

**Active-Site Models of Bacterial Nitric Oxide Reductase Featuring Tris-Histidyl
and Glutamic Acid Mimics: Influence of Carboxylate Ligand on Fe_B Binding and
Heme-Fe/Fe_B Redox Potentials**

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Supporting Information

Preparation of NOR Model Ligands: Compounds **1** (**1a–1c**) were prepared following a scheme recently developed in our laboratory (*Org. Lett.* **2006**, *8*, 923).

Characterization of Compound 1a: A solid. ¹H NMR (500 MHz, CDCl₃): the carboxylic acid proton is not assigned, δ 8.77–8.94 (m, 8H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.38 (d, *J* = 5.5 Hz, 2H), 8.23 (d, *J* = 7.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 1H), 8.03 (d, *J* = 7.0 Hz, 1H), 7.95 (d, *J* = 5.5 Hz, 2H), 7.78–7.88 (m, 5H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52–7.57 (m, 3H), 7.30 (s, 1H), 6.96 (s, 2H), 6.75 (s, 1H), 5.58 (s, 2H), 4.21 (s, 1H), 3.64 (s, 6H), 3.53 (s, 3H), 1.61 (t, *J* = 6.5 Hz, 2H), 1.12 (t, *J* = 6.5 Hz, 2H), 0.84–0.87 (m, 4H), –2.59 (s, 2H); ¹³C NMR (CDCl₃): δ 174.68, 172.15, 159.27, 157.35, 140.83, 140.27, 138.71, 138.59, 138.23, 136.14, 134.91, 134.34, 132.15, 131.40, 130.34, 130.12, 129.63, 129.50, 128.41, 126.25, 125.98, 125.43, 124.43, 123.96, 123.58, 120.27, 116.81, 113.22, 35.33, 33.73, 33.62, 32.32, 29.75, 20.29; MS (ESI): *m/e* 1113.4 for C₆₄H₅₃N₁₄O₆ [M+H]⁺; HRMS (ESI) for C₆₄H₅₃N₁₄O₆ [M+H]⁺ calcd. 1113.4273, found 1113.4279.

Characterization of Compound 1b: A solid. ¹H NMR (500 MHz, CDCl₃): δ 8.85–8.91 (m, 8H), 8.54 (d, *J* = 8.0 Hz, 2H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.25 (s, 1H), 8.09–8.12 (m, 3H), 7.99 (s, 1H), 7.91–7.94 (m, 3H), 7.83–7.86 (m, 3H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.56–7.61 (m, 3H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.02 (s, 2H), 6.94 (s, 1H), 5.61 (s, 1H), 5.16 (s, 2H), 3.66 (s, 6H), 3.58 (s, 3H), 2.79 (s, 3H), 1.49–1.55 (m, 4H), 1.20 (t, *J* = 7.5 Hz, 2H), –2.55 (s, 2H); ¹³C NMR (CDCl₃): δ 173.03, 171.80, 159.09, 158.51, 141.35, 141.22, 138.46, 138.20, 135.42, 135.20, 135.02, 133.45, 133.38, 132.18, 131.79, 131.61, 129.86, 129.71, 129.55, 125.78, 125.68, 124.79, 124.22, 124.12, 123.83, 122.47, 116.31, 115.22, 115.00, 50.83, 34.90, 33.76, 32.18, 23.89, 20.23; MS (ESI): *m/e* 1127.5 for C₆₅H₅₅N₁₄O₆ [M+H]⁺; HRMS (ESI) for C₆₅H₅₅N₁₄O₆ [M+H]⁺ calcd. 1127.4429, found 1127.4425.

Characterization of Compound 1c: A solid. ^1H NMR (500 MHz, CDCl_3): δ 8.86–8.94 (m, 8H), 8.58 (d, $J = 8.0$ Hz, 2H), 8.37 (d, $J = 8.0$ Hz, 3H), 8.10–8.14 (m, 3H), 7.77–7.91 (m, 8H), 7.56–7.62 (m, 3H), 7.48 (t, $J = 8.0$ Hz, 1H), 6.99 (s, 3H), 5.72 (s, 1H), 5.17 (s, 2H), 3.65 (s, 6H), 3.60 (s, 3H), 1.42–1.44 (m, 2H), 0.89–0.93 (m, 2H), 0.50–0.57 (m, 4H), 0.16 (t, $J = 7.5$ Hz, 3H), -2.51 (s, 2H); ^{13}C NMR (CDCl_3): δ 172.68, 159.26, 158.42, 141.34, 141.25, 138.49, 138.25, 135.50, 135.17, 135.09, 133.57, 133.17, 132.06, 131.69, 129.92, 129.69, 129.55, 125.71, 124.64, 124.53, 124.30, 123.73, 122.10, 116.29, 115.42, 114.79, 36.16, 33.80, 33.74, 30.58, 24.77, 21.90, 13.37; MS (ESI): m/e 1096.2 for $\text{C}_{65}\text{H}_{56}\text{N}_{14}\text{O}_4$ $[\text{M}]^+$; HRMS (ESI) for $\text{C}_{65}\text{H}_{56}\text{N}_{14}\text{O}_4$ $[\text{M}+\text{H}]^+$ calcd. 1097.4687, found 1097.4688.

Typical Procedure for Preparation of Diiron Complex 2 (Metalation of compound 1): The reaction was conducted under N_2 atmosphere in a dry glove box (O_2 level < 1 ppm). All solvents and reagents were fully deoxygenated before use. To a stirred solution of compound **1a** (88 mg, 0.08 mmol) in dry THF (8 mL), was added anhydrous FeCl_2 (50 mg, 0.39 mmol) followed by K_2CO_3 (50 mg, 0.36 mmol). The mixture was stirred under N_2 at room temperature overnight. TLC showed completion of the reaction (eluent: $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (NH_3 saturated) = 15/85, v/v). The mixture was evaporated to dryness. The residue was stirred in dry CH_2Cl_2 (10 mL) for 10 min. After filtration, the filtrate was concentrated to dryness to give compound **2a** as a solid (~90 mg, 90%). MS (ESI): m/e 1256.6 for $\text{C}_{64}\text{H}_{49}\text{N}_{14}\text{O}_6\text{ClFe}_2$ $[\text{M}]^+$; HRMS (ESI) for $\text{C}_{64}\text{H}_{49}\text{N}_{14}\text{O}_6\text{ClFe}_2$ $[\text{M}]^+$ calcd. 1256.2347, found 1256.2341.

Table S1. Summary of High Resolution Mass Analysis for Iron Complexes **2a–2c** and **3a–3c** (M^+)

	2a	2b	2c
	$\text{C}_{64}\text{H}_{49}\text{N}_{14}\text{O}_6\text{ClFe}_2$	$\text{C}_{65}\text{H}_{52}\text{N}_{14}\text{O}_6\text{Cl}_2\text{Fe}_2$	$\text{C}_{65}\text{H}_{54}\text{N}_{14}\text{O}_4\text{Cl}_2\text{Fe}_2$
Calculated	1256.2347	1306.2270	1276.2528
Found	1256.2341	1306.2213	1276.2465
	3a	3b	3c
	$\text{C}_{64}\text{H}_{50}\text{N}_{14}\text{O}_6\text{Fe}$	$\text{C}_{65}\text{H}_{52}\text{N}_{14}\text{O}_6\text{Fe}$	$\text{C}_{65}\text{H}_{54}\text{N}_{14}\text{O}_4\text{Fe}$
Calculated	1166.3387	1180.3544	1150.3802
Found	1166.3386	1180.3533	1150.3822

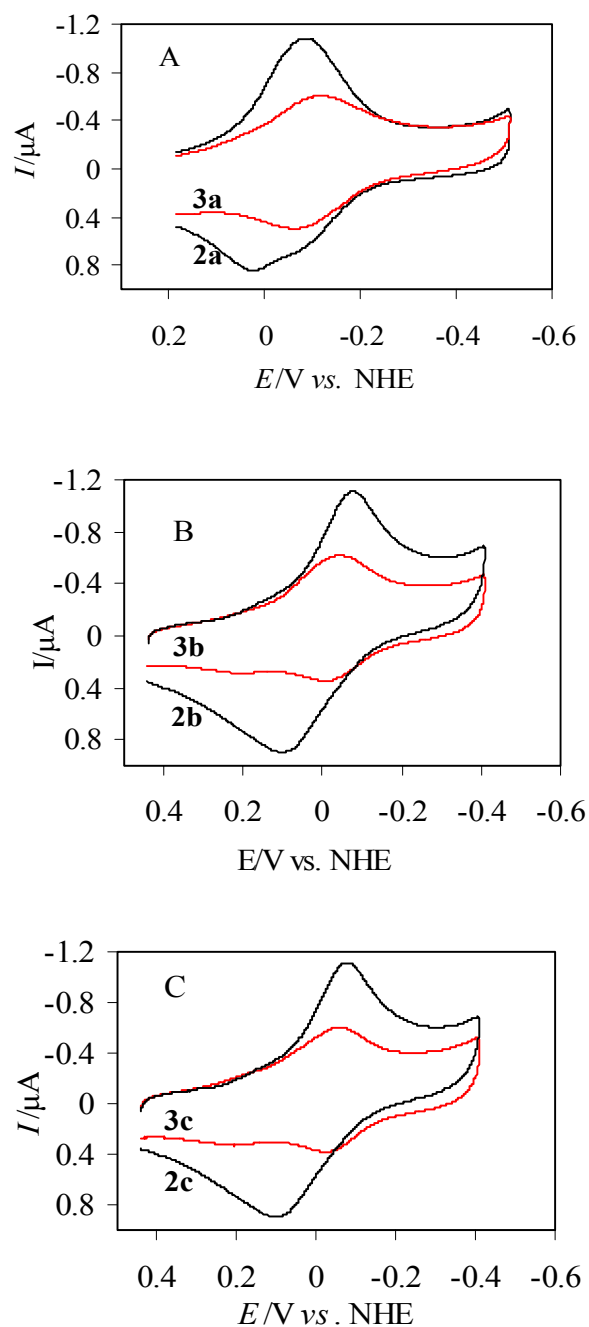


Figure S1. Cyclic Voltammograms (CVs) of Compound **2a**–**2c** and **3a**–**3c** in Anaerobic Phosphate Buffer solution (PBS) at an Edge Plane Graphite (EPG) Electrode, $\nu=10\text{ mV s}^{-1}$, $\Gamma=2.5\text{ nmol cm}^{-2}$, pH=7.0 (A: Compound **2a**/**3a**; B: Compound **2b**/**2c**; C: Compound **2c**/**3c**)