

Supporting Information for:

Structural and Electron-Transfer Characteristics of O-, S-, and Se-Tethered Porphyrin Monolayers on Si(100)

Amir A. Yasseri, Dennis Syomin, Robert S. Loewe,
Jonathan S. Lindsey, Francisco Zaera, and David F. Bocian

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Experimental Section

An A₃B-porphyrin bearing a *meso*-ester group was prepared by mixed-aldehyde condensation of ethyl glyoxylate, mesitaldehyde, and pyrrole using BF₃·O(Et)₂/EtOH cocatalysis^{S1} (Scheme S1). Free base porphyrin **1** was obtained in 2.9% yield. Subsequent metalation with Zn(OAc)₂·2H₂O afforded **Zn-1** in 92% yield. Treatment of **Zn-1** with LiAlH₄ in THF gave the target porphyrin alcohol *mes*-ZnPCH₂OH in 34% yield.

General. All ¹H NMR spectra (300 or 400 MHz) and ¹³C NMR (75 MHz) were collected in CDCl₃ unless noted otherwise. Absorption and fluorescence spectra were collected in toluene at room temperature. Mass spectra of porphyrins were obtained via laser desorption mass spectrometry (LD-MS) without a matrix,^{S2} and by high-resolution fast atom bombardment mass spectrometry (FAB-MS) using a matrix of nitrobenzyl alcohol and polyethylene glycol. Melting points are uncorrected. Silica gel (40 μm average particle size) was used for column chromatography. THF was freshly distilled from sodium as required. Toluene was distilled from CaH₂. CHCl₃ was stabilized with 0.8% ethanol.

5-Ethoxycarbonyl-10,15,20-trimesitylporphyrin (1). Following a standard procedure,^{S1} a solution of mesitaldehyde (2.21 mL, 15.0 mmol), ethyl glyoxylate (1.02 mL, 5.00 mmol, 50% in toluene) and pyrrole (1.39 mL, 20.0 mmol) in CHCl₃ (274 mL) was treated with BF₃·O(Et)₂ (0.618 mL, 4.88 mmol) under argon at room temperature. After 20 min, DIEA (0.850 mL, 4.88 mmol) was added. DDQ (3.41 g, 15.0 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. The mixture was filtered through a silica pad (CH₂Cl₂). The purple fraction was collected, concentrated and chromatographed on silica, affording a purple solid (106 mg, 3%): ¹H NMR δ −2.62 (s, 2H), 1.84–1.86 (m, 21H), 2.62 (s, 3H), 2.64 (s, 6H), 5.07 (q, *J* = 7.2 Hz, 2H), 7.30 (s, 2H), 7.32 (s, 2H), 7.33 (s, 2H), 8.62 (d, *J* = 4.4 Hz, 2H), 8.65 (d, *J* = 4.8 Hz, 2H), 8.79 (d, *J* = 4.8 Hz, 2H), 9.38 (d, *J* = 4.8 Hz, 2H); LD-MS obsd 737.8; FAB-MS obsd 736.3810, calcd 736.3777 (C₅₀H₄₈N₄O₂); λ_{abs} 419, 513, 546, 589, 645 nm.

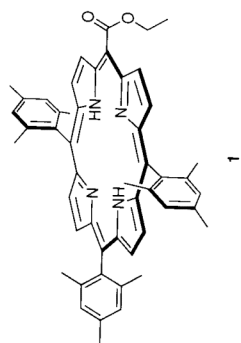
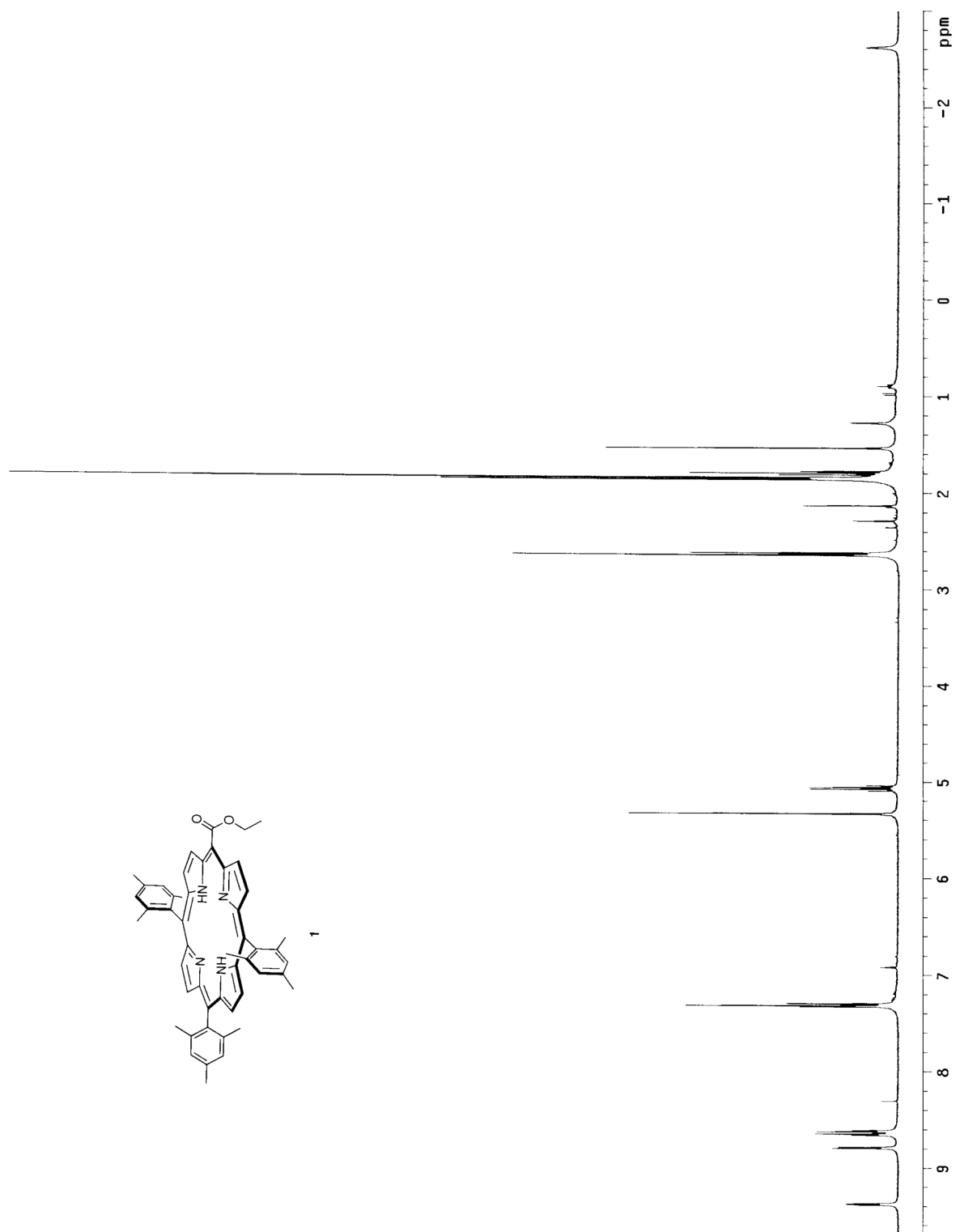
5-Ethoxycarbonyl-10,15,20-trimesitylporphinatozinc(II) (Zn-1). A solution of **1** (100 mg, 0.136 mmol) in CHCl₃ (15 mL) was treated with a solution of Zn(OAc)₂·2H₂O (298 mg, 1.36 mmol) in methanol (3 mL) at room temperature. The reaction was monitored by fluorescence spectroscopy. After the metalation was complete, the mixture was washed with water. The organic phase was dried (Na₂SO₄), concentrated and chromatographed [silica, CHCl₃ → CHCl₃/ethyl acetate (95:5)], affording a purple solid (100 mg, 92%): ¹H NMR δ 1.84–1.86 (m, 21H), 2.60 (s, 3H), 2.63 (s, 6H), 5.02 (q, *J* = 7.2 Hz, 2H), 7.29 (s, 2H), 7.32 (s, 4H), 8.60 (d, *J* = 4.2 Hz, 2H), 8.63 (d, *J* = 4.8 Hz, 2H), 8.72 (d, *J* = 4.8 Hz, 2H), 9.38 (d, *J* = 4.5 Hz, 2H); LD-

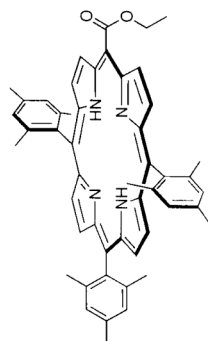
MS obsd 799.8; FAB-MS obsd 799.2997, calcd 799.2990 $[(M + H)^+]$; $M = C_{50}H_{46}N_4O_2Zn$; λ_{abs} 422, 551, 588 nm.

5-Hydroxymethyl-10,15,20-trimesitylporphinatozinc(II) (*mes*-ZnPCH₂OH). A solution of **Zn-1** (95.0 mg, 119 μ mol) in dry THF (8 mL) was treated with LiAlH₄ (14.0 mg, 356 μ mol) and the reaction mixture was stirred at room temperature. After the reaction was completed, methanol (5 mL) was slowly added and the mixture was filtered to remove insoluble compound. After removal of the solvent, the crude product was purified by column chromatography on silica, affording a purple solid (31 mg, 34%): 1.84–1.86 (m, 18H), 2.53 (s, 6H), 2.60 (s, 2H), 2.63 (s, 3H), 6.89 (d, $J = 6.0$ Hz, 2H), 7.28 (s, 2H), 7.31 (s, 4H), 8.60 (s, 2H), 8.73 (d, $J = 4.8$ Hz, 2H), 8.69 (d, $J = 4.4$ Hz, 2H); LD-MS obsd 740.8 $[(M - OH)^+]$, 758.0; FAB-MS obsd 756.28437, calcd 756.2807 ($C_{48}H_{44}N_4OZn$); λ_{abs} 421, 550, 582 nm.

References.

- (S1) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828–836.
(S2) (a) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283–291. (b) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93–99.



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