

Supporting Information

Oxinobactin and Sulfoxinobactin, Abiotic Siderophore Analogues to Enterobactin involving 8-Hydroxyquinoline Subunits. Thermodynamic and Structural Studies.

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Synthesis of oxinobactin precursors.

The organotin catalyst 2,2-dibutyl-1,3,2-dioxastannolane was prepared according to: Deleuze, H.; Maillard, B. *J. Organometallic Chem.* **1995**, 490, C14-C17.

Methyl 8-hydroxyquinoline-7-carboxylate 1. A solution of 8-hydroxyquinoline-7-carboxylic acid (7.85 g; 41.5 mmol) in dry MeOH (220mL), is treated with a solution of BF₃ (50%) in MeOH (33mL, 309 mmol). After refluxing 12h, the solvent was evaporated under vacuum. The residue obtained was dissolved in CH₂Cl₂ (200mL), carefully neutralised with a 4M solution of NaOH and washed with water. After drying over Na₂SO₄, the solvent was removed under vacuum. A pale orange powder was obtained (7.7 g; 97 %). ¹H RMN (CDCl₃, 300 MHz): δ = 4.01 (s, 1H, CH₃), 7.22-7.26 (d, 1H), 7.46-7.52 (dd, 1H), 7.83-7.87 (d, 1H), 8.06-8.10 (dd, 1H), 8.94-8.97 (dd, 1H), 11.86 (s broad, 1H, OH) ppm. ¹³C RMN (CDCl₃, 75.4 MHz): δ = 52.4 (O-CH₃), 109.0 (Cq), 117.5 (C-H), 123.7 (C-H), 125.2 (C-H), 132.1 (Cq), 135.6 (C-H), 139.5 (Cq), 149.8 (C-H), 159.8 (Cq), 170.6 (C=O) ppm.

Methyl 8-(benzyloxy)quinoline-7-carboxylate 2. A solution of methyl 8-hydroxyquinoline-7-carboxylate 1 (7.3 g; 35.9 mmol), benzyl chloride (4.5 g; 36 mmol) and K₂CO₃ (10 g; 72.4 mmol) in dry H₃CCN (180 ml) was refluxed for 14h. After cooling, the solid was filtered off, the filtrate concentrated under vacuum and the very dark oil obtained was purified by chromatography (SiO₂; MeOH/CH₂Cl₂, 1/5). A dark oil was obtained which upon time could solidified (10 g; 34.1 mmol; 95 %). ¹H RMN (CDCl₃, 300 MHz): δ = 3.85 (s, 3H, O-CH₃), 5.52 (s, 2H, O-CH₂), 7.30-7.46 (m, 4H), 7.52-7.55 (d, 1H), 7.59-7.63 (d, 2H), 7.79-7.83 (d, 1H), 8.09-8.12 (d, 1H), 8.97-8.99 (d, 1H) ppm. ¹³C RMN (CDCl₃, 75.4 MHz): δ = 52.1 (O-CH₃), 77.3 (O-CH₂), 122.5 (C-H), 122.9 (C-H), 124.1 (Cq), 126.7 (C-H), 127.7 (C-H), 128.1 (C-H), 128.3 (C-H), 131.3 (Cq), 135.8 (C-H), 137.4 (Cq), 143.1 (Cq), 149.9 (C-H), 155.4 (Cq), 166.7 (C=O) ppm.

8-(benzyloxy)quinoline-7-carboxylic acid 3. A solution of methyl 8-(benzyloxy)quinoline-7-carboxylate 2 (2.10 g; 7.16 mmol) in a mixture of 30 mL of MeOH and 30 mL of THF, was treated with a water solution of 4 M NaOH (0.57 g; 14.3 mmol) during 16h. The resulting solution was acidified

with HCl 2M to pH about 5-6 and 50 mL of water was added. The resulting precipitate was recovered by suction, washed with pentane and dried under vacuum, yielding **3** as orange powder (1.58 g; 80 %). ¹H RMN (CDCl₃, 300 MHz): δ = 5.88 (s, 2H, O-CH₂), 7.32-7.40 (m, 3H), 7.48-7.51 (m, 2H), 7.55-7.59 (dd, 1H), 7.64-7.66 (d, 1H), 8.17-8.20 (d, 1H), 8.21-8.24 (dd, 1H), 9.05-9.07 (dd, 1H), 10.5 (broad s, OH) ppm. ¹³C RMN (CDCl₃, 75.4 MHz): δ = 80 (CH₂), 120.9 (Cq), 123.4 (CH), 124.0 (CH), 127.8 (CH), 128.9 (CH), 129.4 (CH), 132.7 (Cq), 134.8 (CH), 136.4 (Cq), 141.8 (Cq), 150.1 (CH), 154.9 (Cq), 165.1 (CO₂H) ppm.

8-(benzyloxy)quinoline-7-carbonyl fluoride 4. A solution of 8-(benzyloxy)quinoline-7-carboxylic acid **3** (4 g; 14.3 mmol) and cyanuric fluoride (2.29 mL; 14.3 mmol) in 100 mL of CH₂Cl₂ was cooled to 0°C and *N,N*-diisopropylethylamine DIPEA (3.56 mL; 14.3 mmol) was added dropwise. After 30 minutes, the reaction was completed as we can judge by TLC (SiO₂; CH₂Cl₂/acetone, 9/1). The solution is poured in cold water (100 mL) and the organic layer washed with brine before to be drying with Na₂SO₄. After concentration in vacuum, the resulting red oil was purified by chromatography (SiO₂; CH₂Cl₂/acetone, 300/10). A yellow solid was obtained (3 g; 75%). MS (CI, NH₃/isobutane) *m/z*: 282 [M+H]⁺ 100%. Anal. Calcd (%) for C₁₇H₁₂FNO₂: C, 72.60; H, 4.30; N, 4.98. Found: C, 72.40; H, 4.33; N, 5.16. ¹H RMN (CDCl₃, 300 MHz): δ = 5.68 (s, 2H, CH₂), 7.24-7.60 (m, 7H, H Ar), 7.85 (d, 1H, H Ar), 8.20 (d, 1H, H Ar), 9.05 (s, 1H, H Ar) ppm. ¹³C RMN (CDCl₃, 75.4 MHz): δ = 78.0 (CH₂), 117.4 (Cq), 123.3 (C-H), 123.9 (C-H), 127.3 (C-H), 128.3 (C-H), 128.4 (C-H), 128.8 (C-H), 133.2 (Cq), 136.3 (C-H), 136.9 (Cq), 143.2 (Cq), 150.4 (CH), 153.4 (Cq), 158-159 (d, ¹*J*_{C-F}; C=O) ppm. ¹⁹F RMN (CDCl₃, 282.3 MHz): δ = 35.3 (C-F) ppm. IR (ATR) cm⁻¹: ν = 3065 (CH₂), 1700 (ν C-F), 1279 (C=O), 1094 (C-O-).

(3*S*, 7*S*, 11*S*)-3,7,11-tris(tritylamino)-1,5,9-trioxacyclododecane-2,6,10-trione 5. A solution of commercial (2*S*)-methyl 3-hydroxy-2-(tritylamino)propanoate (45 g; 0.124 mol) and 2,2-dibutyl-1,3,2-dioxastannolane (7.30 g; 24.8 mmol) in toluene (250 mL) was refluxed during 3 days in a balloon equipped with a Dean and Stark device. Toluene was removed under vacuum and the thick oil obtained purified by chromatography (SiO₂; CH₂Cl₂/cyclohexane, 2/1). Compound **5** was obtained as a white

powder (30.7 g; 0.031 mol; 75%). F: > 260°C. MS (ESI) m/z : 1011 [M+Na]⁺. ¹H RMN (CDCl₃, 300 MHz): δ = 2.65 (broad s, 3H, NH); 3.30-3.47 (m, 6H), 4.05 (t, 3H, CH) 7.23-7.45 (m, 45H) ppm. ¹³C (CDCl₃, 75.4 MHz): δ = 54.8 (CH), 66.9 (CH₂), 71.6 (Cq), 126.9 (CH), 128.3 (CH), 129.0 (CH), 145.6 (Cq), 172.7 (C=O) ppm.

(3S,7S,11S)-3,7,11-triamino-1,5,9-trioxa-cyclododecane-2,6,10-trione, trishydrochloride 6. Dry solution of HCl was prepared by the reaction of acetyl chloride (0.49 g; 6.70 mmol) and dry ethanol (3 mL): *Cautious, exothermic!* This solution is added to a solution of the tritylated lactone **5** (2.2 g; 2.22 mmol) in dry ethanol (60 mL) and then refluxed for 20 minutes. The resulting solution was concentrated to 30 mL under vacuum and cooled in an ice bath. The resulting solid is filtered, washed with small portions (about 20 mL) of dry ethanol, CHCl₃ and then Et₂O. The tris-hydrochloride salt **6** was obtained as beige powder (0.775 g; 2.09 mmol; 94%). F: > 260°C. MS (ESI), m/z: 284 [M + Na]⁺. ¹H RMN (DMSO, 300 MHz): δ = 4.29-4.34 (d, 3H, CH₂), 4.57 (s, 3H, CH), 5.07-5.11 (d, 3H, CH₂), 9.30 (broad s, 9H, NH) ppm. ¹³C (DMSO, 75.4 MHz): δ = 53.6 (CH), 62.7 (CH₂), 164.9 (C=O) ppm.

N,N',N''-((3S, 7S, 11S)-2, 6, 10-trioxo-1, 5, 9-trioxacyclododecane-3, 7, 11-triyl)tris(8-(benzyloxy)quinoline-7-carboxamide) 7. Under an inert atmosphere of argon, at 0°C, to a solution of the trilactone **6** (0.990 g; 2.67 mmol) and N,N-diisopropyle ethyle amine (1.8 ml; 10.6 mmol) in dry CH₂Cl₂ (90 ml), was added dropwise a solution of 8-(benzyloxy)quinoline-7-carbonyl fluoride **4**, (2.24 g; 7.6 mmol) in dry CH₂Cl₂ (40 ml). Afterward, the solution was kept at room temperature for 24h and the resulting solution was concentrated under vacuum. The resulting oil was triturated in pentane (about 100 mL) and then filtered. The pentane solution was concentrated to dryness and the desired product **7** was obtained after chromatography (SiO₂; CH₂Cl₂/Acetone, 9/1 to 8/2), white foam (1.705 g; 62%). F = 85°C. MS (ESI) m/z : 1045 [M+H]⁺ 100%. Anal. Calcd (%) for C₆₀H₅₀N₆O₁₃ · 1 H₂O: C, 67.79; H, 4.74; N, 7.91. Found: C, 67.53; H, 4.67; N, 7.84. ¹H RMN (CDCl₃, 300 MHz): δ = 4.04-4.23 (m, 6H, CH₂), 4.89-4.97 (m, 3H, CH), 5.57-5.73 (q, 6H, CH₂), 7.23-7.7.26 (m, 9H), 7.40-7.42 (m, 6H), 7.46-7.57 (q + d, 6H), 8.12-8.17 (d + q, 6 H), 8.73 (d, 3H), 8.96-8.98 (dd, 3.9 Hz, 3H) ppm. ¹³C RMN (CDCl₃, 75.4 MHz): δ = 51.7 (CH), 64.2 (CH₂), 78.4 (CH₂), 122.7 (CH), 123.2 (CH), 124.2 (Cq), 127.4 (CH), 128.7

(CH), 129.2 (CH), 131.9 (Cq), 136.3 (CH), 136.4 (Cq), 142.5 (Cq), 149.7 (CH), 154.4 (Cq), 165.2 (Cq), 169.1 (C=O) ppm. FTIR (ATR) cm^{-1} : 3347 (νCH_2 , CH), 3035 (νNH_2), 1745-1650 ($\nu\text{C=O}$), 1191 ($\nu\text{-O}$).

N,N',N''-((3S,7S,11S)-2,6,10-trioxo-1,5,9-trioxacyclododecane-3,7,11-triyl)-tris(2,3-dihydroxybenzamide), enterobactin. ^1H NMR (300 MHz, Acetone- d_6 /TMS): δ = 4.77 (6H, m), 5.15 (3H, m), 6.73 (3H, t), 7.06 (3H, d), 7.28 (3H, d), 7.92 (3H, s), 8.46 (3H, d) ppm. ^{13}C NMR (75.4 MHz, Acetone- d_6 /TMS): δ = 54.39 (CH), 66.60 (CH_2), 116.27 (Cq), 119.51 (CH), 120.72 (CH), 121.12 (CH), 148.27 (Cq), 151.40 (Cq), 170.95 (CO), 172.03 (CO) ppm.

Table S1. X-ray crystallographic data.

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of
F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is

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not relevant to the choice of reflections for refinement. R-factors based

on F^2 are statistically about twice as large as those based on F , and R-

factors based on ALL data will be even larger.

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All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken

into account individually in the estimation of esds in distances, angles

and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

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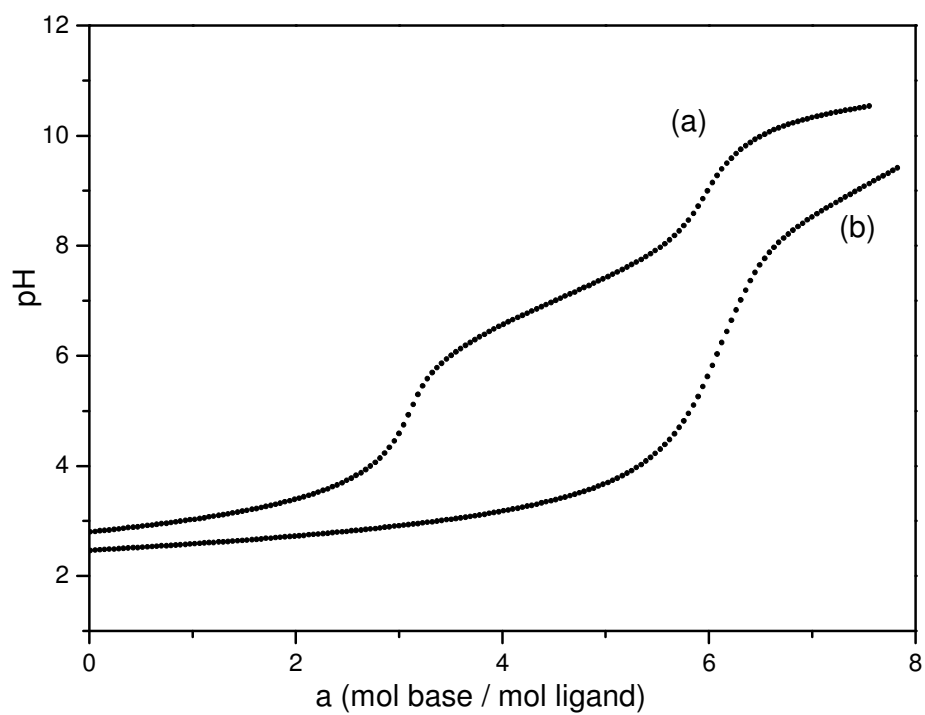


Figure S1. Potentiometric titration curves: (a) [sulfoxinobactine] = 4.8×10^{-4} M; (b) [sulfoxinobactine] / $[\text{Fe}^{3+}] = 1/1$, 4.8×10^{-4} M, Solvent: H_2O , $I = 0.1$ M (NaClO_4), $T = 25.0(2)^\circ\text{C}$.

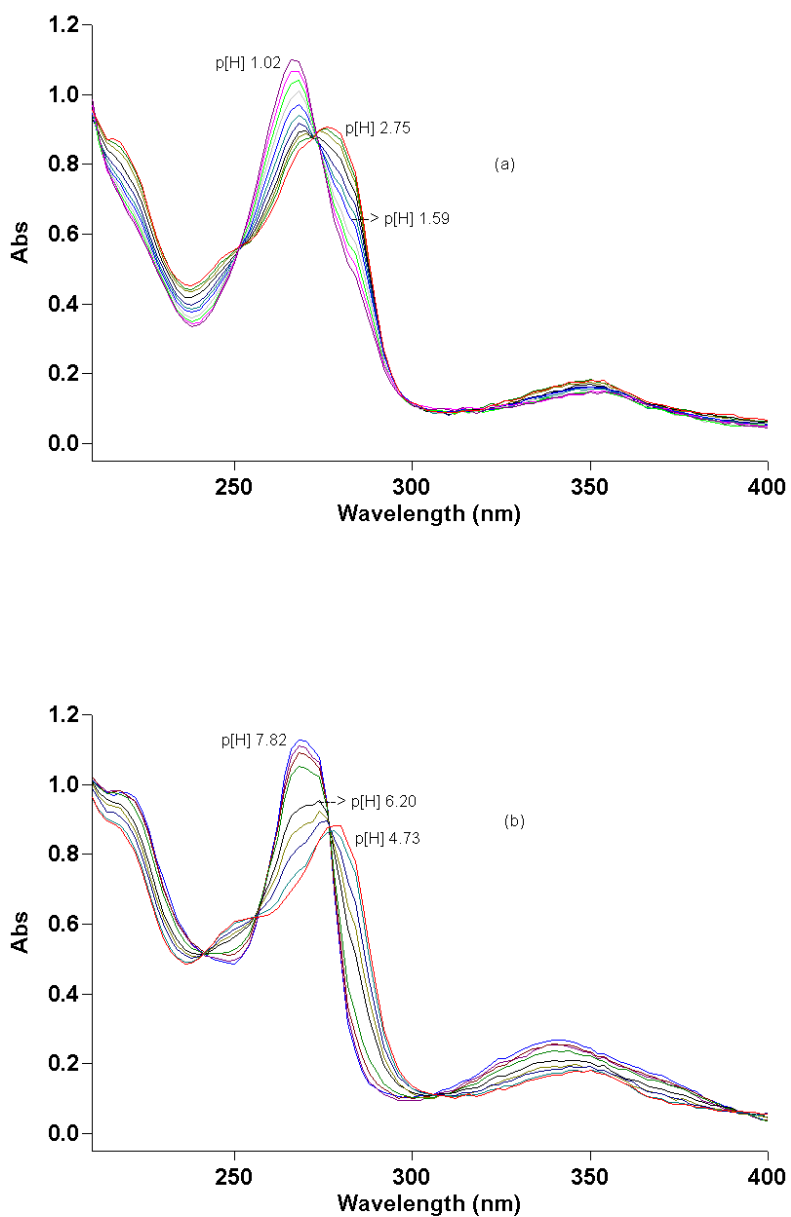


Figure S2. UV-vis absorption spectra of sulfoxinobactine as a function of p[H], (a): p[H] = 1.02, 1.16, 1.29, 1.43, 1.59, 1.74, 1.90, 2.13, 2.35, 2.53, 2.75 ; (b): p[H] = 4.73, 5.03, 5.78, 6.20, 6.80, 7.00, 7.30 and 7.82. [sulfoxinobactin] = 1.5×10^{-5} M, Solvent: H₂O, I = 0.1 M (NaClO₄), T = 25.0(2)°C.

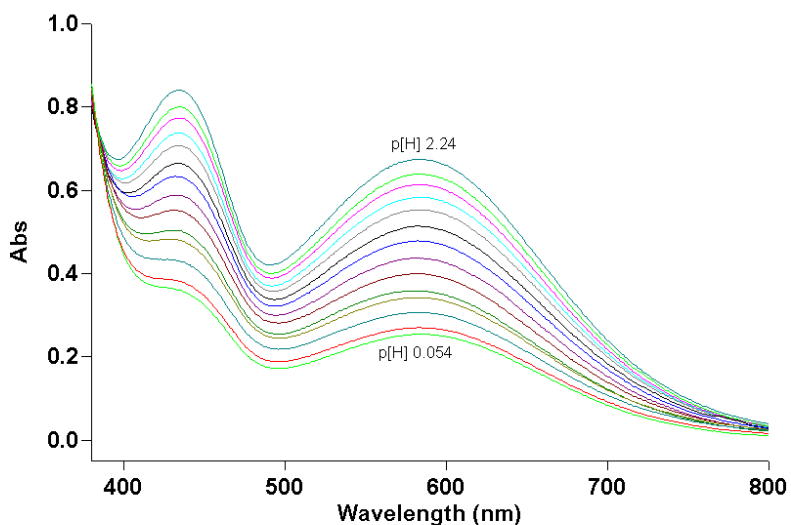


Figure S3 – UV-vis absorption spectra of a Fe^{3+} - sulfoxinobactin mixture at $\text{p[H]} = 0.054$ (bottom), 0.14, 0.32, 0.49, 0.62, 0.79, 0.99, 1.16, 1.34, 1.50, 1.66, 1.75, 1.86 and 2.24 (top). $[\text{Fe}^{3+}] = 1.5 \times 10^{-4} \text{ M}$, $[\text{sulfoxinobactin}] = 1.6 \times 10^{-4} \text{ M}$, Solvent: H_2O , $I = 0.1 \text{ M}$ (NaClO_4), $T = 25.0(2)^\circ\text{C}$.

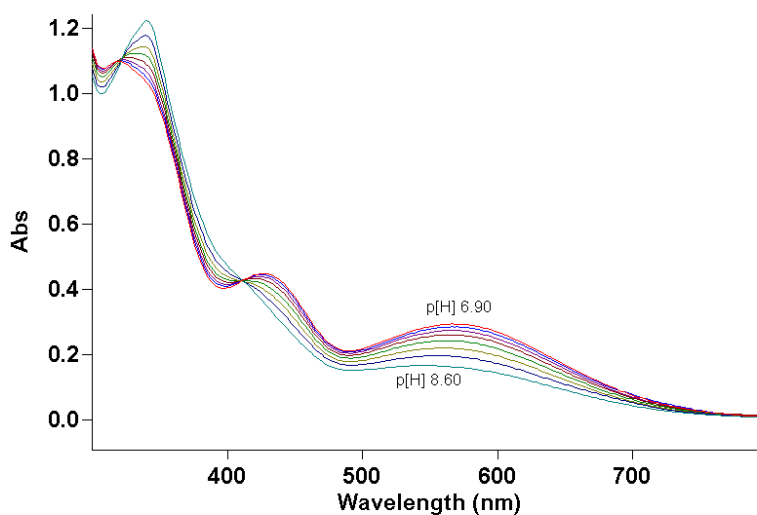


Figure S4 – UV-vis absorption spectra of a Fe^{3+} - sulfoxinobactin mixture at $\text{p[H]} = 6.90$, 7.20, 7.42, 7.61, 7.82, 8.03, 8.28 and 8.60. $[\text{Fe}^{3+}] = 6.8 \times 10^{-5} \text{ M}$, $[\text{sulfoxinobactin}] = 7.6 \times 10^{-5} \text{ M}$, Solvent: H_2O , $I = 0.1 \text{ M}$ (NaClO_4), $T = 25.0(2)^\circ\text{C}$.

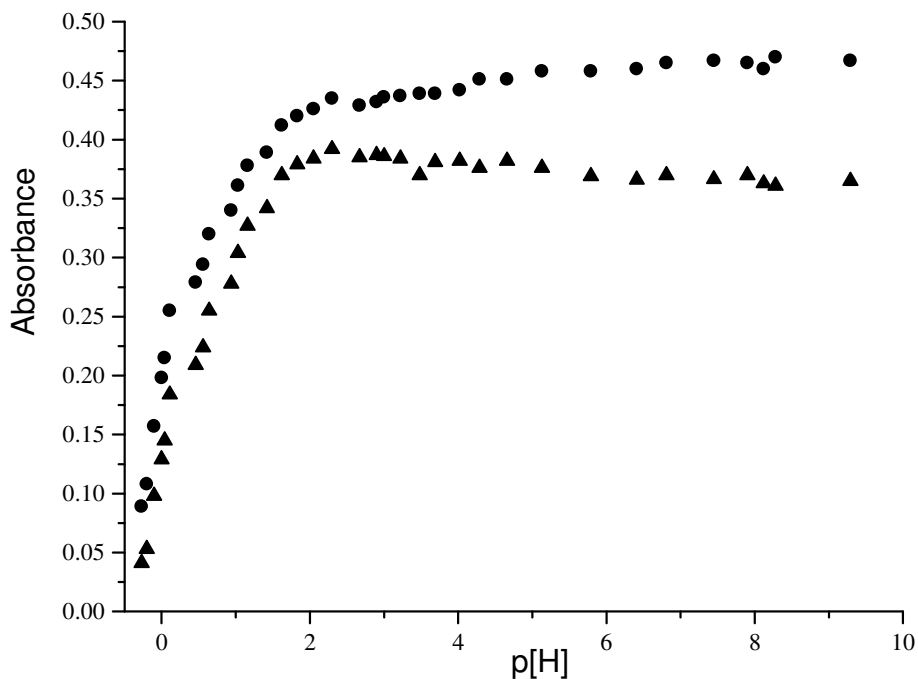


Figure S5. Plot Absorbance versus p[H] at $\lambda = 450$ (●) and 600 nm (▲) for Fe-oxinobactin. $[\text{Fe}^{3+}] = 8.9 \times 10^{-4}$ M, [oxinobactin] = 9.7×10^{-5} M, Solvent: $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (80/20 w/w), $I = 0.1$ M (NaClO_4), $T = 25.0(2)^\circ\text{C}$

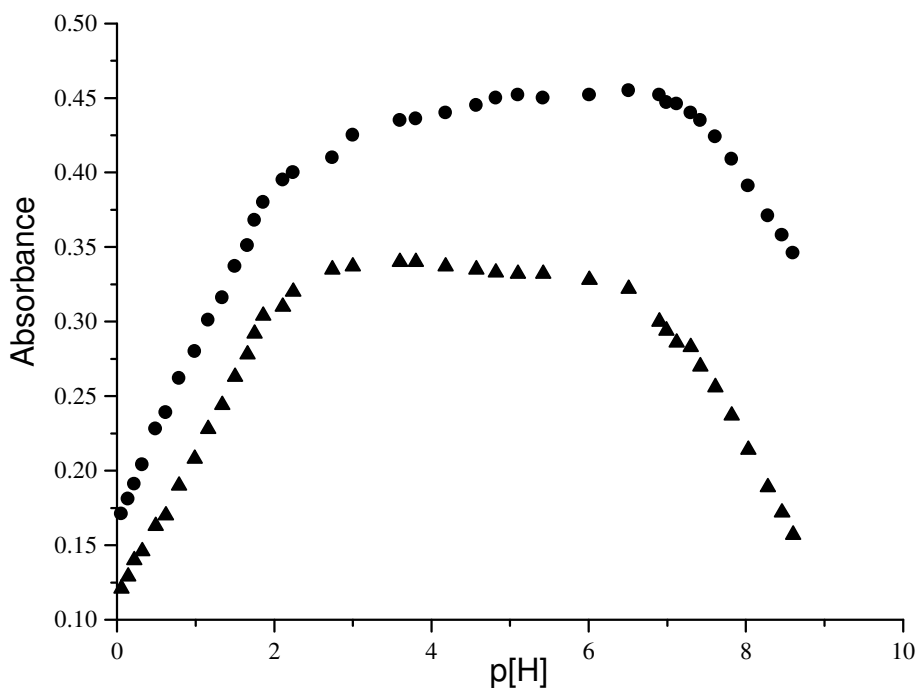


Figure S6. Plot Absorbance versus p[H] at $\lambda = 430$ (●) and 580 nm (▲) for Fe-sulfoxinobactin. $[\text{Fe}^{3+}] = 6.8 \times 10^{-5}$ M, [sulfoxinobactin] = 7.6×10^{-5} M, Solvent: H_2O , $I = 0.1$ M (NaClO_4), $T = 25.0(2)^\circ\text{C}$

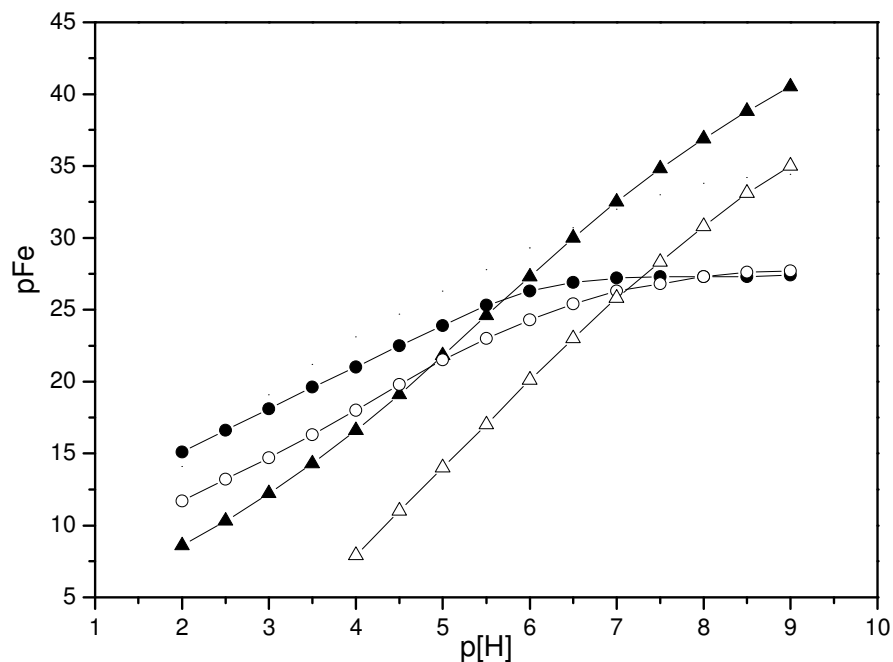


Figure S7. Plot pFe versus p[H]. pFe = $-\log [\text{Fe}^{3+}]$ calculated for $[\text{Fe}]_{\text{tot}} = 10^{-6} \text{ M}$, $[\text{L}]_{\text{tot}} = 10^{-5} \text{ M}$. ▲ enterobactin⁴, △ TRENCAM³⁷, ● hopobactin¹⁸, ○ TRENHOPO¹⁸; pFe were calculated from the protonation and the complexation constants published.

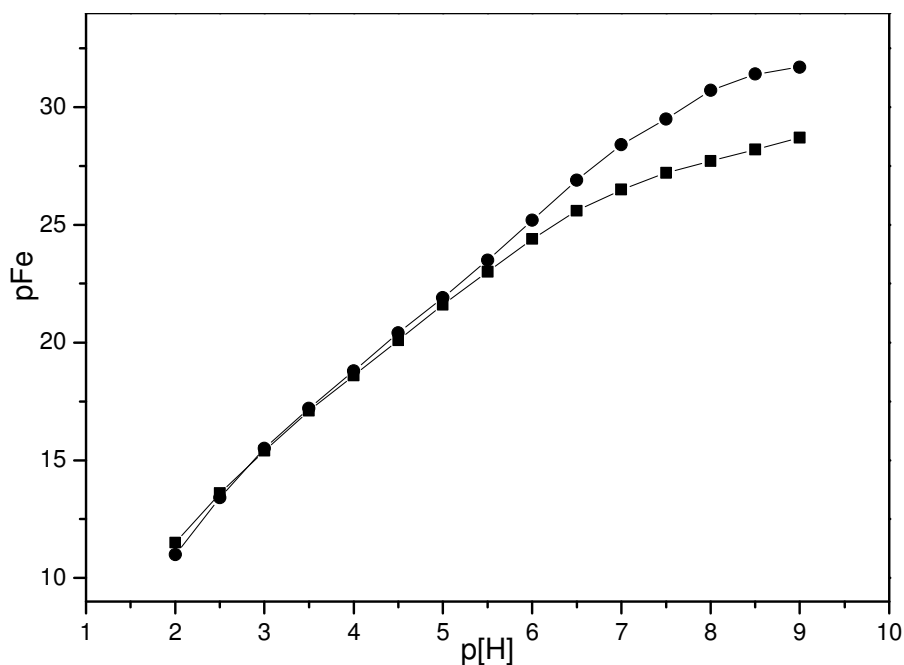


Figure S8. Plot pFe versus p[H]. pFe = $-\log [\text{Fe}^{3+}]$ calculated for $[\text{Fe}]_{\text{tot}} = 10^{-6} \text{ M}$, $[\text{L}]_{\text{tot}} = 10^{-5} \text{ M}$. ■ sulfoxinobactin, ● O-TRENSEX.³¹