

SUPPLEMENTARY INFORMATION

Benzoic hydroxamates-based iron complexes as models compounds for humic substances: synthesis, characterization and algal growth experiments

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Synthesis of hydroxamates

General procedure for preparation of methyl esters

The respective *n*-hydroxy benzoic acid (1 eq, 32 mmol) was dissolved in MeOH (60 mL), and a catalytic amount of sulfuric acid (3 mL) was added. The reaction mixture was stirred at reflux overnight. The resulting mixture was concentrated under reduced pressure and the residue dissolved in EtOAc. The solution was transferred into a separating funnel, washed with saturated NaHCO₃ solution and brine. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated to give the methyl ester **1c–l** in good yield.

Methyl 4-hydroxy-3,5-dimethoxybenzoate (**1c**)

Yield: 3.59 g, 15.9 mmol, 84 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 9.32 (s, 1 H, OH_{Ar}), 7.22 (s, 2 H, H_{Ar}), 3.83 (s, 6 H, OCH_{3Ar}), 3.82 (s, 3 H, OCH_{3ester}) ppm.

Methyl 2-hydroxybenzoate (**1d**)

Yield: 4.98 g, 32.8 mmol, 84 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 10.55 (s, 1 H, OH_{acid}), 7.76 (dd, *J* = 4 Hz, *J* = 2 Hz, 1 H, H_{Ar}), 7.51 (ddd, 1 H, *J* = 6 Hz, *J* = 2 Hz, *J* = 1 Hz, H_{Ar}), 6.98 (dd, *J* = 8 Hz, *J* = 1 Hz, 2 H, H_{Ar}), 6.92 (ddd, 1 H, *J* = 6 Hz, *J* = 1 Hz, H_{Ar}), 3.89 (s, 3 H, OCH_{3ester}) ppm.

Methyl 3-hydroxybenzoate (**1e**)

Yield: 2.24 g, 14.7 mmol, 74 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 9.83 (s, 1 H, OH_{Ar}), 7.42–7.29 (m, 3 H, H_{Ar}), 7.04 (m, 1 H, H_{Ar}), 3.83 (s, 3 H, OCH_{3ester}) ppm.

Methyl 4-hydroxybenzoate (**1f**)

Yield: 4.46 g, 29.3 mmol, 91 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 10.32 (s, 1 H, OH_{Ar}), 7.82 (d, *J* = 2 Hz, 2 H, H_{Ar}), 6.85 (d, *J* = 9 Hz, 2 H, H_{Ar}), 3.78 (s, 3 H, OCH_{3ester}) ppm.

Methyl 2,3-dihydroxybenzoate (**1g**)

Yield: 4.9 g, 29.1 mmol, 90 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 9.91 (s, 2 H, OH_{Ar}), 7.24 (dd, *J* = 8 Hz, *J* = 2 Hz, 1 H, H_{Ar}), 7.04 (dd, *J* = 8 Hz, *J* = 2 Hz, 1 H, H_{Ar}), 6.76 (t, 1 H, *J* = 8 Hz, H_{Ar}), 3.89 (s, 3 H, OCH_{3ester}) ppm.

Methyl 2,4-dihydroxybenzoate (**1h**)

Yield: 4.25 g, 25.3 mmol, 78 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 10.72 (s, 1 H, OH_{Ar}), 10.46 (s, 1 H, OH_{Ar}), 7.64 (d, *J* = 9 Hz, 1 H, H_{Ar}), 6.38 (dd, *J* = 9 Hz, *J* = 3 Hz, 1 H, H_{Ar}), 6.31 (d, 1 H, *J* = 2 Hz, H_{Ar}), 3.84 (s, 3 H, OCH_{3ester}) ppm.

Methyl 3,5-dihydroxybenzoate (**1i**)

Yield: 4.32 g, 25.7 mmol, 79 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 9.60 (s, 2 H, OH_{Ar}), 6.83 (d, J = 3 Hz, 2 H, H_{Ar}), 6.46 (t, 1 H, J = 2 Hz, H_{Ar}), 3.80 (s, 3 H, $\text{OCH}_{3\text{ester}}$) ppm.

Methyl 3-(4-hydroxyphenyl)propanoate (1j)

Yield: 2.03 g, 11.3 mmol, 74 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 9.18 (s, 1 H, OH_{Ar}), 7.01 (d, J = 8 Hz, 2 H, H_{Ar}), 6.70 (d, J = 8 Hz, 2 H, H_{Ar}), 3.58 (s, 3 H, $\text{OCH}_{3\text{ester}}$), 2.76 (t, J = 8 Hz, 2 H, H_{Al}), 2.56 (t, J = 8 Hz, 2 H, H_{Al}) ppm.

Methyl 3-(3,4-dihydroxyphenyl)propanoate (1k)

Yield: 2.07 g, 10.6 mmol, 96.5 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 10.68 (s, 1 H, OH_{Ar}), 7.63 (d, J = 8 Hz, 1 H, H_{Ar}), 6.58 (d, J = 2 Hz, 1 H, H_{Ar}), 6.44 (dd, 1 H, J = 8 Hz, J = 2 Hz, H_{Ar}), 3.58 (s, 3 H, $\text{OCH}_{3\text{ester}}$), 2.67 (t, J = 8 Hz, 2 H, H_{Al}), 2.53 (t, J = 8 Hz, 2 H, H_{Al}) ppm.

Methyl 4-hydroxy-3-methoxybenzoate (1l)

Yield: 5.3 g, 29.1 mmol, 98 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 9.94 (s, 1 H, OH_{acid}), 7.47 (d, J = 9 Hz, 1 H, H_{Ar}), 7.46 (s, 1 H, H_{Ar}), 6.88 (d, J = 8 Hz, 1 H, H_{Ar}), 3.83 (s, 3 H, $\text{OCH}_{3\text{Ar}}$), 3.79 (s, 3 H, $\text{OCH}_{3\text{acid}}$) ppm.

General procedure for preparation of protected methyl esters

To a stirred solution of methyl n-hydroxybenzoate (1eq, 27.6 mmol) in acetone (60 mL), was added potassium carbonate (2.25 eq, 62 mmol or 1.2 eq, 31 mmol) followed by benzyl bromide (2.25 eq, 62 mmol or 1.2 eq, 31 mmol) and refluxed for 10 h. The mixture was filtered, washed with acetone (30 mL), concentrated and dried in vacuo. In order to remove the excess of benzyl bromide the crude oil was suspended in petrol ether (30 mL) and ultrasonicated for approximately 5 min and the solvent was decanted (5x) and finally stored for 2 h at 4°C until a precipitate was formed. The solid was filtered off, washed with petrol ether and dried in vacuo.

Methyl 4-(benzyloxy)-3,5-dimethoxybenzoate (2c)

Yield: 3.30 g, 10.9 mmol, 69 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 7.48–7.27 (m, 5 H, H_{Ar}), 7.25 (s, 2 H, H_{Ar}), 5.01 (s, 2H, CH_{2bn}), 3.86 (s, 3 H, OCH_{3ester}), 3.84 (s, 6 H, OCH_{3Ar}) ppm.

Methyl 2-(benzyloxy)benzoate (2d)

Yield: 4.19 g, 17.3 mmol, 53 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 7.77–6.97 (m, 7 H, H_{Ar}), 5.19 (s, 2H, CH_{2bn}), 3.83 (s, 3 H, OCH_{3ester}) ppm.

Methyl 3-(benzyloxy)benzoate (2e)

Yield: 2.57 g, 10.6 mmol, 74 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): ¹H NMR (DMSO, 500.10 MHz, 25 °C): δ = 7.59–7.29 (m, 9 H, H_{Ar}), 5.18 (s, 2 H, s, 2H, CH_{2bn}), 3.86 (s, 3 H, OCH_{3ester}) ppm.

Methyl 4-(benzyloxy)benzoate (2f)

Yield: 6.59 g, 27.2 mmol, 93 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): ¹H NMR (DMSO, 500.10 MHz, 25 °C): δ = 7.97–7.06 (m, 9 H, H_{Ar}), 5.18 (s, 2 H, s, 2H, CH_{2bn}), 3.81 (s, 3 H, OCH_{3ester}) ppm.

Methyl 2,3-bis(benzyloxy)benzoate (2g)

Yield: 8.12 g, 23.3 mmol, 80 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 7.55–7.16 (m, 13 H, H_{Ar}), 5.22 (s, 2H, CH_{2bn}), 5.02 (s, 2H, CH_{2bn}), 3.79 (s, 3 H, OCH_{3ester}) ppm.

Methyl 2,4-bis(benzyloxy)benzoate (2h)

Yield: 4.46 g, 12.8 mmol, 51 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 7.62–7.17 (m, 13 H, H_{Ar}), 5.24 (s, 2H, CH_{2bn}), 5.19 (s, 2H, CH_{2bn}), 3.81 (s, 3 H, OCH_{3ester}) ppm.

Methyl 3,5-bis(benzyloxy)benzoate (2i)

Yield: 7.64 g, 21.9 mmol, 85 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 7.56–6.91 (m, 8 H, H_{Ar}), 5.15 (s, 4H, CH_{2bn}), 3.84 (s, 3 H, OCH_{3ester}) ppm.

Methyl 3-(4-(benzyloxy)phenyl)propanoate (2j)

Yield: 2.44 g, 9 mmol, 80 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 7.47–6.90 (m, 9 H, H_{Ar}), 5.07 (s, 2H, $\text{CH}_{2\text{bn}}$), 3.58 (s, 3 H, $\text{OCH}_{3\text{ester}}$), 2.79 (t, J = 8 Hz, 2 H, H_{Al}), 2.58 (t, J = 8 Hz, 2 H, H_{Al}) ppm.

Methyl 3-(3,4-bis(benzyloxy)phenyl)propanoate (2k)

Yield: 3.71 g, 9.8 mmol, 63 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 7.52–6.71 (m, 13 H, H_{Ar}), 5.12 (s, 2 H, $\text{CH}_{2\text{bn}}$), 5.09 (s, 2 H, $\text{CH}_{2\text{bn}}$), 2.67 (t, J = 8 Hz, 2 H, H_{Al}), 2.53 (t, J = 8 Hz, 2 H, H_{Al}) ppm.

Methyl 4-(benzyloxy)-3-methoxybenzoate (2l)

Yield: 6.49 g, 23.9 mmol, 82 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 7.62–7.11 (m, 8 H, H_{bn}), 5.17 (s, 2H, $\text{CH}_{2\text{bn}}$), 3.83 (s, 6 H, $\text{OCH}_{3\text{Ar}}$, $\text{OCH}_{3\text{acid}}$) ppm.

General procedure for preparation of protected benzoic acids

The methyl esters (20 mmol) were hydrolyzed using 30% (w/v) aq KOH (2.5 mL) solution in MeOH (40 mL) which was heated at 80 °C for 10 h. After completion of the reaction, the solvent was evaporated. Water (40 mL) was added to the residue and acidified by addition of HCl (5 M) to pH 1. The formed precipitate was collected by filtration, washed with water and dried in vacuo to afford the carboxylic acids **3c–f** as white powders.

4-(Benzyloxy)-3,5-dimethoxybenzoic acid (**3c**)

Yield: 3.00 g, 10.4 mmol, 95.5 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 12.94 (s, 1 H, OH_{acid}), 7.49–7.27 (m, 5 H, H_{bn}), 7.25 (s, 2 H, H_{benz}), 5.00 (s, 2H, CH_{2bn}), 3.84 (s, 6 H, OCH_{3Ar}) ppm.

2-(Benzyloxy)benzoic acid (**3d**)

Yield: 1.38 g, 6.05 mmol, 93 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 12.66 (s, 1 H, OH_{acid}), 7.70–6.99 (m, 9 H, H_{Ar}), 5.21 (s, 2H, CH_{2bn}) ppm.

3-(Benzyloxy)benzoic acid (**3e**)

Yield: 3.00 g, 13.1 mmol, 96 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 13.02 (s, 1 H, OH_{acid}), 7.63–7.19 (m, 9 H, H_{Ar}), 5.18 (s, 2 H, s, 2H, CH_{2bn}) ppm.

4-(Benzyloxy)benzoic acid (**3f**)

Yield: 3.89 g, 17.1 mmol, 63 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 12.65 (s, 1 H, OH_{acid}), 7.98–7.03 (m, 9 H, H_{Ar}), 5.19 (s, 2 H, s, 2H, CH_{2bn}) ppm.

2,3-Bis(benzyloxy)benzoic acid (**3g**)

Yield: 7.6 g, 22.7 mmol, 98 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 7.57–7.10 (m, 13 H, H_{Ar}), 5.19 (s, 2H, CH_{2bn}), 5.02 (s, 2H, CH_{2bn}) ppm.

2,4-Bis(benzyloxy)benzoic acid (**3h**)

Yield: 4.26 g, 13.1 mmol, 99.5 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 7.55–7.19 (m, 13 H, H_{Ar}), 5.16 (s, 2H, CH_{2bn}), 5.04 (s, 2H, CH_{2bn}) ppm.

3,5-Bis(benzyloxy)benzoic acid (**3i**)

Yield: 5.9 g, 17.7 mmol, 81 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 7.58–6.86 (m, 8 H, H_{Ar}), 5.14 (s, 4H, CH_{2bn}) ppm.

3-(4-(Benzyloxy)phenyl)propanoic acid (**3j**)

Yield: 1.79 g, 7 mmol, 77 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 12.09 (s, 1 H, OH_{acid}), 7.48–6.88 (m, 9 H, H_{Ar}), 5.07 (s, 2H, CH_{2bn}), 2.76 (t, *J* = 8 Hz, 2 H, H_{Al}), 2.49 (t, *J* = 8 Hz, 2 H, H_{Al}) ppm.

3-(3,4-Bis(benzyloxy)phenyl)propanoic acid (3k)

Yield: 3.54 g, 9.78 mmol, 99 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 7.49–6.70 (m, 13 H, H_{Ar}), 5.10 (s, 2 H, $\text{CH}_{2\text{bn}}$), 5.08 (s, 2H, $\text{CH}_{2\text{bn}}$), 2.74 (t, J = 8 Hz, 2 H, H_{Al}), 2.49 (t, J = 8 Hz, 2 H, H_{Al}) ppm.

4-(Benzyloxy)-3-methoxybenzoic acid (3l)

Yield: 5.49 g, 21.3 mmol, 89 %. ^1H NMR (DMSO- d_6 , 500.10 MHz, 25 °C): δ = 7.58–7.07 (m, 8 H, H_{bn}), 5.17 (s, 2H, $\text{CH}_{2\text{bn}}$), 3.81 (s, 3 H, $\text{OCH}_{3\text{Ar}}$) ppm.

General procedure for preparation of protected hydroxamic acidsⁱ

To a solution of the benzoic acid (0.88 g, 10 mmol) in diethyl ether (30 mL) ethyl chloroformate (1.3 g, 12 mmol) and *N*-methylmorpholine (1.3 g, 13 mmol) were added at 0 °C and the mixture was stirred for 30 min. The formed solid was filtered off and the filtrate was added to freshly prepared methanolic hydroxylamine (0.5 g, 15 mmol) solution. The reaction mixture was stirred at room temperature for 45 min. The formed white precipitate was filtered off and washed with diethyl ether. The crude hydroxamic acid was recrystallized from EtOAc or EtOAc/PE (8:2) to give the respective hydroxamic acid as white powder.

***N*-Hydroxycinnamamide (4b)**

Yield: 0.272 g, 1.7 mmol, 17 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 10.75 (s, 1 H, NH_{acid}), 9.07 (s, 1 H, OH_{acid}), 7.47 (d, *J* = 16 Hz, 1 H, H_{Al}), 7.60–7.35 (m, 5 H, H_{Ar}), 6.48 (d, *J* = 16 Hz, 1 H, H_{Al}) ppm.

4-(Benzyloxy)-*N*-hydroxy-3,5-dimethoxybenzamide (4c)

Yield: 1.10 g, 3.6 mmol, 35 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 11.15 (s, 1 H, NH_{acid}), 9.03 (s, 1 H, OH_{acid}), 7.49–7.28 (m, 5 H, H_{bn}), 7.11 (s, 2 H, H_{benz}), 4.96 (s, 2H, CH_{2bn}), 3.83 (s, 6 H, OCH_{3Ar}) ppm.

2-(Benzyloxy)-*N*-hydroxybenzamide (4d)

Yield: 1.38 g, 5.7 mmol, 94 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 11.20 (s, 1 H, NH_{acid}), 9.09 (s, 1 H, OH_{Ar}), 7.56–7.30 (m, 9 H, H_{Ar}), 7.16 (t, *J* = 9 Hz, 1 H, H_{Ar}), 7.01 (t, *J* = 7 Hz, 1 H, H_{Ar}), 5.23 (s, 2H, CH_{2bn}) ppm.

3-(Benzyloxy)-*N*-hydroxybenzamide (4e)

Yield: 0.779 g, 3.2 mmol, 32 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 11.10 (s, 1 H, NH_{acid}), 9.05 (s, 1 H, OH_{acid}), 7.51–7.12 (m, 9 H, H_{Ar}), 5.15 (s, 2 H, s, 2H, CH_{2bn}) ppm.

4-(Benzyloxy)-*N*-hydroxybenzamide (4f)

Yield: g, 0.67, 2.8 mmol, 31 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 11.10 (s, 1 H, NH_{acid}), 8.91 (s, 1 H, OH_{acid}), 7.81–7.00 (m, 9 H, H_{Ar}), 5.17 (s, 2H, CH_{2bn}) ppm.

2,3-Bis(benzyloxy)-*N*-hydroxybenzamide (4g)

Yield: g, 2.31, 6.6 mmol, 75 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 10.74 (s, 1 H, NH_{acid}), 9.11 (s, 1 H, OH_{acid}), 7.56–6.94 (m, 13 H, H_{Ar}), 5.21 (s, 2H, CH_{2bn}), 5.02 (s, 2H, CH_{2bn}) ppm.

2,4-Bis(benzyloxy)-*N*-hydroxybenzamide (4h)

Yield: 1.4 g, 4 mmol, 67 %. ¹H NMR (DMSO-*d*₆, 500.10 MHz, 25 °C): δ = 10.76 (s, 1 H, NH_{acid}), 9.17 (s, 1 H, OH_{acid}), 7.55–6.95 (m, 13 H, H_{Ar}), 5.21 (s, 2H, CH_{2bn}), 5.02 (s, 4H, CH_{2bn}) ppm.

3,5-Bis(benzyloxy)-*N*-hydroxybenzamide (4i)

Yield: 1.65 g, 4.7 mmol, 53.6 %. ESI-MS: m/z 196 [L-H]⁻. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 11.24 (s, 1 H, NH_{acid}), 9.10 (s, 1 H, OH_{acid}), 7.49–6.79 (m, 8 H, H_{Ar}), 5.14 (s, 4H, CH_{2bn}) ppm.

3-(4-(Benzyloxy)phenyl)-*N*-hydroxypropanamide (4j)

Yield: 1.49 g, 5.5 mmol, 79 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 10.37 (s, 1 H, NH_{acid}), 8.69 (s, 1 H, OH_{acid}), 7.46–6.88 (m, 9 H, H_{Ar}), 5.06 (s, 2H, CH_{2bn}), 2.74 (t, J = 8 Hz, 2 H, H_{Al}), 2.22 (t, J = 8 Hz, 2 H, H_{Al}) ppm.

3-(3,4-Bis(benzyloxy)phenyl)-*N*-methylpropanamide (4k)

Yield: 3.45 g, 9.14 mmol, 93 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 10.38 (s, 1 H, NH_{acid}), 8.72 (s, 1 H, OH_{acid}), 7.50–6.69 (m, 13 H, H_{Ar}), 5.10 (s, 2 H, CH_{2bn}), 5.08 (s, 2 H, CH_{2bn}), 2.74 (t, J = 8 Hz, 2 H, H_{Al}), 2.23 (t, J = 8 Hz, 2 H, H_{Al}) ppm.

4-(Benzyloxy)-*N*-hydroxy-3-methoxybenzamide (4l)

Yield: 0.568 g, 2.1 mmol, 30 %. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 11.11 (s, 1 H, NH_{acid}), 8.94 (s, 1 H, OH_{acid}), 7.48–7.04 (m, 8 H, H_{bn}), 5.14 (s, 2H, CH_{2bn}), 3.81 (s, 3 H, OCH_{3Ar}) ppm.

General procedure for preparation of hydroxamic acids

A catalytic amount of Pd/C (10 wt. % loading) was added to a solution of protected hydroxamic acid in methanol (dried over mol sieves) under an argon atmosphere. The suspension was put stirred for 4h under an H₂ atmosphere until the hydroxamic acid was completely dissolved. The solution was filtered off, concentrated and dried in vacuo yielding pure hydroxamic acids.

N,4-Dihydroxy-3,5-dimethoxybenzamide (5c)

Yield: 0.765 g, 3.6 mmol, 99.5 %. ESI-MS: m/z 163 [L-H]⁻. Anal. Calcd for C₉H₁₁NO₅ · 0.1 C₇H₆: C, 52.38; H, 5.35; N, 6.30; found: C, 52.79; H, 5.73; N, 6.33. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 11.15 (s, 1 H, OH_{Ar}), 8.89 (s, 1 H, OH_{acid}), 7.10 (s, 2 H, H_{benz}), 3.80 (s, 6 H, OCH_{3Ar}) ppm. ¹³C NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 168.9 (C=O), 145.4 (C_q), 143.8 (C_q), 125.8 (C_q), 119.2 (CH_{ar}), 116.2 (CH_{ar}), 115.9 (CH_{ar}), 34.9 (CH₂), 30.8 (CH₂) ppm.

N,2-Dihydroxybenzamide (5d)

Yield: 0.742 g, 4.8 mmol, 85%. ESI-MS: m/z 152 [L-H]⁻. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 12.22 (s, 1 H, NH_{acid}), 11.42 (s, 1 H, OH_{acid}), 9.32 (s, 2 H, OH_{Ar}), 7.68 (dd, J = 4 Hz, J = 2 Hz, 1 H, H_{Ar}), 7.39 (m, 1 H, H_{Ar}), 6.91 (dd, J = 1 Hz, 1 H, H_{Ar}), 6.87 (m, 1 H, H_{Ar}), ppm.

N,3-Dihydroxybenzamide (5e)

Yield: 0.193 g, 1.3 mmol, 39 %. ESI-MS: m/z 176 [L+Na]⁺. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 10.98 (s, 1 H, NH_{acid}), 9.51 (s, 1 H, OH_{acid}), 9.07 (s, 1 H, OH_{Ar}), 7.23 (t, J = 8 Hz, 1 H, H_{Ar}), 7.15 (t, J = 2 Hz, 1 H, H_{Ar}), 6.90 (dd, J = 4 Hz, J = 1.5 Hz, 1 H, H_{Ar}), ppm.

N,4-Dihydroxybenzamide (5f)

Yield: 0.420 g, 2.7 mmol, 99.5 %. ESI-MS: m/z 152 [L-H]⁻. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 10.15 (s, 1 H, OH_{acid}), 9.04 (s, 1 H, OH_{Ar}), 7.62 (d, J = 9 Hz, 2 H, H_{Ar}), 6.80 (d, J = 8 Hz, 2 H, H_{Ar}), ppm.

N,2,3-Trihydroxybenzamide (5g)

Yield: 0.918 g, 5.4 mmol, 83 %. ESI-MS: m/z 192 [L+Na]⁺. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 12.29 (s, 1 H, NH_{acid}), 11.46 (s, 1 H, OH_{acid}), 9.30 (s, 2 H, OH_{Ar}), 7.12 (dd, J = 8 Hz, J = 2 Hz, 2 H, H_{Ar}), 6.91 (dd, J = 8 Hz, J = 2 Hz, 2 H, H_{Ar}), 6.66 (t, J = 8 Hz, 1 H, H_{Ar}), ppm

N,2,4-Trihydroxybenzamide (5h)

Yield: 0.673 g, 3.9 mmol, 99.4 %. ESI-MS: m/z 170 [L+H]⁺. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 11.2 (s, 1 H, NH_{acid}), 10.09 (s, 1 H, OH_{acid}), 9.13 (s, 2 H, OH_{Ar}), 7.53 (dd, J = 9 Hz, J = 2 Hz, 2 H, H_{Ar}), 6.28 (dd, J = 8 Hz, J = 2 Hz, 2 H, H_{Ar}), 6.26 (t, J = 3 Hz, 1 H, H_{Ar}), ppm

N,3,5-Trihydroxybenzamide (5i)

Yield: 0.718 g, 3.6 mmol, 99.3 %. ESI-MS: m/z 192 [L+Na]⁺. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 9.60 (s, 2 H, OH_{Ar}), 6.58 (d, J = 2 Hz, 2 H, H_{Ar}), 6.37 (s, 1 H, H_{Ar}), ppm.

N-Hydroxy-3-(4-hydroxyphenyl)propanamide (5j)

Yield: 0.699 g, 3.8 mmol, 99.7 %. ESI-MS: m/z 180 [L-H]⁻. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 10.38 (s, 1 H, NH_{acid}), 9.19 (s, 1 H, OH_{acid}), 8.69 (s, 1 H, OH_{Ar}), 6.98 (d, J = 8 Hz, 2 H, H_{Ar}), 6.67 (d, J = 8 Hz, 2 H, H_{Ar}), 2.69 (t, J = 8 Hz, 2 H, H_{Al}), 2.20 (t, J = 8 Hz, 2 H, H_{Al}) ppm.

3-(3,4-dihydroxyphenyl)-N-hydroxypropanamide (5k)

Yield: 0.885 g, 4.5 mmol, 95.7 %. ESI-MS: m/z 196 [L-H]⁻. Anal. Calcd for C₉H₁₁NO₄ · 0.5 H₂O: C, 52.40; H, 5.87; N, 6.79; found: C, 52.38; H, 5.87; N, 6.41. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 10.33 (s, 1 H, NH_{acid}), 8.67 (s, 2 H, OH_{Ar}), 6.61 (d, J = 8 Hz, J = 2 Hz, 2 H, H_{Ar}), 6.57 (d, J = 2 Hz, 1 H, H_{Ar}), 6.42 (dd, J = 8 Hz, J = 2 Hz, 1 H, H_{Ar}), 2.63 (t, J = 8 Hz, 2 H, H_{Al}), 2.16 (t, J = 8 Hz, 2 H, H_{Al}) ppm. ¹³C NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 168.9 (C=O), 145.4 (C_q), 143.8 (C_q), 125.8 (C_q), 119.2 (CH_{ar}), 116.2 (CH_{ar}), 115.9 (CH_{ar}), 34.9 (CH₂), 30.8 (CH₂) ppm.

N,3-Dihydroxy-4-methoxybenzamide (5l)

Yield: 0.362 g, 2 mmol, 95 %. ESI-MS: m/z 182 [L]⁻. ¹H NMR (DMSO-d₆, 500.10 MHz, 25 °C): δ = 9.61 (s, 1 H, NH_{acid}), 7.80 (s, 2 H, OH_{acid}), 7.35 (d, J = 3 Hz, 1 H, H_{Ar}), 7.26 (dd, J = 8 Hz, J = 2 Hz, 1 H, H_{Ar}), 7.09 (s, 1 H, OH_{Ar}), 6.83 (d, J = 8 Hz, 1 H, H_{Ar}), 3.80 (s, 3 H, OCH_{3Ar}) ppm.

Time dependent UV-vis spectra in seawater

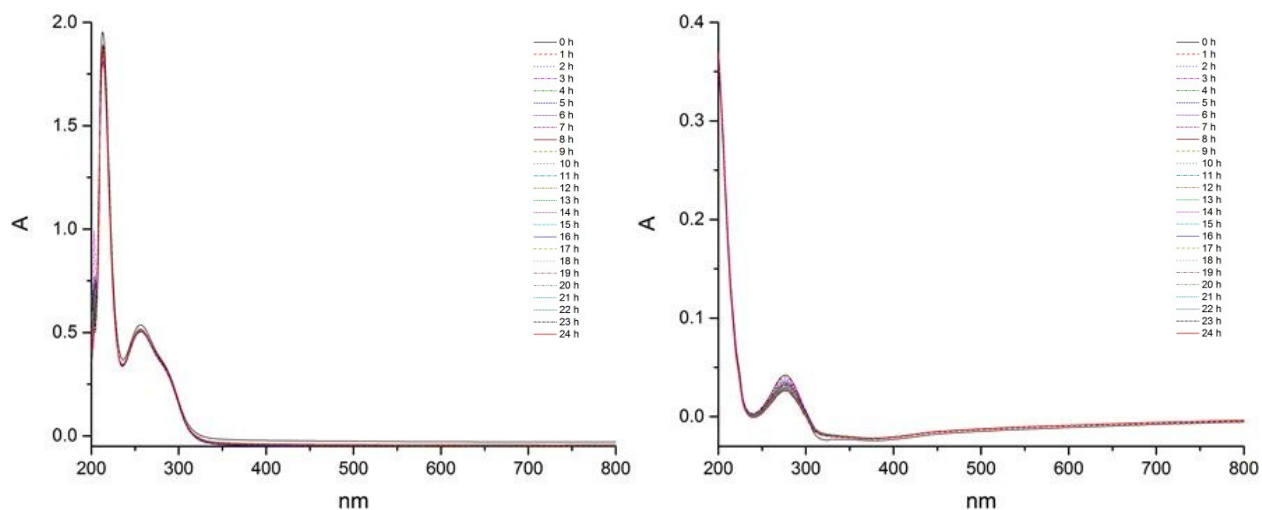


Figure S1. Time dependent UV-vis spectra of **6a** (left) and **6b** (right) in seawater.

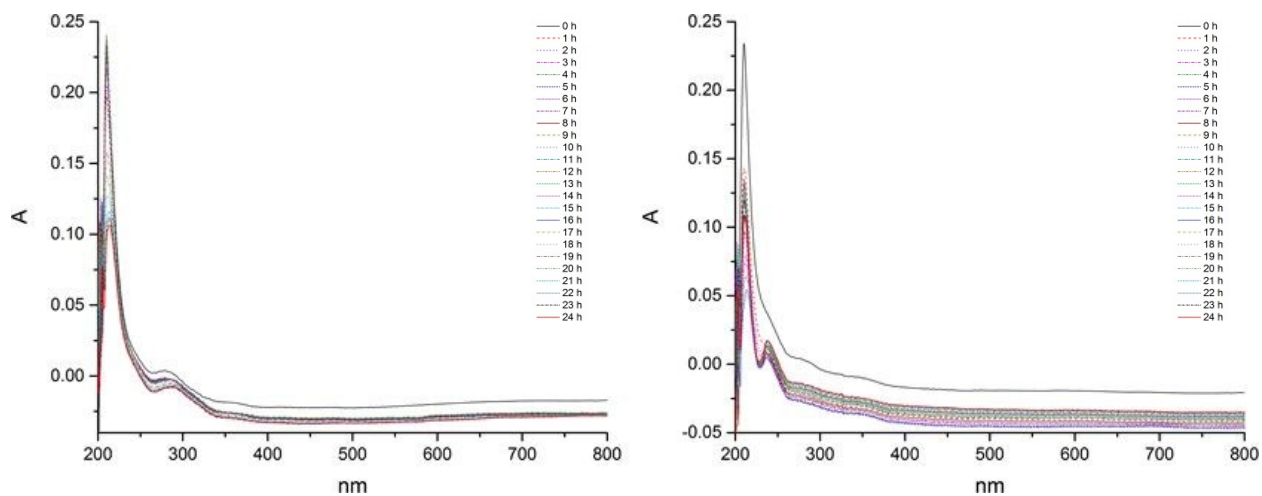


Figure S2. Time dependent UV-vis spectra of **6c** (left) and **6d** (right) in seawater.

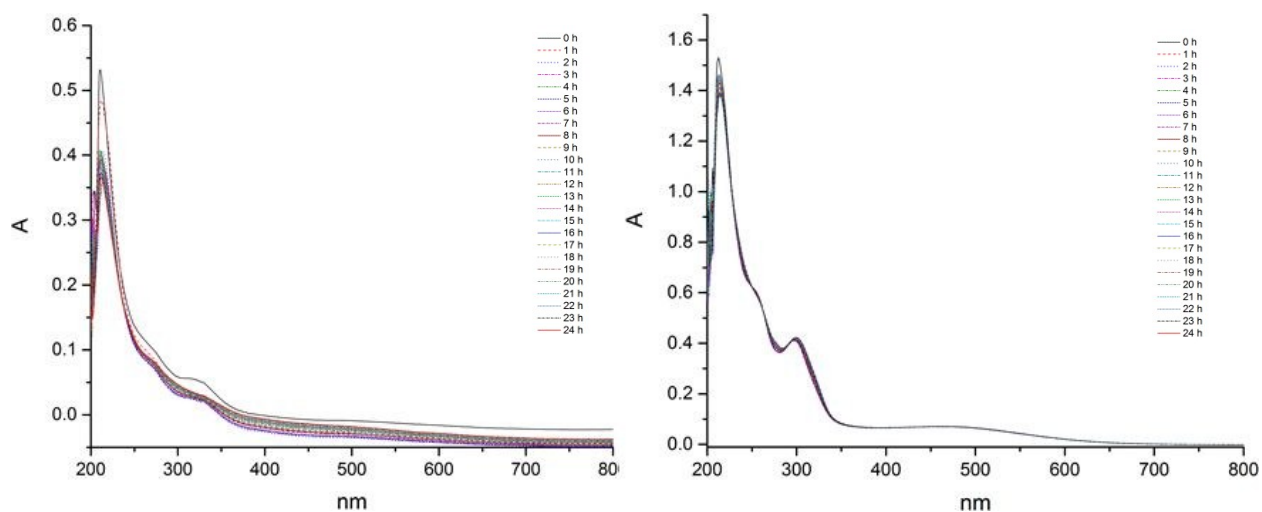


Figure S3. Time dependent UV-vis spectra of **6g** (left) and **6h** (right) in seawater.

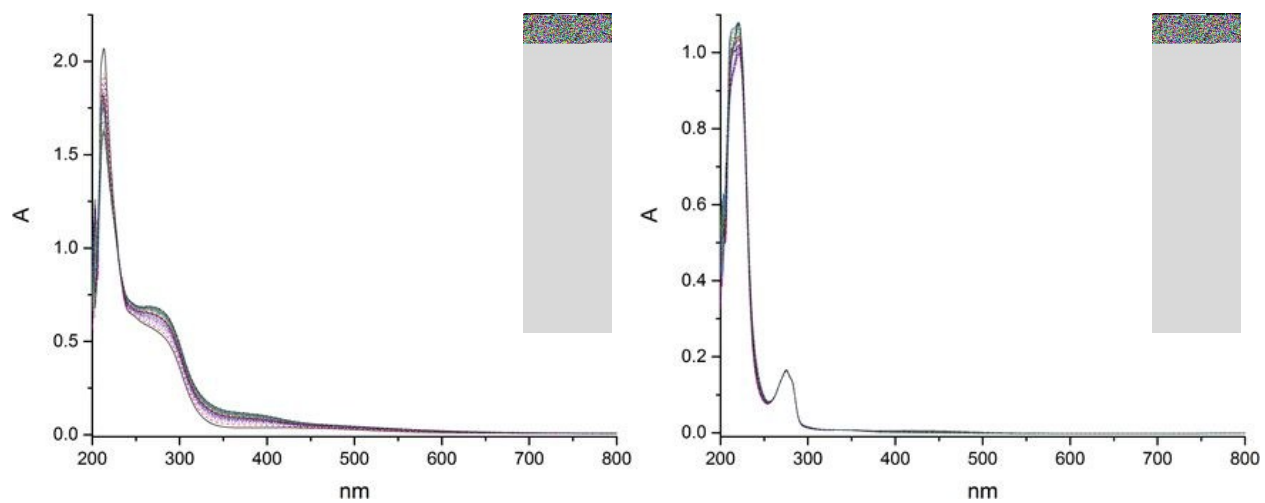


Figure S4. Time dependent UV-vis spectra of **6i** (left) and **6j** (right) in seawater.

Time dependent UV-vis spectra in distilled water

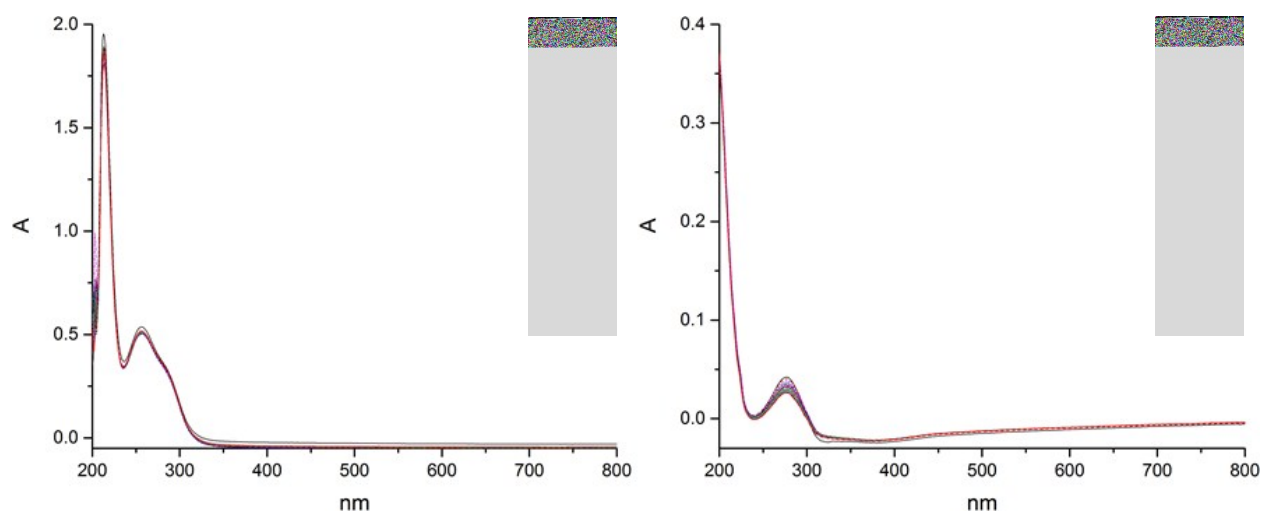


Figure S5. Time dependent UV-vis spectra of **6a** (left) and **6b** (right) in distilled water.

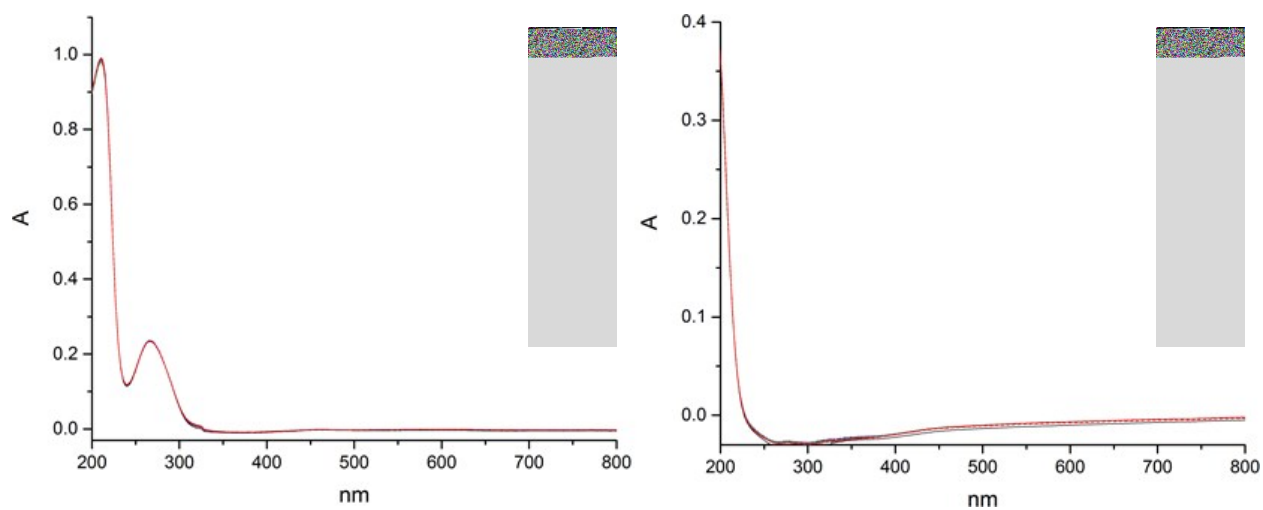


Figure S6. Time dependent UV-vis spectra of **6c** (left) and **6d** (right) in distilled water.

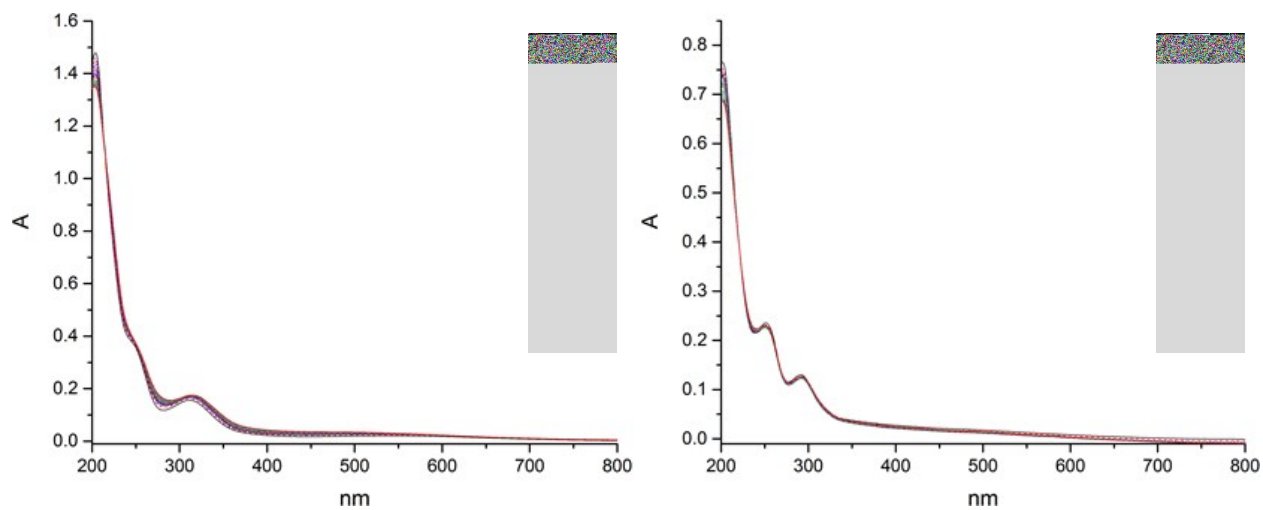


Figure S7. Time dependent UV-vis spectra of **6g** (left) and **6h** (right) in distilled water.

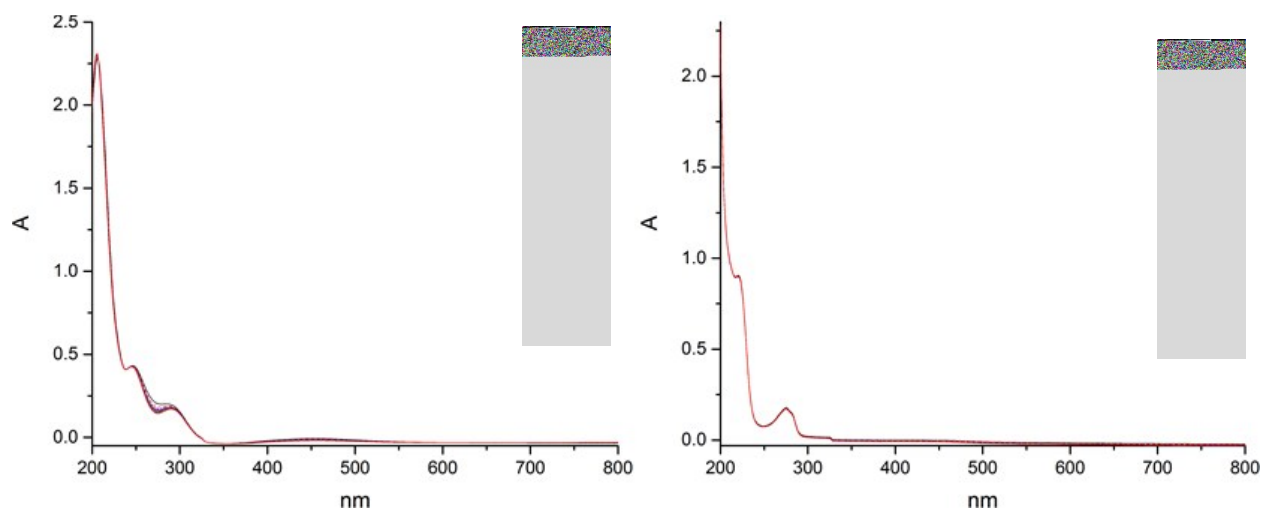


Figure S8. Time dependent UV-vis spectra of **6i** (left) and **6j** (right) in distilled water.

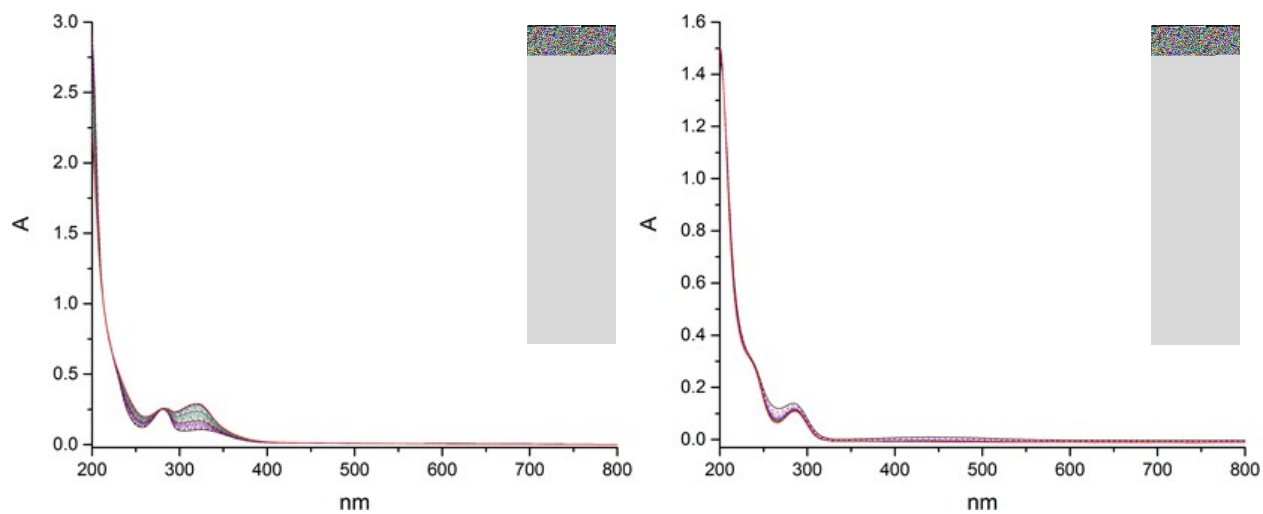


Figure S9. Time dependent UV-vis spectra of **6k** (left) and **6e** (right) in distilled water

Time dependent UV-vis spectra in distilled water at pH 11

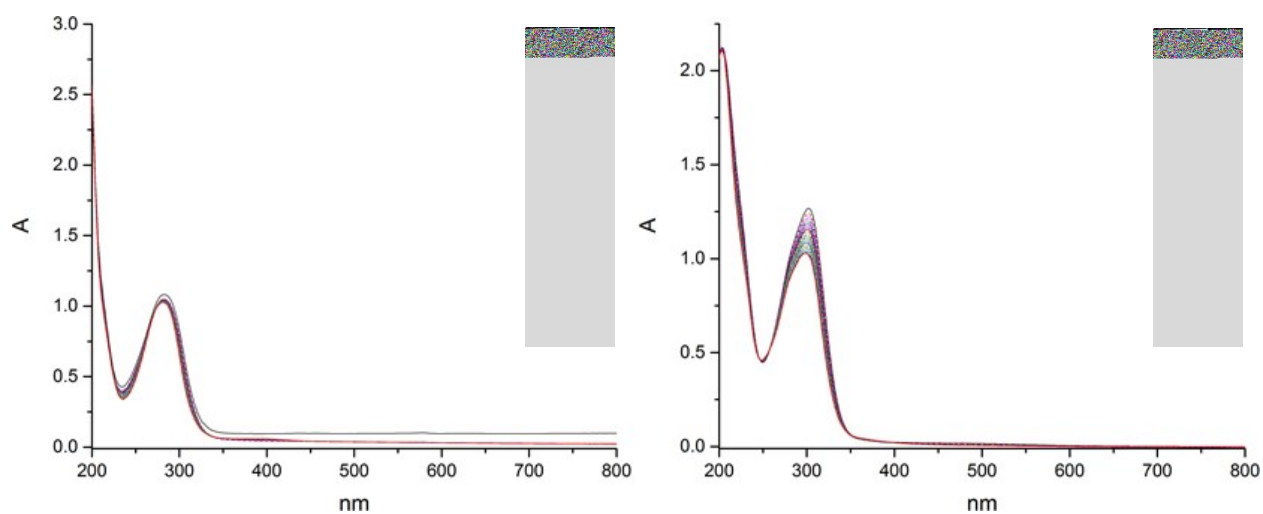


Figure S10. Time dependent UV-vis spectra of **6f** (left) and **6l** (right) in distilled water at pH 11

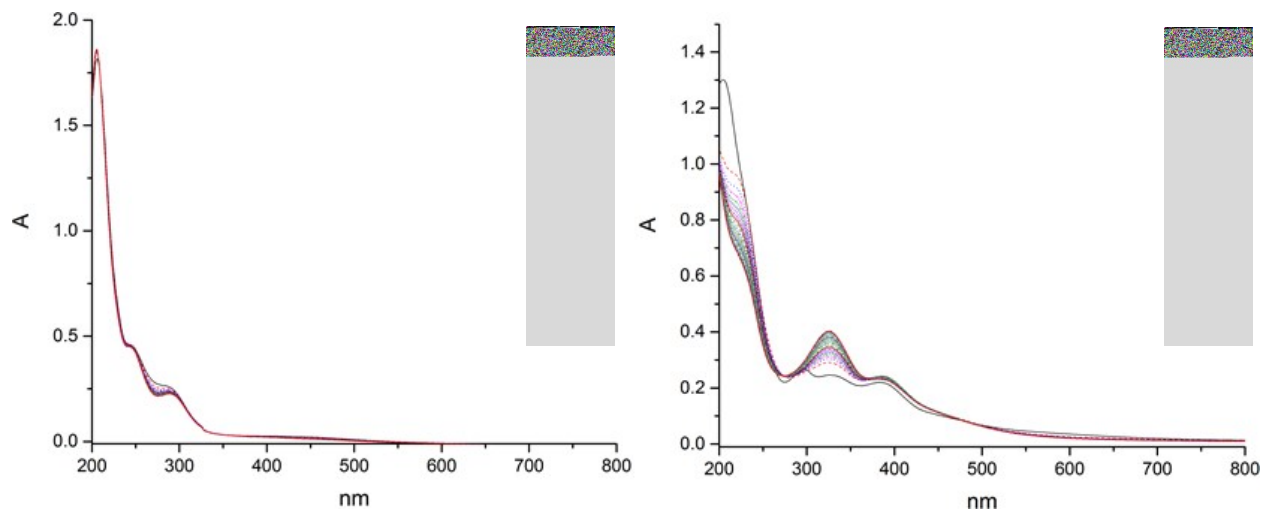


Figure S11. Time dependent UV-vis spectra of **6i** (left) and **6k** (right) in distilled water at pH 11

*Time dependent UV-vis spectra of **6e** distilled water and seawater with EDTA*

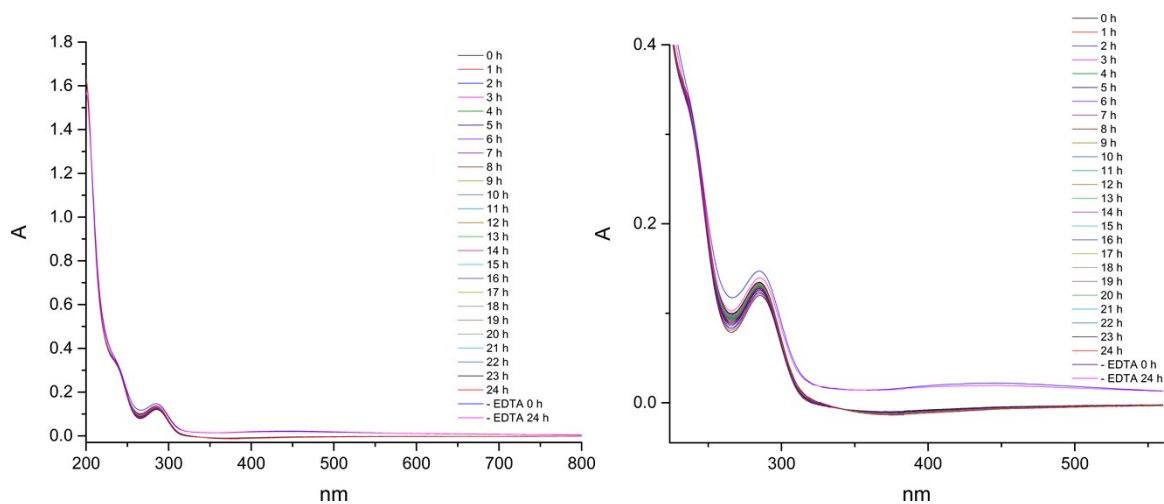


Figure S12. Time dependent UV-vis spectra of **6e** treated with EDTA in distilled water (left – whole spectra, right – enlarged area, pH: distilled water = 5.71, distilled water + **6e** = 5.64, distilled water + **6e** + EDTA = 4.62). Used concentration of **6e** and EDTA was 25 nM. The time dependent measurement was carried out at 25 °C.

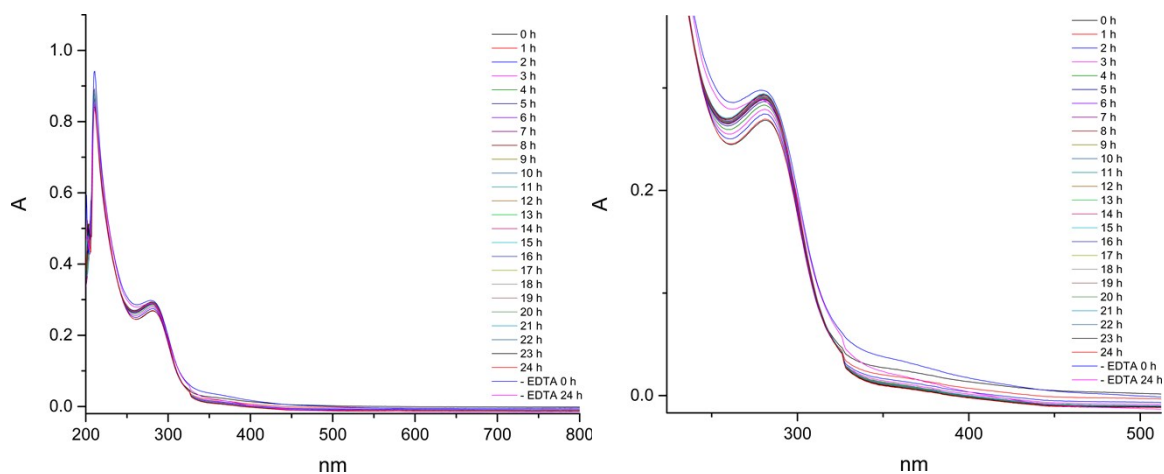


Figure S13. Time dependent UV-vis spectra of **6e** treated with EDTA in seawater (left – whole spectra, right – enlarged area, pH: seawater = 8.15, seawater + **6e** = 8.01, distilled water + **6e** + EDTA = 7.75). Used concentration of **6e** and EDTA was 25 nM. The time dependent measurement was carried out at 25 °C.

Crystallographic parameters and X-ray structures

Experimental parameters and CCDC Codes of the X-ray diffraction measurements are listed in Table S1–S13. Distortion parameters for all diffraction measurements are listed in Table S14.

Sample	Machine	Source	Temp.	Detector Distance	Time/Frame	#Frames	Frame width	CCDC
	Bruker		[K]	[mm]	[s]		[°]	
6a	D8	Mo	100 (2)	35	60	741	0.4	1436734
6b	D8	Mo	100 (2)	40	96	2442	0.4	1436733
6d	D8	Mo	100 (2)	35	48	1426	0.4	1436732
6e	D8	Mo	100 (2)	40	48	334	0.4	1436731
6g	D8	Mo	100 (2)	35	96	600	0.4	1436730
6j	D8	Mo	100 (2)	34	24	2665	0.4	1436729

Table S1. Experimental parameters and CCDC-Codes.

1. 6a.

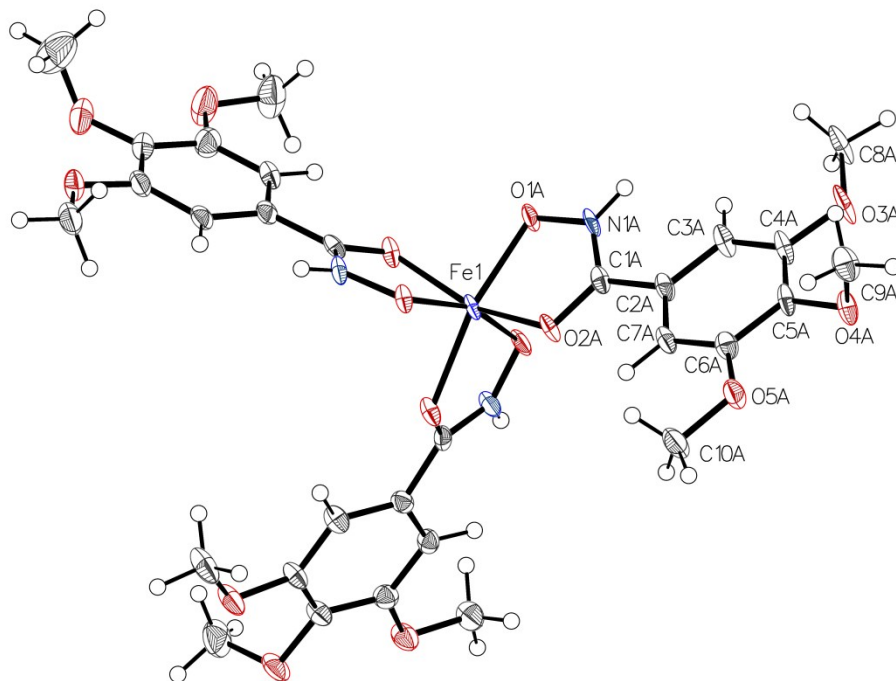


Figure S14. Asymmetric Unit of **6a**, drawn with 50% displacement ellipsoids. Co-crystallized water and disorder omitted for clarity. The target molecule could be determined in good quality but apart from some possible to refine located (still generating non confidentially short interactions) water positions, it was not possible to install satisfying solvent models for still available volume. The help of solvent mask ("squeeze") was required to finalize the crystallographic data. Two voids (each 51.8 Å³, 3.6 respectively 3.5 e⁻) were excluded from the original hkl-file.

Chemical formula	C30H44FeN3O19	Crystal system	triclinic	
Formula weight [g/mol]	806.53	Space group	<i>P</i> -1	
Temperature [K]	100	Z	2	
Measurement method	$\backslash\Phi$ and $\backslash\omega$ scans	Volume [Å³]	1874.03(18)	
Radiation (Wavelength [Å])	MoK α (λ = 0.71073)	Unit cell dimensions [Å] and [°]	12.0485(7)	69.9928(19)
Crystal size [mm³]	0.124 × 0.069 × 0.009		13.2910(7)	78.6474(19)
Crystal habit	clear brown plate		13.4446(7)	68.339(2)
Density (calculated) [g/cm³]	1.429	Absorption coefficient [mm⁻¹]	0.484	
Abs. correction Tmin	0.906	Abs. correction Tmax	1	
Abs. correction type	multi-scan	F(000) [e⁻]	846	

Table S2. Sample and crystal data of **6a**.

Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16	Theta range for data collection [°]	4.678 to 50.7	
Reflections number	18793	Data / restraints / parameters	6846/7/499	
Refinement method	Least squares	Final R indices	all data	R1 = 0.0896, wR2 = 0.1622
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$		I>2σ(I)	R1 = 0.0600, wR2 = 0.1507
Goodness-of-fit on F²	1.042	Weighting scheme	w=1/[σ ² (F _o ²)+(0.0838P) ² +2.2433P]	
Largest diff. peak and hole [e Å⁻³]	1.32/-0.67		where P=(F _o ² +2F _c ²)/3	

Table S3. Data collection and structure refinement of **6a**.

2. 6b.

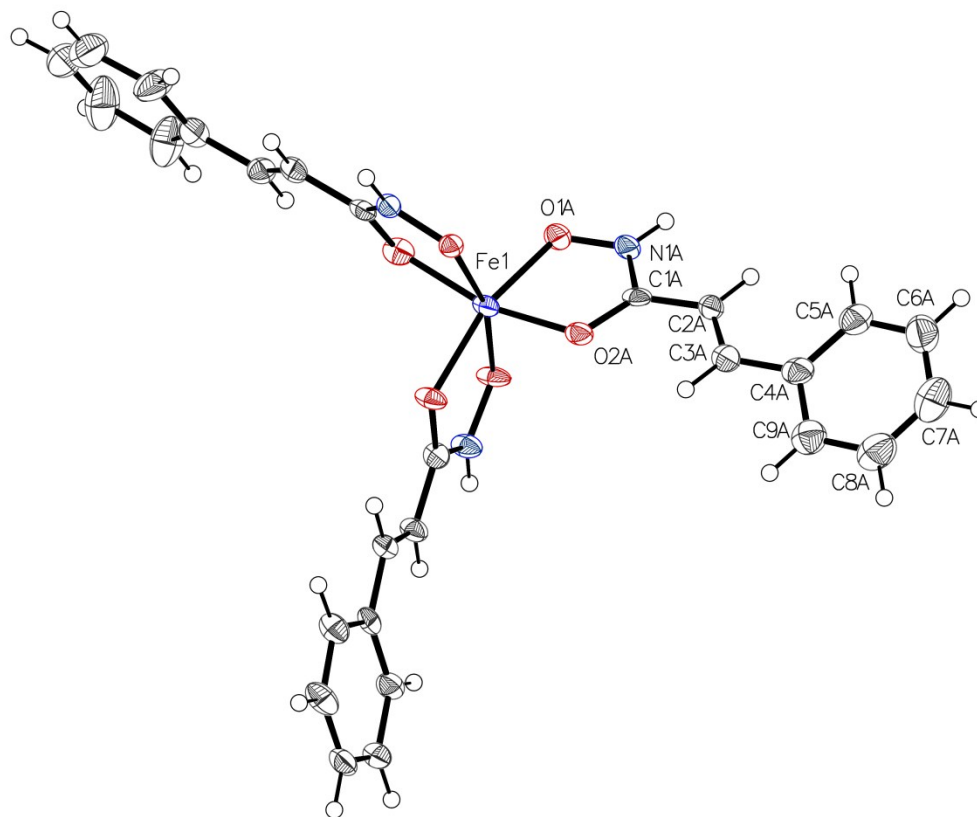


Figure S15. Asymmetric Unit of **6b**, drawn with 50% displacement ellipsoids. Co-crystallized ethanol, water and disorder omitted for clarity. The percentage of main residue disorder is 22% (solvent disorder 100%).

Chemical formula	C ₂₈ H ₃₀ .2FeN ₃ O ₇ .3	Crystal system	monoclinic	
Formula weight [g/mol]	591.01	Space group	<i>P</i> 2 ₁ / <i>c</i>	
Temperature [K]	100	Z	4	
Measurement method	\Φ and \ω scans	Volume [Å³]	3211.5(5)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	Unit cell dimensions [Å] and [°]	16.0853(15)	90
Crystal size [mm³]	0.22 × 0.2 × 0.01		28.696(3)	96.758(3)
Crystal habit	clear red plate		7.0062(6)	90
Density (calculated) [g/cm³]	1.222	Absorption coefficient [mm⁻¹]	0.515	
Abs. correction Tmin	0.6763	Abs. correction Tmax	0.7452	
Abs. correction type	multi-scan	F(000) [e⁻]	1234	

Table S4. Sample and crystal data of **6b**.

Index ranges	$-19 \leq h \leq 19, -34 \leq k \leq 34, -8 \leq l \leq 8$	Theta range for data collection [°]	3.816 to 50.698	
Reflections number	72071	Data / restraints / parameters	5869/6/414	
Refinement method	Least squares	Final R indices	all data	R1 = 0.1101 wR2 = 0.1899
Function minimized	$\sum w(F_o^2 - F_c^2)^2$		$I > 2\sigma(I)$	R1 = 0.0729 wR2 = 0.1747
Goodness-of-fit on F^2	1.105	Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0855P)^2 + 6.6742P]$	
Largest diff. peak and hole [$e \text{ \AA}^{-3}$]	0.1/-0.66		where $P = (F_o^2 + 2F_c^2)/3$	

Table S5. Data collection and structure refinement of **6b**.

3. 6d.

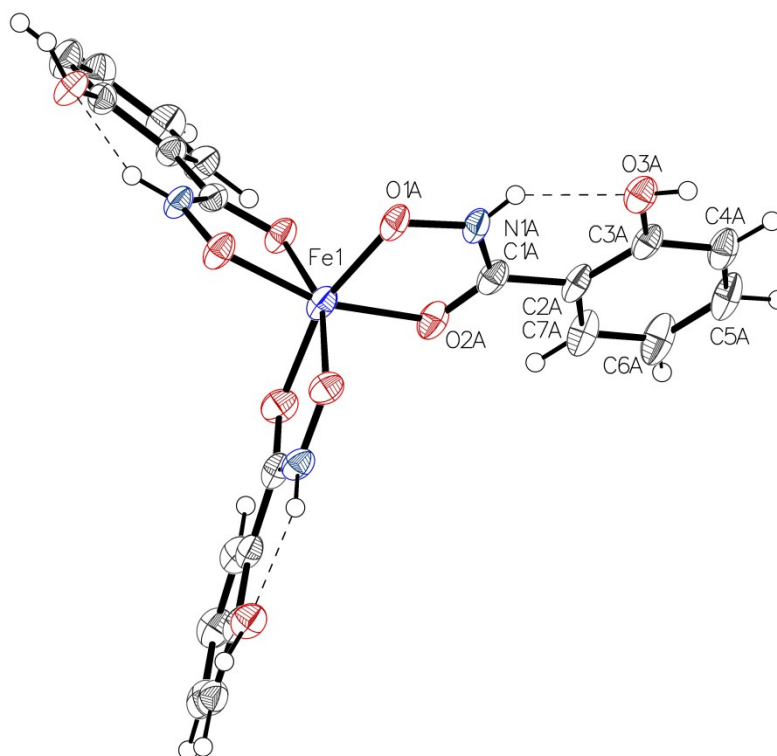


Figure S16. Asymmetric Unit of **6d**, drawn with 50% displacement ellipsoids. Co-crystallized acetone omitted for clarity. The acetone occupancy is refined with 0.5. The solvent model is fixed with restraints and influences the quality of the refinement as visible in the weighting scheme. Three moderate intramolecular hydrogen bonds, following the classification of Jeffreyⁱⁱ, N1A-H...O3A (2.677(6) Å and 128.9°), N1B-H...O3B (2.643(6) Å and 130.8°), N1C-H...O3C (2.648(5) Å and 129.5°) could be tagged.

Chemical formula	C _{25.5} H ₂₇ FeN ₃ O _{10.5}	Crystal system	monoclinic	
Formula weight [g/mol]	599.35	Space group	C2/c	
Temperature [K]	100	Z	8	
Measurement method	$\backslash\Phi$ and $\backslash\omega$ scans	Volume [Å³]	6720.1(6)	
Radiation (Wavelength [Å])	MoK α ($\lambda = 0.71073$)	Unit cell dimensions [Å] and [°]	23.1974(8)	90
Crystal size / [mm³]	0.146 × 0.114 × 0.043		13.7678(8)	109.575(3)
Crystal habit	clear red block		22.3320(11)	90
Density (calculated) / [g/cm³]	1.185	Absorption coefficient / [mm⁻¹]	0.5	
Abs. correction Tmin	0.675	Abs. correction Tmax	0.746	
Abs. correction type	multi-scan	F(000) [e⁻]	2488	

Table S6. Sample and crystal data of **6d**.

Index ranges	$-27 \leq h \leq 27, -16 \leq k \leq 16, -26 \leq l \leq 26$	Theta range for data collection [°]	3.682 to 50.696	
Reflections number	53729	Data / restraints / parameters	6162/21/364	
Refinement method	Least squares	Final R indices	all data	R1 = 0.1097, wR2 = 0.2701
Function minimized	$\sum w(F_o^2 - F_c^2)^2$		I>2 σ (I)	R1 = 0.0898, wR2 = 0.2531
Goodness-of-fit on F²	1.084	Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1382P)^2+60.2699P]$	
Largest diff. peak and hole [e Å⁻³]	1.42/-1.20		where $P=(F_o^2+2F_c^2)/3$	

Table S7. Data collection and structure refinement of **6d**.

4. 6e.

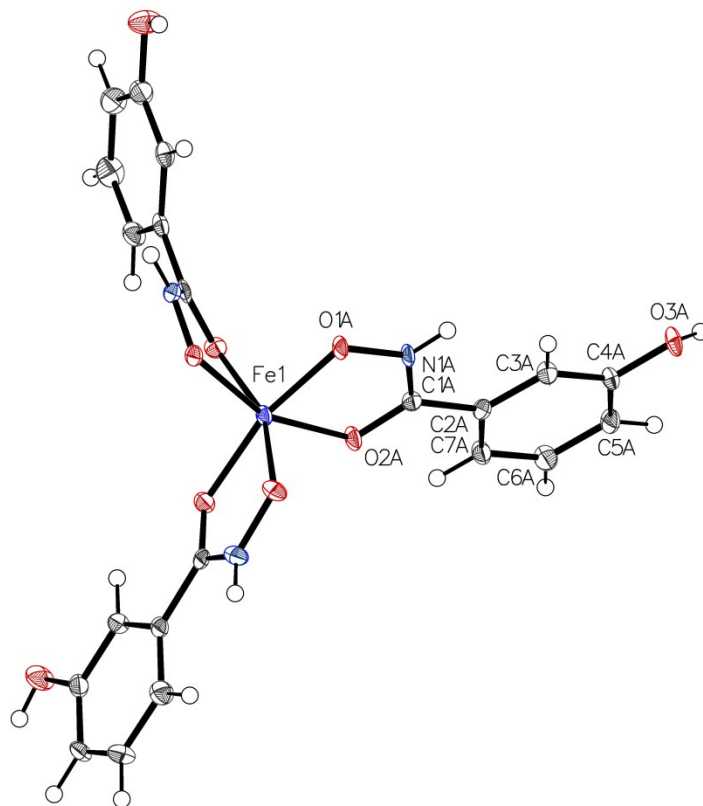


Figure S17. Asymmetric Unit of 6e, drawn with 50% displacement ellipsoids. Co-crystallized acetone omitted for clarity. The assembly of strongest Q-peaks and the presence of one solvent accessible void (38 Å³) is a matter of conjecture for small amounts of disordered methanol and water instead of one acetone. In this context the not satisfying low value of second weighting scheme parameter should be mentioned.

Chemical formula	C ₂₇ H ₃₀ FeN ₃ O ₁₁	Crystal system	orthorhombic	
Formula weight [g/mol]	628.39	Space group	<i>Pbca</i>	
Temperature [K]	100	Z	8	
Measurement method	\Φ and \ω scans	Volume [Å³]	6032.9(4)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	Unit cell dimensions [Å] and [°]	11.1864(4)	90
Crystal size [mm³]	0.29 × 0.08 × 0.026		21.2415(7)	90
Crystal habit	clear red block		25.3894(9)	90
Density (calculated) [g/cm³]	1.384	Absorption coefficient [mm⁻¹]	0.562	
Abs. correction Tmin	0.5959	Abs. correction Tmax	0.7460	
Abs. correction type	multi-scan	F(000) [e⁻]	2616	

Table S8. Sample and crystal data of 6e.

Index ranges	$-12 \leq h \leq 13, -25 \leq k \leq 25, -30 \leq l \leq 28$	Theta range for data collection [°]	3.208 to 50.698	
Reflections number	21591	Data / restraints / parameters	5496/0/386	
Refinement method	Least squares	Final R indices	all data	R1 = 0.0642 wR2 = 0.1162
Function minimized	$\sum w(F_o^2 - F_c^2)^2$		$I > 2\sigma(I)$	R1 = 0.0480 wR2 = 0.1104
Goodness-of-fit on F^2	1.074	Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 9.9934P]$	
Largest diff. peak and hole [$e \text{ \AA}^{-3}$]	0.73/-0.40		where $P = (F_o^2 + 2F_c^2)/3$	

Table S9. Data collection and structure refinement of **6e**.

6g.

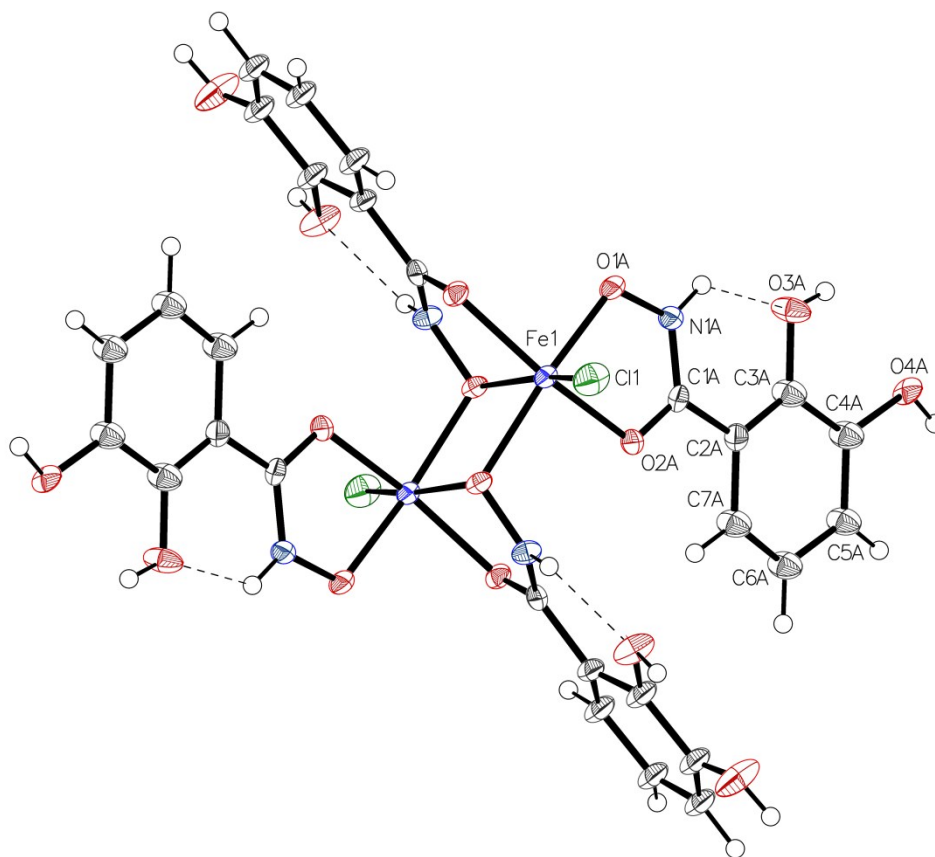


Figure S18. Molecular structure of **6g**, drawn with 50% displacement ellipsoids. Co-crystallized methanol, diethyl ether and disorder omitted for clarity. The percentage of main residue disorder is 42% (solvent disorder 100%). Two intramolecular hydrogen bonds (N1A-H...O3A, N1B-H...O3B, values because of disorder not listed, but geometric properties tag them as moderate following the classification of Jeffrey¹ in the asymmetric unit are co-responsible to the molecular structure.

Chemical formula	C38H52Cl2Fe2N4O20	Crystal system	monoclinic	
Formula weight [g/mol]	1067.43	Space group	$P2_1/c$	
Temperature [K]	100	Z	2	
Measurement method	$\backslash\Phi$ and $\backslash\omega$ scans	Volume [Å³]	2417.2(2)	
Radiation (Wavelength [Å])	MoK α ($\lambda = 0.71073$)	Unit cell dimensions [Å] and [°]	12.4686(6)	90
Crystal size [mm³]	0.08 × 0.06 × 0.06		11.1309(5)	94.456(3)
Crystal habit	clear orange block		17.4694(10)	90
Density (calculated) [g/cm³]	1.467	Absorption coefficient [mm⁻¹]	0.789	
Abs. correction Tmin	0.6382	Abs. correction Tmax	0.7452	
Abs. correction type	multi-scan	F(000) [e⁻]	1108	

Table S10. Sample and crystal data of **6g**.

Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 13, -19 ≤ l ≤ 21	Theta range for data collection [°]	4.342 to 50.7	
Reflections number	10928	Data / restraints / parameters	4359/29/313	
Refinement method	Least squares	Final R indices	all data	R1 = 0.0802 wR2 = 0.1202
Function minimized	$\sum w(F_o^2 - F_c^2)^2$		$I > 2\sigma(I)$	R1 = 0.0498 wR2 = 0.1086
Goodness-of-fit on F²	1.057	Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0419 P)^2 + 3.5548P]$	
Largest diff. peak and hole [e Å⁻³]	0.53/-0.54		where $P = (F_o^2 + 2F_c^2)/3$	

Table S11. Data collection and structure refinement of **6g**.

5. 6j.

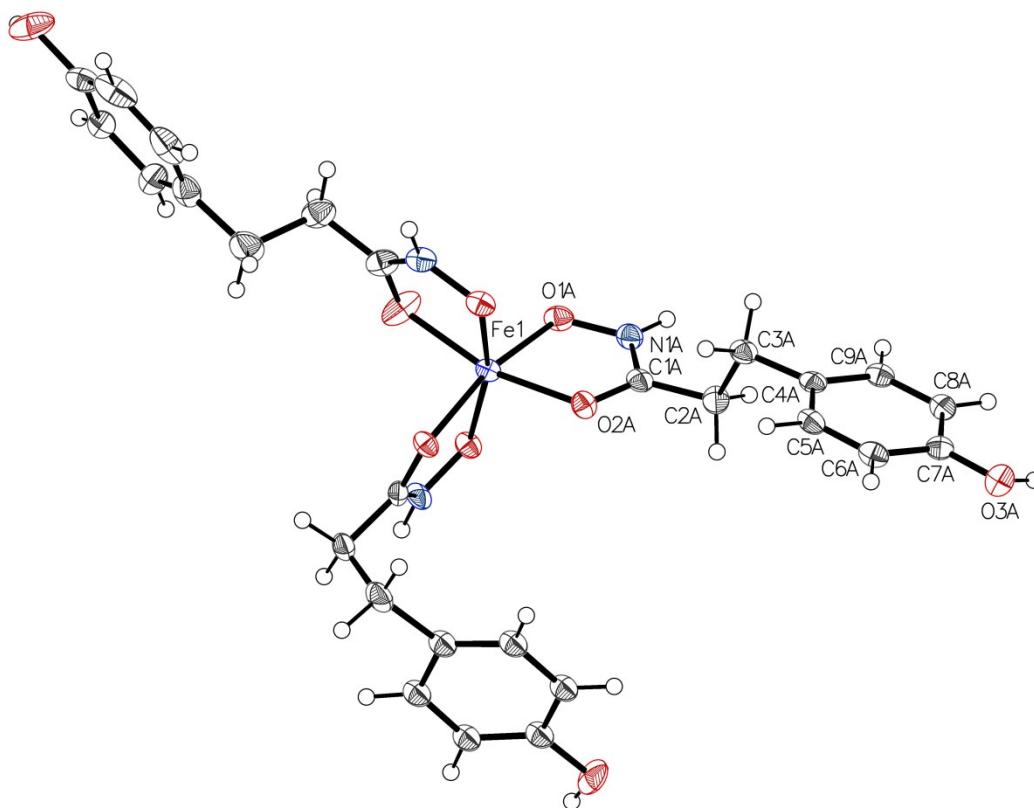


Figure S19. Asymmetric Unit of **6j**, drawn with 50% displacement ellipsoids. Co-crystallized water and disorder omitted for clarity. The percentage of main residue disorder is 18% (solvent disorder 50%).

Chemical formula	C ₂₇ H ₃₄ FeN ₃ O ₁₁	Crystal system	monoclinic	
Formula weight [g/mol]	632.42	Space group	<i>P</i> 2 ₁ / <i>n</i>	
Temperature [K]	100	Z	4	
Measurement method	\Φ and \ω scans	Volume [Å³]	2870.8(2)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	Unit cell dimensions [Å] and [°]	15.9200(7)	90
Crystal size [mm³]	0.265 × 0.168 × 0.085		11.6967(5)	104.5149(15)
Crystal habit	clear red block		15.9254(6)	90
Density (calculated) [g/cm³]	1.463	Absorption coefficient [mm⁻¹]	0.59	
Abs. correction Tmin	0.6983	Abs. correction Tmax	0.7460	
Abs. correction type	multi-scan	F(000) [e⁻]	1324	

Table S12. Sample and crystal data of **6j**.

Index ranges	$-19 \leq h \leq 19, -14 \leq k \leq 14, -19 \leq l \leq 19$	Theta range for data collection [°]	4.18 to 50.692	
Reflections number	100539	Data / restraints / parameters	5251/9/402	
Refinement method	Least squares	Final R indices	all data	R1 = 0.0462 wR2 = 0.1097
Function minimized	$\sum w(F_o^2 - F_c^2)^2$		$I > 2\sigma(I)$	R1 = 0.0446 wR2 = 0.1087
Goodness-of-fit on F^2	1.183	Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 5.2426P]$	
Largest diff. peak and hole [e Å ⁻³]	0.68/-0.34		where $P = (F_o^2 + 2F_c^2)/3$	

Table S13. Data collection and structure refinement of 6j.

6. Determination of Distortion in Coordination Polyhedra following K. Robinson⁺²

Sample	Geometry	Volume	Quadratic Elongation	Angle Variance
		[Å ³]		[° ²]
6a	Octahedral meridional	10.450	1.030	103.72
6b	Octahedral meridional	10.594	1.018	61.39
6d	Octahedral facial	10.461	1.025	85.2
6e	Octahedral facial	10.460	1.027	93.16
6g	Octahedral	11.284	1.030	87.01
6j	Octahedral meridional	10.588	1.020	68.89

Table S14.

Composition of enriched seawater medium for algae experiments

Full medium ³	Medium -Fe	Medium -EDTA	Medium + model compounds
200 mL of filtered artificial seawater ⁴	200 mL of filtered artificial seawater	200 mL of filtered artificial seawater	200 mL of filtered artificial seawater
0.2 mL of micronutrient solution ³	0.2 mL of micronutrient solution	0.2 mL of micronutrient solution	0.2 mL of micronutrient solution
0.2 mL of vitamin solution ³	0.2 mL of vitamin solution	0.2 mL of vitamin solution	0.2 mL of vitamin solution
0.2 mL of 0.88 M NaNO ₃	0.2 mL of 0.88 M NaNO ₃	0.2 mL of 0.88 M NaNO ₃	0.2 mL of 0.88 M NaNO ₃
0.2 mL of 0.1 M Na ₂ SiO ₃ ·9H ₂ O	0.2 mL of 0.1 M Na ₂ SiO ₃ ·9H ₂ O	0.2 mL of 0.1 M Na ₂ SiO ₃ ·9H ₂ O	0.2 mL of 0.1 M Na ₂ SiO ₃ ·9H ₂ O
0.2 mL of 0.036 M NaH ₂ PO ₄ ·H ₂ O	0.2 mL of 0.036 M NaH ₂ PO ₄ ·H ₂ O	0.2 mL of 0.036 M NaH ₂ PO ₄ ·H ₂ O	0.2 mL of 0.036 M NaH ₂ PO ₄ ·H ₂ O
-	-	-	0.007 mM of model compound

Table S15.

Cyclic voltammograms

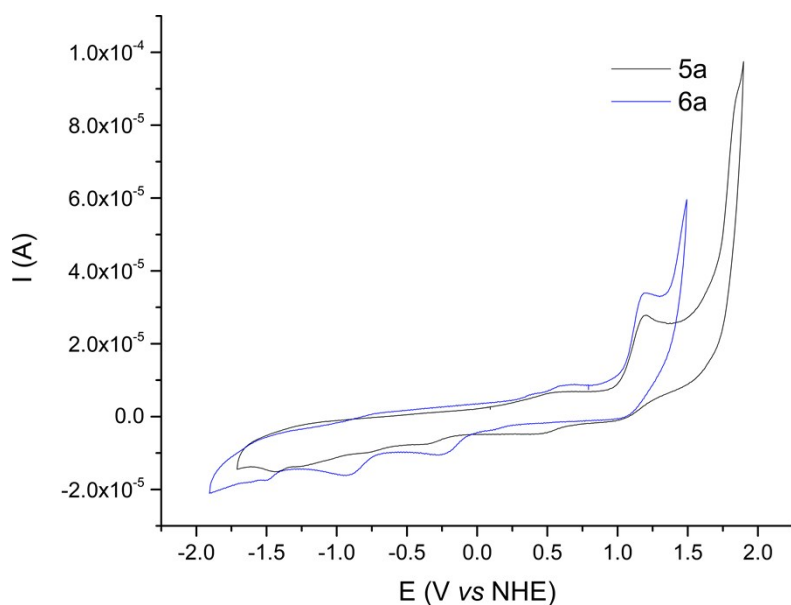


Figure S20. Cyclic voltammograms of complex **6a** and ligand **5a** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

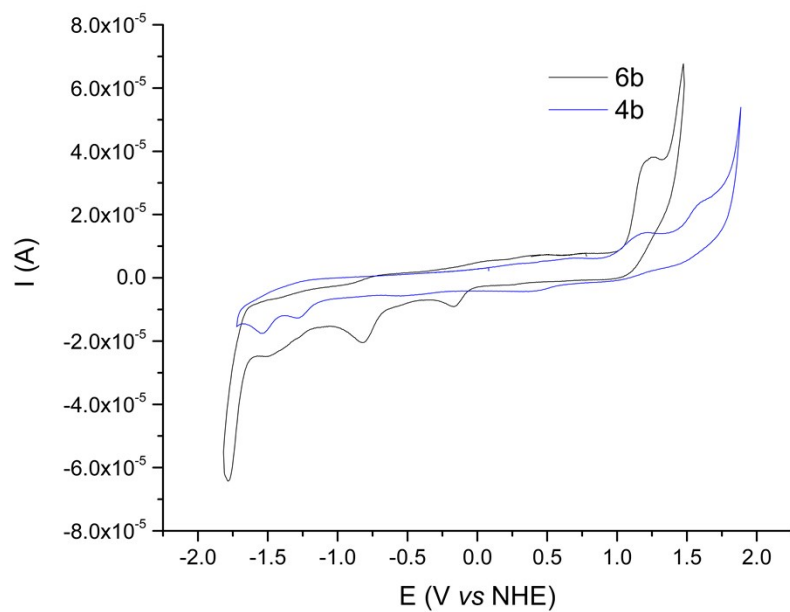


Figure S21. Cyclic voltammograms of complex **6b** and ligand **4b** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

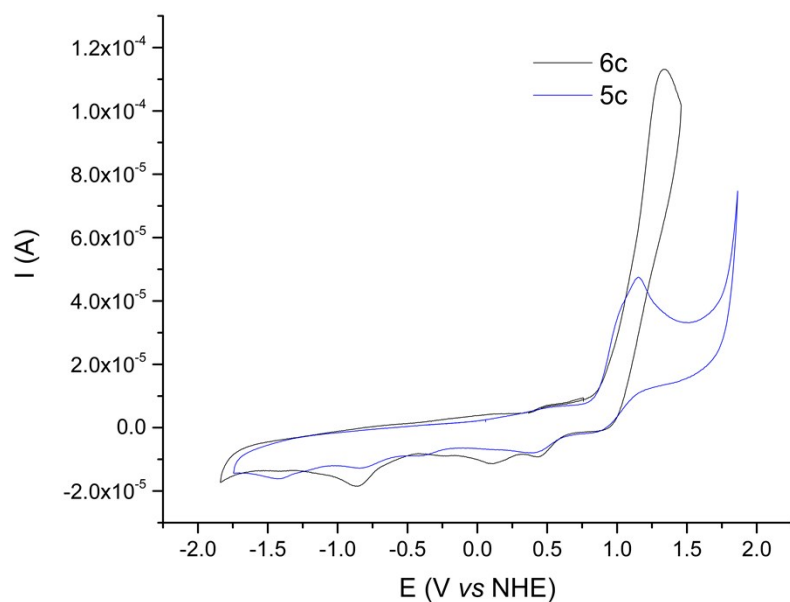


Figure S22. Cyclic voltammograms of complex **6c** and ligand **5c** in DMF solution containing 0.10 M [n-Bu₄N][BF₄] at a scan rate 0.20 V s⁻¹ using a glassy carbon working electrode.

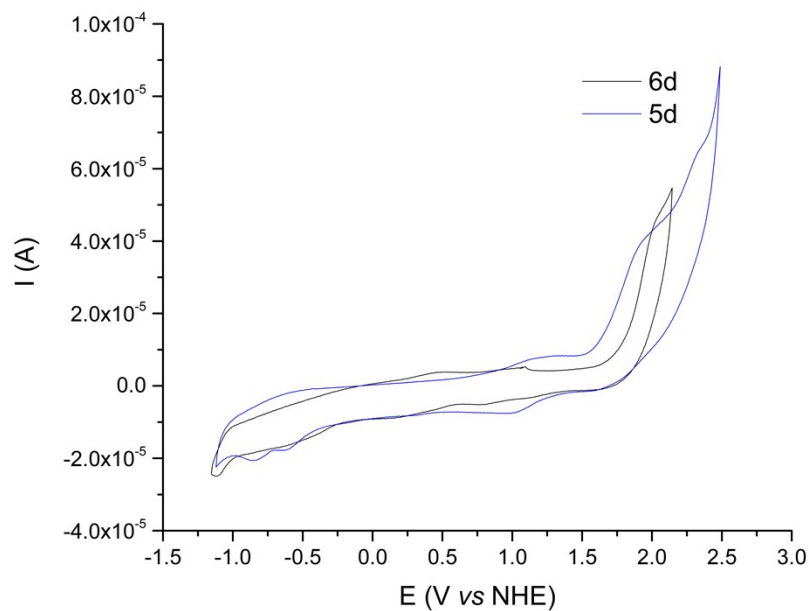


Figure S23. Cyclic voltammograms of complex **6d** and ligand **5d** in DMF solution containing 0.10 M [n-Bu₄N][BF₄] at a scan rate 0.20 V s⁻¹ using a glassy carbon working electrode.

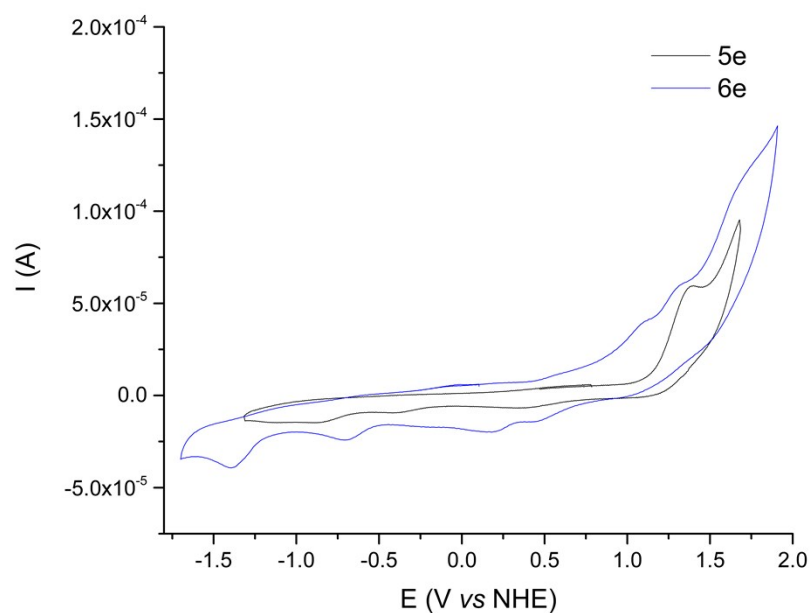


Figure S24. Cyclic voltammograms of complex **6e** and ligand **5e** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

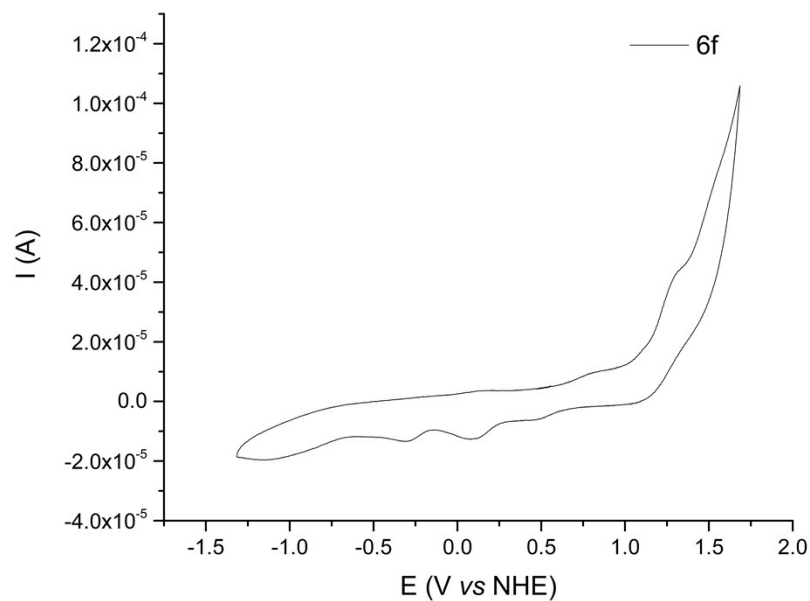


Figure S25. Cyclic voltammograms of complex **6f** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

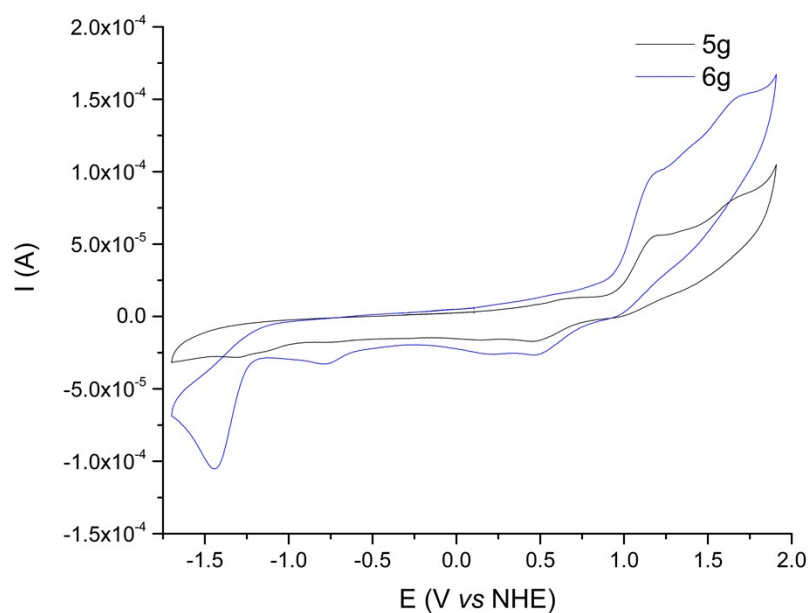


Figure S26. Cyclic voltammograms of complex **6g** and ligand **5g** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

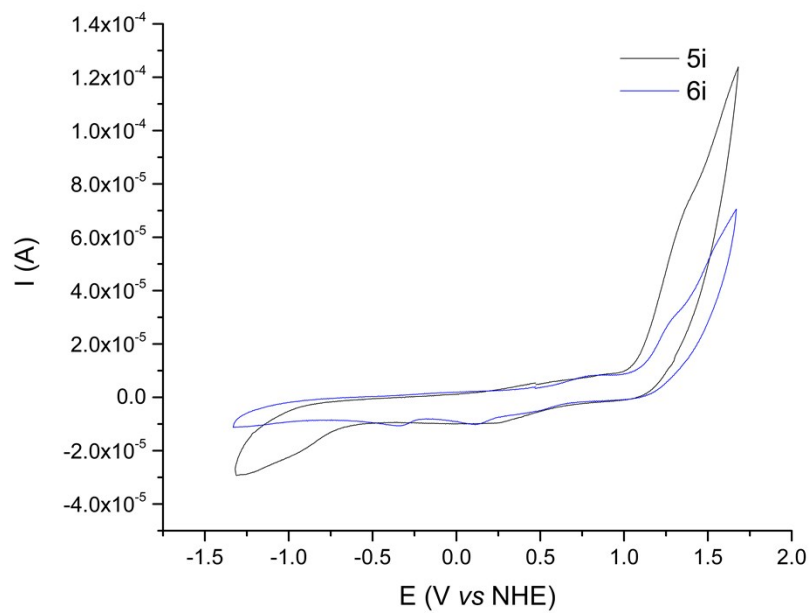


Figure S27. Cyclic voltammograms of complex **6h** and ligand **5h** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

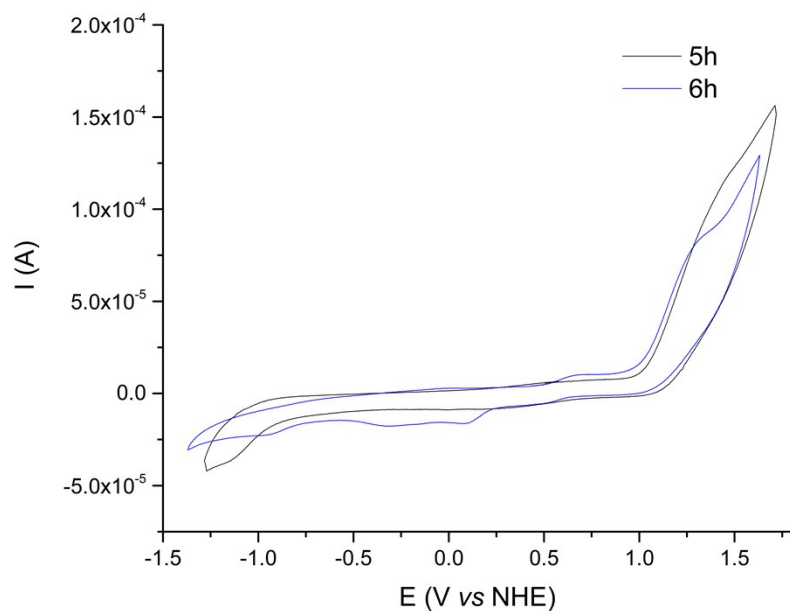


Figure S28. Cyclic voltammograms of complex **6i** and ligand **5i** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

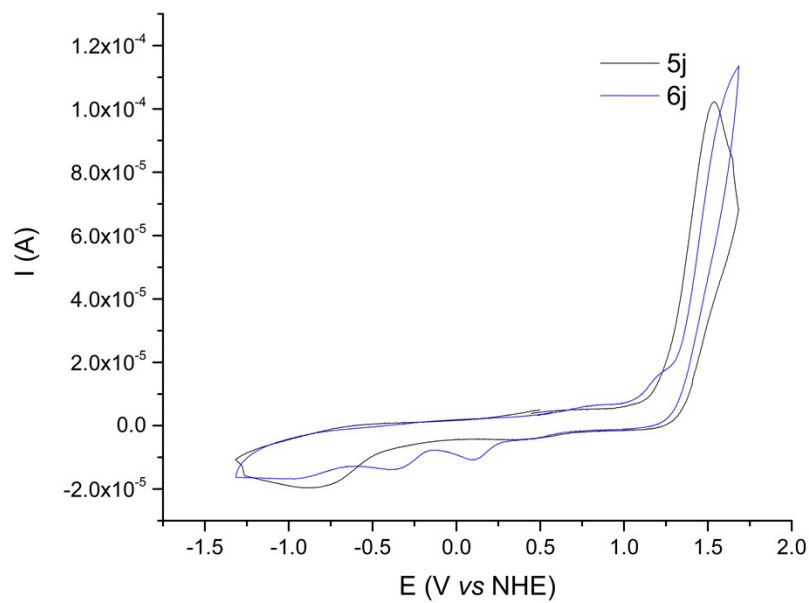


Figure S29. Cyclic voltammograms of complex **6j** and ligand **5j** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

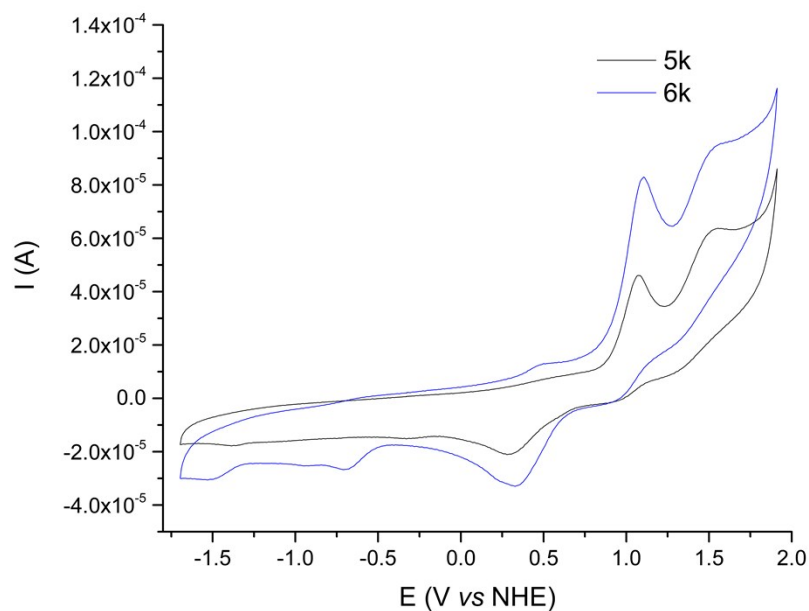


Figure S30. Cyclic voltammograms of complex **6k** and ligand **5k** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

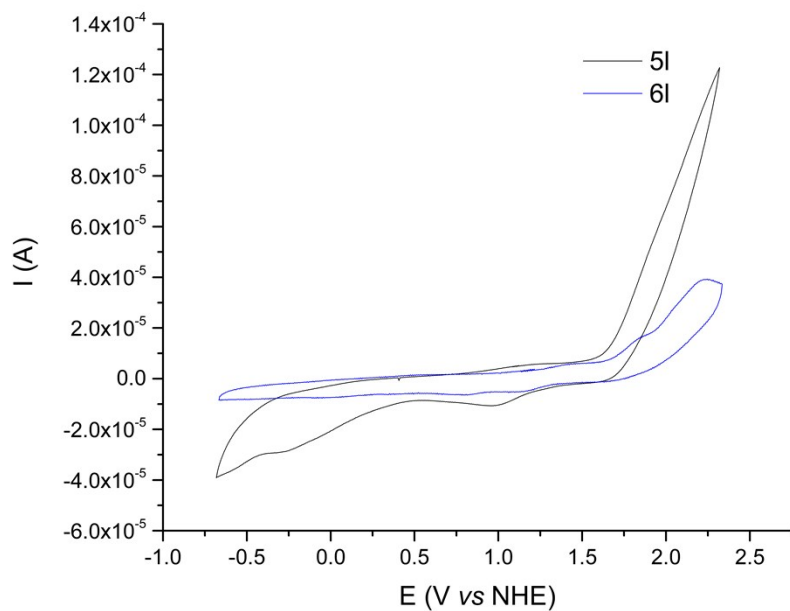


Figure S31. Cyclic voltammograms of complex **6l** and ligand **5l** in DMF solution containing 0.10 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at a scan rate 0.20 V s^{-1} using a glassy carbon working electrode.

1. G. A. Jeffrey, *Crystallography Reviews*, 2003, **9**, 135–176.
 2. Keith Robinson, G. V. Gibbs and P. H. Ribbe, *Science, New Series*, 1971, **172**, 567-570.
 3. R. R. Guillard and J. H. Ryther, *Can J Microbiol*, 1962, **8**, 229-&.
 4. D. R. Kester, I. W. Duedall, D. N. Connors and Pytkowic.Rm, *Limnol Oceanogr*, 1967, **12**, 176-&.
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