Supporting Information
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Supporting Information

Efficient One-Pot Regioselective Synthesis of 2,3-Dibromo-5,10,15,20-tetraarylporphyrins from 5,10,15,20-Tetraarylchlorins

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I. Experimental details and characterization data for all new compounds

Materials and Instrumentations:

NMR spectra were recorded at 300 MHz for $^1$H and 282 MHz for $^{19}$F NMR spectra. Deuterated solvents for $^1$H NMR were purchased from Cambridge Isotope Laboratories, Aldrich or Acros. MS were recorded on a Hewlett-Packard HP-5989A spectrometer. UV – vis spectra were measured at 20 °C with a Varian Cary 100 spectrophotometer. Elementary analyses were obtained on a Perkin Elmer 2400 Series II Elemental Analyzer. TLC analyses were performed on silica gel plate and column chromatography over silica gel (mesh 300 – 400), which were both obtained from Qingdao Ocean Chemicals. Unless otherwise noted, reagents were commercial available and used as received.

5,10,15,20-tetraarylchlorins 2 were synthesized according to the literature method.$^1$

5,10,15,20-tetraphenylchlorin (2a)$^1$: purple crystals; 730 mg, yield 73%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.57 (d, $J = 3.9$ Hz, 2H, $\beta$-H), 8.42 (s, 2H, $\beta$-H), 8.17 (d, $J = 3.9$ Hz, 2H, $\beta$-H), 8.11 (d, $J = 5.7$ Hz, 4H, o-Ph-H), 7.87 (d, $J = 4.8$ Hz, 4H, o-Ph-H), 7.68 – 7.69 (m, 12H, m-Ph-H & p-Ph-H), 4.16 (s, 4H, CH$_2$), – 1.45 (s, 2H, NH); MS (MALDI) m/z 616.3 (M$^+$).

5,10,15,20-tetra($p$-chlorophenyl)chlorin (2b): purple crystals; 736 mg, yield 60%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J = 4.5$ Hz, 2H, $\beta$-H), 8.40 (s, 2H, $\beta$-H), 8.18 (d, $J = 4.5$ Hz, 2H, $\beta$-H), 8.02 (d, $J = 7.8$ Hz, 4H, o-Ph-H), 7.80 (d, $J = 7.8$ Hz, 4H, o-Ph-H), 7.67 (d, $J = 7.5$ Hz, 8H, m-Ph-H), 4.15 (s, 4H, CH$_2$), – 1.52 (s, 2H, NH); UV – vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (relative intensity) 419 (1.00), 519 (0.09), 545 (0.06), 599 (0.04), 652 (0.19) nm; MS (MALDI) m/z 754.1 (M$^+$). Anal. Caled for C$_{44}$H$_{28}$Cl$_4$N$_4$·0.5H$_2$O (from CH$_2$Cl$_2$/wet CH$_3$OH): C, 69.21; H, 3.83; N, 7.34. Found: C, 69.35; H, 3.68; N, 7.34.
5,10,15,20-tetra(p-trifluoromethylphenyl)chlorin (2c): purple crystals; 1230 mg, yield 85%.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.82 (s, 2H, $\beta$-H), 8.54 (d, $J = 4.5$ Hz, 2H, $\beta$-H), 8.35 (d, $J = 9.0$ Hz, 4H, o-Ph-H), 8.22 (d, $J = 7.5$ Hz, 4H, o-Ph-H), 8.16 (d, $J = 4.5$ Hz, 2H, $\beta$-H), 7.96 – 8.06 (m, 8H, m-Ph-H), 4.15 (s, 4H, CH$_2$), 1.49 (s, 2H, NH); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ – 58.3 (s, 12F); UV – vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (relative intensity) 417 (1.00), 515 (0.07), 544 (0.04), 597 (0.03), 652 (0.15) nm; MS (MALDI) $m/z$ 888.2 (M$^+$). Anal. Calcd for C$_{48}$H$_{28}$F$_{12}$N$_4$: C, 64.87; H, 3.18; N, 6.30. Found: C, 64.66; H, 3.11; N, 6.30.

Synthesis of 12,13-Dibromo-2,3-dihydro-5,10,15,20-tetraphenylchlorin 3a.

5,10,15,20-tetraphenylchlorin 2a (124 mg, 0.2 mmol) and NBS (80 mg, 0.44 mmol) were added to a Schlenk flask (50 mL). The flask was then evacuated and backfilled with nitrogen (three cycles). Then dry chloroform (ethanol free, 20 mL) was charged with a syringe. The reaction mixture was stirred and heated under reflux for 4 h. After being cooled to room temperature, triethylamine (1 mL) was added to neutralize the acids produced in the reaction. Then the reaction mixture was quickly filtered through a short silica plug (300 – 400 mesh, eluting with CH$_2$Cl$_2$). The filtrate was concentrated and recrystallized from CH$_2$Cl$_2$/MeOH to give pure products 3a.

12,13-Dibromo-2,3-dihydro-5,10,15,20-tetraphenylchlorin (3a): purple crystals; 151 mg, yield 98%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.51 (d, $J = 2.7$ Hz, 2H, $\beta$-H), 8.08 (d, $J = 2.7$ Hz, 2H, $\beta$-H), 8.02 (d, $J = 6.0$ Hz, 4H, o-Ph-H), 7.82 (d, $J = 6.0$ Hz, 4H, o-Ph-H), 7.67 – 7.70 (m, 12H, m-Ph-H & p-Ph-H), 4.07 (s, 4H, CH$_2$), 1.40 (s, 2H, NH); UV – vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (relative intensity) 428 (1.00), 529 (0.08), 598 (0.05), 650 (0.10) nm; MS (MALDI) $m/z$ 774.1 (M$^+$). Anal. Calcd for C$_{44}$H$_{30}$Br$_2$N$_4$·2H$_2$O (from CH$_2$Cl$_2$/wet CH$_3$OH): C, 65.20; H, 4.23; N, 6.91. Found: C, 65.00; H, 4.01; N, 6.90.

Synthesis of Zinc 12,13-Dibromo-2,3-dihydro-5,10,15,20-tetraphenylchlorin Zn3a.

Zn3a was synthesized according to the literature method.$^2$ 12,13-Dibromo-2,3-dihydro-5,10,15,20-tetraphenylchlorin 3a (77 mg, 0.1 mmol) and zinc acetate
dihydrate (66 mg, 0.3 mmol) were added to a Schlenk flask (20 mL). The flask was then evacuated and backfilled with nitrogen (three cycles). Then pyridine (10 mL) was charged with a syringe. The reaction mixture was stirred and heated at 100 °C under nitrogen for 1 h. To the cooled reaction mixture, benzene (20 mL) and distilled water (20 mL) were added. The organic layer was quickly washed with distilled water and brine and then filtered through a short silica plug (300 – 400 mesh, eluting with CH₂Cl₂). The filtrate was concentrated and recrystallized from CH₂Cl₂/MeOH to give mono-pyridinate complex of Zn₃a.

Zinc 12,13-Dibromo-2,3-dihydro-5,10,15,20-tetraphenylchlorin (Zn₃a): purple crystals; 66 mg, yield 72%. ¹H NMR (300 MHz, CDCl₃) δ 8.36 (d, J = 4.2 Hz, 2H, β-H), 7.96 (d, J = 4.2 Hz, 2H, β-H), 7.86 (d, J = 7.2 Hz, 4H, o-Ph-H), 7.77 (d, J = 7.2 Hz, 4H, o-Ph-H), 7.59 – 7.61 (m, 12H, m-Ph-H & p-Ph-H), 3.97 (s, 4H, CH₂); UV – vis (CH₂Cl₂) λₓᵧ (relative intensity) 424 (1.00), 553 (0.05), 619 (0.08) nm; MS (MALDI) m/z 836.0 (M⁺). Anal. Calcd for C₄₄H₂₈Br₂N₄Zn·C₅C₅N·4H₂O (from CH₂Cl₂/wet CH₃OH/pyridine): C, 59.50; H, 4.18; N, 7.08. Found: C, 59.68; H, 3.86; N, 7.08.


5,10,15,20-tetraarylchlorin 2 (0.2 mmol) and NBS (80 mg, 0.44 mmol) were added to a Schlenk flask (50 mL). The flask was then evacuated and backfilled with nitrogen (three cycles). Then dry chloroform (ethanol free, 20 mL) was charged with a syringe. The reaction mixture was stirred and heated under reflux for 4 h. After being slightly cooled, a solution of DDQ (184 mg, 0.8 mmol) in toluene (2 mL) was added, and the mixture was refluxed for further 1 h. After being cooled to room temperature, triethylamine (1 mL) was added to neutralize the acids produced in the reaction. Then the reaction mixture was filtered through a short silica plug (300 – 400 mesh, eluting with CH₂Cl₂). The filtrate was evaporated to dryness and the resulting solid was purified by flash chromatography (silica gel, 300 – 400 mesh, petroleum ether/CH₂Cl₂ as eluent) to yield the products 4.

2,3-Dibromo-5,10,15,20-tetraphenylporphyrin (4a): purple crystals; 148 mg, yield 96%. ¹H NMR (300 MHz, CDCl₃) δ 8.86 – 8.89 (m, 4H, β-H), 8.71 (s, 2H, β-H), 8.20 (d, J = 6.0 Hz, 4H, o-Ph-H), 8.16 (d, J = 6.3 Hz, 4H, o-Ph-H), 7.78 (bs, 12H, m-Ph-H & p-Ph-H), −2.83 (s, 2H, NH); MS (MALDI) m/z 772.1 (M⁺).
2,3-Dibromo-5,10,15,20-tetra(p-chlorophenyl)porphyrin (4b): purple crystals; 172 mg, yield 95%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.85 (s, 4H, $\beta$-H), 8.68 (s, 2H, $\beta$-H), 8.11 (d, $J = 6.0$ Hz, 4H, $o$-Ph-H), 8.05 (d, $J = 6.6$ Hz, 4H, $o$-Ph-H), 7.74 – 7.76 (m, 8H, $m$-Ph-H), – 2.93 (s, 2H, NH); UV – vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (relative intensity) 425 (1.00), 522 (0.06), 599 (0.02), 687 (0.05) nm; MS (MALDI) $m/z$ 909.9 (M$^+$). Anal. Calcd for C$_{44}$H$_{24}$Br$_2$Cl$_4$N$_4$·0.5H$_2$O (from CH$_2$Cl$_2$/wet CH$_3$OH): C, 57.49; H, 2.74; N, 6.09. Found: C, 57.39; H, 2.60; N, 6.16.

2,3-Dibromo-5,10,15,20-tetra(p-trifluoromethylphenyl)porphyrin (4c): purple crystals; 200 mg, yield 96%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.83 (s, 4H, $\beta$-H), 8.66 (s, 2H, $\beta$-H), 8.33 (d, $J = 7.2$ Hz, 4H, $o$-Ph-H), 8.27 (d, $J = 7.8$ Hz, 4H, $o$-Ph-H), 8.05 – 8.07 (m, 8H, $m$-Ph-H), – 2.91 (s, 2H, NH); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ – 61.9 (s, 6F), – 62.1 (s, 6F); UV – vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (relative intensity) 418 (1.00), 517 (0.06), 596 (0.02), 656 (0.03) nm; MS (MALDI) $m/z$ 1044.0 (M$^+$). Anal. Calcd for C$_{48}$H$_{24}$Br$_2$F$_{12}$N$_4$·0.3 C$_6$H$_{14}$ (from CH$_2$Cl$_2$/hexane): C, 55.88; H, 2.66; N, 5.23. Found: C, 55.77; H, 2.56; N, 5.41.

**Typical Procedure for the Synthesis of 2,3,12,13-tetrabromo-5,10,15,20-tetraarylporphyrins 5.**

5,10,15,20-tetraarylporphyrin 1 (0.5 mmol) and NBS (580 mg, 3.25 mmol) were dissolved in chloroform (ethanol free, 60 mL). The reaction mixture was stirred and heated under reflux for 4 h. After being cooled to room temperature, triethylamine (3 mL) was added to neutralize the acids produced in the reaction. Then the reaction mixture was filtered through a short silica plug (300 – 400 mesh, eluting with CH$_2$Cl$_2$). The filtrate was evaporated to dryness and the resulting solid was purified by flash chromatography (silica gel, 300 – 400 mesh, CH$_2$Cl$_2$ as eluent) to yield the products 5. The spectroscopic data were in agreement with literature values.$^{4,5}$
2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrin (5a): purple crystals; 386 mg, yield 83%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.70 (s, 4H, $\beta$-H), 8.18 (d, $J$ = 6.0 Hz, 8H, o-Ph-H), 7.79 (bs, 12H, m-Ph-H & p-Ph-H), – 2.83 (s, 2H, NH); MS (MALDI) m/z 929.9 (M$^+$).

2,3,12,13-Tetrabromo-5,10,15,20-tetrakis(p-methylphenyl)porphyrin (5d): purple crystals; 394 mg, yield 80%. MS (MALDI) m/z 986.0 (M$^+$). The title compound was insoluble in common solvents and no $^1$H NMR spectrum was obtained.

2,3,12,13-Tetrabromo-5,10,15,20-tetrakis(p-methoxyphenyl)porphyrin (5e): purple crystals; 347 mg, yield 66%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.69 (s, 4H, $\beta$-H), 8.11 (d, $J$ = 7.5 Hz, 8H, o-Ph-H), 7.33 (d, $J$ = 7.5 Hz, 8H, p-Ph-H), – 2.72 (s, 2H, NH); MS (MALDI) m/z 1049.9 (M$^+$).
2,3,12,13-Tetrabromo-5,10,15,20-tetrakis(3’,5’-di-tert-butylphenyl)porphyrin (5f): purple crystals; 420 mg, yield 61%. $^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 8.82 (s, 4H, $\beta$-H), 7.97 (s, 8H, $o$-Ph-H), 7.80 (s, 4H, $p$-Ph-H), 1.52 (s, 72H, CH$_3$), – 2.94 (s, 2H, NH); MS (MALDI) m/z 1378.4 (M$^+$$)$. 

Reference:
Ⅱ. Copies of $^1$H NMR and $^{19}$F NMR spectra for key and new compounds

Figure S1. 300 MHz $^1$H NMR of 2a in CDCl$_3$

Figure S2. 300 MHz $^1$H NMR of 2b in CDCl$_3$
Figure S3. 300 MHz $^1$H NMR of 2c in CDCl$_3$

Figure S4. 282 MHz $^{19}$F NMR of 2c in CDCl$_3$
Figure S5. 300 MHz $^1$H NMR of 3a in CDCl$_3$

Figure S6. 300 MHz $^1$H NMR of 4a in CDCl$_3$
Figure S7. 300 MHz $^1$H NMR of 4b in CDCl$_3$

Figure S8. 300 MHz $^1$H NMR of 4c in CDCl$_3$
Figure S9. 282 MHz $^{19}$F NMR of 4c in CDCl$_3$

Figure S10. 300 MHz $^1$H NMR of 5a in CDCl$_3$
Figure S11. 300 MHz $^1$H NMR of 5e in CDCl$_3$

Figure S12. 300 MHz $^1$H NMR of 5f in CDCl$_3$