Materials and Methods.

All chemicals were purchased from commercial sources and used without further purification. Solvents were dried using a Solvent Purification System (SPS). Melting points were measured on a Büchi B-540 apparatus. NMR spectra were performed on Bruker Avance 400 (H: 400 MHz, 13C: 100 MHz) and 500 (H: 500 MHz, 13C: 125 MHz) Ultrashield spectrometers. Deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm, and are referred to the residual peak of the solvent. Mass analysis was performed in Waters LCT Premier (ESI or APCI mode), Waters GCT (EI and CI ionization modes) or Bruker MALDI-TOF spectrometers. UV spectra were recorded on a Shimadzu UV-1700 UV-Vis spectrophotometer. Thin layer chromatography (TLC) was performed on Alugram Sil G-25/UV254-coated aluminium sheets (Macherey-Nagel) and Alumina 60A F254 coated glass (SDS).

5-[4-(methoxycarbonyl)phenyl]-10,15,20-tri-p-tolylporphyrin (2)

To a solution of 4-methoxycarbonylbenzaldehyde (0.680 g, 4.14 mmol) and p-tolualdehyde (1.47 mL, 12.42 mmol) in refluxing propionic acid (140 mL) was added dropwise a solution of pyrrole (1.30 mL, 18.63 mmol) over a period of 30 minutes. The reaction mixture was stirred for an additional 3h, then cooled to RT. The solvent was removed under reduced pressure. The black tar-like residue was passed through a Florisil column using chloroform as eluent. The resulting purple crude product was purified by column chromatography over silica using chloroform as eluent followed by a second chromatographic purification using chloroform/hexane (6:4) as eluent. The desired porphyrin was precipitated from dichloromethane by addition of methanol to yield 2 as purple solid (0.260 g, 9.0%). Mp: >400°C (dec.). 1H NMR (400 MHz, CDCl3) 8.92 (m, 6H, Hc, Hd & He), 8.82 (m, 2H, Hf), 8.47 (d, 2H, 8.0 Hz, Hh), 8.35 (d, 2H, 8.0 Hz, Hg), 8.13 (d, 6H, 7.6 Hz, Hb), 7.57 (d, 6H, 7.6 Hz, Ha), 4.14 (s, 3H, OMe), 2.72 (s, 9H, Me), -2.69 (s, 2H).

NH). $^{13}$C NMR (100 MHz, CDCl$_3$) 167.3, 147.2, 139.2, 139.1, 137.4, 134.6, 134.5, 129.5, 127.9, 127.4, 120.7, 120.4, 118.2, 52.4, 21.5.

$^{5-}$[4-(methoxycarbonyl)phenyl]-10,15,20-tri-$p$-tolyl aluminium(III) porphyrin methoxide (3)

Free base porphyrin $^2$ (0.210 g, 0.29 mmol) was dissolved in dichloromethane (20 mL) and AlMe$_3$ (2.0 M in toluene, 0.440 mL) was added quickly. After stirring for 0.5 h at room temperature, the reaction was quenched by addition of 20 mL methanol and the mixture was evaporated to dryness under reduced pressure. Purification was carried out by passing the crude over a plug of neutral alumina using DCM/MeOH (99:1) as eluent. When all the yellow side-product had eluted, polarity was increased to 3% methanol. The purified product was subsequently precipitated from DCM with hexane to yield 3 as a dark-purple solid (0.220 g, 98%). Mp: >400ºC (dec). $^1$H NMR (400 MHz, MeOD) 9.05 (m, 6H, H$_c$, H$_d$ & H$_e$), 8.98 (m, 2H, H$_f$), 8.48 (d, 2H, 8.1 Hz, H$_h$), 8.36 (d, 2H, 8.1 Hz, H$_g$), 8.11 (d, 6H, 7.8 Hz, H$_b$), 7.64 (d, 6H, 7.6 Hz, H$_a$), 4.13 (s, 3H, OMe), 2.74 (s, 9H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) 169.5, 150.3, 150.2, 150.1, 149.4, 149.3, 141.3, 139.9, 136.5, 136.3, 134.0, 133.8, 133.7, 133.1, 131.8, 129.8, 129.4, 123.2, 122.9, 120.8, 53.8, 22.42. UV-vis (MeOH): $\lambda_{max}$/nm ($\varepsilon$/dm$^3$mol$^{-1}$cm$^{-1}$) 420 (7.1 $\times$ 10$^4$), 556 (2.3 $\times$ 10$^5$), 597 (1.2 $\times$ 10$^4$). EI-MS: m/z = 771 [M$^-$] & 793 [M+Na$^-$]

$^{5-}$[4-(carboxylic acid)phenyl]-10,15,20-tri-$p$-tolyl aluminium(III) porphyrin acetate (1)
Methyl ester 3 (0.129 g, 0.17 mmol) was dissolved in methanol (20 mL) and 1 M LiOH in water (4 mL) was added. The solution was stirred overnight at 50°C and then the excess methanol was removed by evaporation under reduced pressure. To the resulting suspension of 4 in water was added AcOH (3mL) and the suspension was extracted with dichloromethane. The organic layer was dried over Na₂SO₄ and evaporated to dryness to quantitatively give 1 as a purple/red solid. ¹H NMR (400 MHz, MeOD + 10μL AcOH) 9.16 (m, 8H, β-pyrrole), 8.48 (d, 2H, 7.7 Hz, H₂), 8.33 (d, 2H, 7.7 Hz, H₃), 8.12 (d, 6H, 7.3 Hz, H₄), 7.67 (d, 6H, 7.3 Hz, H₅), 2.75 (s, 9H, Me), -2.24 (bs, 3H, CH₃, acetate).

**Self-assembly of 1 into cyclic trimer 1₃**

A solid sample of 1 was dried *in vacuo* overnight at 60°C to remove all residual acetic acid and to exchange the axial acetate for the carboxylate that is part of 1. The resulting self-assembled aggregates were taken up in pyridine to form 1₃. ¹H NMR (400 MHz, pyridine-d₅) 9.38 (d, 2H, 4.7 Hz, HIV), 9.27 (d, 2H, 4.7 Hz, HIII), 9.15 (d, 2H, 4.7 Hz, HII), 8.60 (d, 2H, 4.7 Hz, HI), 8.55 & 8.34 (bs, 1H, H₁), 8.20 & 7.92 (bs, 1H, H₂), 7.56 (bs, 2H, H₃), 7.50 (d, 1H, 8.0 Hz, H₄), 7.45 (d, 4H, 7.8 Hz, H₅), 7.34 (bs, 1H, H₆), 6.57 (d, 1H, 7.0 Hz, H₇), 4.44 (d, 1H, 6.3 Hz, H₈), 2.60 (s, 3H, H₂), 2.54 (s, 6H, H₁). UV-vis (MeOH): λ max/nm
(ε/dm³mol⁻¹cm⁻¹) 429 (5.5 x 10⁵), 565 (1.9 x 10⁴), 606 (1.4 x 10⁴). Maldi-TOF-MS: m/z = 725 [M (I) - OAc]⁺, 1449 [M (I₂)]⁺, 2175 [M (I₃)]⁺.
**Dosy NMR**
Spectra were recorded of 0.02M solutions of methyl ester 3 and aggregates of 1 in pyridine-d₅ (Figure S1).

**Figure S1.** DOSY-spectra of 0.02 M solutions of 3 (red) and 1₃ (blue) in pyridine-d₅. The black line represents the logD of residual pyridine.
Maldi-TOF
A Maldi-TOF mass spectrum of $1_n$ was recorded from a solution of 1 in 1-methyl imidazole with dichloromethane as cosolvent. Pyrene was used as matrix (Figure S2).

\[ \text{Figure S2. Maldi-TOF spectrum of 1 from a solution in 1-methylimidazole/dichloromethane.} \]
Calculation of hydrodynamic radius $r_{\text{calc}}^2$

The average radius ($r_{\text{calc}}$) of the gas phase-minimized structures was calculated by averaging the $x$-, $y$- and $z$-values shown in Figure S3: $r_{\text{calc}} = 0.5 \cdot (x + y + z)/3$.

![Figure S3](image_url)

**Figure S3.** Minimized structures by CAChe of A) $1_3$ and B) $2$ and the values for their length, width and height. Pyridine molecules have been omitted because of their fast exchange on the NMR time-scale.

Also hydrodynamic radii were determined for hypothetical tetrameric and dimeric assemblies of $1$, $1_4$ and $1_2$, respectively (Figure S4).

---

Figure S4. Minimized structures by CAChe of A) 14 and B) 12 and the values for their length, width and height. Pyridine molecules have been omitted because of their fast exchange on the NMR time-scale.