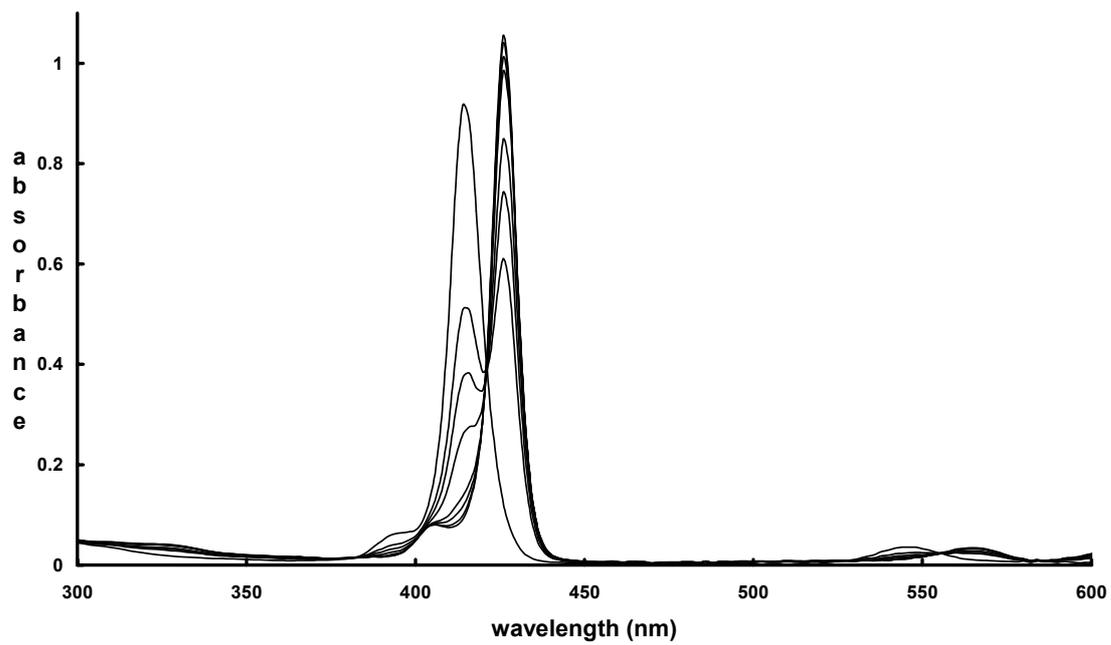
### *Association constant determination - UV/Vis titration*

A stock solution of 3 was prepared at a concentration of  $2 \times 10^{-6}$  M. A known amount was added to a 1 cm cuvette. To this was added 1 - 5  $\mu$ L of a concentrated solution of either 4-*tert*-butylpyridine or *N*-methylimidazole. The spectra were recorded from 200 - 800 nm. The association constant was determined from either the disappearance of the peak at 414 nm or the appearance at 426 nm. The association constants were averaged over three separate titrations.

#### **Complex 3 and 4-*tert*-butylpyridine**

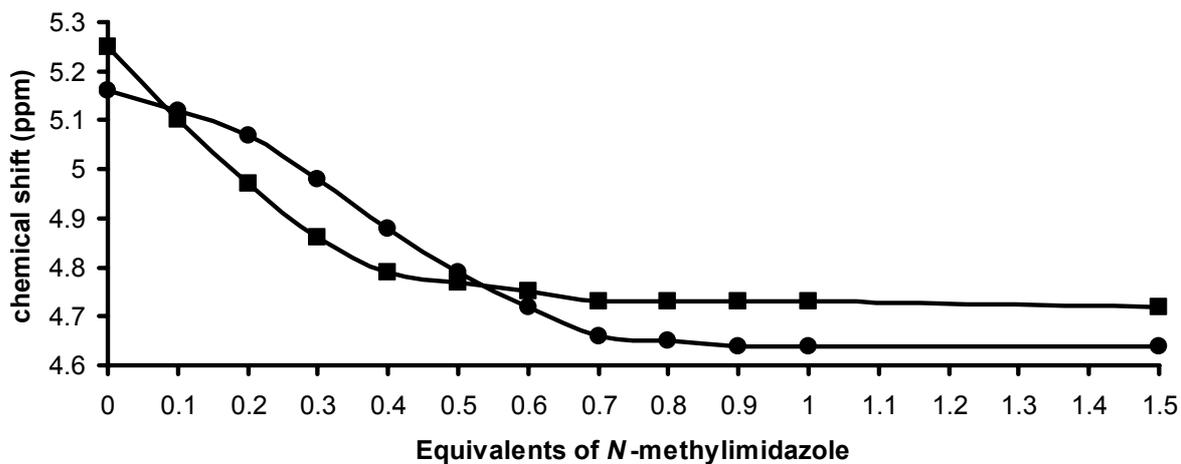
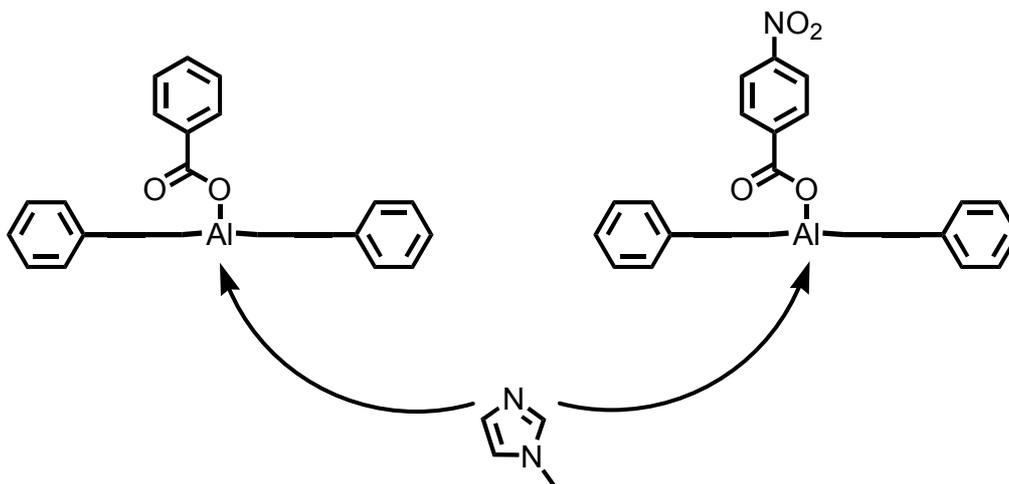


### Complex 3 and N-methylimidazole



### Competition Experiment

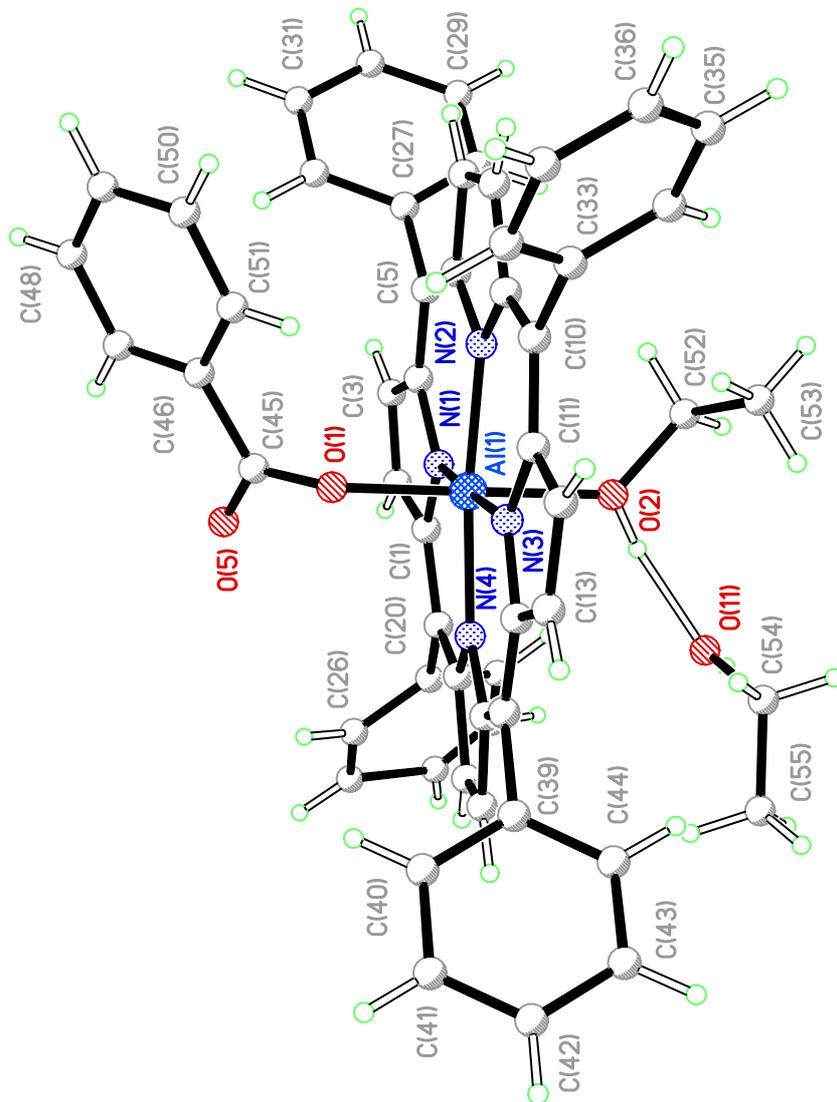
Equal molar quantities of both complex **3** and a *para*-nitro version (see below) were dissolved in 0.75 ml of CDCl<sub>3</sub> and placed into an NMR tube. A stock solution of *N*-methylimidazole was titrated in at every 0.1 equivalents. The <sup>1</sup>H NMR spectrum was recorded.



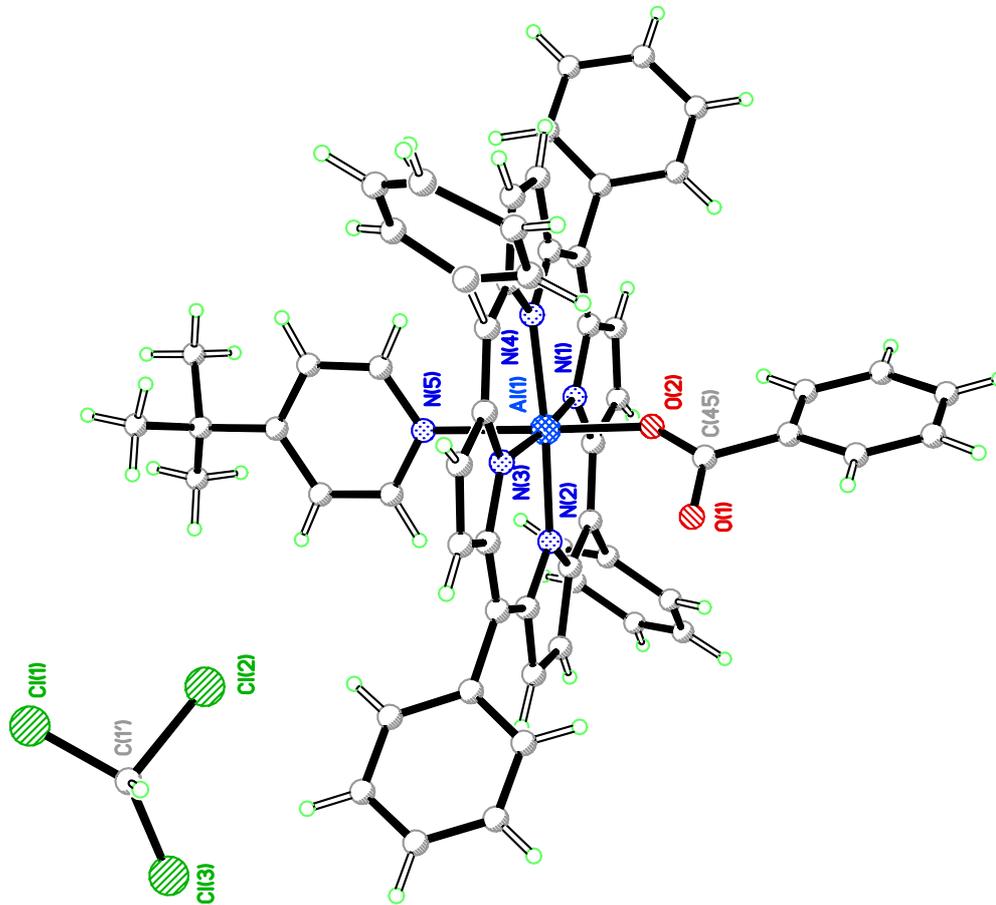
Plot construct monitoring the *ortho*-proton on each of complex **3** (●) and the *para*-nitro version (■)

*X-Ray Crystallography- Crystal Data*

Molecular Structure of complex **3**

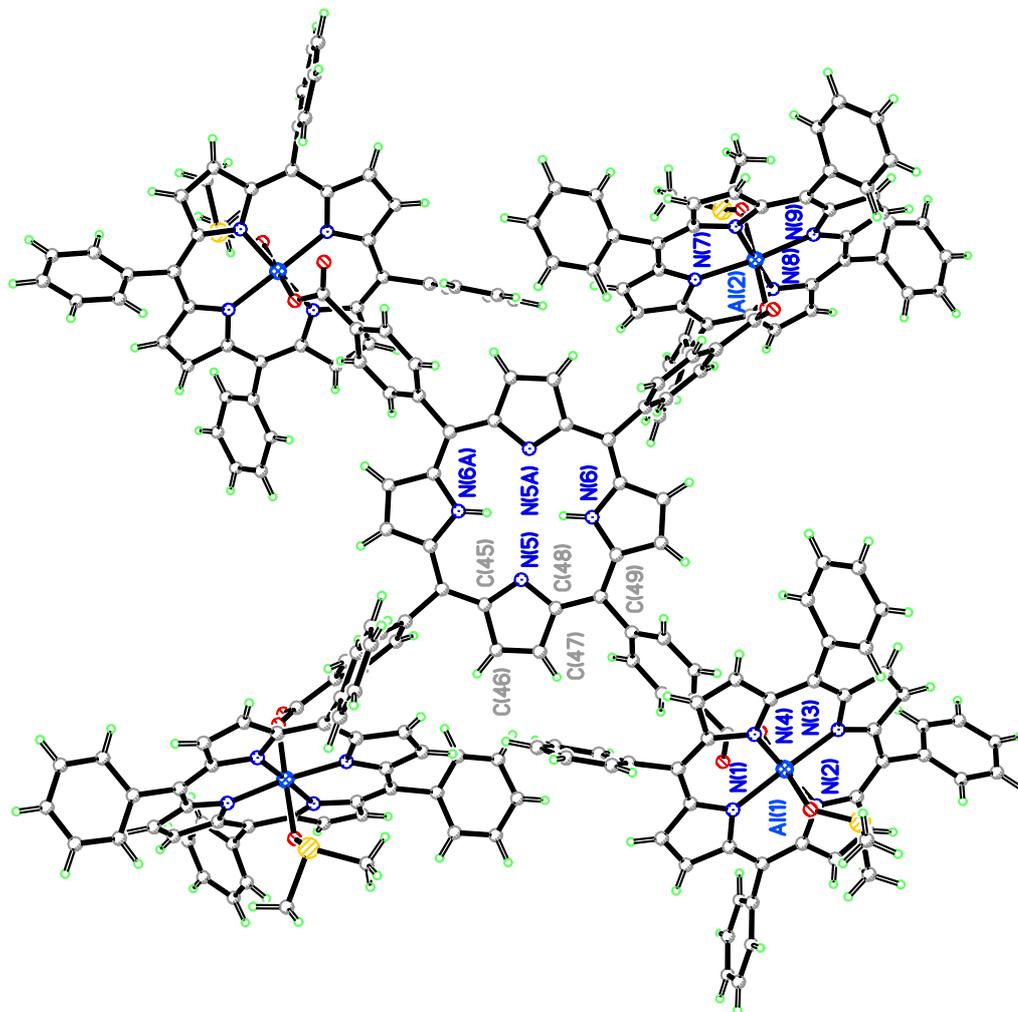


Molecular Structure of complex **3**\* 4-*tert*-butylpyridine



## Molecular Structure of complex 6

Note : There is DMSO molecule coordinated to each of the aluminium(III) centre in the sixth coordination site. While the rest are 'free'. Atoms labelled "A" are related by symmetry (inversion centre).



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,  $\beta = 108.394(2)^\circ$ ,  $V = 4404.2(13)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.100$  mm<sup>-1</sup>,  $T = 150(2)$  K, dark red plates; 6652 independent measured reflections ( $R_{\text{int}} = 0.0895$ ),  $F^2$  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,  $\beta = 94.962(1)^\circ$ ,  $V = 5198.5(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.164$  mm<sup>-1</sup>,  $T = 220(2)$  K, 7369 independent measured reflections ( $R_{\text{int}} = 0.027$ ),  $F^2$  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,  $P-1$  (No. 2),  $a = 17.0248(14)$ ,  $b = 18.7182(16)$ ,  $c = 19.0603(16)$  Å,  $\alpha = 104.949(1)^\circ$ ,  $\beta = 105.955(1)^\circ$ ,  $\gamma = 94.339(1)$ ,  $V = 5571.7(8)$  Å<sup>3</sup>,  $Z = 1$ ,  $\mu(\text{Mo-K}\alpha) = 0.21$  mm<sup>-1</sup>,  $T = 150(2)$  K, 15881 independent measured reflections ( $R_{\text{int}} = 0.028$ ),  $F^2$  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.