# 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.<sup>1</sup> The *tetrakis*(triphenylphosphine) palladium(0) catalyst  $[Pd(PPh_3)_4]$  was synthesised from palladium(II) chloride (Precious Metals Online) according to the literature procedure.<sup>2</sup> The synthesis of the free base ligands 2, 2'-[(1R,2R)-1,2-Cyclohexanediylbis(nitrilomethylidine)]bis[4-bromo-phenol] (1),<sup>3</sup> 2, 2'-[1,2-Phenylenediyl bis(nitrilomethylidine)]bis[4-bromo-phenol] (2),<sup>4</sup> and 2, 2'-[4,5-Dimethyl-1,2-phenylenediyl bis(nitrilomethylidine)]bis[4-bromo-phenol] (3) <sup>5</sup> 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). (1*R*,2*R*)-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.<sup>6</sup> 186–188 °C) <sup>1</sup>**H NMR** (200 MHz, *d*<sub>6</sub>-DMSO)  $\delta$  (ppm) 13.36 (s, 1H), 8.48 (s, 1H), 7.59 (d, <sup>4</sup>*J*<sub>*H*-*H*</sub> = 2.6 Hz, 1H), 7.41 (dd, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 8.9 Hz, <sup>4</sup>*J*<sub>*H*-*H*</sub> = 2.6 Hz, 1H), 6.80 (d, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 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.<sup>3</sup>

# 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.<sup>7</sup> 216–218 °C) <sup>1</sup>**H NMR** (400 MHz, *d*<sub>6</sub>-DMSO)  $\delta$  (ppm) 12.90 (s, 1H), 8.91 (s, 1H), 7.89 (d, <sup>4</sup>*J*<sub>*H*-*H*</sub> = 2.6 Hz, 1H), 7.54 (dd, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 8.8 Hz, <sup>4</sup>*J*<sub>*H*-*H*</sub> = 2.6 Hz, 1H), 7.40–7.48 (m, 2H), 6.94 (d, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 8.8 Hz, 1H). The characterisation data matched that reported in the literature.<sup>4</sup>

#### 2, 2'-[4,5-Dimethyl-1,2-phenylenediyl 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-*o*-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.<sup>5</sup> 241–245 °C) <sup>1</sup>**H NMR** (400 MHz, *d*<sub>6</sub>-DMSO)  $\delta$  (ppm) 8.91 (s, 1H), 7.87 (d, <sup>4</sup>J<sub>H-H</sub> = 2.5 Hz, 1H), 7.52 (dd, <sup>3</sup>J<sub>H-H</sub> = 8.8 Hz, <sup>4</sup>J<sub>H-H</sub> = 2.5 Hz, 1H), 7.28 (m, 1H), 6.92 (d, <sup>3</sup>J<sub>H-H</sub> = 8.8 Hz, 1H), 2.30 (s, 3H). The characterisation data matched that reported in the literature.<sup>5</sup>

#### 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 N<sub>2</sub> for 20 minutes. Under N<sub>2</sub>, **1** (0.480 g, 1.00 mmol) was dissolved in EtOH and to this solution was added Co(OAc)<sub>2</sub>•4H<sub>2</sub>O (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 the N<sub>2</sub> atmosphere 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 H<sub>2</sub>O (3 × 50 mL). The organic layer was collected, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to yield the product as a dark brown powder (Yield: 0.544 g, 95%) **M.P.** 297–299 °C **ATR-IR** (cm<sup>-1</sup>)  $v_{C=N} = 1638$  **UV-Vis-NIR**  $\lambda$ (KBr, cm<sup>-1</sup>) 12435, 17886 (sh), 25002, 30029, 34708 **MS** (**ESI+**, **DMF/MeOH**) *m/z* calculated for C<sub>20</sub>H<sub>18</sub>Br<sub>2</sub>CoN<sub>2</sub>O<sub>2</sub> [M-Cl]<sup>+</sup>: 537.12, found: 536.93 **Elemental Analysis** calculated for C<sub>20</sub>H<sub>18</sub>Br<sub>2</sub>ClCoN<sub>2</sub>O<sub>2</sub>: 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 N<sub>2</sub> for 20 min. Under an atmosphere of N<sub>2</sub>, **2** (0.348 g, 0.735 mmol) was dissolved in EtOH and Co(OAc)<sub>2</sub>•4H<sub>2</sub>O (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 N<sub>2</sub> 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 H<sub>2</sub>O (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<sup>-1</sup>)  $v_{C=N} = 1613$  **UV-Vis-NIR**  $\lambda$ (KBr, cm<sup>-1</sup>) 12154 (sh), 16485 (sh), 20187, 21376, 30377 **MS (ESI+, DMF/MeOH)** *m/z* calculated for C<sub>20</sub>H<sub>12</sub>Br<sub>2</sub>CoN<sub>2</sub>O<sub>2</sub> [M-Cl]<sup>+</sup>: 531.07, found: 530.93 **Elemental Analysis** calculated for C<sub>20</sub>H<sub>18</sub>Br<sub>2</sub>ClCoN<sub>2</sub>O<sub>2</sub>: C 42.4, H 2.1, N 4.9%, found C 42.1, H 2.1, N 4.8%.

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

EtOH (20 mL) was degassed with N<sub>2</sub> for 20 min. Under an atmosphere of N<sub>2</sub>, **3** (0.250 g, 0.500 mmol) was dissolved in EtOH and Co(OAc)<sub>2</sub>•4H<sub>2</sub>O (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 N<sub>2</sub> 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 H<sub>2</sub>O (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<sup>-1</sup>)  $v_{C=N} = 1622$  **UV-Vis-NIR**  $\lambda$ (KBr, cm<sup>-1</sup>) 14948 (sh), 21928,

25426, 29681 MS (ESI+, DMF/MeOH) m/z calculated for  $C_{22}H_{16}Br_2CoN_2O_2$  [M-Cl]<sup>+</sup>: 558.89, found: 558.80 Elemental Analysis calculated for  $C_{20}H_{18}Br_2ClCoN_2O_2$ : 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.

**Col** (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<sup>-1</sup>)  $v_{C=C} = 2192$ ,  $v_{C=N} = 1595$  **UV-Vis-NIR**  $\lambda$ (KBr, cm<sup>-1</sup>) 16050, 22280, 30520 **Elemental Analysis** Found: C 73.8, H 4.6, N 4.3%.

# POPCo2.

**Co2** (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<sup>-1</sup>)  $v_{C=C} = 2195$ ,  $v_{C=N} = 1592$  **UV-Vis-NIR**  $\lambda$ (KBr, cm<sup>-1</sup>) 16720, 22350, 31320 **Elemental Analysis** Found: C 70.7, H 4.3, N 4.6%.

## POPCo3.

**Co3** (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<sup>-1</sup>)  $v_{C=C} = 2203$ ,  $v_{C=N} = 1595$  **UV-Vis-NIR**  $\lambda$ (KBr, cm<sup>-1</sup>) 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<sup>-1</sup>)  $v_{C=C} = 2195$ , **UV-Vis-NIR**  $\lambda$ (KBr, cm<sup>-1</sup>) 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  $CO_2$ , and that the concentration of  $CO_2$  is large in comparison to that of the analyte), it is possible to calculate kinetic data for the interaction of salen complexes with  $CO_2$ . Upon comparison of the peak currents for salen

complexes in the presence of CO<sub>2</sub> with the absence of CO<sub>2</sub>, an expression for  $k_{cat}[Q]$ , or TOF, in terms of the  $i_p$  ratio, which can be directly examined from CV.

$$k[Q] = \frac{F \nu n_p^{-3}}{RT} \left[ \frac{0.4463}{n_{cat}} \right]^2 \left[ \frac{i_{cat}}{i_p} \right]^2$$
(1)

i<sub>cat</sub>

where F = Faraday constant (C mol<sup>-1</sup>), v = scan rate (V s<sup>-1</sup>), n<sub>p</sub> = number of electrons facilitated by the redox process, R = universal gas constant (J mol<sup>-1</sup> K<sup>-1</sup>), T = temperature (K), n<sub>cat</sub> = number of electrons facilitated in the catalytic transformation,  $i_{cat}$  = peak catalytic current (mA/cm<sup>2</sup>),  $i_p$  = peak current under N<sub>2</sub> (mA/cm<sup>2</sup>).

Low pressure CO<sub>2</sub> 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 CO<sub>2</sub> was determined by comparing CO<sub>2</sub> isotherms at 288, 298 and 308 K. Isosteric heat of adsorption calculations ( $Q_{st}$ ) for CO<sub>2</sub> at these temperatures were undertaken using the Clausius-Clapeyron equation

$$(\ln P)_n = -\left(\frac{Q_{st}}{R}\right)\left(\frac{1}{T}\right) + C$$
(2)

where P = pressure (mbar), n = amount of gas adsorbed (mol/mol), T = temperature (K), R = universal gas constant (J mol<sup>-1</sup> K<sup>-1</sup>) and C = constant).

The selectivity (*S*) for adsorption of  $CO_2$  over  $N_2$  was estimated from the single-component  $N_2$  and  $CO_2$  room temperature isotherm data. The values for this approximation are derived from an approximate flue gas composition of 15%  $CO_2$ , 75%  $N_2$  and 10% other gases, at a total pressure of 1 bar.

$$S = \frac{\left(\frac{q_{CO_2}}{q_{N_2}}\right)}{\left(\frac{p_{CO_2}}{p_{N_2}}\right)}$$
(3)

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<sup>-1</sup>.



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  $v_{C=N}$  stretch from the discrete complexes to the POPs, while the  $v_{C=C}$  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 (vi) POPCo2 (v) 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

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



Figure S4: <sup>13</sup>C CPTOSS of **Co2** (above) and **POPCo2** (below). The full <sup>13</sup>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 S5: <sup>13</sup>C CPTOSS of **Co3** (above) and **POPCo3** (below) the aromatic salen POPs, as well as the POP made in the absence of salen metal complex. The full <sup>13</sup>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: <sup>13</sup>C CPTOSS of **POPTPA**. The full <sup>13</sup>C NMR spectra are plotted in blue, while the spectra in red are the nonprotonated or methyl carbon species detected after 40 µs 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  $[(n-C_4H_9)_4N]PF_6/DMF$  as the supporting electrolyte under N<sub>2</sub>, scan rate: 0.1 V s<sup>-1</sup>, Fc (1 mM) was used as an internal standard).



Figure S10: Solid state CV of **A POPCo1** upon progressively extending the potential window to  $E_{pc} = -1.39$  (black), -1.58 (red), -1.96 (blue), -2.17 (green), -2.36 V vs. Fc<sup>0</sup>/Fc<sup>+</sup> (purple) **B POPCo2** upon progressively extending the potential window to  $E_{pc} = -1.42$  (black), -1.62 (blue), -2.01 (green), -2.41 (magenta) and -2.58 V vs. Fc<sup>0</sup>/Fc<sup>+</sup> (yellow) and **C POPCo3** upon progressively extending the potential window to -1.36 (black), -2.35 (magenta) and -2.55 V vs. Fc<sup>0</sup>/Fc<sup>+</sup> (yellow), **b**) under N<sub>2</sub> (black), CO<sub>2</sub> (red) and CO<sub>2</sub> with TFE (0.14 mmol-blue, 0.28 mmol-green) (0.1 M LiBF<sub>4</sub>/MeCN as the supporting electrolyte, scan rate: 0.025 V s<sup>-1</sup>, 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<sup>+</sup> and **B** -1.0 to -1.5 V vs. Ag/Ag<sup>+</sup> **C Co2** (0.51 mM) upon changing the potential from 0.1 to -0.3 V vs. Ag/Ag<sup>+</sup> and **D** -1.0 to -1.5 V vs. Ag/Ag<sup>+</sup> **E Co3** (0.32 mM) upon changing the potential from +0.1 to -0.4 V vs. Ag/Ag<sup>+</sup> and **F** -0.8 to -1.4 V vs. Ag/Ag<sup>+</sup>. 0.1 M [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]PF<sub>6</sub>/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<sup>+</sup>, **B** -0.8 to -1.4 V vs. Ag/Ag<sup>+</sup> and **C** of **POPCo2** upon changing the potential from -0.9 to -1.3 V vs. Ag/Ag<sup>+</sup> (0.1 M [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]PF<sub>6</sub>/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 N<sub>2</sub>(black), CO<sub>2</sub> (red) and CO<sub>2</sub> with TFE (2.1 mmol) as a proton source (blue) **B Co2** (1 mM) under saturation conditions of N<sub>2</sub> (black), CO<sub>2</sub> (red) and CO<sub>2</sub> with TFE (6.3 mmol) as a proton source (blue) **C Co3** (1 mM) under saturation conditions of N<sub>2</sub> (black), CO<sub>2</sub> (red) and CO<sub>2</sub> with TFE (2.1 mmol) as a proton source (blue) **C co3** (1 mM) under saturation conditions of N<sub>2</sub> (black), CO<sub>2</sub> (red) and CO<sub>2</sub> with TFE (2.1 mmol) as a proton source (blue) **C co3** (1 mM) under saturation conditions of N<sub>2</sub> (black), CO<sub>2</sub> (red) and CO<sub>2</sub> with TFE (2.1 mmol) as a proton source (blue) (0.1 M [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]PF<sub>6</sub>/DMF as the supporting electrolyte, scan rate: 0.1 V s<sup>-1</sup>, Fc (1 mM) was used as an internal standard).



Figure S14: Plot of **A** current density  $(i_{cat})$  vs.  $[CO_2]^{0.5}$  for solution state CV of **Co2** (1 mM) under CO<sub>2</sub>, demonstrating a first order kinetic relation in  $[CO_2]$  **B**  $i_{cat}$  vs. [TFE] for solution state CV of **Co2** (1 mM) under CO<sub>2</sub> saturation, demonstrating a second order kinetics relation in [TFE] and **C**  $i_{cat}$  vs. [**Co2**] for solution state CV of **Co2** under CO<sub>2</sub> saturation, demonstrating a first order kinetic relation in [**CO2**].



Figure S15: Plot of **A** current density  $(i_{cat})$  vs.  $[CO_2]^{0.5}$  for solution state CV of **Co3** (1 mM) under CO<sub>2</sub>, demonstrating a first order kinetic relation in  $[CO_2]$  **B**  $i_{cat}$  vs. [TFE] for solution state CV of **Co3** (1 mM) under CO<sub>2</sub> saturation, demonstrating a second order kinetics relation in [TFE] and **C**  $i_{cat}$  vs. [**Co2**] for solution state CV of **Co3** under CO<sub>2</sub> saturation, demonstrating a first order kinetic relation in [**Co3**].



Figure S16: Production of H<sub>2</sub> (black) and CO (red) from CO<sub>2</sub> 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 [( $n-C_4H_9$ )\_4N]PF\_6/DMF/MeCN(8:2) with TFE (0.63 M) as the supporting electrolyte under CO<sub>2</sub>, E<sub>pc</sub> = -1.85 V vs. Ag/Ag<sup>+</sup>).



Figure S17: <sup>1</sup>H NMR of the **Co2** bulk electrolysis solution after work up from CPE in D<sub>2</sub>O at 300 MHz under CO<sub>2</sub> saturation after 30 min (black), 60 min (red), 90 min (blue), 120 min (cyan) and in the absence of CO<sub>2</sub> after 120 min (orange). The peak at  $\delta = 8.00$  ppm corresponds to the generation of formic acid. Spectra were referenced to D<sub>2</sub>O.  $E_{pc} = -1.85$  V vs. Ag/Ag<sup>+</sup>.



Figure S18: Solid state CV of **A POPCo1 B POPCo2** and **C POPCo3** under  $N_2$  (black) and under CO<sub>2</sub> (red) with TFE (0.14 mmol-blue, 0.28 mmol-green) (0.1 M LiBF<sub>4</sub>/MeCN as the supporting electrolyte, scan rate: 0.025 V s<sup>-1</sup>, Fc (1 mM) was used as an internal standard).  $N_1$  denotes the new

## References

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