Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Unexpected bromination ring opening of tetraarylporphyrins

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Instrumentation and Materials:

^{1}H(300MHz) and ^{19}F(282MHz) NMR spectra were recorded with a Brucker AM-300 or Varian-360L spectrometer. Chemical shifts are reported in parts per million (ppm) relative to TMS as an internal standard (δ_{TMS} = 0 ppm) for ^{1}H NMR spectra and $CFCl_3$ as an external standard (negative for upfield) for ^{19}F NMR spectra. Deuterated solvents for NMR were purchased from Cambridge Isotope Laboratories, Aldrich or Acros. MS and HRMS were recorded on a Hewlett-Packard HP-5989A spectrometer and a Finnigan MAT-8483 mass spectrometer. UV-vis spectra were measured with a Varian Cary 100 spectrophotometer. Elementary analyses were obtained on a Perkin Elmer 2400 Series II Elemental Analyzer. TLC analysis 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. NBS was crystallized from hot water and dried at room temperature in vacuum overnight.

General procedure for synthesis of various biladienes Zn2 from the bromination ring opening of various meso-tetraarylporphyrins H_2TAP(1):

H_2TAP(**1**) (100 mg, 1.0 equiv.) was dissolved in CH_2Cl_2/MeOH (9:1 vol./vol.) (20 mL). NBS (20 equiv.) and $Zn(OAc)_2{\cdot}2H_2O$ (5.0 equiv.) was added. The reaction mixture was stirred under air at room temperature for 30 min. The resulting bright red solution was evaporated to dryness, the residue was purified twice by silica gel column chromatography using CH_2Cl_2 and petrol ether as eluant to provide the pure desired **Zn2**. Yields are lower due to part decomposition of the products during silica gel column purification.

Zn2a: (Yield: 32%) (Found: C, 37.98; H, 2.21; N, 3.46. $C_{47}H_{29}N_4O_3Br_9Zn$ requires C, 38.08; H, 1.97; N, 3.78.); UV-vis λ_{max} (CH_2Cl_2, relative intensity)/nm: 387 (1.0), 504 (9.5), 532 (sh, 3.6), 565 (2.4); δ_H (300MHz, $CDCl_3$, Me_4Si) 2.90 (s, 3H, MeO), 3.11-3.17 (m, 3H, MeO), 3.36 (s, 3H, MeO), 7.24-7.81 (m, 20H, Ph-H); MS (MALDI) m/z: 1407.5 (M^+-Zn).

Zn2b: (Yield: 46%) (Found: C, 38.76; H, 2.94; N, 3.21. $C_{51}H_{37}N_4O_3Br_9Zn{\cdot}2H_2O$ requires C, 38.91; H, 2.62; N, 3.56.); UV-vis λ_{max} (CH_2Cl_2, relative intensity)/nm: 395 (1.0), 518 (7.4), 536 (sh, 5.3); δ_H (300MHz, $CDCl_3$, Me_4Si) 2.32 (s, 6H, Ph-*Me*), 2.45 (d, 6H, Ph-*Me*), 2.79 (br s, 9H, MeO), 7.03-7.37 (m, 16H, Ph-H); MS (MALDI) m/z: 1527.5 (M^+).

Zn2c: (Yield: 40%) (Found: C, 38.47; H, 2.64; N, 3.17. $C_{51}H_{37}N_4O_7Br_9Zn$ requires C, 38.23; H, 2.33; N, 3.50.); UV-vis λ_{max} (CH_2Cl_2, relative intensity)/nm: 409 (1.0), 502 (sh, 5.2), 528 (10.8); δ_H (300MHz, $CDCl_3$, Me_4Si) 3.93 (s, 12H, Ph-*MeO*), 4.03 (s, 9H, MeO), 7.04 (d, J = 8.7Hz, 8H, Ph-H), 7.16 (d, J = 8.1Hz, 8H, Ph-H); MS (MALDI) m/z: 1591.0 (M^+).

Zn2d: (Yield: 38%) (Found: C, 34.22; H, 2.20; N, 3.06. $C_{47}H_{25}N_4O_3Cl_4Br_9Zn{\cdot}2.5H_2O$ requires C, 33.90; H, 1.82; N, 3.36.); UV-vis λ_{max} (CH_2Cl_2, relative intensity)/nm: 385 (1.0), 522 (7.1), 540 (sh, 5.2); δ_H (300MHz, $CDCl_3$, Me_4Si) 2.77 (br s, 9H, MeO), 7.13-7.49 (m, 16H, Ph-H); MS (MALDI) m/z: 1607.3 (M^+).

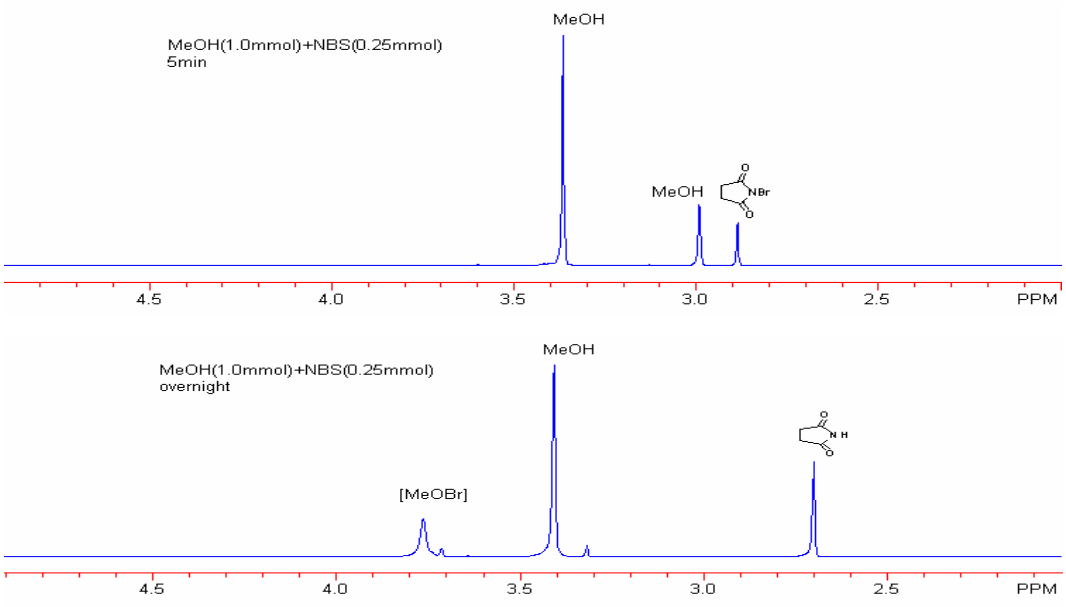
Zn2e: (Yield: 25%) UV-vis λ_{max} (CH_2Cl_2, relative intensity)/nm: 506 (1.4), 519 (1.4), 540 (1.0); δ_H (300MHz, $CDCl_3$, Me_4Si) 2.80 (br s, 9H, MeO), 7.31-7.76 (m, 16H, Ph-H); δ_F (282MHz, $CFCl_3$) –62.87 (m, 12F, CF_3); MS (MALDI) m/z: 1743.4 (M^+). HRMS (MALDI) found: 1743.36714. $C_{51}H_{25}N_4O_3F_{12}Br_9Zn^+$ requires: 1743.3624.

Cu2a: (Yield: 11%) (Found: C, 38.62; H, 2.26; N, 3.58. $C_{47}H_{29}N_4O_3Br_9Cu$ requires C, 38.13; H, 1.97; N, 3.78.); UV-vis λ_{max} (CH_2Cl_2, relative intensity)/nm: 416 (1.0), 507 (5.7), 557 (sh, 1.8); MS (MALDI) m/z: 1455.4 (M^+-MeO).

General procedure for the synthesis of various brominated porphyrins:

The starting porphyrin (100 mg, 1.0 equiv.) was dissolved in CH_2Cl_2/MeOH (9:1 vol./vol.) (50 mL). For meso-tetraarylporphyrin H_2TAP(**1**), the mixture was heated to reflux and NBS (1.1 equiv.) was added. After 5-30 min, the reaction mixture was cooled to room temperature and evaporated to dryness. The resulting residue was purified by dry column chromatography to provide the β-monobrominated porphyrins H_2TAP(Br)(**3**) in 32-48% yields. For 5,10-diphenylporphyrin H_2DPP(**4**), NBS (1.1 equiv. or 2.0 equiv.) was added. The reaction mixture was stirred under air at room temperature for 5 min and quenched with acetone (5 ml). The solvent was evaporated to dryness. The resulting residue was purified by dry column chromatography to yield H_2DPP(Br)(**5**) in 62% yield or washed with several portions of methanol and pumped dry to give H_2DPP$(Br)_2$(**6**) in 91% yield. An analytical sample was recrystallized from CH_2Cl_2/MeOH.

H_2T(p-CF_3)PP(Br)(**3e**): (Yield: 32%) (Found: C, 58.77; H, 3.00; N, 5.66. $C_{48}H_{25}N_4F_{12}Br{\cdot}H_2O$ requires C, 58.61; H, 2.77; N, 5.70.); UV-vis λ_{max} (CH_2Cl_2, relative intensity)/nm: 377 (2.8), 453 (36.0), 611 (1.0), 664 (4.3); δ_H (300MHz, $CDCl_3$, Me_4Si) -2.91 (br s, 2H, NH), 8.00-8.06 (m, 8H, Ph-H), 8.19-8.34 (m, 8H, Ph-H), 8,72-8.89 (m, 7H, β-H); δ_F (282 MHz, $CFCl_3$) -62.48 (m, 12F, CF3); MS (MALDI) m/z: 965.1 (M^++1).



^{1}H NMR spectrum of reaction system of NBS (0.25 mmol) and MeOH (1 mmol) in $CDCl_3$ (0.5 mL)