

Supporting information for Chemical Communication

## Large-scale synthesis of alkyne-linked tripodal porphyrins via palladium-mediated coupling conditions

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### General Procedures

3,5-di-*tert*-butylbenzaldehyde<sup>1</sup> and the linkers **2**<sup>2</sup> and **3**<sup>3</sup> were prepared according to the published procedures. All other chemicals were purchased from Aldrich or Avocado in reagent grade quality or better and used without further purification. All <sup>1</sup>H NMR measurements were carried out at room temperature in deuteriochloroform and recorded on a Bruker DRX-500 instrument. Chemical shifts are quoted in parts per million with reference to residual protons of the deuterated solvent for the <sup>1</sup>H. The coupling constants are reported in hertz (Hz). Triethylamine (Et<sub>3</sub>N) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were distilled from CaH<sub>2</sub> under argon. Pyrrole was freshly distilled before use. Preparative thin layer chromatography was carried out on silica gel plates loaded with Merck silica gel 60 PF<sub>254</sub>. Column chromatography was performed on Merck 60 silica gel (230–400 mesh). 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 10-mm path quartz cell versus a pure-solvent reference. Elemental analyses were performed in the University of Cambridge, UK.

### 5-(3'-Iodophenyl)-10,15,20-tris(3'',5''-di-*tert*-butylphenyl)zincporphyrin (**1**)

3,5-di-*tert*-butylbenzaldehyde (6.66 g, 30.58 mmol), 3-iodobenzaldehyde (1.42 g, 6.12 mmol) and pyrrole (1.70 mL, 24.40 mmol) in propionic acid (100 mL) were heated to reflux for 6 h. The reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (300 mL) and Et<sub>3</sub>N (15 mL) was added. The organic layer was washed with H<sub>2</sub>O (4 × 300 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure to leave a black solid. The crude mixture was treated with excess Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (15 g) in CHCl<sub>3</sub>/MeOH mixture (10% MeOH) and gently heated for 10 mins. The solution was washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography on silica gel eluted with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/3) and the second fraction was collected. The fraction was purified again by column chromatography under the same conditions to yield **1** as purple solid (1.08 g, 16%). Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub> solution layered with MeOH afforded **1** of higher purity. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.06–9.03 (m, 6H, β-pyrrole), 8.96 (d, 2H, β-pyrrole), 8.65 (dd, <sup>3</sup>J<sub>ab</sub> ≈ <sup>3</sup>J<sub>ad</sub> = 1.6, 1H, H<sub>a</sub>), 8.26 (ddd, <sup>3</sup>J<sub>bc</sub> = 7.5, <sup>3</sup>J<sub>ba</sub> ≈ <sup>3</sup>J<sub>bd</sub> = 1.6, 1H, H<sub>b</sub>), 8.16–8.10 (m, 7H, ArH), 7.84–7.81 (m, 3H, ArH), 7.52 (dd, <sup>3</sup>J<sub>cb</sub> ≈ <sup>3</sup>J<sub>cd</sub> = 7.5, 1H, H<sub>c</sub>), 1.57–1.55 (4 singlets, 54H, <sup>1</sup>BuH) ; MALDI-TOF MS (m/z): required 1138.4323, found 1138.3114;

$\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 422, 548, 580 (log [ $\epsilon/M^{-1}cm^{-1}$ ] 5.8, 4.6, 4.5); elemental analysis for C<sub>68</sub>H<sub>75</sub>N<sub>4</sub>Zn·1CH<sub>3</sub>OH: calcd. C 70.73, H 6.71, N 4.78; found C 70.40, H 6.66, N 4.68.

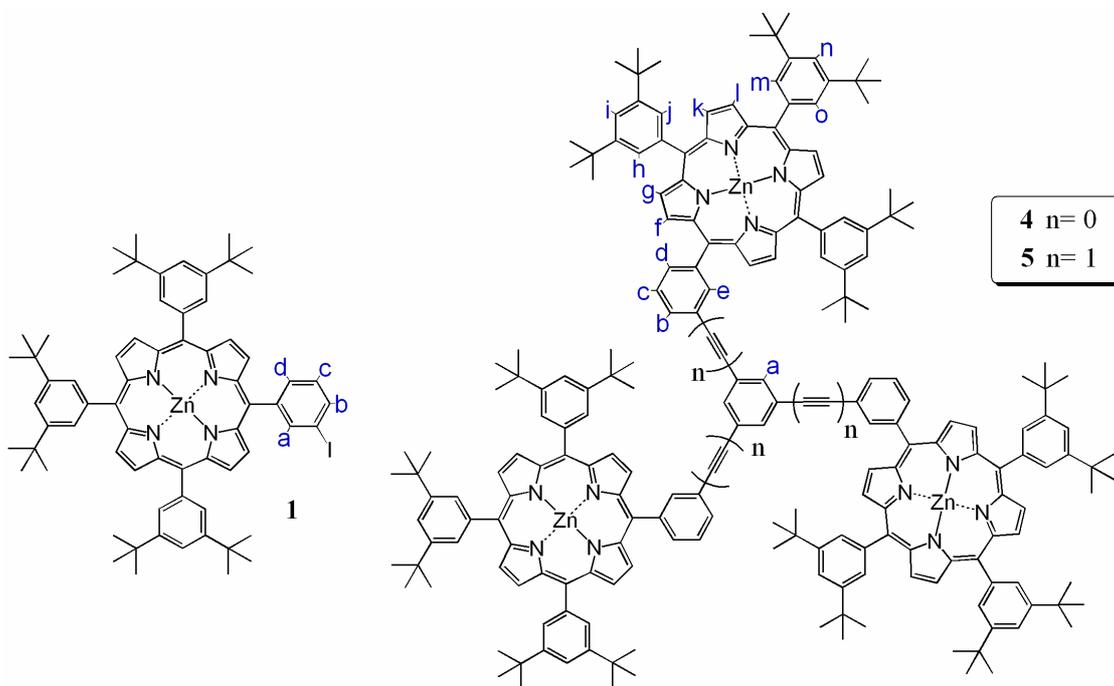
#### Zinc Trimer (4)

Tribornic ester **2** (40 mg, 0.09 mmol), zinc porphyrin monomer **1** (0.33 g, 0.29 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.06 g, 0.53 mmol) were added to a biphasic mixture of toluene (10 mL), ethanol (4 mL) and distilled H<sub>2</sub>O (3 mL). The solution was degassed for 30 minutes before Pd(PPh<sub>3</sub>)<sub>4</sub> (18 mg, 0.02 mmol) was added. The reaction mixture was heated to 80 °C and stirred under argon for 4 days. The mixture was cooled down to room temperature and the aqueous layer was discarded. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The reaction mixture was purified by preparative TLC on silica gel eluted with pentane/CH<sub>2</sub>Cl<sub>2</sub>/CHCl<sub>3</sub> (4/1/1) to yield **4** as purple solid (221 mg, 80%). Recrystallisation from CHCl<sub>3</sub> solution layered with MeOH afforded **1** of higher purity. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.00 (d, <sup>3</sup>J<sub>lk</sub> = 4.5, 6H, H<sub>l</sub>), 8.97 (d, <sup>3</sup>J<sub>kl</sub> = 4.5, 6H, H<sub>k</sub>), 8.95 (d, <sup>3</sup>J<sub>fg</sub> = 4.5, 6H, H<sub>f</sub>), 8.88 (d, <sup>3</sup>J<sub>gf</sub> = 4.5, 6H, H<sub>g</sub>), 8.66 (dd, <sup>4</sup>J<sub>eb</sub>  $\approx$  <sup>4</sup>J<sub>ed</sub> = 1.7, 3H, H<sub>e</sub>), 8.32 (s, 3H, H<sub>a</sub>), 8.18 (ddd, <sup>3</sup>J<sub>dc</sub> = 7.7, <sup>4</sup>J<sub>db</sub>  $\approx$  <sup>4</sup>J<sub>de</sub> = 1.7, 3H, H<sub>d</sub>), 8.13 (ddd, <sup>3</sup>J<sub>bc</sub> = 7.7, <sup>4</sup>J<sub>bd</sub>  $\approx$  <sup>4</sup>J<sub>be</sub> = 1.7, 3H, H<sub>b</sub>), 8.10 (dd, <sup>4</sup>J<sub>mn</sub>  $\approx$  <sup>4</sup>J<sub>mo</sub> = 1.6 or <sup>4</sup>J<sub>om</sub>  $\approx$  <sup>4</sup>J<sub>on</sub> = 1.6, 3H, H<sub>m</sub> or H<sub>o</sub>), 8.08 (dd, <sup>4</sup>J<sub>mn</sub>  $\approx$  <sup>4</sup>J<sub>mo</sub> = 1.6 or <sup>4</sup>J<sub>om</sub>  $\approx$  <sup>4</sup>J<sub>on</sub> = 1.6, 3H, H<sub>m</sub> or H<sub>o</sub>), 8.05 (dd, <sup>4</sup>J<sub>hi</sub>  $\approx$  <sup>4</sup>J<sub>hj</sub> = 1.6 or <sup>4</sup>J<sub>jh</sub>  $\approx$  <sup>4</sup>J<sub>ji</sub> = 1.6, 6H, H<sub>h</sub> or H<sub>j</sub>), 7.93 (dd, <sup>4</sup>J<sub>hi</sub>  $\approx$  <sup>4</sup>J<sub>hj</sub> = 1.6 or <sup>4</sup>J<sub>jh</sub>  $\approx$  <sup>4</sup>J<sub>ji</sub> = 1.6, 6H, H<sub>h</sub> or H<sub>j</sub>), 7.81 (dd, <sup>4</sup>J<sub>nm</sub>  $\approx$  <sup>4</sup>J<sub>no</sub> = 1.6, 3H, H<sub>n</sub>), 7.73 (dd, <sup>3</sup>J<sub>cb</sub>  $\approx$  <sup>3</sup>J<sub>cd</sub> = 7.7, 3H, H<sub>c</sub>), 7.72 (dd, <sup>4</sup>J<sub>ih</sub>  $\approx$  <sup>4</sup>J<sub>ij</sub> = 1.6, 6H, H<sub>i</sub>), 1.54 (s, 27H, <sup>1</sup>BuH), 1.53 (s, 27H, <sup>1</sup>BuH), 1.50 (s, 54H, <sup>1</sup>BuH), 1.34 (s, 54H, <sup>1</sup>BuH); MALDI-TOF MS (m/z): required 3109.6084, found 3109.3374;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 422, 548, 584 (log [ $\epsilon/M^{-1}cm^{-1}$ ] 5.9, 4.6, 4.1); elemental analysis for C<sub>210</sub>H<sub>228</sub>N<sub>12</sub>Zn<sub>3</sub>·1CHCl<sub>3</sub>: calcd. C 78.32, H 7.13, N 5.19; found C 77.99, H 7.22, N 5.20.

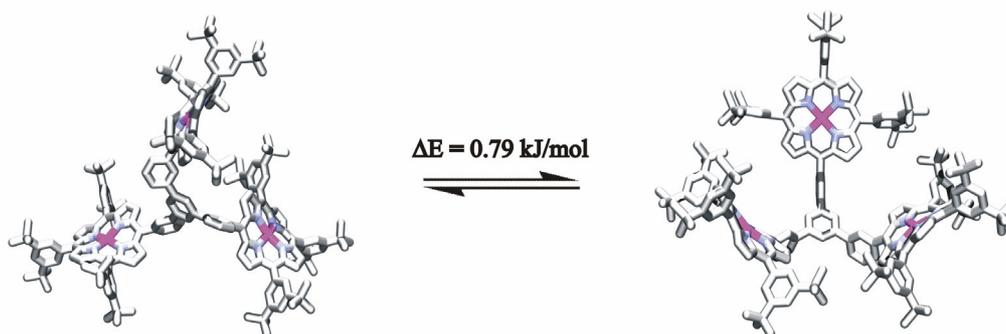
#### Zinc Trimer (5)

1,3,5-triethylbenzene **3** (5.20 mg, 0.03 mmol), zinc porphyrin monomer **1** (0.20 g, 0.15 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (6.40 mg, 0.07 mmol) and AsPh<sub>3</sub> (0.11 g, 0.35 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) and Et<sub>3</sub>N (4 mL). The solution was saturated with argon (three freeze-thaw cycles) and stirred at room temperature for 3 days, after which the solvent was removed under reduced pressure. The reaction mixture was purified by preparative TLC on silica gel eluted with pentane/CH<sub>2</sub>Cl<sub>2</sub>/CHCl<sub>3</sub> (4/1/1) to yield **2** as purple solid (102 mg, 91%). **1** (45 mg) could be recovered in the purification. Recrystallisation from CHCl<sub>3</sub> solution layered with MeOH afforded **2** of higher purity. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.02 (d, <sup>3</sup>J<sub>kl</sub>  $\approx$  <sup>3</sup>J<sub>lk</sub> = 4.8, 6H, H<sub>k</sub> or H<sub>l</sub>), 9.00 (d, <sup>3</sup>J<sub>kl</sub>  $\approx$  <sup>3</sup>J<sub>lk</sub> = 4.8, 6H, H<sub>k</sub> or H<sub>l</sub>), 8.98 (d, <sup>3</sup>J<sub>gf</sub> = 4.6, 6H, H<sub>g</sub>), 8.93 (d, <sup>3</sup>J<sub>fg</sub> = 4.6, 6H, H<sub>f</sub>), 8.40 (dd, <sup>4</sup>J<sub>eb</sub>  $\approx$  <sup>4</sup>J<sub>ed</sub> = 1.6, 3H, H<sub>e</sub>), 8.20 (ddd, <sup>3</sup>J<sub>dc</sub> = 7.7, <sup>4</sup>J<sub>db</sub>  $\approx$  <sup>4</sup>J<sub>de</sub> = 1.6, 3H, H<sub>d</sub>), 8.11 (dd, <sup>4</sup>J<sub>mn</sub>  $\approx$  <sup>4</sup>J<sub>mo</sub> = 1.7 or <sup>4</sup>J<sub>om</sub>  $\approx$  <sup>4</sup>J<sub>on</sub> = 1.7, 3H, H<sub>m</sub> or H<sub>o</sub>), 8.09–8.07 (m, 9H, H<sub>m</sub> or H<sub>o</sub> and H<sub>h</sub> or H<sub>j</sub>), 8.05 (dd, <sup>4</sup>J<sub>hi</sub>  $\approx$  <sup>4</sup>J<sub>hj</sub> = 1.6 or <sup>4</sup>J<sub>jh</sub>  $\approx$  <sup>4</sup>J<sub>ji</sub> = 1.6, 6H, H<sub>h</sub> or H<sub>j</sub>), 7.90 (ddd, <sup>3</sup>J<sub>bc</sub> = 7.7, <sup>4</sup>J<sub>bd</sub>  $\approx$  <sup>4</sup>J<sub>be</sub> = 1.6, 3H, H<sub>b</sub>), 7.81 (dd, <sup>4</sup>J<sub>nm</sub>  $\approx$  <sup>4</sup>J<sub>no</sub> = 1.7, 3H, H<sub>n</sub>), 7.77 (dd, <sup>4</sup>J<sub>ih</sub>  $\approx$  <sup>4</sup>J<sub>ij</sub> = 1.6, 6H, H<sub>i</sub>), 7.72 (s, 3H, H<sub>a</sub>), 7.70 (dd, <sup>3</sup>J<sub>cb</sub>  $\approx$  <sup>3</sup>J<sub>cd</sub> = 7.7, 3H, H<sub>c</sub>), 1.54 (2 singlets, 54H, <sup>1</sup>BuH), 1.52 (s, 54H, <sup>1</sup>BuH), 1.45 (s, 54H, <sup>1</sup>BuH); MALDI-TOF MS (m/z): required 3181.6084, found 3181.3665;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 422, 548, 584 (log [ $\epsilon/M^{-1}cm^{-1}$ ] 6.1, 4.8, 4.4); elemental analysis for C<sub>216</sub>H<sub>228</sub>N<sub>12</sub>Zn<sub>3</sub>·3CH<sub>3</sub>OH: calcd. C 80.16, H 7.28, N 5.12; found C 79.71, H 7.09, N 4.92.

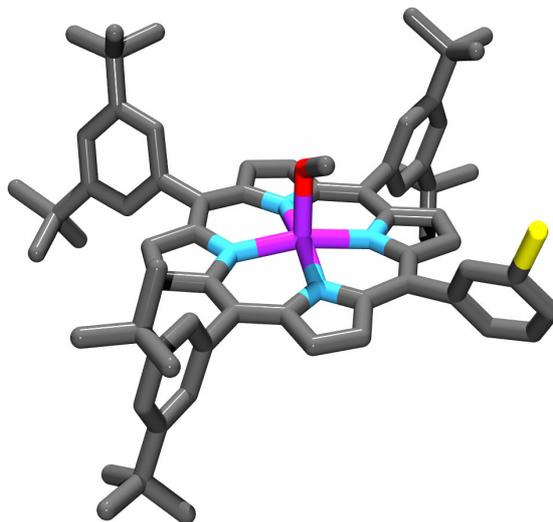
**NMR labelling scheme for zinc monomer 1 and zinc trimers 4 and 5**



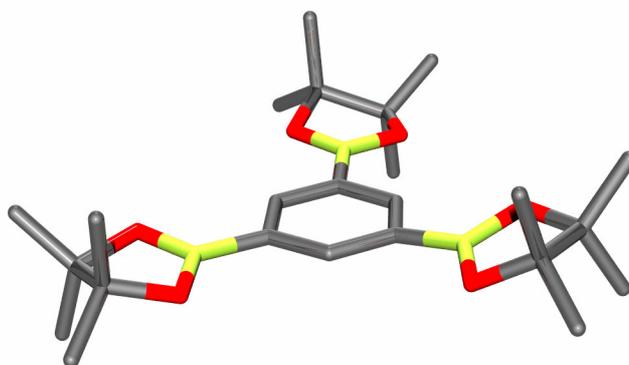
**Fig. S1.** Gas phase optimised geometries (PC Spartan, PM3 level) of the zinc trimer 4: propeller-shaped conformer (left) and bowl-shaped conformer (right).



**Fig. S2.** Molecular structure of zinc porphyrin monomer **1**. Hydrogen atoms have been omitted for clarity. (Key: grey-carbon, blue-nitrogen, purple-zinc, yellow-iodine)



**Fig. S3.** Molecular structure of triboronic ester **2**. Hydrogen atoms and solvent molecules have been omitted for clarity. (Key: grey-carbon, red-oxygen, yellow-boron)



X-ray quality crystals of **1** were obtained from a  $\text{CH}_2\text{Cl}_2$  solution layered with MeOH. X-ray quality crystals of **2** were grown from slow evaporation of the MeOH solution. Data were collected at 180 K on a Nonius KappaCCD with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The images were processed with the DENZO and SCALEPACK programs.<sup>4</sup> The structures were solved by direct methods using the program SIR92.<sup>5</sup> The refinement (on F) and graphical calculations were performed using the CRYSTALS<sup>6</sup> program suite.

## References

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