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Extraordinary behavior of 5-(3,4-dihydroxyphenyl)-10,15,20-tris(*N*-methylpyridinium-3-yl)porphyrin triiodide in titration with bases and in albumin oxidation

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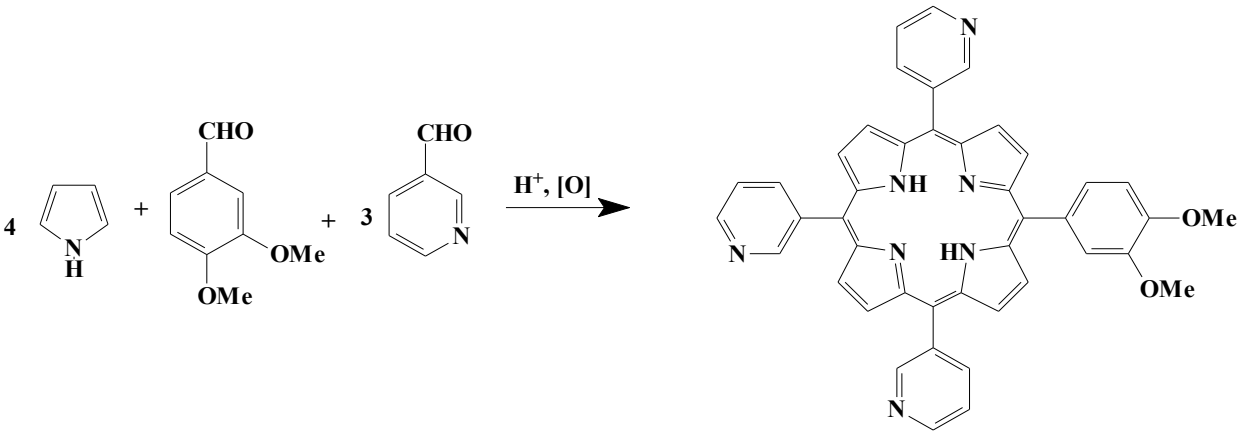
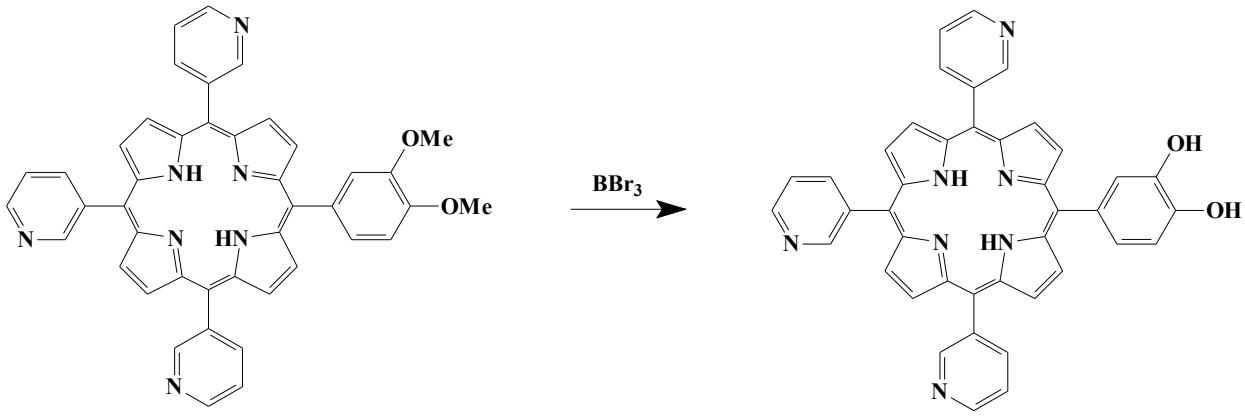
5-(3,4-Dimethoxyphenyl)-10,15,20-tris(3-pyridyl)porphyrin



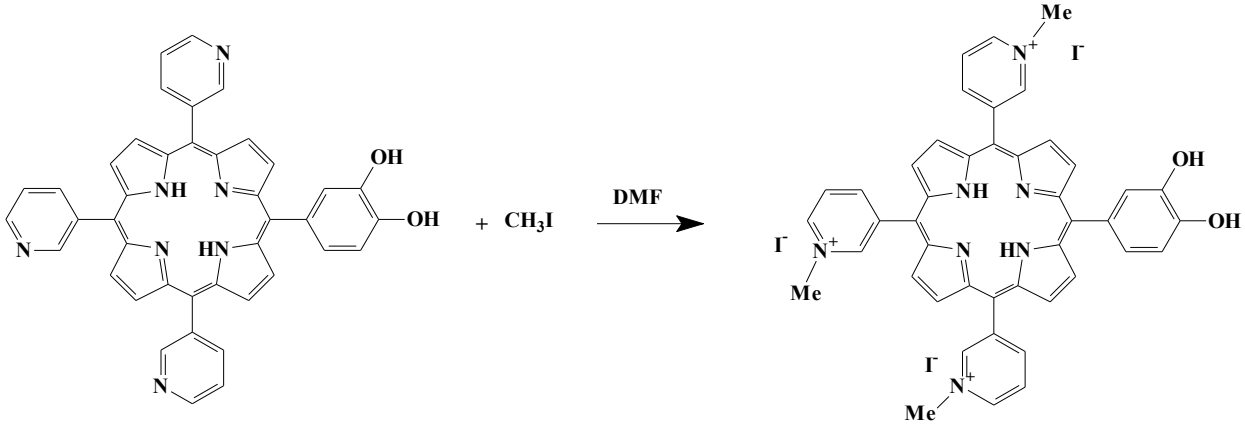
A mixture of pyrrole (10 ml, 0.144 mol), 3,4-dimethoxybenzaldehyde (6.66 g, 0.036 mol) and pyridine-3-carbaldehyde (10.15 ml, 0.108 mol) was added to a boiling solution of propionic anhydride (35 ml, 0.27 mol) in propionic acid (500 ml) with nitrogen flushing within 10 minutes. The mixture was boiled for 1.5 hours in air flow. Propionic acid was distilled off under vacuum with a water bath heating. The residue was treated with a mixture of methanol (300 ml) and concentrated ammonia solution (30 ml). The porphyrin precipitate was filtered off, washed with methanol (10 ml), and dried at room temperature to constant weight. For purification, porphyrin was dissolved in dichloromethane (150 ml) and chromatographed on a column (3×50 cm) with Al_2O_3 (III grade of activity according to Brockmann), eluting with dichloromethane (MS MALDI-TOF control) to afford the title product. For better purification, the product was rechromatographed on a column (1.5×70 cm) with Al_2O_3 eluting with dichloromethane. The eluate was evaporated to 5 ml volume, the product was precipitated with methanol (50 ml) and dried at room temperature to constant weight. Yield 1.4 g (15%). UV-Vis spectrum (λ_{max}, nm (log ε), $CHCl_3$): 645 (4.61); 588 (4.60); 546 (4.50); 510 (4.62); 416 (5.87) ^{1}H NMR ($CDCl_3$): 9.50 s (3H, 2'-HPy), 9.11 d (3H, 6'-HPy), 9.02 d (2H, 8.12-H), 8.93 d (4H, 3,7,13,17-H), 8.56 d (2H, 2,18-H), 8.43 d (3H, 4'-HPy), 7.91 d (3H, 5'-HPy), 7.65 s (1H, 4"-HPh), 7.58 s (1H, 6"-HPh), 7.34 s (1H, 2"-HPh), 4.18 s (3H, OMe), 4.03 s (3H, OMe), –2.78 bs (2H, NH). MS MALDI-TOF: *m*/*z* Calc: $C_{43}H_{31}N_7O_2$: 677.25; Found: 677.27 $[M]^+$.

5-(3,4-Dihydroxyphenyl)-10,15,20-tris(3-pyridyl)porphyrin



To a solution of 5-(3,4-dimethoxyphenyl)-10,15,20-tri**s**(3-pyridyl)porphyrin (108 mg, 1.6 mmol) from the previous step in dry chloroform (30 ml), BBr_3 (1 ml, 6.4 mmol) was added with stirring. The mixture was stirred at room temperature for 1 h, then methanol (3 ml) and 20% ammonia solution (3 ml) were added successively. The chloroform solution was chromatographed on a column (1.5×25 cm) with silica gel (L 100/250), eluting with chloroform with a variable amount of methanol. The proper fractions were evaporated to 5 ml, the product was precipitated with hexane (50 ml), and dried at room temperature to constant weight. Yield 103 mg (99%). (silufol, diethyl ether). UV-Vis spectrum (λ_{max}, nm (log ε), pyridine): 656 (3.79); 598 (3.67); 561 (4.11); 521 (4.16); 426 (5.64). ^{1}H NMR (d-Pr^{i}OD) 9.33 s (3H, 2'-HPy), 9.03 d (3H, 6'-HPy), 8.77 bs (2H, 8,12-H), 8.62 s (4H, 3,7,13,17-H), 8.57 d (2H, 2,18-H), 7.95 dd (3H, 4'-HPy), 7.75 dd (3H, 5'-HPy), 7.64 s (1H, 4"-HPh), 7.46 s (1H, 6"-HPh), 7.28 s (1H, 2"-HPh), –2.79 bs (2H, NH). IR spectrum, (см$^{-1}$) (KBr): ν_{OH} 3460; δ_{OH} 1357; δ_{CO} 1253. MS MALDI-TOF: *m*/*z* Calc: $C_{41}H_{27}N_7O_2$: 649.70; Found: 649.78 $[M]^+$.

5-(3,4-Dihydroxyphenyl)-10,15,20-tris(*N*-methylpyridinum-3-yl)porphyrin triiodide



A mixture of 5-(3,4-dihydroxyphenyl)-10,15,20-tris(3-pyridyl)porphyrin (150 mg, 0.29 mmol) from the previous step and iodomethane (0.5 ml, 0.46 mmol) was refluxed in DMF (30 ml) for 1 h. The solution was cooled and diluted with benzene (30 ml). The precipitate was filtered off, washed sequentially with benzene and acetone, and dried at room temperature to constant weight. Yield 297 mg. (90%).^{1}H NMR δ, ppm: 9.38 s (3H, 2'-HPy), 9.15 m (3H, 6'-HPy), 8.90 bs (2H, 8,12-H), 8.59 s (4H, 3,7,13,17-H), 8.29 d (2H, 2,18-H), 7.99 d (3H, 4'-HPy), 7.75 d (3H, 5'-HPy), 7.17 s (1H, 4"-HPh), 7.06 s (1H, 6"-HPh), 6.96 s (1H, 2"-HPh), 2.89 s (2H, NMe), 2.73 s (1H, NMe). (D_2O). MS MALDI-TOF: *m*/*z* Calc: $C_{44}H_{36}I_3N_7O_2$: 1075.01; Found: 1074.88 $[M]^+$.