Electroactive Co(III) Salen Metal Complexes and the Electrophoretic Deposition of their Porous Organic Polymers onto Glassy Carbon

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Synthesis

The synthesis of tris(p-ethynylphenyl)amine (TPA) was carried out according to the literature procedure.1 The tetrakis(triphenylphosphine) palladium(0) catalyst [Pd(PPh3)4] was synthesised from palladium(II) chloride (Precious Metals Online) according to the literature procedure.2 The synthesis of the free base ligands 2, 2′-[(1R,2R)-1,2-Cyclohexanediylbis(nitrilomethylidine)]bis[4-bromo-phenol] (1), 3 2, 2′-[1,2-Phenylenediyl bis(nitrilomethylidine)]bis[4-bromo-phenol] (2), 4 and 2, 2′-[4,5-Dimethyl-1,2-phenylenediyl bis(nitrilomethylidine)]bis[4-bromo-phenol] (3) 5 have previously been reported and their synthetic methods were adapted.

Salen backbones

2, 2′-[(1R,2R)-1,2-Cyclohexanediylbis(nitrilomethylidine)]bis[4-bromo-phenol] (1).

5-Bromosalicylaldehyde (1.20 g, 6.00 mmol) was dissolved in degassed MeOH (10 mL). (1R,2R)-diaminocyclohexane (0.332 g, 3.00 mmol) was added, upon which the solution immediately turned bright yellow. The reaction was heated at 80 °C for 2 h. The bright yellow precipitate was separated from the mixture via centrifugation and the yellow solid was washed with cold MeOH (3 × 3 mL) and dried to yield a bright yellow powder (Yield: 1.13 g, 79%). M.P. 185–187 °C (lit.6 186–188 °C) 1H NMR (200 MHz, d6-DMSO) δ (ppm) 13.36 (s, 1H), 8.48 (s, 1H), 7.59 (d, J_H-H = 2.6 Hz, 1H), 7.41 (dd, J_H-H = 8.9 Hz, J_H-H = 2.6 Hz, 1H), 7.40–7.48 (m, 2H), 6.80 (d, J_H-H = 8.9 Hz, 1H), 3.39–3.45 (m, 1H), 1.35–1.98 (m, 2H). The characterisation data matched that reported in the literature.3

2, 2′-[1,2-Phenylenediyl bis(nitrilomethylidine)]bis[4-bromo-phenol] (2).

5-Bromosalicylaldehyde (0.600 g, 3.00 mmol) was dissolved in degassed MeOH (10 mL). o-Phenylenediamine (0.162 g, 1.50 mmol) was added, upon which the solution turned bright orange immediately. The reaction was heated at 80 °C for 2 h. The bright orange precipitate was separated from the reaction mixture via centrifugation and the solid was washed with cold ether (3 × 5 mL) and dried to yield a bright orange powder (Yield: 0.614 g, 87%). M.P. 216–217 °C (lit.7 216–218 °C) 1H NMR (400 MHz, d6-DMSO) δ (ppm) 12.90 (s, 1H), 8.91 (s, 1H), 7.59 (d, J_H-H = 2.6 Hz, 1H), 7.54 (dd, J_H-H = 8.8 Hz, J_H-H = 2.6 Hz, 1H), 7.40–7.48 (m, 2H), 6.94 (d, J_H-H = 8.8 Hz, 1H). The characterisation data matched that reported in the literature.4

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2, 2’-[4,5-Dimethyl-1,2-phenylenediy]bis(nitrilomethylidine)bis[4-bromo-phenol] (3).

5-Bromosalicylaldehyde (0.600 g, 3.00 mmol) was dissolved in degassed MeOH (10 mL). 4,5-Dimethyl-phenylenediamine (0.204 g, 1.50 mmol) was added to the solution, which turned bright orange immediately. The reaction was heated at 80 °C for 2 h. The precipitate that formed was separated from the reaction mixture via centrifugation and was washed with cold ether (3 × 5 mL) and dried to yield a bright orange powder (Yield: 0.741 g, ×98%). M.P. 241–243 °C (lit. 241–245 °C).

H NMR (400 MHz, d6-DMSO) δ (ppm) 8.91 (s, 1H), 7.87 (d, JH-H = 2.5 Hz, 1H), 7.52 (dd, JH-H = 8.8 Hz, JH-H = 2.5 Hz, 1H), 7.28 (m, 1H), 6.92 (d, JH-H = 8.8 Hz, 1H), 2.30 (s, 3H). The characterisation data matched that reported in the literature.

Co(III) salen metal complexes.

2, 2’-[1R,2R]-1,2-Cyclohexanediylbis(nitrilomethylidine)bis[4-bromo-phenol]Co(III) chloride (Co1).

EtOH (50 mL) was degassed with N2 for 20 minutes. Under N2, 1 (0.480 g, 1.00 mmol) was dissolved in EtOH and to this solution was added Co(OAc)2•4H2O (0.273 g, 1.10 mmol), upon which the solution turned brown. The solution was stirred at room temperature for 2 h, prior to the removal of N2 and the addition of LiCl (0.187 g, 4.41 mmol). The mixture was allowed to stir in air at room temperature for 2 d. The excess EtOH was removed in vacuo and the residue dissolved in DCM (150 mL) and washed with H2O (3 × 50 mL). The organic layer was collected, dried over Na2SO4 and evaporated to yield the product as a dark brown powder (Yield: 0.544 g, 95%). M.P. 297–299 °C.

ATR-IR (cm−1) νC=N = 1638 UV-Vis-NIR λ(KBr, cm−1) 12435, 17886 (sh), 25002, 30029, 34708 MS (ESI+, DMF/MeOH) m/z calculated for C20H18Br2CoN2O2[M-Cl]+: 537.12, found: 536.93 Elemental Analysis calculated for C20H18Br2ClCoN2O2: C 42.0, H 3.2, N 4.9%, found C 41.6, H 3.2, N 4.8%.

2, 2’-[1,2-Phenylenediyl bis(nitrilomethylidine)bis[4-bromo-phenol]Co(III) chloride (Co2).

EtOH (50 mL) was degassed with N2 for 20 min. Under an atmosphere of N2, 2 (0.348 g, 0.735 mmol) was dissolved in EtOH and Co(OAc)2•4H2O (0.202 g, 0.810 mmol) was added to this solution, upon which the solution turned brown. The solution was stirred at room temperature for 2 h, prior to the removal of N2 and the addition of LiCl (0.136 g, 3.21 mmol). The mixture was allowed to stir in air at room temperature for 2 d. The excess EtOH was removed and the residue washed with H2O (30 mL), EtOH (30 mL) and diethyl ether (30 mL) to yield the product as a dark brown powder (Yield: 0.314 g, 76%). M.P. 330–333 °C.

ATR-IR (cm−1) νC=N = 1613 UV-Vis-NIR λ(KBr, cm−1) 12154 (sh), 16485 (sh), 20187, 21376, 30377 MS (ESI+, DMF/MeOH) m/z calculated for C20H12Br2CoN2O2 [M-Cl]+: 531.07, found: 530.93 Elemental Analysis calculated for C20H12Br2ClCoN2O2: C 42.0, H 3.2, N 4.9%, found C 41.6, H 3.2, N 4.8%.

2, 2’-[4,5-Dimethyl-1,2-phenylenediyl bis(nitrilomethylidine)bis[4-bromo-phenol] (Co3).

EtOH (20 mL) was degassed with N2 for 20 min. Under an atmosphere of N2, 3 (0.250 g, 0.500 mmol) was dissolved in EtOH and Co(OAc)2•4H2O (0.127 g, 0.510 mmol) was added to this solution, upon which the solution turned brown. The solution was stirred at room temperature for 2 h, prior to the removal of N2 and the addition of LiCl (0.086 g, 2.04 mmol). The mixture was allowed to stir in air at room temperature for 2 d. The excess EtOH was removed and the residue was washed with H2O (30 mL), EtOH (30 mL) and diethyl ether (30 mL) to yield the product as a dark brown powder (Yield: 0.256 g, 87%). M.P. > 350 °C ATR-IR (cm−1) νC=N = 1622 UV-Vis-NIR λ(KBr, cm−1) 14948 (sh), 21928,
25426, 29681 MS (ESI+, DMF/MeOH) m/z calculated for C_{22}H_{16}Br_{2}CoN_{2}O_{2} [M-Cl]^+: 558.89, found: 558.80

**Elemental Analysis** calculated for C_{20}H_{16}Br_{2}ClCoN_{2}O_{2}: C 44.4, H 2.7, N 4.7%, found C 44.7, H 3.0, N 4.8%.

**POPs containing Co(III) salen complexes.**

**General procedure for the synthesis of POPs.**

A solution of toluene/EtOH (2:1) was degassed with N\(_2\) for 20 min. The *bis*-bromo salen metal complex, TPA, [Pd(PPh\(_3\))\(_4\)] were suspended in the degassed solution and stirred away from light for 15 min. CuI was added and the reaction heated at 85 °C for 72 h. The solid was collected by filtration, washed with DMF (100 mL), toluene (100 mL), MeOH (100 mL) and extracted *via* a Soxhlet washing procedure with MeOH for 48 h. The fluffy brown solid was dried under vacuum overnight.

**POPCo1.**

Co\(_1\) (0.115 g, 0.202 mmol), TPA (0.255 g, 0.804 mmol), [Pd(PPh\(_3\))\(_4\)] (0.080 g, 0.069 mmol) and CuI (0.040 g, 0.210 mmol) were all combined in solution (15 mL) and reacted according to the general procedure to afford the polymer (Yield: 0.312 g) M.P. > 350 °C ATR-IR (cm\(^{-1}\)) \(\nu_{C≡C} = 2192, \nu_{C=N} = 1595\) UV-Vis-NIR \(\lambda(KBr, cm^{-1})\) 16050, 22280, 30520 **Elemental Analysis** Found: C 73.8, H 4.6, N 4.3%.

**POPCo2.**

Co\(_2\) (0.113 g, 0.200 mmol), TPA (0.255 g, 0.804 mmol), [Pd(PPh\(_3\))\(_4\)] (0.080 g, 0.069 mmol) and CuI (0.040 g, 0.210 mmol) were all combined in solution (15 mL) and reacted according to the general procedure to afford the polymer (Yield: 0.209 g). M.P. > 350 °C ATR-IR (cm\(^{-1}\)) \(\nu_{C≡C} = 2195, \nu_{C=N} = 1592\) UV-Vis-NIR \(\lambda(KBr, cm^{-1})\) 16720, 22350, 31320 **Elemental Analysis** Found: C 70.7, H 4.3, N 4.6%.

**POPCo3.**

Co\(_3\) (0.120 g, 0.203 mmol), TPA (0.255 g, 0.804 mmol), [Pd(PPh\(_3\))\(_4\)] (0.080 g, 0.069 mmol) and CuI (0.040 g, 0.210 mmol) were all combined in solution (15 mL) and reacted according to the general procedure to afford the polymer (Yield: 0.290 g). M.P. > 350 °C ATR-IR (cm\(^{-1}\)) \(\nu_{C≡C} = 2203, \nu_{C=N} = 1595\) UV-Vis-NIR \(\lambda(KBr, cm^{-1})\) 15780, 20940, 30120, 34870 **Elemental Analysis** Found: C 75.6, H 4.4, N 4.3%.

**POPTPA.**

TPA (0.200 g, 0.630 mmol), [Pd(PPh\(_3\))\(_4\)] (0.080 g, 0.069 mmol) and CuI (0.040 g, 0.210 mmol) were combined in solution (15 mL) and reacted according to the general procedure to afford the polymer (Yield: 0.136 g). M.P. > 350 °C ATR-IR (cm\(^{-1}\)) \(\nu_{C≡C} = 2195, \) UV-Vis-NIR \(\lambda(KBr, cm^{-1})\) 21540, 32400 **Elemental Analysis** Found: C 71.0, H 4.0, N 3.6%. 


Calculations

If an electrochemical system obeys pseudo-first order kinetics (proof that the reaction is first order in the analyte and the concentration of CO₂, and that the concentration of CO₂ is large in comparison to that of the analyte), it is possible to calculate kinetic data for the interaction of salen complexes with CO₂. Upon comparison of the peak currents for salen complexes in the presence of CO₂ with the absence of CO₂, an expression for \( k_{\text{cat}}[Q] \), or TOF, in terms of the \( \frac{i_{\text{cat}}}{i_p} \) ratio, which can be directly examined from CV.

\[
k_{Q} = \frac{F \nu n_p}{RT} \left[ \frac{0.4463}{n_{\text{cat}}} \right]^2 \left[ \frac{i_{\text{cat}}}{i_p} \right]^2
\]  

where \( F = \) Faraday constant (C mol\(^{-1}\)), \( \nu = \) scan rate (V s\(^{-1}\)), \( n_p = \) number of electrons facilitated by the redox process, \( R = \) universal gas constant (J mol\(^{-1}\) K\(^{-1}\)), \( T = \) temperature (K), \( n_{\text{cat}} = \) number of electrons facilitated in the catalytic transformation, \( i_{\text{cat}} = \) peak catalytic current (mA/cm\(^2\)), \( i_p = \) peak current under N\(_2\) (mA/cm\(^2\)).

Low pressure CO₂ measurements (up to 1 bar) were carried out at three temperatures (typically 288, 298 and 308 K) on the ASAP2020 or 3-Flex as described above. The data were modelled using a virial equation or the interpolation function before applying the Clausius-Clapeyron relation. The heat of adsorption for CO₂ was determined by comparing CO₂ isotherms at 288, 298 and 308 K. Isosteric heat of adsorption calculations \((Q_{st})\) for CO₂ at these temperatures were undertaken using the Clausius-Clapeyron equation

\[
(\ln P)_n = -\left(\frac{Q_{st}}{R} \frac{1}{T}\right) + C
\]

where \( P = \) pressure (mbar), \( n = \) amount of gas adsorbed (mol/mol), \( T = \) temperature (K), \( R = \) universal gas constant (J mol\(^{-1}\) K\(^{-1}\)) and \( C = \) constant.

The selectivity \((S)\) for adsorption of CO₂ over N\(_2\) was estimated from the single-component N\(_2\) and CO₂ room temperature isotherm data. The values for this approximation are derived from an approximate flue gas composition of 15% CO₂, 75% N\(_2\) and 10% other gases, at a total pressure of 1 bar.

\[
S = \frac{q_{\text{CO}_2}}{q_{N_2}} \frac{p_{\text{CO}_2}}{p_{N_2}}
\]

where \( q = \) quantity of gas adsorbed (mmol g\(^{-1}\)), \( p = \) partial pressure at which each gas is adsorbed).
Figure S1: TGA of POPCo1 (black), POPCo2 (red) and POPCo3 (blue) taken from 25 to 650 °C. The temperature was ramped at 1 °C min⁻¹.

Figure S2: Solid State ATR-IR measurements of (i) Co1 (ii) Co2 (iii) Co3 (iv) POPCo1 (v) POPCo2 and (vi) POPCo3. * denotes the shift in the νC=N stretch from the discrete complexes to the POPs, while the νC≡C stretch appears in the polymers but not in the discrete complexes.
Figure S3: Solid State UV-Vis-NIR measurements of (i) Co1 (ii) Co2 (iii) Co3 (iv) POPCo1 (v) POPCo2 (vi) POPCo3. * denotes the shift in bands from the discrete complexes to the POPs, while the T denotes the band that appears from the TPA co-ligand.

Table S1: ICP-OES results for Co(III) salen polymers

| POP     | Suspected Co content (%) | Found (%) |
|---------|--------------------------|-----------|
| POPCo1  | 8.38                     | 6.31      |
| POPCo2  | 8.45                     | 6.65      |
| POPCo3  | 8.13                     | 5.83      |

Figure S4: $^{13}$C CPTOSS of Co2 (above) and POPCo2 (below). The full $^{13}$C NMR spectra are plotted in blue, while the spectra in red are the non-protonated or methyl carbon species detected after 40 μs of dipolar dephasing. Residual ethanol is denoted with a #, while residual triethylamine is noted with a *
Figure S5: $^{13}$C CPTOSS of $\text{Co}_3$ (above) and $\text{POPCo}_3$ (below) the aromatic salen POPs, as well as the POP made in the absence of salen metal complex. The full $^{13}$C NMR spectra are plotted in blue, while the spectra in red are the non-protonated or methyl carbon species detected after 40 $\mu$s of dipolar dephasing. Residual ethanol is denoted with a #, while residual triethylamine is noted with a *.

Figure S6: $^{13}$C CPTOSS of $\text{POPTPA}$. The full $^{13}$C NMR spectra are plotted in blue, while the spectra in red are the non-protonated or methyl carbon species detected after 40 $\mu$s of dipolar dephasing. Residual triethylamine is noted with a *.
Figure S7: DFT pore size distributions for POPCo1 (black), POPCo2 (red) and POPCo3 (blue).

Figure S8: Isosteric heats of adsorption for POPCo1 (black), POPCo2 (red) and POPCo3 (blue).
Figure S9: Solution state CV of A Co1 (1 mM), B Co2 (1 mM) and C Co3 (1 mM). (0.1 M [(n-C4H9)4N]PF6/DMF as the supporting electrolyte under N2, scan rate: 0.1 V s⁻¹, Fc (1 mM) was used as an internal standard).

Figure S10: Solid state CV of A POPCo1 upon progressively extending the potential window to Epc = −1.39 (black), −1.58 (red), −1.96 (blue), −2.17 (green), −2.36 V vs. Fe⁰/Fe⁺ (purple) B POPCo2 upon progressively extending the potential window to Epc = −1.42 (black), −1.62 (blue), −2.01 (green), −2.41 (magenta) and −2.58 V vs. Fe⁰/Fe⁺ (yellow) and C POPCo3 upon progressively extending the potential window to −1.36 (black), −2.35 (magenta) and −2.55 V vs. Fe⁰/Fe⁺ (yellow), b) under N2 (black), CO2 (red) and CO2 with TFE (0.14 mmol-blue, 0.28 mmol-green) (0.1 M LiBF4/MeCN as the supporting electrolyte, scan rate: 0.025 V s⁻¹, Fc (1 mM) was used as an internal standard).
Figure S11: Solution state UV-Vis-NIR SEC of A Co1 (0.61 mM) upon changing the potential from +0.1 to −0.2 V vs. Ag/Ag⁺ and B −1.0 to −1.5 V vs. Ag/Ag⁺. C Co2 (0.51 mM) upon changing the potential from 0.1 to −0.3 V vs. Ag/Ag⁺ and D −1.0 to −1.5 V vs. Ag/Ag⁺. E Co3 (0.32 mM) upon changing the potential from +0.1 to −0.4 V vs. Ag/Ag⁺ and F −0.8 to −1.4 V vs. Ag/Ag⁺. 0.1 M [(n-C₅H₉)₄N]PF₆/DMF as the supporting electrolyte.
Figure S12: Solid state Vis-NIR SEC of POPCo1 upon changing the potential from A +0.1 to −0.4 V vs. Ag/Ag⁺, B −0.8 to −1.4 V vs. Ag/Ag⁺ and C of POPCo2 upon changing the potential from −0.9 to −1.3 V vs. Ag/Ag⁺ (0.1 M [(n-C₄H₉)₄N]PF₆/MeCN as the supporting electrolyte. The insets show the polymers during the experiment.

Figure S13: Solution state CV showing the electrochemical response of A Co1 (1 mM) under saturation conditions of N₂ (black), CO₂ (red) and CO₂ with TFE (2.1 mmol) as a proton source (blue) B Co2 (1 mM) under saturation conditions of N₂ (black), CO₂ (red) and CO₂ with TFE (6.3 mmol) as a proton source (blue) C Co3 (1 mM) under saturation conditions of N₂ (black), CO₂ (red) and CO₂ with TFE (2.1 mmol) as a proton source (blue) (0.1 M [(n-C₄H₉)₄N]PF₆/DMF as the supporting electrolyte, scan rate: 0.1 V s⁻¹, Fc (1 mM) was used as an internal standard).
Figure S14: Plot of \( i_{\text{cat}} \) vs. \( [\text{CO}_2]^{0.5} \) for solution state CV of \( \text{Co}_2 \) (1 mM) under \( \text{CO}_2 \), demonstrating a first order kinetic relation in \( [\text{CO}_2] \). B \( i_{\text{cat}} \) vs. \([\text{TFE}]\) for solution state CV of \( \text{Co}_2 \) (1 mM) under \( \text{CO}_2 \) saturation, demonstrating a second order kinetics relation in \( [\text{TFE}] \) and C \( i_{\text{cat}} \) vs. \([\text{Co}_2]\) for solution state CV of \( \text{Co}_2 \) under \( \text{CO}_2 \) saturation, demonstrating a first order kinetic relation in \([\text{Co}_2]\).

Figure S15: Plot of \( i_{\text{cat}} \) vs. \( [\text{CO}_2]^{0.5} \) for solution state CV of \( \text{Co}_3 \) (1 mM) under \( \text{CO}_2 \), demonstrating a first order kinetic relation in \( [\text{CO}_2] \). B \( i_{\text{cat}} \) vs. \([\text{TFE}]\) for solution state CV of \( \text{Co}_3 \) (1 mM) under \( \text{CO}_2 \) saturation, demonstrating a second order kinetics relation in \( [\text{TFE}] \) and C \( i_{\text{cat}} \) vs. \([\text{Co}_2]\) for solution state CV of \( \text{Co}_2 \) under \( \text{CO}_2 \) saturation, demonstrating a first order kinetic relation in \([\text{Co}_2]\).
Figure S16: Production of H₂ (black) and CO (red) from CO₂ by A Co₂ (3.60 mM) with TFE (0.63 M) and B Co₃ (1.11 mM) and (0.14 M) during CPE (0.1 M [(n-C₄H₉)₄N]PF₆/DMF/MeCN(8:2) with TFE (0.63 M) as the supporting electrolyte under CO₂, E_{pc} = −1.85 V vs. Ag/Ag⁺.

Figure S17: ¹H NMR of the Co₂ bulk electrolysis solution after work up from CPE in D₂O at 300 MHz under CO₂ saturation after 30 min (black), 60 min (red), 90 min (blue), 120 min (cyan) and in the absence of CO₂ after 120 min (orange). The peak at δ = 8.00 ppm corresponds to the generation of formic acid. Spectra were referenced to D₂O. E_{pc} = −1.85 V vs. Ag/Ag⁺.
Figure S18: Solid state CV of A POPCo1 B POPCo2 and C POPCo3 under N\textsubscript{2} (black) and under CO\textsubscript{2} (red) with TFE (0.14 mmol-blue, 0.28 mmol-green) (0.1 M LiBF\textsubscript{4}/MeCN as the supporting electrolyte, scan rate: 0.025 V s\textsuperscript{-1}, Fc (1 mM) was used as an internal standard). N\textsubscript{i} denotes the new

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