

Supporting Information

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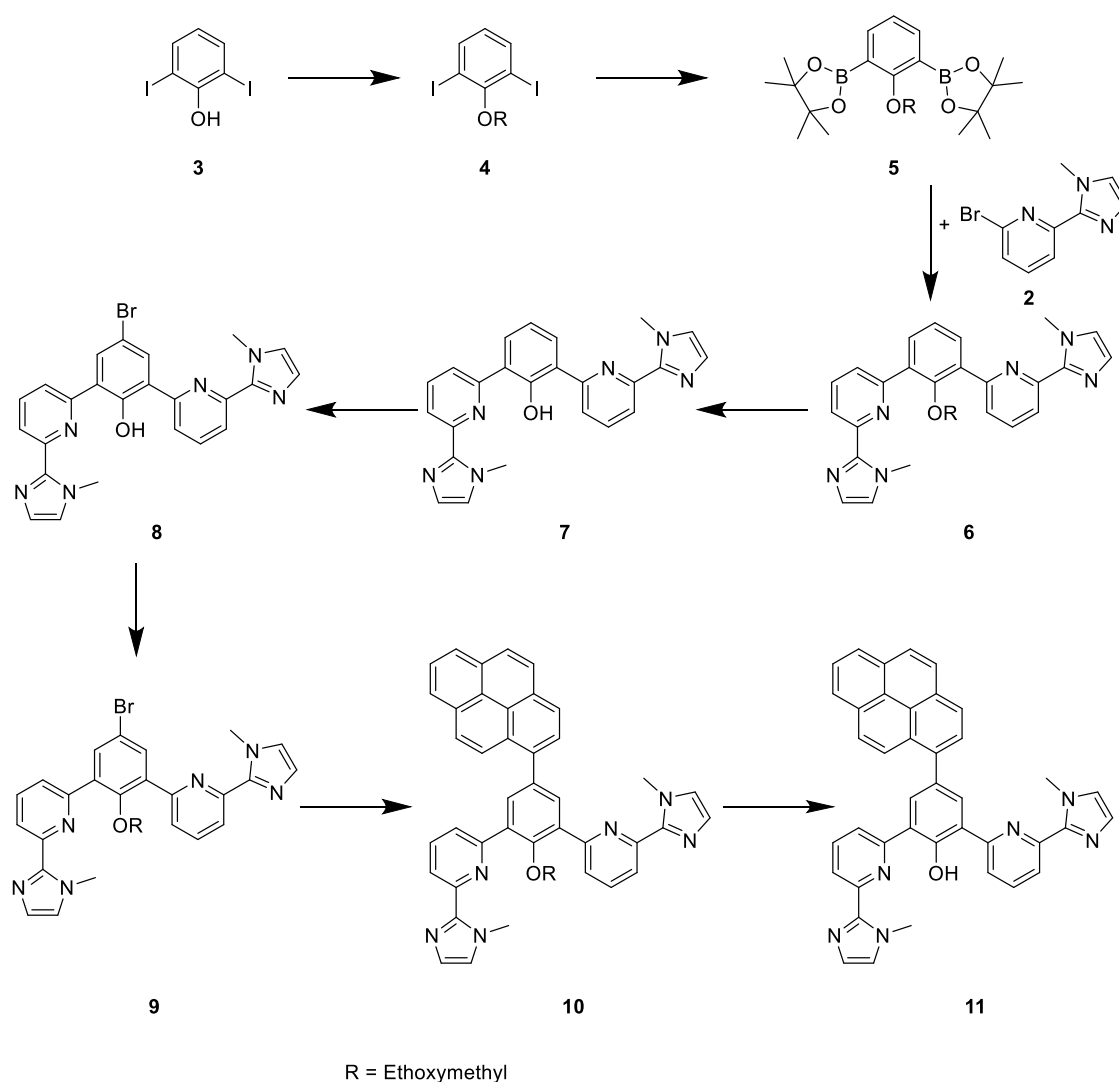
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Experimental Section

General

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded with a Bruker Avance 300 NMR spectrometer (^1H 300 MHz, ^{13}C 75.4 MHz) with CDCl_3 , $[\text{D}_6]\text{-DMSO}$ or $[\text{D}_7]\text{-dmf}$ as the solvent at 25 °C. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were calibrated against the residual protons and natural-abundance ^{13}C resonances of the deuterated solvents (CDCl_3 $\delta_{\text{H}} = 7.26$ ppm, $[\text{D}_6]\text{-DMSO}$ $\delta_{\text{H}} = 2.50$ ppm and $[\text{D}_7]\text{-dmf}$ $\delta_{\text{H}} = 8.03, 2.92, 2.75$ ppm). Microanalyses were performed with an Elementar Vario El II elemental analyser. Mass spectra were recorded using a Bruker APEX IV micrOTOF or a Bruker Autoflex Speed mass spectrometer.

Synthesis



Scheme S 1. Ligand Synthesis.

2-Bromo-6-(1-methylimidazole-2-yl)pyridine, **2**, was prepared according to a literature procedure.¹

2,6-Diiodophenol, **3**

2,6-Diiodophenol was prepared according to a modified literature procedure.² Iodine (32.3 g, 127 mmol, 1.48 eq.) was suspended in deionised water (425 mL) and phenol (8.09 g, 86.0 mmol, 1.00 eq.) was added. Hydrogenperoxide (35% in water, 21.9 mL, 255 mmol, 2.97 eq.) was slowly added

and the mixture stirred for 22 hours. A solution of sodium thiosulfate (44.2 g) in water (100 mL) was added and the mixture was extracted with dichloromethane (dcm) (3 x 200 mL). The combined organic phases were washed with sodium thiosulfate solution in water (10%, 100 mL) and saturated NaCl solution (100 mL). After drying over MgSO₄ the solvent was removed under reduced pressure. The product was obtained in 35% yield as a white solid after column chromatography on silica gel using hexane:ethyl acetate in a ratio of 20:1 as eluent.

2-(Ethoxymethoxy)-1,3-diiodobenzene, **4**

3 (1.26 g, 3.64 mmol, 1.00 eq.) was dissolved in dry dcm (5 mL) and dry triethylamine (1.00 mL, 7.01 mmol, 1.93 eq.) was added at 0 °C. Chloromethylethylether (0.68 mL, 7.33 mmol, 2.01 eq.) was added after stirring the mixture for 10 minutes at 0 °C. Subsequently, the mixture was stirred for 90 minutes at 0 °C and 20 minutes at rt. Water (10 mL) was added, the aqueous phase was extracted with dcm (2 x 10 mL), the combined organic phases were washed with saturated NaCl solution (15 mL), and dried over MgSO₄. Evaporation of the solvent yielded the pure product in 90% yield as a colourless oil.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.78 (d, ³J_{HH} = 7.8 Hz, 4-CH, 6-CH, 2H), 6.56 (t, ³J_{HH} = 7.8 Hz, 5-CH, 1H), 5.19 (s, OCH₂O, 2H), 4.03 (q, ³J_{HH} = 7.1 Hz, OCH₂Me, 2H), 1.31 (t, ³J_{HH} = 7.1 Hz, CH₃, 3H).

¹³C-NMR (75.4 MHz, CDCl₃, ppm): δ = 156.4 (2-C_q), 140.3 (4-CH, 6-CH), 127.9 (5-CH), 98.7 (OCH₂O), 91.8 (1-C_q, 3-C_q), 66.9 (OCH₂Me), 15.3 (CH₃).

MS (ESI MeOH): *m/z* = 426.8660 [M+Na]⁺.

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 686 (s), 736 (w), 765 (s), 797 (m), 846 (m), 921 (s), 1022 (m), 1065 (s), 1086 (m), 1117 (s), 1153 (s), 1227 (m), 1271 (w), 1387 (s), 1429 (s), 1458 (w), 1546 (m), 1857 (w), 1916 (w), 2885 (w), 2929 (m), 2973 (m), 3063 (w).

2-(Ethoxymethoxy)-1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzene, **5**

4 (1.35 g, 3.34 mmol, 1.00 eq.), Bispinacolatodiboron (2.59 g, 10.2 mmol, 3.05 eq.), potassium *tert*-butoxide (966 mg, 10.0 mmol, 2.99 eq.), copper(I)iodide (125 mg, 656 μmol, 0.20 eq.) and triphenylphosphine (228 mg, 869 μmol, 0.26 eq.) were suspended in dry thf (35 mL) and the mixture stirred at rt for five days. Diethylether (25 mL) was added and the mixture filtered through Celite. The residue was flushed with diethylether (60 mL) and the solvent of the filtrate was removed under reduced pressure. Column chromatography on silica with hexane:ethylacetate (ratio of 40:1 to 15:1 to 10:1) gave the product in 66% yield as slightly yellow oil.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.81 (d, ³J_{HH} = 7.3 Hz, 4-CH, 6-CH, 2H), 7.09 (t, ³J_{HH} = 7.3 Hz, 5-CH, 1H), 5.19 (s, OCH₂O, 2H), 3.83 (q, ³J_{HH} = 7.1 Hz, OCH₂Me, 2H), 1.33 (s, C_qCH₃, 24H), 1.19 (t, ³J_{HH} = 7.1 Hz, OCH₂CH₃, 3H).

¹³C-NMR (75.4 MHz, CDCl₃, ppm): δ = 168.0 (2-C_q), 140.0 (4-CH, 6-CH), 139.5 (1-C_q, 3-C_q), 123.0 (5-CH), 100.3 (OCH₂O), 83.7 (OC_qMe₂), 65.4 (OCH₂Me), 25.0 (C_qCH₃), 15.3 (CH₂CH₃).

MS (ESI MeOH): *m/z* = 422.2871 [M+NH₄]⁺, 427.2429 [M+Na]⁺.

IR (ATR, cm⁻¹): 661 (m), 783 (w), 848 (s), 882 (m), 966 (s), 1067 (m), 1133 (s), 1211 (m), 1257 (m), 1277 (m), 1331 (s), 1371 (s), 1439 (w), 1463 (m), 1590 (m), 2931 (w), 2977 (m).

2-(Ethoxymethoxy)-1,3-bis(2-(1-methylimidazole-2-yl)pyridine-6-yl)benzene, **6**

5 (1.81 g, 4.48 mmol, 1.00 eq.), **2** (2.42 g, 10.2 mmol, 2.28 eq.), bis(dibenzylidenacetone)palladium (42.0 mg, 73.0 μmol, 0.02 eq.), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos; 72.0 mg, 175 μmol, 0.04 eq.), and potassium phosphate (3.79 g, 17.9 mmol, 4.00 eq.) were dissolved in degassed toluene (30 mL). Subsequently, degassed water (3 mL) was added and the mixture was heated to 100 °C for three days. After cooling to rt, dcm (60 mL) and water (30 mL) were added. The aqueous phase was

extracted with dcm (2 x 40 mL and 1 x 20 mL), the combined organic phases were washed with saturated NaCl solution (20 mL), and dried over MgSO₄. Column chromatography on silica with hexane:ethylacetate in a ratio 1:1 to ethylacetate:triethylamine in a ratio of 1:0.05 as eluent yielded the product as pale yellow solid in 85% yield.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 8.20-8.13 (m, Py-5-CH, 2H), 7.84-7.78 (m, 4-CH, 6-CH, Py-3-CH, Py-4-CH, 6H), 7.37 (t, ³J_{HH} = 7.7 Hz, 5-CH, 1H), 7.14 (d, ³J_{HH} = 1.1 Hz, Im-4-CH, 2H), 6.99 (d, ³J_{HH} = 1.1 Hz, Im-5-CH, 2H), 4.57 (s, OCH₂O, 2H), 4.21 (s, NCH₃, 6H), 3.03 (q, ³J_{HH} = 7.1 Hz, OCH₂Me, 2H), 0.70 (t, ³J_{HH} = 7.1 Hz, CH₂CH₃, 3H).

¹³C-NMR (75.4 MHz, CDCl₃, ppm): δ = 155.2 (Py-2-C_q/Py-6-C_q), 153.2 (2-C_q), 150.8 (Py-2-C_q/Py-6-C_q), 145.0 (Im-2-C_q), 136.8 (3-Py-CH/4-Py-CH), 135.4 (1-C_q, 3-C_q), 131.8 (4-CH,6-CH), 128.3 (Im-4-CH), 124.8 (5-CH), 124.6 (Im-5-CH), 124.0 (Py-3-CH/Py4-CH), 120.9 (Py-5-CH), 98.7 (OCH₂O), 65.4 (OCH₂Me), 36.8 (NCH₃), 14.8 (CH₂CH₃).

MS (ESI MeOH): *m/z* = 467.2190 [M+H]⁺, 489.2002 [M+Na]⁺.

IR (KBr, cm⁻¹): $\tilde{\nu}$ = 627 (w), 724 (m), 765 (m), 796 (s), 821 (m), 938 (s), 1069 (m), 1105 (m), 1158 (m), 1210 (m), 1281 (m), 1372 (m), 1454 (s), 1476 (s), 1568 (s), 1592 (m), 2895 (m), 2895 (m), 2935 (m), 2955 (m), 2972 (m), 3069 (w), 3097 (w), 3128 (w).

2,6-Bis(2-(1-methylimidazole-2-yl)pyridine-6-yl)phenol, **7**

6 (2.19 g, 4.69 mmol, 1.00 eq.) was dissolved in ethanol (120 mL), hydrochloric acid (37%, 8 mL) was added, and the mixture was stirred for 24 hours at rt. Subsequently, the pH was adjusted to pH 8 by adding sodium hydroxide solution (30%) and sodium carbonate solution (10%). The crude product was extracted with dcm (1 x 80 mL and 2 x 40 mL), the combined organic phases were washed with saturated NaCl solution (20 mL), and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was washed with diethylether (3 x 20 mL). After drying *in vacuo* the product was obtained as a colourless solid in 86% yield.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 14.30 (s, OH, 1H), 8.08 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.1 Hz, Py-5-CH, 2H), 7.99 (dd, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.1 Hz, Py-3-CH, 2H), 7.94 (d, ³J_{HH} = 7.8 Hz, 3-CH, 5-CH, 2H), 7.89 (t, ³J_{HH} = 7.9 Hz, Py-4-CH, 2H), 7.15 (d, ³J_{HH} = 1.1 Hz, Im-4-CH, 2H), 7.08 (t, ³J_{HH} = 7.8 Hz, 4-CH, 1H), 7.01 (d, ³J_{HH} = 1.1 Hz, Im-5-CH, 2H), 4.11 (s, NCH₃, 6H).

¹³C-NMR (75.4 MHz, CDCl₃, ppm): δ = 157.3 (1-C_q), 155.7 (2-C_q, 6-C_q), 148.8 (Py-2-C_q), 145.0 (Im-2-C_q), 137.8 (4-Py-CH), 130.5 (3-CH, 5-CH), 128.7 (Im-4-CH), 124.6 (Im-5-CH), 121.7 (Py-3-CH), 121.5 (Py-5-CH), 119.2 (4-CH), 36.3 (NCH₃).

MS (ESI MeOH): *m/z* = 409.1773 [M+H]⁺, 431.1590 [M+Na]⁺.

IR (KBr, cm⁻¹): $\tilde{\nu}$ = 631 (m), 677 (m), 716 (s), 732 (s), 788 (m), 823 (m), 842 (w), 920 (w), 1042 (m), 1088 (m), 1134 (w), 115 (w), 1249 (w), 1274 (m), 1286 (m), 1367 (w), 1421 (m), 1446 (s), 1473 (s), 1510 (w), 1570 (s), 1597 (m), 2853 (w), 2921 (w), 2946 (w), 3056 (w), 3088 (w), 3133 (w), 3415 (w).

4-Bromo-2,6-bis(2-(1-methylimidazole-2-yl)pyridine-6-yl)phenol, **8**

7 (1.65 g, 4.04 mmol, 1.04 eq.) was dissolved in pyridine (150 mL) and the solution was cooled to 0 °C. In the absence of light, a solution of bromine (200 μL, 3.90 mmol, 1.00 eq.) in tetrachloromethane (6 mL) was added dropwise. The solution was stirred for three hours at 0 °C in the dark. Subsequently, a solution of sodium thiosulfate (10%, 60 mL) in water was added and the mixture was stirred for further 15 minutes at rt. The pH was adjusted to 8 with sodium carbonate solution (10%) and the product was extracted with dcm (1 x 120 mL and 3 x 60 mL). The combined organic phases were washed with saturated NaCl solution (40 mL) and the aqueous solution was extracted with dcm (150 mL). The combined organic phases were dried over MgSO₄, the solvent was removed under reduced pressure. The

crude product was dissolved in a small amount of dcm and filtered. Drying of the filtrate *in vacuo* yielded the product as a mixture with **7** in a ratio of 1:0.18 as a brown solid.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 8.11 (dd, $J_{\text{HH}} = 7.6$ Hz, $J_{\text{HH}} = 1.3$ Hz, Py-CH, 2H), 8.05 (s, Ph-CH, 2H), 8.09 (s, Ar-CH, 2H), 7.99-7.87 (m, Ar-CH, 4H), 7.16 (d, $^3J_{\text{HH}} = 1.1$ Hz, Im-4-CH, 2H), 7.02 (d, $^3J_{\text{HH}} = 1.1$ Hz, Im-5-CH, 2H), 4.10 (s, NCH₃, 6H).

¹³C-NMR (75.4 MHz, CDCl₃, ppm): δ = 156.4 (C_q), 154.3 (Ph-C_q), 148.9 (C_q), 144.7 (Im-2-C_q), 138.0 (Py-CH), 132.7 (Ph-CH), 128.8 (Im-4-CH), 126.2 (C_q), 124.7 (Im-5-CH), 122.0 (Py-CH), 121.7 (Py-CH), 111.4 (Ph-C_q), 36.2 (NCH₃).

MS (ESI MeOH): $m/z = 487.0874$ [M+H]⁺, 511.0664 [M+Na]⁺.

5-Bromo-2-(ethoxymethoxy)-1,3-bis(2-(1-methylimidazole-2-yl)pyridine-6-yl)benzene, **9**

8 (1.51 g, 3.10 mmol, 1.00 eq.) was dissolved in dry thf (60 mL) and the solution was cooled to 0 °C. Sodium hydride (60% in mineral oil, 208 mg, 5.20 mmol, 1.68 eq.) was added in small portions and the mixture was stirred at 0 °C for 50 minutes. Chloromethylethylether (570 μL, 6.14 mmol, 1.98 eq.) was added dropwise at 0 °C and the solution was stirred for 165 minutes at rt. Water (50 mL) was slowly added to the solution at 0 °C and the mixture was extracted with dcm (4 x 50 mL). The combined organic phases were washed with saturated NaCl solution (50 mL) and dried over MgSO₄. Column chromatography on silica with ethylacetate:triethylamine (1:0.01) yielded the product as a mixture with **6** in a ratio of 1:0.22 as light yellow solid.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 8.11 (dd, $J_{\text{HH}} = 6.5$ Hz, $J_{\text{HH}} = 2.6$ Hz, Py-CH, 2H), 7.94 (s, Ph-CH, 2H), 7.86-7.79 (m, Py-CH, 4H), 7.15 (d, $^3J_{\text{HH}} = 1.1$ Hz, Im-4-CH, 2H), 7.01 (d, $^3J_{\text{HH}} = 1.1$ Hz, Im-5-CH, 2H), 4.56 (s, OCH₂O, 2H), 4.21 (s, NCH₃, 6H), 3.02 (q, $^3J_{\text{HH}} = 7.0$ Hz, OCH₂Me, 2H), 0.69 (t, $^3J_{\text{HH}} = 7.0$ Hz, OCH₂CH₃, 3H).

¹³C-NMR (75.4 MHz, CDCl₃, ppm): δ = 153.8 (C_q), 152.3 (Ph-2-C_q), 150.9 (C_q), 144.8 (Im-2-C_q), 137.1 (C_q), 137.0 (Py-CH), 134.3 (Ph-CH), 128.4 (Im-4-CH), 124.8 (Im-5-CH), 123.9 (Py-CH), 121.4 (Py-CH), 117.8 (Ph-C_q), 98.8 (OCH₂O), 65.6 (OCH₂Me), 36.9 (NCH₃), 14.8 (OCH₂CH₃).

MS (ESI MeOH): $m/z = 547.1278$ [M+H]⁺, 569.1085 [M+Na]⁺.

2-(Ethoxymethoxy)-1,3-bis(6-(1-methylimidazol-2-yl)pyridin-2-yl)-5-(pyren-1-yl)benzene **10**

9 (200 mg, 367 μmol, 1.00 eq.), 1-pyreneboronic acid (99.0 mg, 402 μmol, 1.10 eq.), potassium phosphate (158 mg, 744 μmol, 2.03 eq.), bis(dibenzylideneacetone)palladium (3.0 mg, 5.22 μmol, 0.01 eq.) and SPhos (3.6 mg, 8.77 μmol, 0.02 eq.) were suspended in degassed toluene (6 mL) and degassed water (0.6 mL). The mixture was heated to 100 °C for three days. After cooling to room temperature, water (5 mL) and dcm (10 mL) were added and the phases were separated. The aqueous phase was extracted with dcm (10 mL and 2 x 5 mL) and the combined organic phases were washed with saturated aqueous NaCl and dried over MgSO₄. The solvent was removed under reduced pressure. Purification by column chromatography over silica with ethylacetate:triethylamine (1:0.02) yielded the product as a mixture with **6** in ratio of 1:0.07 as yellow solid.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 8.43 (d, $J_{\text{HH}} = 9.3$ Hz, Pyr-CH, 1H), 8.24-8.16 (m, Ar-CH 5H), 8.12 (s, Ar-CH, 2H), 8.09 (s, Ar-CH, 2H), 8.07-7.96 (m, Ar-CH, 5H), 7.88 (t, $J_{\text{HH}} = 7.8$ Hz, Ar-CH, 2H), 7.12 (d, $^3J_{\text{HH}} = 1.0$ Hz, Im-4-CH, 2H), 6.94 (d, $^3J_{\text{HH}} = 0.9$ Hz, Im-5-CH, 2H), 4.74 (s, OCH₂O, 2H), 4.17 (s, NCH₃, 6H), 3.15 (q, $^3J_{\text{HH}} = 7.1$ Hz, OCH₂Me, 2H), 0.78 (t, $^3J_{\text{HH}} = 7.1$ Hz, OCH₂CH₃, 3H).

¹³C-NMR (75.4 MHz, CDCl₃, ppm): δ = 155.0, 152.6, 150.8, 144.9 (Im-2-C_q), 137.6, 136.9, 136.9, 135.3, 133.8, 131.6, 131.0, 130.8, 128.5, 128.2 (Im-4-CH), 127.7, 127.7, 127.6, 127.5, 126.2, 125.4, 125.4, 125.2, 125.0, 125.0, 124.9, 124.7 (Im-5-CH), 124.1, 121.0, 98.9 (OCH₂O), 65.6 (OCH₂Me), 36.9 (NCH₃), 14.8 (OCH₂CH₃).

MS (ESI MeOH): $m/z = 334.1440 [M+2H]^{2+}$, 667.2809 $[M+H]^+$, 689.2627 $[M+Na]^+$, 1333.5558 $[2M+H]^+$.

2,6-Bis(6-(1-methylimidazol-2-yl)pyridin-2-yl)-4-(pyren-1-yl)phenol **11**

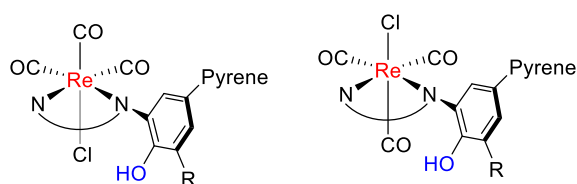
10 (39.0 mg, 58.8 μmol , 1.00 eq.) was dissolved in ethanol (10 mL) and hydrochloric acid (37%, 0.6 mL) added dropwise. The solution was stirred at rt for 21.5 hours. The pH was adjusted to 8 by adding aqueous NaOH (30%) and aqueous NaHCO_3 (10%) solution. Water (10 mL) and dcm (30 mL) were added and the phases were separated. The aqueous phase was extracted with dcm (2 x 20 mL) and the combined organic phases were washed with saturated aqueous NaCl (10 mL) and dried over MgSO_4 . Drying in vacuo yielded the product as yellow solid in 53% yield.

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , ppm): $\delta = 14.54$ (s, OH, 1H), 8.31 (d, $J_{\text{HH}} = 9.3$ Hz, Pyr-CH, 1H), 8.22-7.95 (m, Ar-CH, 12H), 8.08 (s, 3-CH, 5-CH, 2H), 7.86 (t, $J_{\text{HH}} = 8.0$ Hz, Ar-CH, 2H), 7.15 (d, $^3J_{\text{HH}} = 1.0$ Hz, Im-4-CH, 2H), 6.95 (d, $^3J_{\text{HH}} = 0.8$ Hz, Im-5-CH, 2H), 4.06 (s, NCH_3 , 6H).

$^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3 , ppm): $\delta = 156.8$, 155.4, 148.8, 144.8 (Im-2- C_q), 137.9, 137.2, 132.5, 131.9, 131.6, 131.0, 128.7 (Im-4-CH), 128.6, 127.7, 127.6, 127.5, 126.2, 125.3, 125.2, 125.2, 125.0, 124.9, 124.9, 124.6, 124.4, 121.8, 121.6, 36.3 (NCH_3).

MS (ESI MeOH): $m/z = 609.2367 [M+H]^+$, 631.2196 $[M+Na]^+$.

IR (ATR, cm^{-1}): 680 (s), 701 (s), 720 (s), 798 (s), 813 (s), 845 (m), 919 (m), 1019 (s), 1038 (s), 1080 (m), 1259 (m), 1340 (w), 1408 (w), 1431 (m), 1449 (m), 1565 (m), 2859 (w), 2962 (w), 3033 (w), 3097 (w).



Scheme S 2. Schematic representation of the isomers.

X-Ray Refinement

X-ray data were collected with a Bruker D8 VENTURE CMOS diffractometer by use of ω and φ scans (graphite monochromated $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods and refined on F^2 using all reflections with SHELX-2014/7.³ Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 1.2 / 1.5 Ueq(C). Absorption correction was performed by the multi-scan method with the program SADABS V2014/4.⁴ The unit cell contained solvent molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.⁵ The number of electrons and the void volume may count for 17-18 molecules of diethyl ether or dimethyl formamide. The structure was uploaded to the CCDC Database and can be obtained free of charge from <https://www.ccdc.cam.ac.uk>, no. 1973247.

Table S 1. Crystal data and refinement details for **1**.

empirical formula	C ₄₆ H ₂₈ Cl ₂ N ₆ O ₇ Re ₂ , 6[C ₃ H ₇ NO]
formula weight	1658.62
<i>T</i> [K]	100(2)
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> [Å]	8.9050(9)
<i>b</i> [Å]	20.176(3)
<i>c</i> [Å]	20.556(2)
α [°]	92.208(4)
β [°]	97.473(3)
γ [°]	99.790(5)
<i>V</i> [Å ³]	3601.6(7)
<i>Z</i>	4
ρ [g/cm ³]	1.529
<i>F</i> (000)	1652
μ [mm ⁻¹]	3.468
<i>T</i> _{min} / <i>T</i> _{max}	0.6445 / 0.7458
θ -range [°]	2.193 - 29.221
<i>hkl</i> -range	-12 - 9, ± 27 , ± 28
measured refl.	183498
unique refl. [<i>R</i> _{int}]	19341 [0.1433]
observed refl. (<i>I</i> > 2 σ (<i>I</i>))	12815
data / restraints / param.	19341 / 0 / 568
goodness-of-fit (<i>F</i> ²)	1.047
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0437, 0.0899
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0874, 0.1006
resid. el. dens. [e/Å ³]	-1.590 / 2.157

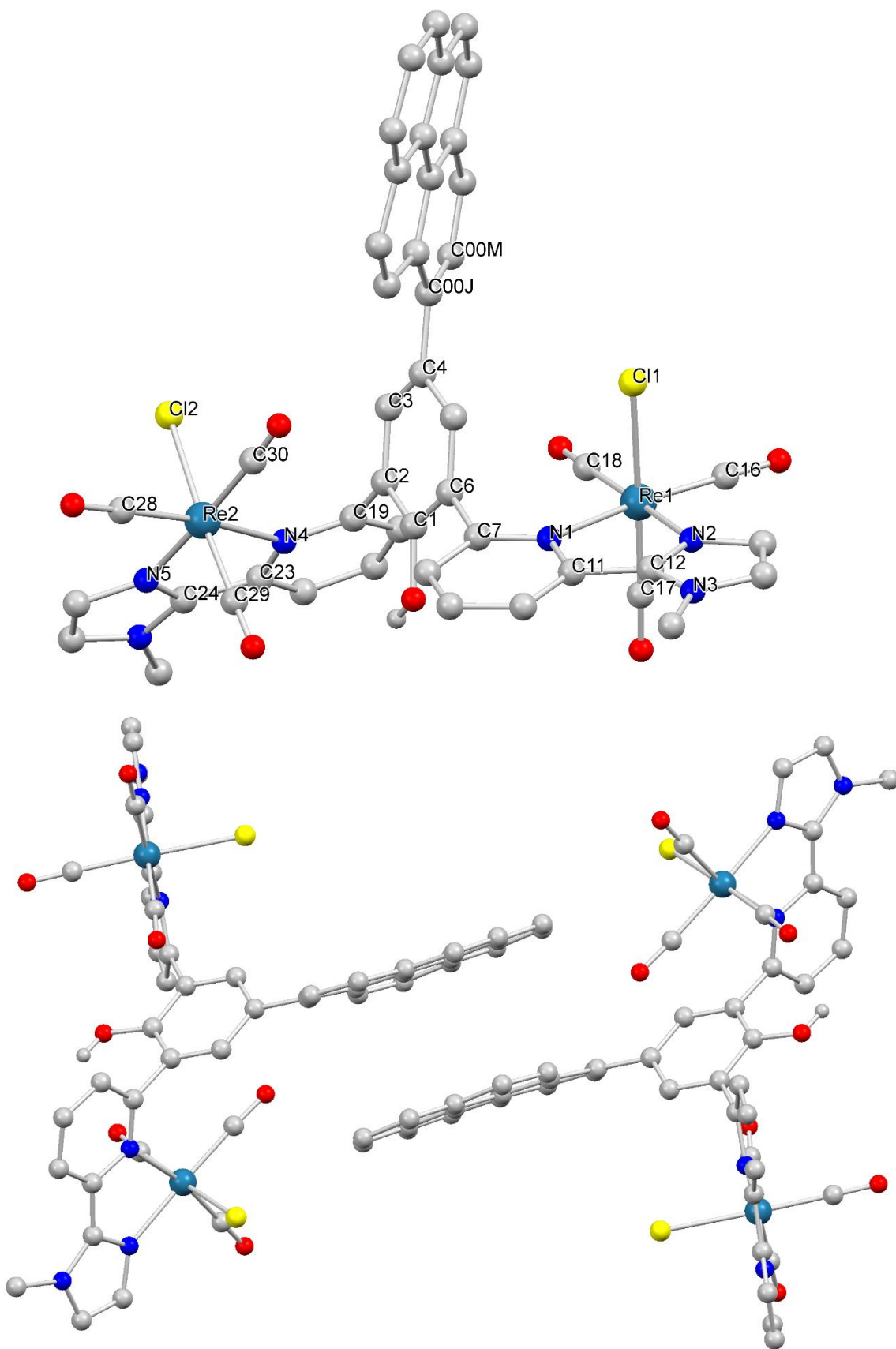


Figure S 1. Molecular structure of 1. Most hydrogen atoms were omitted for clarity.

Table S 2. Selected torsion angles /° of **1**.

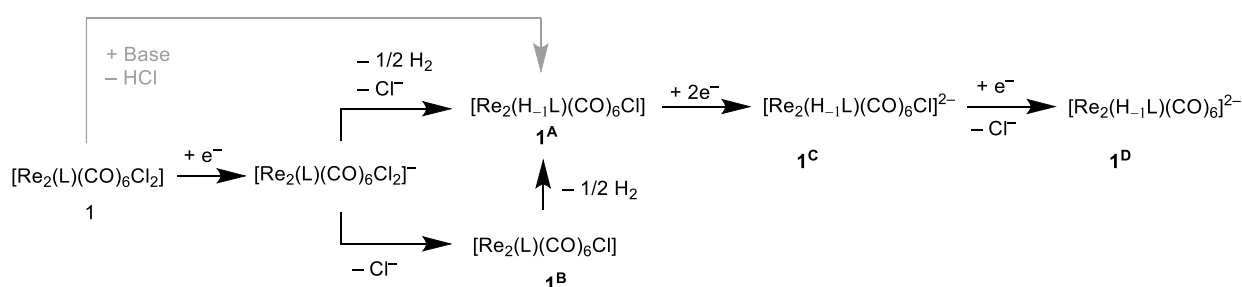
Atoms	Angle
N5-C24-C23-N4	2.3(6)
N4-C19-C2-C1	85.2(5)
N1-C11-C12-N2	-4.5(6)
N1-C7-C6-C1	117.4(5)
C00M-C00J-C4-C3	-44.7(6)

Electrochemical Measurements

CV Measurements

The cell was prepared in a nitrogen filled glovebox with dry solvents. All CV measurements have been conducted with a glassy carbon (GC) working electrode, a platinum wire counter electrode, and a diluted silver/silver nitrate electrode (organic solvents), or a SCE electrode (water). All data in organic solvents were referenced internally vs. $\text{Fc}^{+/0}$. All data in water were referenced vs. SCE. All measurements have been conducted with a Gamry Reference 600 or 600+ potentiostat. In the CO_2 reduction experiments, the sealed cell was purged with CO_2 (quality 5.3) for 10 minutes. iR compensation was applied by the positive feedback method, which is implemented in the software.

Conversion of the potentials: $\text{Fc}^{+/0}$ exhibits a standard reduction potential of 0.40 V vs. NHE in water⁶ and the SCE exhibits a standard reduction potential of 0.24 V vs. NHE.⁷



Scheme S 3. Proposed coupled electrochemical and chemical steps during reduction of **1** under N_2 .

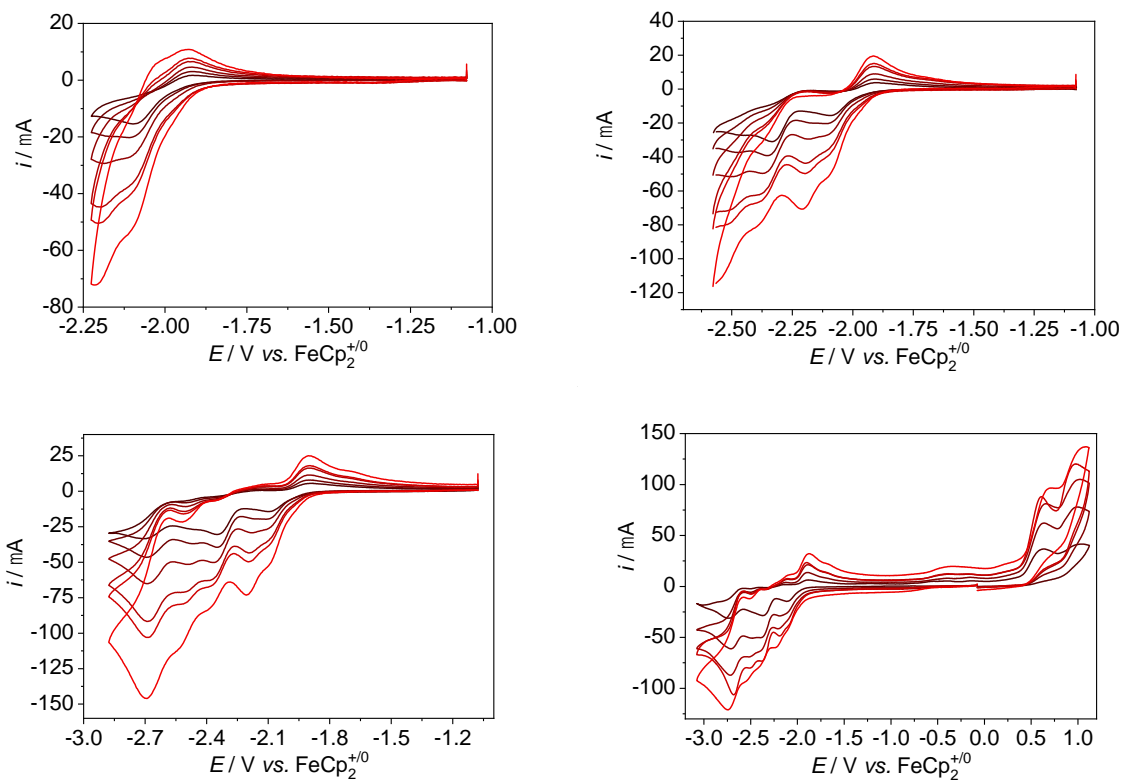


Figure S 2. Scan rate dependent CV data of **1** under N_2 atmosphere, *dmf*, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$, $v = 0.1, 0.2, 0.4, 0.8, 1, 2 \text{ Vs}^{-1}$.

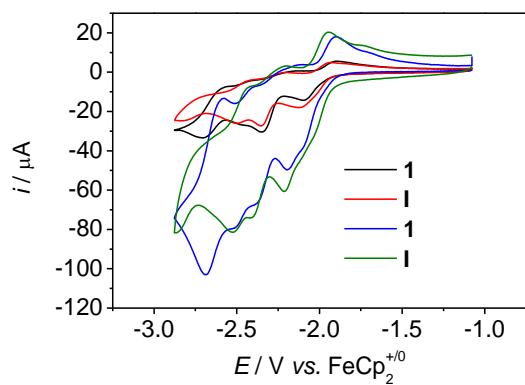


Figure S 3. Overlay of the CV data of **1** and **I** under N_2 atmosphere, in *dmf*, $c_{\text{complex}} \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$, $v = 0.1$ and 1 Vs^{-1} .

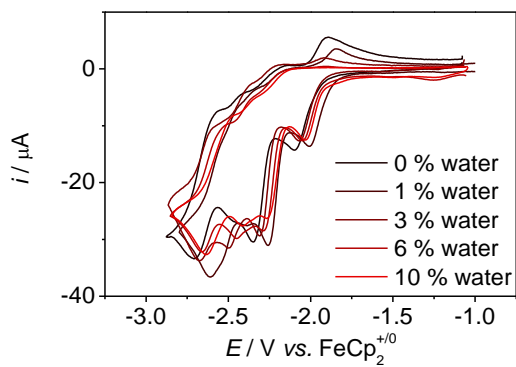


Figure S 4. CV data of **1** in dmf with various amounts of water under N_2 atmosphere, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$, $v = 0.1 \text{ Vs}^{-1}$.

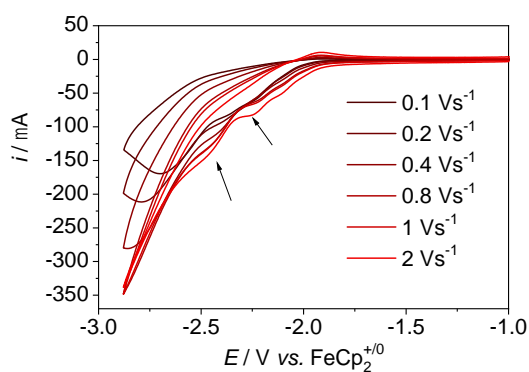


Figure S 5. Scan rate dependent CV data of **1** under CO_2 atmosphere 0% water, dmf, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$. The arrows indicate the first and second wave.

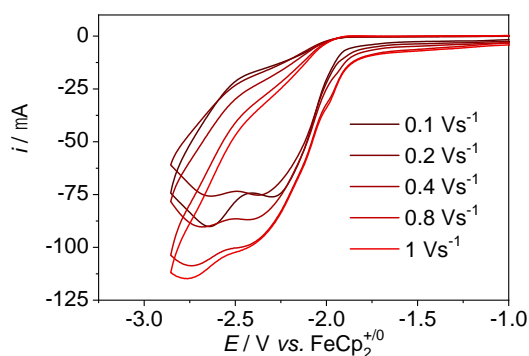


Figure S 6. Scan rate dependent CV data of **1** under CO_2 atmosphere, 6% water, dmf, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

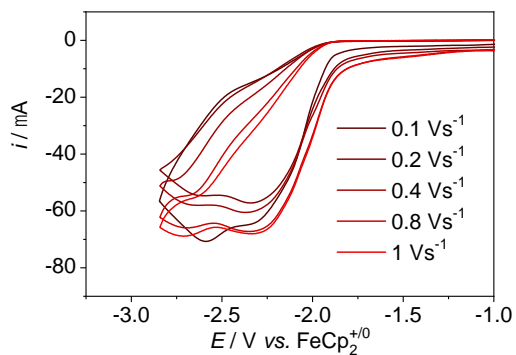


Figure S 7. Scan rate dependent CV data of **I** under CO_2 atmosphere, 10% water, dmf, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

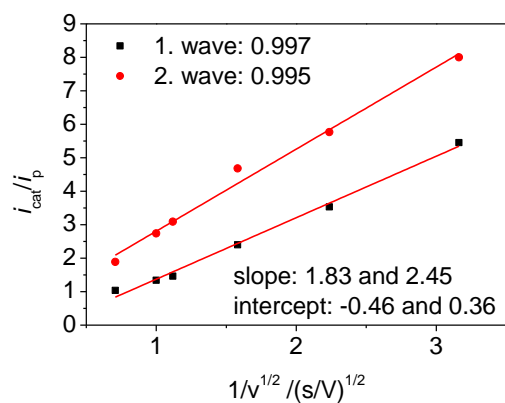


Figure S 8. Catalytic current of **I** over i_p versus the reciprocal square root of the scan rate, under CO_2 atmosphere, 0% water, dmf, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

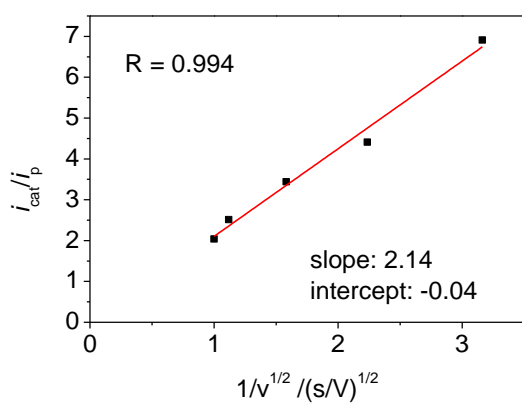


Figure S 9. Catalytic current of **I** over i_p versus the reciprocal square root of the scan rate, under CO_2 atmosphere, 6% water, dmf, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

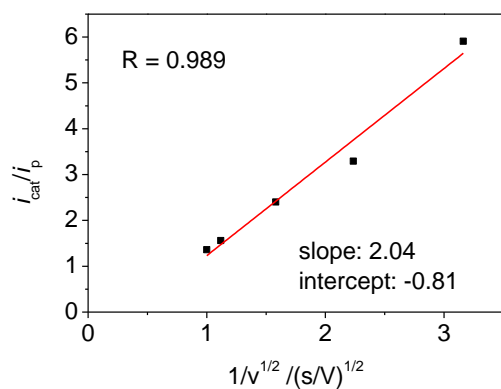


Figure S 10. Catalytic current of **1** over i_p versus the reciprocal square root of the scan rate, under CO_2 atmosphere, 10% water, dmf, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

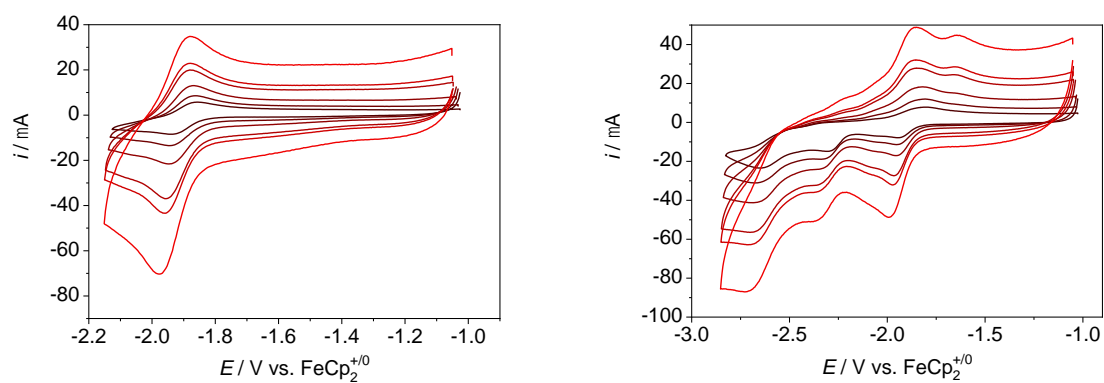


Figure S 11. Scan rate dependent CV data of **1** + LDA under N_2 atmosphere, dmf, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$, $v = 0.1, 0.2, 0.4, 0.8, 1, 2 \text{ Vs}^{-1}$.

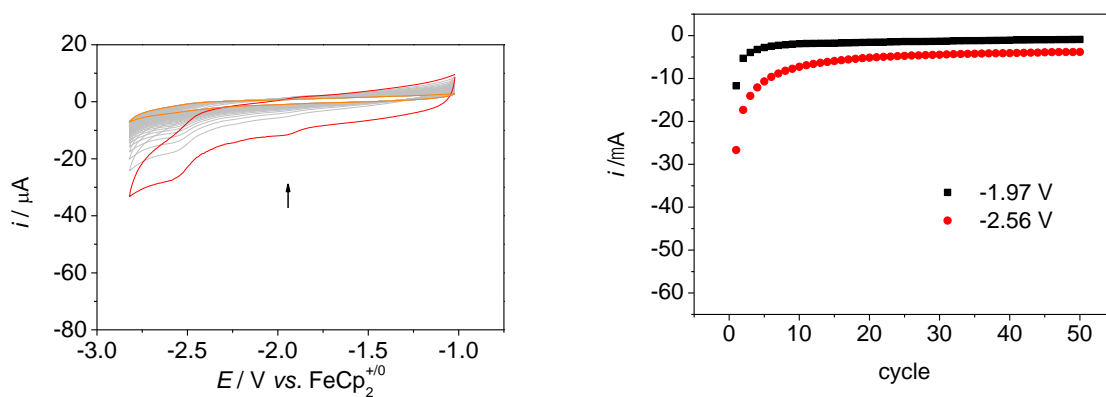


Figure S 12. Left: 50 CV scans of **1**@MWCNT under N_2 atmosphere in dmf + 10% water, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$; $v = 0.1 \text{ Vs}^{-1}$. right: current vs. cycles at representative potentials.

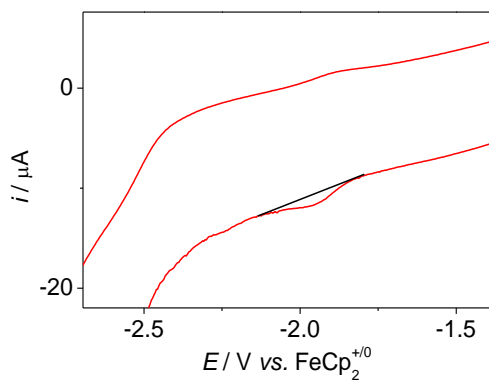


Figure S 13. Magnification of the first CV scan of 1@MWCNT to highlight the integral, N_2 atmosphere in $dmf + 10\%$ water, $v = 0.1 \text{ Vs}^{-1}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

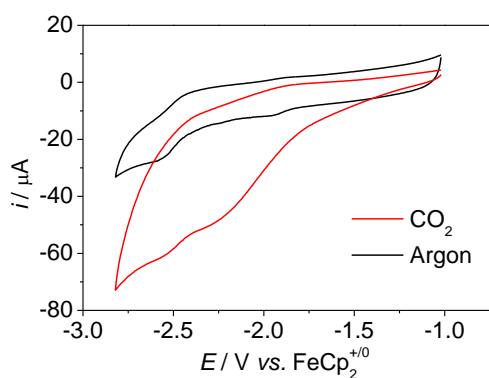


Figure S 14. CV of 1@MWCNT under N_2 and CO_2 atmosphere in $dmf + 10\%$ water, $v = 0.1 \text{ Vs}^{-1}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

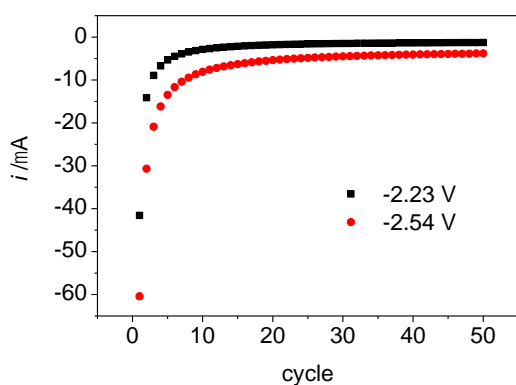


Figure S 15. Presentation of the peak current at selected potentials vs. cycles of the experiment of 1@MWCNT under CO_2 atmosphere in $dmf + 10\%$ water, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$, CV data are depicted in Figure 6.

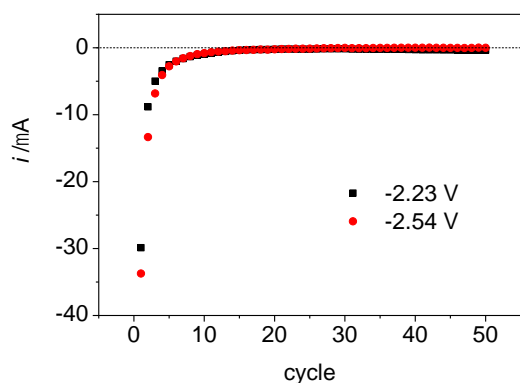


Figure S 16. Difference between the peak current under CO_2 atmosphere and under N_2 atmosphere at selected potentials vs. cycles; dmf +10% water, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$, CV data of the experiments are depicted in Figure 6 and Figure S 12.

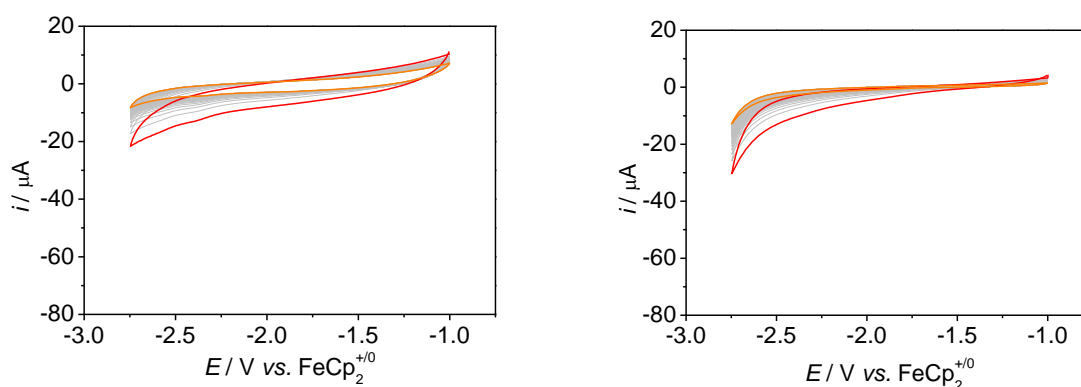


Figure S 17. 50 CV scans of bare MWCNT under N_2 (left) and CO_2 (right) atmosphere in dmf +10 % water, $\nu = 0.1 \text{ Vs}^{-1}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

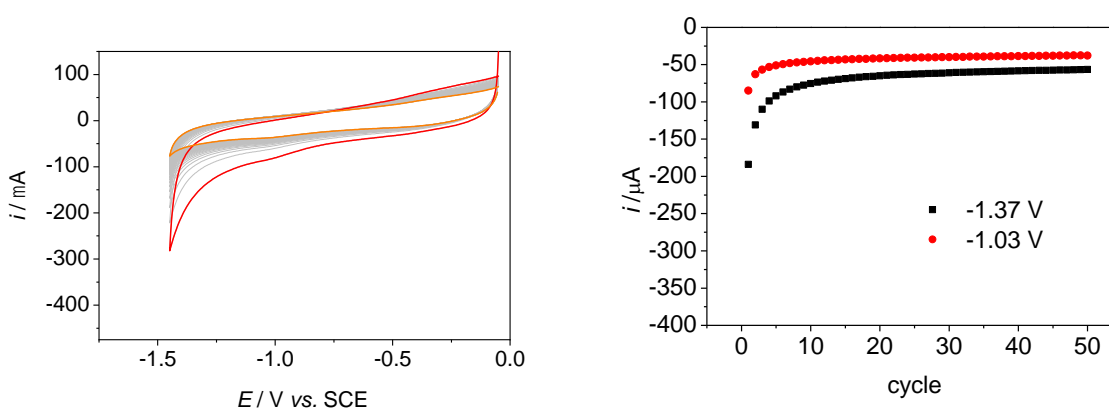


Figure S 18. Left: 50 CV scans of I@MWCNT under Ar atmosphere in water, 0.5 M NaHCO_3 ; right: current vs. cycles at the representative potentials of -1.03 and -1.37 V vs. SCE .

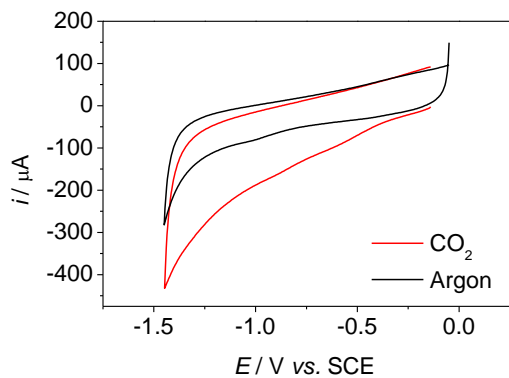


Figure S 19. CV of **1@MWCNT** under Ar and CO_2 atmosphere in water, $\nu = 0.1 \text{ Vs}^{-1}$, 0.5 M NaHCO_3 .

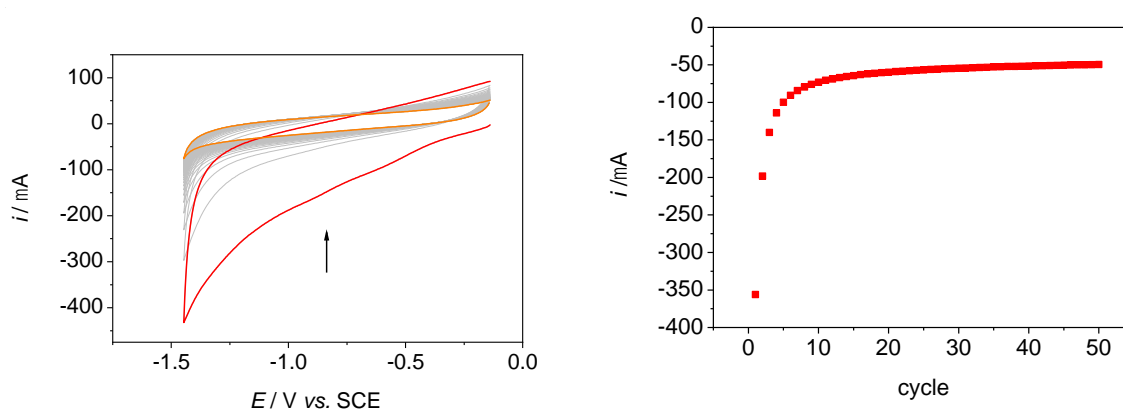


Figure S 20. Left: 50 CV scans of **1@MWCNT** under CO_2 atmosphere in water, 0.5 M NaHCO_3 ; right: current vs. cycles the representative potential of -1.37 V vs. SCE .

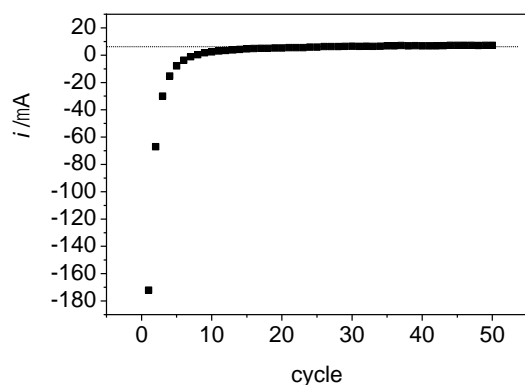


Figure S 21. Difference between the peak current under CO_2 atmosphere and under N_2 atmosphere at $-1.37 \text{ V (vs. SCE)}$ vs. cycles, water, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$, CV data of the experiments are depicted in Figure S 18 and Figure S 20.

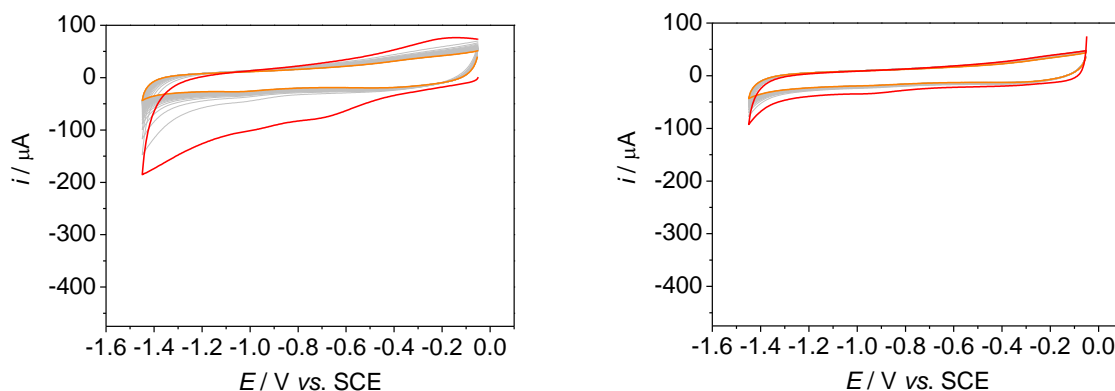


Figure S 22. 50 CV scans of bare MWCNT under N₂ (left) and CO₂ (right) atmosphere in water, 0.5 M NaHCO₃.

CPE measurements

In the CPE experiments, the counter electrode was separated from the bulk solution by a sample holder with a porous glass frit, a 3 mm glassy carbon rod was used as working electrode, and a Pt spiral electrode as counter electrode. In heterogeneous CPE experiments a 1 cm² GC plate coated with MWCNT was used as a working electrode. CO and H₂ were detected and quantified with a Shimadzu GC-2014 equipped with a thermal conductivity detector (TCD) and a ShinCarbon ST 80/100 silco column. Methane was used as an internal standard in order to determine n_{H_2} and n_{CO} . FE were calculated according to $n(\text{measured})_{\text{H}_2/\text{CO}}/(Q/2F)$, Q = electric charge. Calibration curves for CH₄/H₂ and CH₄/CO were determined separately by injecting known quantities of the mixtures.

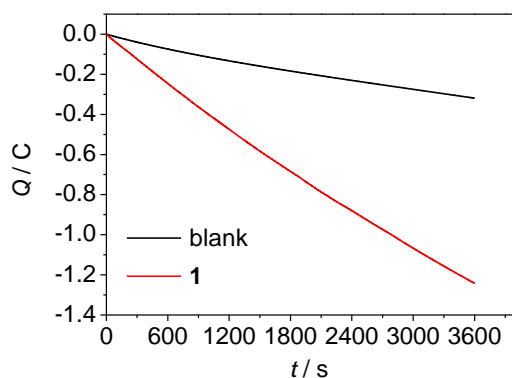


Figure S 23. Charge build-up during the electrolysis experiment ($E_{\text{appl.}} = -2.20$ V vs. FeCp₂⁺⁰) of **1** in dmf + 10% water under CO₂ atmosphere, $c_1 \sim 1$ mM, 0.1 M ⁿBu₄NPF₆.

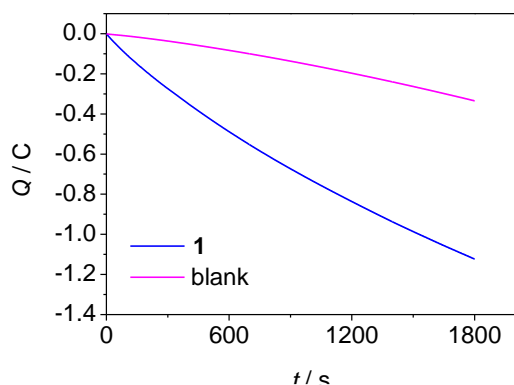


Figure S 24. Charge build-up during the electrolysis experiment ($E_{\text{appl.}} = -2.50 \text{ V vs. FeCp}_2^{+/0}$) of **1** in *dmf* + 10% water under CO_2 atmosphere, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

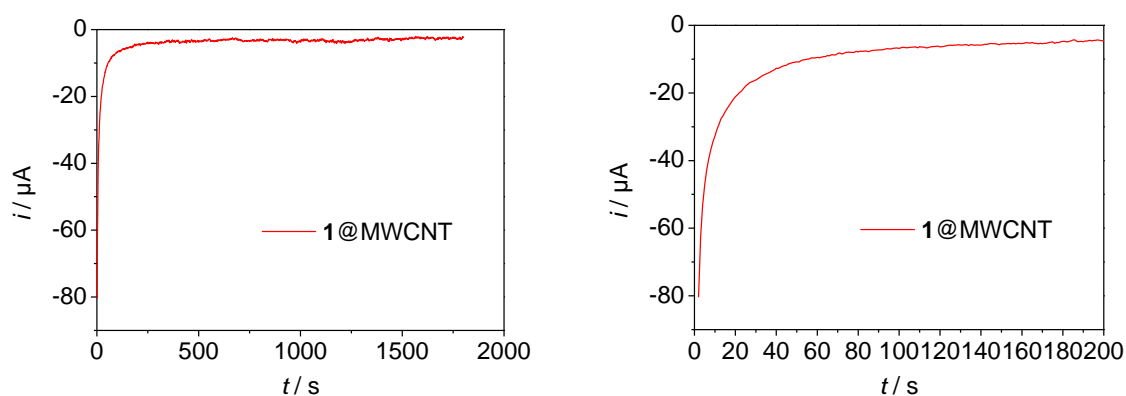


Figure S 25. Current versus time during the electrolysis experiment ($E_{\text{appl.}} = -2.20 \text{ V vs. FeCp}_2^{+/0}$) of **1@MWCNT** in *dmf* + 10% water, under CO_2 atmosphere, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$, $\Phi = 3 \text{ mm}$ disc electrode, the right graph is a magnification of the first 200 s.

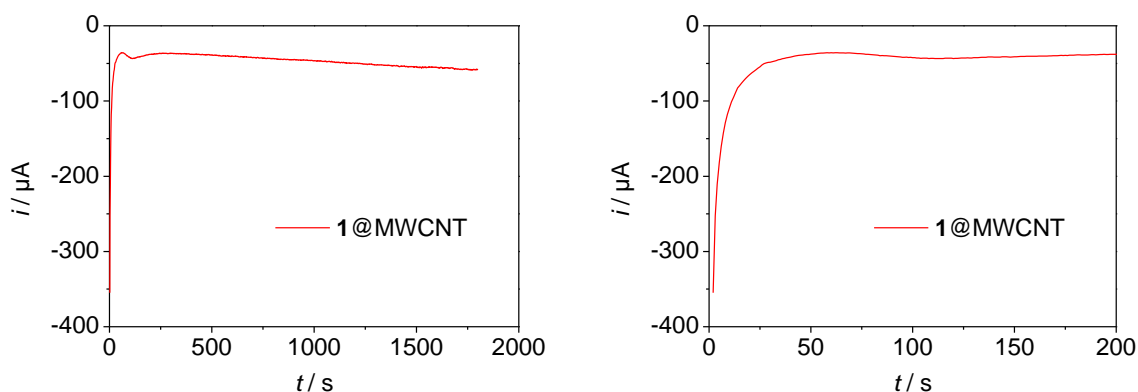


Figure S 26. Current versus time during the electrolysis experiment ($E_{\text{appl.}} = -1.37 \text{ V vs. SCE}$) of **1@MWCNT** in water under CO_2 atmosphere, 0.5 M NaHCO_3 , $\Phi = 3 \text{ mm}$ disc electrode, the right graph is a magnification of the first 200 s.

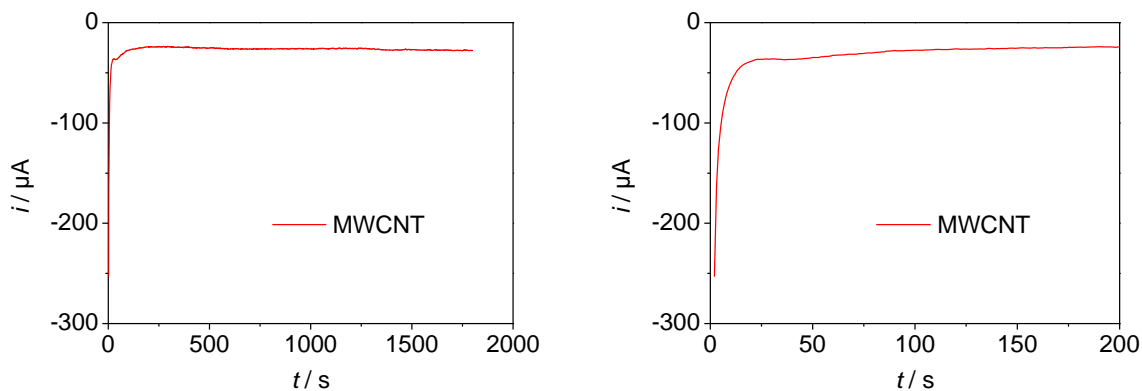


Figure S 27. Current versus time during the electrolysis experiment ($E_{\text{appl.}} = -1.37 \text{ V vs. SCE}$) of MWCNT in water under CO_2 atmosphere, 0.5 M NaHCO_3 , $\Phi = 3 \text{ mm}$ disc electrode, the right graph is a magnification of the first 200 s.

Table S 3. Results of the CPE experiments of **1** in $\text{dmf} + 10\%$ water under CO_2 atmosphere, $c_1 \sim 1 \text{ mM}$, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$. Average of two runs.

E / V^0	$FE(\text{CO}) / \%$	$FE(\text{H}_2) / \%$
-2.20	45 (71 μL)	35 (55 μL)
-2.50	30 (31 μL)	20 (18 μL)

Table S 4. Results of the 30 min CPE experiment of MWCNT in water under CO_2 atmosphere, 0.5 M NaHCO_3 .

$E / \text{V vs. SCE}$	$FE(\text{CO}) / \%$	$FE(\text{H}_2) / \%$
-1.37	0 (0 μL)	65 (48 μL)

IR-Spectroelectrochemical and IR Measurements

IR-SEC experiments were conducted in an OTTLE cell.⁸ The cell is equipped with a platinum working electrode, pseudo-Ag-reference electrode, and a platinum counter electrode. The IR spectra were recorded with a Bruker Vertex 70 IR spectrometer.

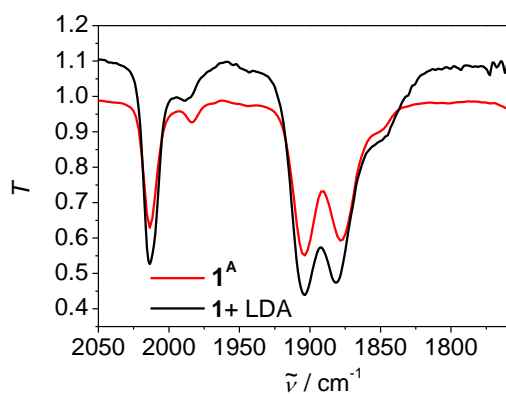


Figure S 28. IR spectra of 1^A (black) as recorded during IR-SEC of **1**, $0.1\text{ M } n\text{-Bu}_4\text{NPF}_6$, dmf, and IR of **1** + LDA (red).

SEM Images

A FEI Nova NanoSEM and a Nova Nano Lab 600 SEM was used for surface topology investigation.

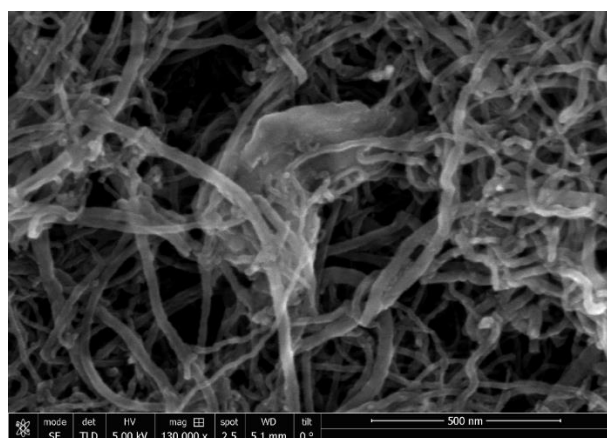


Figure S 29. SEM picture of the electrode surfaces after decorating with MWCNT.

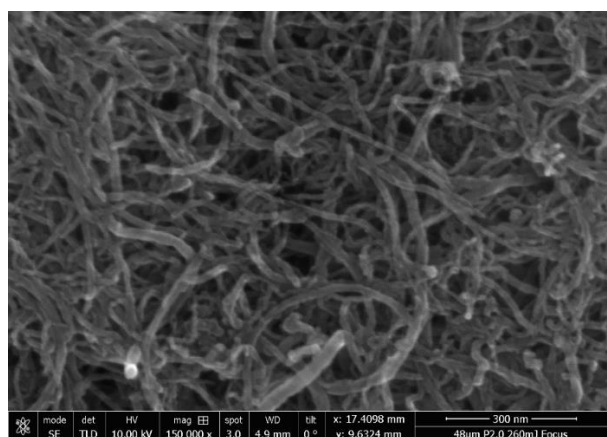


Figure S 30. SEM picture of the electrode surfaces after decorating with MWCNT and soaking in a solution of **1**.

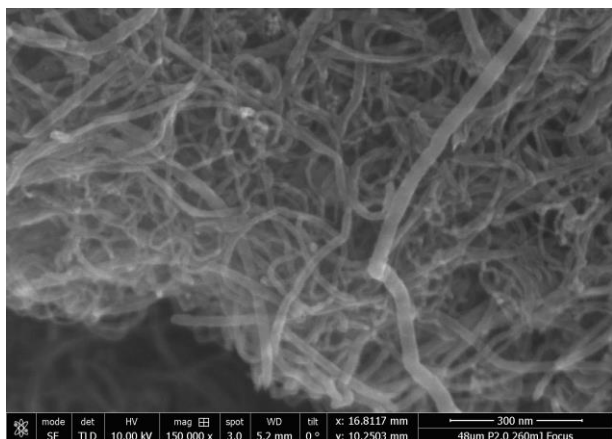


Figure S 31. SEM picture of the electrode surfaces after 7200 s of electrolysis under CO_2 -atmosphere; $\text{dmf} + 10\%$ water, $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

XPS Data

XPS data were collected using a hemispherical XPS analyser (SPECS PHOIBOS 100) with a monochromatic X-ray source (SPECS FOCUS 500 monochromator, $\text{Al } K_\alpha$ radiation, 1486.74 eV). Fine spectra were collected at a normal angle from the surface. The pass energy was set to 10 eV for fine spectra with step sizes of 0.05 eV.

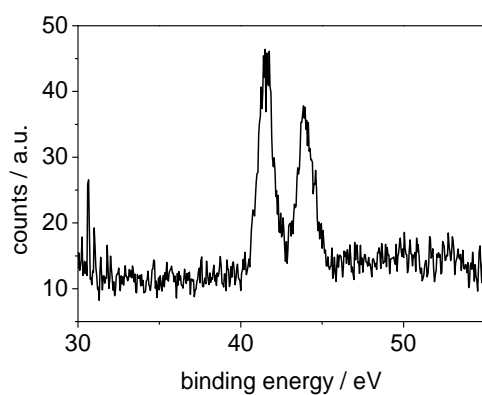


Figure S 32. XPS data at the Re edge of the electrode surface of **1**@MWCNT prior catalysis.

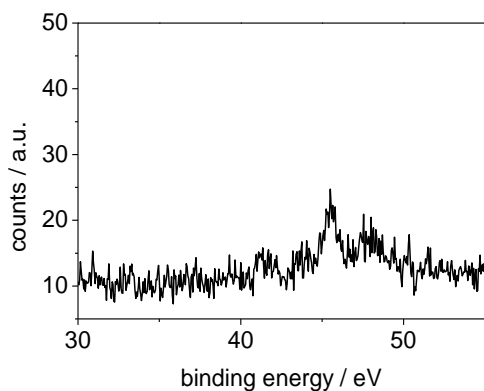


Figure S 33. XPS data at the Re edge of the electrode surface of **1**@MWCNT after 30 min. CPE experiment at -2.20 V vs. $Fc^{+/0}$ in dmf + 10% water under CO_2 atmosphere, 0.1 M nBu_4NPF_6 .

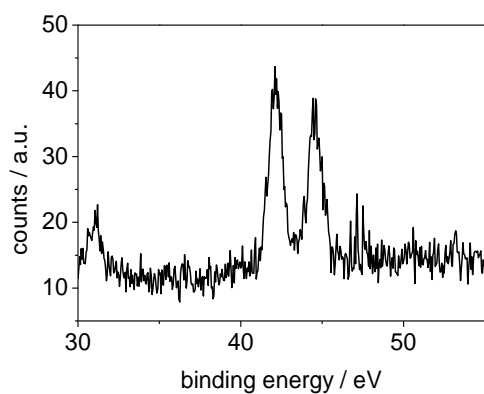


Figure S 34. XPS data at the Re edge of the electrode surface of **1**@MWCNT after 30 min. CPE experiment in water under CO_2 atmosphere, 0.5 M $NaHCO_3$.

NMR Spectrum

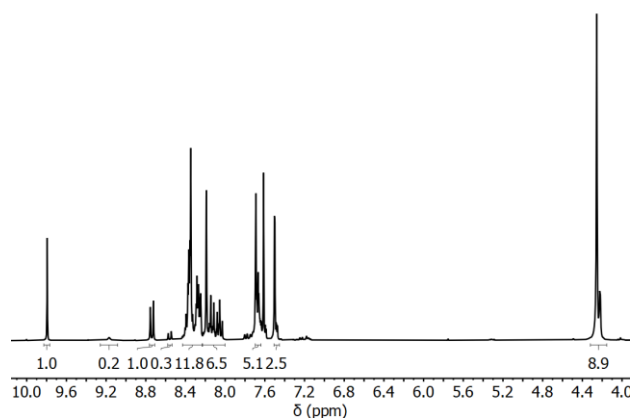


Figure S 35. 1H -NMR spectrum of **1** in $dms0-d_6$.

References

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- 1 A. Wilting, M. Kügler and I. Siewert, *Z. Anorg. Allg. Chem.*, 2015, **641**, 2498-2505.
 - 2 R. D. C. Gallo, K. S. Gebara, R. M. Muzzi and C. Raminelli, *J. Braz. Chem. Soc.* 2010, **21**, 770-774.
 - 3 G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **64**, 112–122.
 - 4 SADABS V2014/4, Bruker AXS Inc., Madison, WI, USA.
 - 5 (a) A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13. (b) P. van der Sluis, A. L. Spek, *Acta Cryst.* 1990, **A46**, 194-201.
 - 6 I. M. Kolthoff and M. K. Chantooni, *J. Phys. Chem.* 1972, **76**, 2024-2034.
 - 7 Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications*. 2nd ed.; Wiley: New York, **2001**.
 - 8 M. Krejčík, M. Danek and F. Hartl, *J. Electroanal. Chem. Interfacial Electrochem.* 1991, **317**, 179–187.