

***In-situ* reversible conversion of porphyrin aggregate morphologies**

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Electronic Supplementary Information

Materials and methods:

All the starting materials were purchased from commercial sources and used without further purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon or nitrogen atmosphere. ¹H and ¹³C NMR spectra of compounds were collected on a 400 MHz spectrometer at room temperature. **5a**¹, **1a**¹ and **4**² were synthesized according to the published procedures.

Instruments and Experimental Techniques

Optical Measurements:

UV-visible absorption spectra were recorded on a HITACHI U2800A spectrophotometer.

Preparation of samples:

Solutions (0.1 mM) of compounds **1b**, **2**, or **3** were prepared by adding a pure or mixed solvent to a glass vial containing the solid sample. Dissolution of solid samples was achieved by gentle shaking of the vial. The solutions (5 or 10 μL) were then dropcast onto the substrates using a micro-pipette and the solvent was evaporated in air.

Scanning electron microscopy:

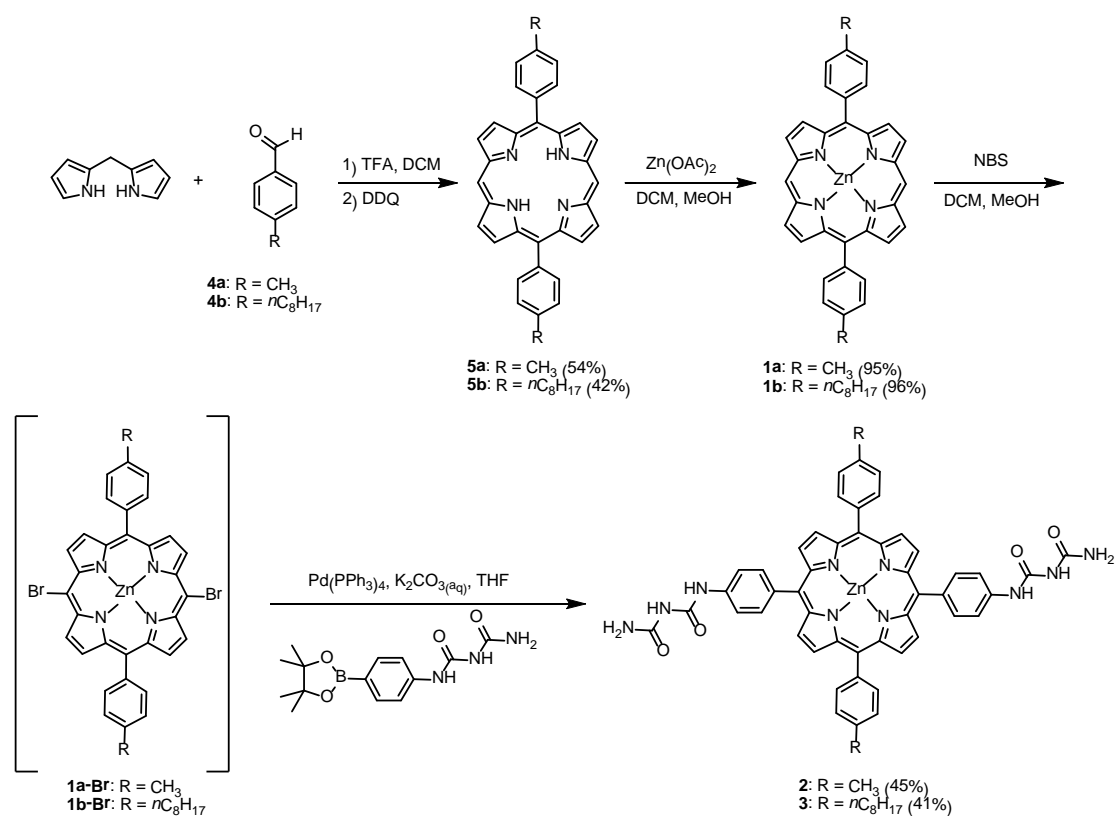
Samples were prepared by drop-casting solutions of compounds **1b**, **2**, or **3** (0.1 mM) onto a flat SiO₂/Si substrate. The samples were imaged using a FEI Nova NanoSEM 200 in low-vacuum mode with no conductive overcoat. The chamber pressure was maintained at 0.45 Torr water or THF vapor using a differential pumping system. An immersion lens was employed and the secondary electrons amplified by gas vapor and collected by an electrode mounted on the pole piece.

Transmission electron microscopy:

Samples were dropcast onto a 200 mesh copper grid coated with formvar film stabilized with vacuum-evaporated carbon and dried under air. The samples were examined using a Hitachi H-7650 electron microscope operating at 75 kv.

Crystal structure determination:

Crystallographic data were collected at 295(2) K on a Oxford Gemini A CCD diffractometer using graphite-monochromatized Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Cell parameters were retrieved and refined using CrysAlis Pro software on all observed reflections. Data reduction was performed with the CrysAlis Pro software. The structures were solved and refined with SHELXL programs. The hydrogen atoms were included in calculated positions and refined using a riding mode.



Scheme S1 Synthesis of porphyrin derivatives **2**, and **3**.

Synthetic procedures:

Synthesis of 5,15-Bis(4-octylphenyl)porphyrin (5b). A solution of dipyrromethane (191 mg, 1.3 mmol) and 4-octylbenzaldehyde (282 mg, 1.3 mmol) in dry CH₂Cl₂ (250 mL) was stirred under N₂ for 15 min. TFA (55 μ L, 0.85 mmol) was added to the solution via syringe, the flask was shielded from light, and the solution was stirred for 16 h at room temperature. DDQ (0.5 g, 2.17 mmol) was added, and the solution was

stirred for an additional 2 h. The crude product was purified by flash column chromatography on silica gel (DCM) to afford pure **5b** (190 mg, 42% yield) as a purple solid. ¹H NMR (CDCl₃, 400 MHz) δ 10.30 (s, 2H), 9.38 (d, *J* = 4.8 Hz, 4H), 9.12 (d, *J* = 4.8 Hz, 4H), 8.18 (d, *J* = 7.6 Hz, 4H), 7.62 (d, *J* = 7.6 Hz, 4H), 3.00 (t, *J* = 7.6 Hz, 4H), 1.97 (quin, *J* = 7.6 Hz, 4H) 1.65-1.01 (m, 20H), 0.99 (t, *J* = 6.8 Hz, 6H), -3.05 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 147.3, 145.1, 142.4, 138.6, 134.8, 131.5, 131.1, 127.0, 119.3, 105.1, 36.0, 32.0, 31.7, 29.7, 29.6, 29.4, 22.8, 14.2; HRMS (*m/z*, FAB⁺) [*M*⁺ + H] Calcd for C₄₈H₅₅N₄ 687.4427, found 687.4426.

Synthesis of [5,15-Bis(4-octylphenyl)porphyrinato]zinc(II) (1b). A saturated solution of Zn(OAc)₂ in methanol (20 mL) was added to a solution of **5b** (1.374 g, 2 mmol) in CHCl₃ (300 mL) and the resulting mixture was stirred for 3 h at 60 °C. Then, the organic residue was washed with water, dried over anhydrous Na₂SO₄, and evaporated. The crude product was purified by column chromatography on silica gel (DCM) to afford pure **2** (96%, 1.44 g) as a purple solid. ¹H NMR (CDCl₃, 400 MHz) δ 10.27 (s, 2H), 9.41 (d, *J* = 4.4 Hz, 4H), 9.16 (d, *J* = 4.4 Hz, 4H), 8.16 (d, *J* = 7.6 Hz, 4H), 7.60 (d, *J* = 7.6 Hz, 4H), 3.00 (t, *J* = 7.6 Hz, 4H), 1.97 (quin, *J* = 7.6 Hz, 4H), 1.64-1.41 (m, 20H), 0.98 (t, *J* = 6.8 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 150.3, 149.2, 142.2, 139.8, 134.6, 132.6, 131.6, 126.7, 120.3, 106.1, 36.0, 32.0, 31.7, 29.7, 29.4, 22.8, 14.2; HRMS (*m/z*, FAB⁺) Calcd for C₄₈H₅₂N₄Zn 748.3483, found 748.3477.

Synthesis of [5,15-Bis(benzenebiuret)-10,20-Bis(4-methylphenyl)porphyrinato]zinc(II) (2). A mixture of **1a** (673 mg, 1.21 mmol), NBS (476 mg, 2.67 mmol) was dissolved in DCM/MeOH = 9/1 and stirred at 0 °C for 10 min. The crude product (**1a-Br**) was concentrated and washed by MeOH and acetone, which was used directly for the next step without further purification. A mixture of Pd(PPh₃)₄ (116 mg, 0.1 mmol), K₂CO₃ (3.75 ml, 2M, 7.5 mmol) **1a-Br** (711 mg, 1.0 mmol), 4-pinacolboronic ester-benzenebiuret (**4**) (763 mg, 2.5 mmol) in degassed THF (40 mL) was refluxed for two days. The reaction was quenched by adding water and extracted with DCM and THF. The combined organic solution was washed with brine and dried over MgSO₄. The crude product was purified by column chromatography on silica gel (THF/DCM = 1/2) to afford pure **2** (45%, 450 mg) as a purple solid. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 10.34 (s, 2H), 9.05 (s, 2H), 8.79 (d, *J* = 4.8 Hz, 4H), 8.77 (d, *J* = 4.8 Hz, 4H), 8.09 (d, *J* = 8.4 Hz, 4H), 8.04 (d, *J* = 8.0 Hz, 4H), 7.85 (d, *J* = 8.4 Hz, 4H), 7.58 (d, *J* = 8.0 Hz, 4H), 2.66 (s, 6H); ¹³C NMR (DMSO-*d*₆, 400 MHz) δ 155.6, 152.3, 149.4, 149.3, 139.9, 137.6, 137.4, 136.6, 134.1, 131.5, 127.2, 120.3, 119.8,

117.2, 21.0; HRMS (m/z , FAB⁺) Calcd for C₅₀H₄₈N₁₀O₄Zn 906.2369, found 906.2380.

Synthesis of [5,15-Bis(benzenebiuret)-10,20-Bis(4-octylphenyl)porphyrinato]zinc(II) (3). A mixture of **1b** (87 mg, 0.13 mmol), NBS (51 mg, 0.29 mmol) was dissolved in DCM/MeOH = 9/1 and stirred at 0 °C for 10 min. The crude product (**1b-Br**) was concentrated and washed by MeOH and acetone, which was applied directly for the next step without further purification. A mixture of Pd(PPh₃)₄ (40 mg, 0.035 mmol), K₂CO₃ (828 mg, 6 mmol) **1b-Br** (100 mg, 0.11 mmol), 4-pinacolatoboronic ester-benzenebiuret (**4**) (305 mg, 1 mmol) in degassed THF (10 mL) and water (3 mL) was refluxed for two days. The reaction was quenched by adding water and extracted with THF. The combined organic solution was washed with brine and dried over MgSO₄. The crude product was purified by column chromatography on silica gel (THF/DCM = 1/2) to afford pure **3** (41%, 55 mg) as a purple solid. ¹H NMR (DMSO-d₆, 400 MHz) δ 10.35 (s, 2H), 9.05 (s, 2H), 8.78(d, J = 4.8 Hz, 4H), 8.75 (d, J = 4.8 Hz, 4H), 8.09 (d, J = 8.0 Hz, 4H), 8.03 (d, J = 8.0 Hz, 4H), 7.86 (d, J = 8.0 Hz, 4H), 7.54 (d, J = 8.0 Hz, 4H), 2.89 (t, J = 7.2 Hz, 4H), 1.85 (quin, J = 7.2 Hz 4H), 1.50-1.32 (m, 20H), 0.90 (t, J = 7.2 Hz 6H); ¹³C NMR (DMSO-d₆, 100 MHz) δ 156.3, 153.0, 150.1 150.0, 142.1, 140.7, 138.3, 138.1, 135.4, 134.8, 132.2, 132.1, 127.1, 121.0, 120.5, 117.8, 35.8, 32.0, 31.7, 29.6, 29.4, 22.8, 14.7; HRMS (m/z , FAB⁺) Calcd for C₆₄H₆₆N₁₀O₄Zn 1102.4560, found 1102.4563.

References

- 1 A. Osuka, S. Marumo, N. Mataga, S. Taniguchi, T. Okada, I. Yamazaki, Y. Nishimura, T. Ohno and K. Nozaki, *J. Am. Chem. Soc.* 1996, **118**, 155.
- 2 F.-C. Fang, C.-C. Chu, C.-H. Huang, G. Raffy, A. Del Guerzo, K.-T. Wong and D. M. Bassani, *Chem. Commun.* 2008, 6369.

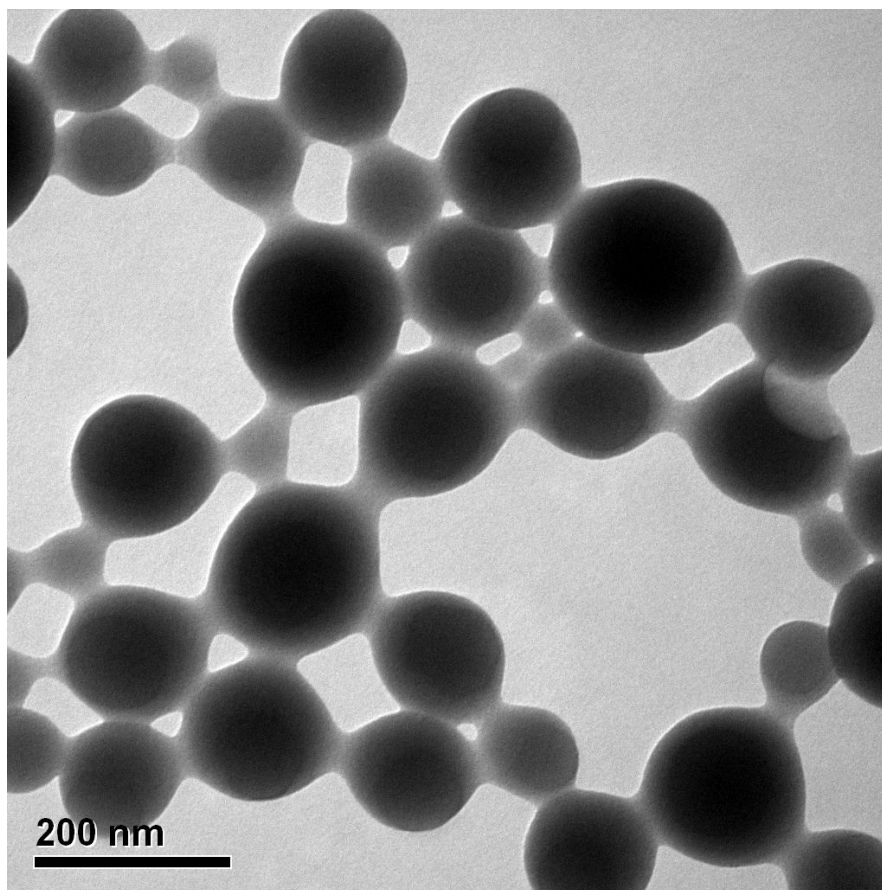


Figure. S1 TEM of **2** prepared in THF/MeOH (10:1, v/v), showing hollow sphere structures.

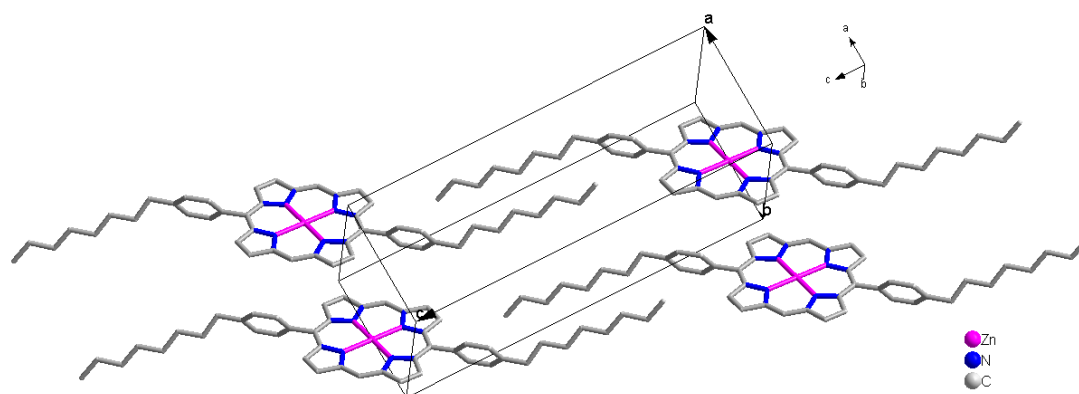


Figure. S2 Crystal packing of compound **1b** in a unit cell. The hydrogen atoms are omitted for clarity.

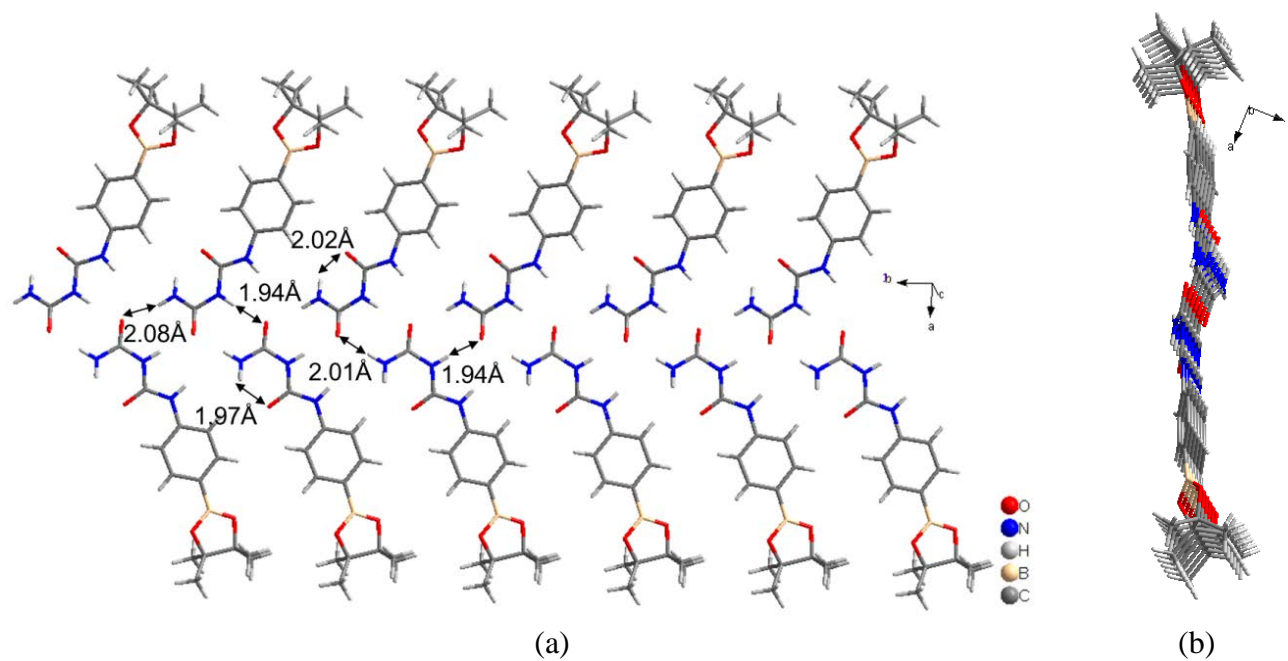


Figure. S3 Crystal packing of 4-pinacolboronic ester-benzenebiuret (**4**). The hydrogen atoms are omitted for clarity. (a) Top view of *ab*-plane. (b) Side view from *b*-axis.

Table S1. The crystal data of **1b** and **4**

	1b	4
Empirical formula	C ₄₈ H ₅₂ N ₄ Zn	C ₁₄ H ₂₀ BN ₃ O ₄
Formula weight	750.31	305.14
Crystal dimensions/mm ³	0.30×0.15×0.10	0.25×0.20×0.15
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pca2(1)
<i>a</i> /Å	8.5569(2)	19.8063(6)
<i>b</i> /Å	9.8055(2)	7.1749(3)
<i>c</i> /Å	23.4743(6)	22.0931(8)
α (deg)	81.298(2)	90.00
β (deg)	89.186(2)	90.00
γ (deg)	89.346(2)	90.00
Cell volume/Å ³	1946.65(8)	3139.6(2)
Z	2	8
Density (calc)/g cm ⁻³	1.280	1.291
<i>F</i> (000)	796	1296
Temperature/K	200(2)	150(2)
Wavelength/Å	1.54178	1.54178
No. of reflns collected	12010	9810
No. of indep reflns (<i>R</i> _{int})	12010(0.0000)	4131(0.0395)
<i>R</i> (<i>F</i>), <i>wR</i> 2 [<i>I</i> >2σ(<i>I</i>)]	0.0473, 0.1254	0.0544, 0.1423
<i>R</i> (<i>F</i>), <i>wR</i> 2 (all data)	0.0631, 0.1387	0.0581, 0.1564

