Rhenium Coordination-Induced Conformational Modulation in Nitrogen-Doped Nanographene

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1. General Information

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. All reagents and starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. Synthesis of nanographene **2**, **3**, **4a** and **4b** was already reported in our lab.¹ All solvents were distilled before use in the reactions. The reactions were usually carried out under a nitrogen atmosphere with magnetic stirring. NMR spectra were recorded with Varian NMR 200MHz, NMR JEOL 400MHz, Varian VNMRS 600MHz spectrometers at room temperature (unless otherwise noted). Proton assignment was carried out by 2D NMR experiments: COSY, NEOSY and REOSY where possible. High-resolution mass spectra (HRMS) were measured with a Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer. The emission and absorption spectra were measured in Jasco FP-8350 Spectrofluorometer and Jasco V-770 Spectrophotometer, respectively.

Cyclic voltammetry (CV) and Controlled potential electrolysis (CPE) were conducted using a Zahner Zennium pro instrument equipped with a three-electrode cell. using glassy carbon as the working electrode, Pt wire as the counter electrode, Ag/Ag⁺ electrode as the reference electrode at a scan rate of 100 mVs^{-1} . All measurements were referenced to ferrocene (Fc^{+/0}) as internal standard. Sample solutions, with 0.1 mM compound and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in THF was employed as the supporting electrolyte. Prior to each measurement, the solution was degassed by nitrogen bubbling for several minutes, and a continuous flow of nitrogen was maintained over the solution throughout the experiment.

Controlled-potential electrolysis (CPE) was conducted in a specially designed singlecompartment cell. This apparatus included a glassy carbon plate (15 mm x 10 mm x 1 mm) as a working electrode, a Pt wire counter electrode, and, Ag/Ag^+ reference electrode. The CPE experiments were performed in THF contain 0.5mM catalyst, 1.5 mM AcOH and 0.1 M TBAPF₆. The CPE solutions were purged with N₂ gas for 20 min before the electrolysis. Applied potentials in CPE experiments were determined by cyclic voltammetry. Gaseous products after the CPE experiments were analyzed using 1ml sample aliquots taken from the headspace of the electrochemical cell and injected on a Shimadzu NexisnGc-2030 gas chromatography instrument equipped with a BID detector using helium as a carrier gas at a flow rate of 10.68 mL/min.

2. Experimental Procedure



Scheme S1: Synthetic procedure for the synthesis of nanographene 2, 3, (P,P,M,M,M)-4 and (P,P,M,P,M)-4.

Compound 1 (50 mg, 0.04 mmol) was dissolved in a mixture of DCM and methanesulfonic acid (8:2), and was treated with 136 mg (0.6 mmol) of DDQ in an inert atmosphere for 12 hours at 0 °C. After completion of the reaction, it was quenched with addition of a saturated of NaHCO₃ solution, and extracted with CH₂Cl₂. The combined extracts were washed with brine, dried over anhydrous MgSO₄ and the solvent was evaporated in vacuo. The crude product was isolated by preparative thin layer chromatography (toluene: methanol, 25:1) to afford the desired compounds, **2**, **3**, (P,P,M,M,M)-**4**, and (P,P,M,P,M)-**4**.

Compound 1

¹H NMR (400 MHz, CDCl₃): δ 8.80(s, 4H^a), 8.08(s, 8H^b), 7.98(s,4H^e), 7.19(d, J= 8Hz, 8H^d), 6.99(d, J= 8Hz, 8H^c), 1.20 (s,36H^f), 0.59 (s,18H^g), ¹³C NMR (400 MHz, CDCl₃): δ 158.08, 155.92, 150.22, 146.15, 138.93, 138.77, 134.49, 133.47, 132.89, 131.33, 127.74, 126.59, 126.11, 124.98, 34.70, 34.52, 31.21, 31.05. HR-MS (ESI-TOF): m/z calcd. for C₈₈H₈₆N₈ [M+H]⁺: 1255.70475, found: 1255.70482.

Compound 2

¹H NMR (400 MHz, CD₂Cl₂): $\delta = 9.86$ (d, J=4Hz, 2H, H^b), 9.65 (s, 2H, H^a), 9.34 (s, 2H, H^d), 9.21 (d, J=4Hz, 2H, H^c), 8.8 (s, 2H, H^h), 8.32 (s, 4H, H^g), 7.52 (d, J=8Hz, 4H, H^f), 7.35 (d, J = 8Hz, 4H, H^e), 1.80 (s, 18H, Hⁱ), 1.49 (s, 18H, H^j), 1.43 ppm (s, 18H, H^k). ¹³C NMR (600 MHz, CD₂Cl₂): δ 158.36, 156.84,

156.33, 155.49, 151.03, 147.95, 143.96, 140.24, 139.30, 138.28, 134.89, 134.84, 133.98, 132.59, 132.33, 131.88, 130.17, 129.27, 128.79, 128.46, 127.83, 127.36, 126.69, 126.09, 125.53, 124.20, 123.31, 123.15, 122.0, 119.84, 119.46, 115.98, 39.10, 36.36, 34.91, 34.63, 31.98, 31.41. HR-MS (ESI-TOF): m/z calcd. for C₈₈H₇₆N₈ [M+H]⁺: 1245.6263, found: 1245.62657.

Compound 3

¹H NMR (600 MHz, CDCl₃): $\delta = 10.30(s, 1H, H^a/H^i), 10.29(s, 1H, H^a/H^i), 10.10(d, J=1.8Hz, 1H, H^b), 10.07(d, J=1.8Hz, 1H, H^s), 9.44(s, 1H, H^h), 9.43(s, 1H, H^g), 9.39(d, J=1.8Hz, 1H, H^c), 9.33(s, 1H, H^d), 9.31(s, 1H, H^q), 9.26(d, J=2.4Hz, 1H, H^r), 9.16(s, 1H, H^k), 8.84(s, 1H, H^i), 8.65(d, J=3Hz, 1H, H^j/H^l), 8.57(d, J=3Hz, 1H, H^1/H^i), 8.11(d, J=8.4Hz, 1H, H^e), 7.61-7.62(m, 2H, H^f and H^n/H^o), 7.48-7.46(m, 2H, H^o/H^n and H^m/H^p)7.16(dd, J=1.8, 7.8Hz, 1H, H^p/H^m), 1.89(s, 9H, H^u), 1.81(s, 9H, H^z), 1.60(s, 9H, H^w), 1.48(s, 9H, H^v), 1.45(s, 9H, H^x), 1.42(s, 9H, H^y).$ ¹³C NMR (600 MHz, CDCl₃): δ 159.03, 157.92, 157.10, 156.98, 156.75, 155.73, 155.03, 153.10, 151.86, 151.42, 151.05, 147.78, 147.66, 144.22, 143.52, 140.70, 138.28, 136.24, 132.24, 131.89, 131.72, 131.61, 131.09, 130.12, 129.97, 129.78, 129.47, 129.37, 129.27, 128.84, 128.15, 127.92, 127.75, 127.61, 127.36, 126.61, 126.56, 126.44, 126.00, 125.93, 125.62, 124.38, 124.24, 123.28, 123.12, 122.73, 122.05, 121.76, 121.69, 121.59, 120.84, 119.9, 119.85, 119.5, 115.96, 115.88, 38.88, 38.57, 36.24, 36.20, 35.39, 34.80, 34.43, 34.10, 31.98, 31.96, 31.37, 31.32. HR-MS (ESI-TOF): m/z calcd. for C₈₈H₇₄N₈ [M+H]⁺: 1243.6093, found: 1243.6109.

Compound (P,P,M,M,M)-4

¹H NMR (600 MHz, CDCl₃): $\delta = 10.25$ (s, 2H, H^a), 10.1 (d, J=1.8Hz, 2H, H^b), 9.74 (s, 2H, H^h), 9.56 (s, 2H, Hⁱ), 9.47 (d, J=2.4Hz, 2H, H^g), 9.45 (d, J=1.8Hz, 2H, H^c), 9.422 (s, 2H, H^d), 8.21 (d, J = 9Hz, 2H, H^e), 7.68 (dd, J = 2.4, 8.7 Hz, 2H, H^f), 1.90 (s, 18H, H^j), 1.65 (s, 18H, H^l), 1.52 ppm (s, 18H, H^k), ¹³C NMR (600 MHz, CDCl₃): δ 157.84, 156.67, 156.07, 155.35, 151.75, 151.17, 150.87, 147.56, 143.47, 133.79, 132.86, 132.05, 130.70, 129.82, 129.22, 129.10, 129.02, 128.99, 127.65, 127.61, 127.53, 125.85, 124.40, 123.72, 123.19, 123.04, 121.85, 121.49, 120.82, 119.70, 118.95, 115.66, 38.73, 36.25, 35.45, 34.16, 32.02, 31.41. HR-MS (ESI-TOF): m/z calcd. for C₈₈H₇₂N₈ [M+H]⁺: 1241.5936, found: 1241.5953.

Compound (P,P,M,P,M)-4

¹H NMR (400 MHz, CDCl₃): δ = 10.40 (s, 2H, H^a), 10.19 (d, J=2Hz, 2H, H^b), 9.88 (s, 2H, H^h), 9.56 (s, 2H, Hⁱ), 9.53 (d, J=1.6Hz, 2H, H^c), 9.47 (d, J=2.4Hz, 2H, H^g), 9.29 (s, 2H, H^d), 8.18 (d, *J* = 9.2Hz, 2H, H^e), 7.763 (d, *J* = 10.8Hz, 2H, H^f), 1.90 (s, 18H, H^j), 1.66 (s, 18H, H^l), 1.45 ppm (s, 18H, H^k).

Synthesis of Compound 2Re, 3Re, 4Re.

In a 10 mL round-bottom flask, 0.44 mmol of Re(CO)₅Cl and 0.4 mmol of the Nanographene ligand **2**, **3** or **4** were combined with 5 mL of toluene, stirred under reflux for 4 hours. During reaction, the solution's color transitioned from orange-red to green. After the 4-hour reflux, the reaction mixture was taken off heat and allowed to cool. The solvent was subsequently removed and was purified using thin-layer chromatography with a Toluene:MeOH ratio of 25:1. The desired complex was obtained as a green solid.

2Re

Yield=64%.

¹H NMR (400 MHz, CD_2Cl_2): δ = 10.44 (s, 2H, H^a), 10.12 (d, J=2 H_Z, 2H, H^b), 9.38 (s, 2H, H^d), 9.38 (d, J=2 H_Z, 2H, H^c), 8.83(s, 2H, H^h), 8.34 (d, J=16 H_Z, 4H, H^g), 7.50 (m, 4H, H^f), 7.29 (m, 4H, H^e), 1.82 (s, 18H, Hⁱ), 1.44 (s, 18H, H^j), 1.41 ppm (s, 18H, H^k)

¹³C NMR (400 MHz, CD_2Cl_2): $\delta = 196.93$, 187.42, 157.95, 157.13, 156.59, 156.10, 151.44, 150.88, 148.73, 144.34, 140.22, 138.78, 131.74, 131.40, 131.38, 130.49, 128.80, 127.42, 126.67, 126.52, 126.46, 126.45, 123.60, 123.29, 120.32, 119.65, 114.78, 38.83, 36.24, 34.63, 34.30, 31.60, 31.11.

HRMS(([M-Cl]⁺) calculated for [M-Cl]⁺ = 1515.55982; detected [M-Cl]⁺: 1515.5638

FTIR v_{co} (cm⁻¹): 1903 (m), 1926 (m), and 2025 (s) in CH₂Cl₂

3Re1

Yield= (27%).

¹H NMR (600 MHz, CD₂Cl₂): $\delta = 10.45$ (s, 1H, H^a/H^t), 10.44(s, 1H, H^a/H^t), 10.17(d, J=2.4Hz, 1H, H^b), 10.13(d, J=1.8Hz, 1H, H^s), 9.561(d, J=1.8Hz, 1H, H^c), 9.44(d, J=2.4Hz 1H, H^g), 9.438(s, 1H, H^q), 9.429(s, 1H, H^d), 9.425(d, J=1.8Hz, 1H, H^r), 9.394(s, 1H, H^h), 9.123(s, 1H, H^k), 8.811(s, 1H, Hⁱ), 8.65(d, J=3Hz, 1H, H^j/H¹), 8.53(d, J=3Hz, 1H, H^l/H^j), 8.05(d, J=8.4Hz, 1H, H^e), 7.62-7.58(m, 2H, H^f and Hⁿ /H^o), 7.50(dd, J=1.8, 7.8Hz, 1H, H^o/Hⁿ), 7.46(dd, J=2.4, 7.8Hz, 1H, H^p/H^m), 7.16(dd, J=1.8, 7.8Hz, 1H, H^m/H^p), 1.87(s, 9H, H^u), 1.82(s, 9H, H^z), 1.57(s, 9H, H^w), 1.48(s, 9H, H^v), 1.45(s, 9H, H^x), 1.43(s, 9H, H^y).

¹³C NMR (600 MHz, CD₂Cl₂): δ = 197, 189, 159.32, 158.251, 157.492, 157.348, 157.11, 156.99, 155.41, 153.40, 152.24, 151.74, 151.71, 151.43, 149.006, 148.87, 145.13, 144.68, 141.04, 138.55, 138.51, 136.49, 136.26, 134.752, 132.66, 132.300, 132.13, 131.479, 131.168, 130.754, 130.589, 130.383, 129.904,

129.580, 129.541, 129.462, 129.396, 128.671, 128.320, 128.195, 127.561, 127.050, 126.935, 126.832, 126.732, 126.689, 126.483, 125.295, 124.976, 124.407,124.214, 123.855, 123.563, 123.128, 122.020, 121.957, 121.160, 120.720, 120.676, 119.933, 115.206, 39.32, 38.94, 36.59, 36.55, 35.59, 34.99, 34.623, 34.20, 31.93, 31.90, 31.42, 31.36.

HRMS(([M-Cl]⁺) calculated for [M-Cl]⁺: 1513.54417, found: 1513.5450.

FTIR v_{co} (cm⁻¹): 1903 (m), 1926 (m), and 2025 (s) in CH₂Cl₂

3Re2

Yield= (27%).

¹H NMR (600 MHz, CD₂Cl₂): $\delta = 10.45$ (s, 1H, H^a/H^t), 10.44(s, 1H, H^a/H^t), 10.17(d, J=1.8Hz, 1H, H^b), 10.129(d, J=1.8Hz, 1H, H^s), 9.56(d, J=2.4Hz, 1H, H^c), 9.45(d, J=1.8Hz 1H, H^g), 9.437(s, 1H, H^d), 9.428(s, 1H, H^q), 9.424(d, J=1.8Hz, 1H, H^r), 9.394(s, 1H, H^h), 9.12(s, 1H, H^k), 8.8(s, 1H, Hⁱ), 8.62(d, J=3Hz, 1H, H^j/H¹), 8.55(d, J=3Hz, 1H, H¹/H^j), 8.08(d, J=8.4Hz, 1H, H^e), 7.60-7.58(m, 2H, H^f and Hⁿ/H^o), 7.50(dd, J=1.8, 7.8Hz, 1H, H^o/Hⁿ), 7.43(dd, J=1.8, 7.8Hz, 1H, H^p/H^m), 7.18(dd, J=2.4, 7.8Hz, 1H, H^m/H^p), 1.88(s, 9H, H^u), 1.81(s, 9H, H^z), 1.58(s, 9H, H^w), 1.478(s, 9H, H^v), 1.45(s, 9H, H^x), 1.43(s, 9H, H^y).

¹³C NMR (600 MHz, CD₂Cl₂): $\delta = 197$, 188, 159.31, 158.241, 157.503, 157.394, 157.10, 156.976, 155.406, 153.366, 152.218, 151.73, 151.43, 149.022, 148.85, 145.23, 145.136, 144.524, 143.635, 141.070, 138.508, 136.491, 136.194, 134.70, 132.661, 132.319, 132.189, 131.471, 131.108, 130.767, 130.581, 130.391, 129.892, 129.637, 129.579, 129.538, 129.476, 129.411, 128.635, 128.139, 128.195, 127.580, 127.030, 126.932, 126.826, 126.729, 126.686, 126.465, 125.298, 125.140, 125.028, 124.420, 124.211, 123.849, 123.581, 123.103, 121.953, 121.205, 120.673, 119.93, 115.198, 39.30, 38.95, 36.59, 36.55, 35.59, 34.99, 34.623, 34.19, 31.94, 31.90, 31.42, 31.36.

HRMS(([M-Cl]⁺) calculated for [M-Cl]⁺: 1513.54417, found: 1513.5424.

FTIR v_{co} (cm⁻¹): 1903 (m), 1926 (m), and 2025 (s) in CH₂Cl₂

4Re1

Yield= (31%).

¹H NMR (600 MHz, CD_2Cl_2): δ = 10.46 (s, 2H, H^a/H^r), 10.19 (t, J=1.8, 2.4H_Z, 2H, H^b/H^q), 9.72 (s, 2H, H^h/H^k), 9.62 (dd, J=1.6 H_Z, 2H, H^c/H^p), 9.52-9.51(m, 2H, H^d/H^o), 9.51(s, 2H, Hⁱ/H^j), 9.48 (q, J=2.4, 1.8H_Z, 2H, H^a/H^k), 9.62 (dd, J=1.6 H_Z, 2H, H^c/H^p), 9.52-9.51(m, 2H, H^d/H^o), 9.51(s, 2H, Hⁱ/H^j), 9.48 (q, J=2.4, 1.8H_Z, 2H, H^k/H^k), 9.62 (dd, J=1.6 H_Z, 2H, H^c/H^p), 9.52-9.51(m, 2H, H^d/H^o), 9.51(s, 2H, Hⁱ/H^j), 9.48 (q, J=2.4, 1.8H_Z), 9.51(s, 2H, H^k/H^k), 9.62 (dd, J=1.6 H_Z, 2H, H^k/H^k), 9.52-9.51(m, 2H, H^k/H^k), 9.51(s, 2H, H^k/H^k), 9.48 (q, J=2.4, 1.8H_Z), 9.51(s, 2H, H^k/H^k), 9.

2H, H^g/H^l), 8.14 (m, J=2, 6.4H_Z, 2H, H^e/Hⁿ), 7.66(q, J=8.4, 9.6, 9H_Z, 2H, H^f/H^m), 1.90 (d, J=3 H_Z, 18H, H^s/H^x), 1.62 (d, J=2.4 H_Z, 18H, H^u/H^v), 1.51 ppm (d, J=4.8 H_Z, 18H, H^t/H^w)

¹³C NMR (600 MHz, CD_2Cl_2): $\delta = 197.15$, 196.35, 160.41, 158.14, 157.57, 157.07, 156.39, 152.72, 152.25, 152.10, 151.75, 151.72, 151.50, 151.47, 149.17, 148.93, 148.86, 144.43, 144.42, 143.80, 141.06, 140.91, 137.46, 136.34, 136.12, 133.85, 132.09, 130.68, 130.36, 129.57, 129.41, 129.17, 128.47, 127.91, 127.09, 126.77, 126.53, 125.28, 124.47, 123.81, 123.37, 121.71, 121.19, 120.80, 120.56, 119.95, 115.25, 39.07, 39.02, 36.62, 35.98, 35.76, 35.63, 34.29, 34.21, 31.96, 31.49, 31.42, 29.45.

 $HRMS(([M-C1]^+) \text{ calculated for } [M-C1]^+ = 1511.52852 \text{ ; detected } [M-C1]^+: 1511.5319.$

FTIR v_{co} (cm⁻¹): 1902 (m), 1926 (m), and 2025 (s) in CH₂Cl₂

4Re2

Yield= (41%).

¹H NMR (600 MHz, CD_2Cl_2): δ = 10.47 (s, 2H, H^a/H^r), 10.23 (s, 2H, H^b/H^q), 9.86 (s, 2H, H^h/H^k), 9.69 (d, J=1.8 H_Z, 2H, H^c/H^p), 9.54(s, 2H, Hⁱ/H^j), 9.50 (s, 2H, H^g/H^l), 9.42 (br, 2H, H^d/H^o), 8.18 (br, 2H, H^e/Hⁿ), 7.78 (br, 2H, H^f/H^m), 1.92 (s, 18H, H^s/H^x), 1.66 (s, 18H, H^u/H^v), 1.48 ppm (s, 18H, H^t/H^w)

¹³C NMR (600 MHz, CD_2Cl_2): $\delta = 197.18$, 158.14, 157.51, 157.28, 157.17, 157.08, 156.39, 156.25, 152.26, 152.10, 151.93, 151.76, 151.50, 149.16, 148.95, 145.09, 144.56, 144.44, 143.80, 136.32, 136.16, 133.83, 132.65, 132.10, 131.92, 131.09, 130.70, 130.37, 129.61, 129.57, 129.42, 129.16, 129.12, 128.55, 128.12, 127.97, 127.22, 127.10, 126.77, 126.55, 125.40, 125.34, 125.23, 124.47, 124.05, 123.82, 123.37, 123.26, 121.71, 121.20, 120.80, 120.75, 120.57, 120.29, 120.16, 119.94, 115.50, 115.25, 39.07, 39.00, 36.65, 35.76, 35.63, 34.30, 34.21, 32.00, 31.49, 31.42, 31.42, 29.45.

 $HRMS(([M-C1]^+) \text{ calculated for } [M-C1]^+ = 1511.52852 \text{ ; detected } [M-C1]^+: 1511.5279.$

FTIR v_{co} (cm⁻¹): 1902 (m), 1926 (m), and 2025 (s) in CH₂Cl₂



Figure S1. Pictorial representation of TLC image of the nanographene 4 reacting with $Re(CO)_5Cl$ using Toluene: MeOH (25:1) as the eluent.



Figure S2. All possible stereoisomers of 4Re2 contain nanographene moiety with C_2 symmetry.

Similar to the first band, the second band also consisted of four different structures **4Re2-a**, **4Re2a'**, **4Re2-b**, and **4Re2-b'** Compounds **4Re2-a** and **4Re2-b** are stereoisomers and differ in the orientation of the Cl atom, and **4Re2-a'** and **4Re2-b'** are also stereoisomers. Additionally, **4Re2-a'** and **4Re2-b'** are enantiomers of **4Re2-a** and **4Re2-b**, respectively.



Figure S3. Four different structures of **4Re2**. **4Re2-a** and **4Re2-a**' are enantiomers, and **4Re2-b** and **4Re2-b**' are also enantiomers.



Figure S4. Pictorial representation of TLC image of the nanographene **3** reacting with $Re(CO)_5Cl$ using Toluene: MeOH (25:1) as the eluent.









Figure S5. Possible structure of **3Re1** and **3Re2**.

3. NMR spectra



Figure S6. ¹H NMR spectrum of compound **1** in CDCl₃ (400 MHz, 298 K)



Figure S7. ¹³C NMR spectrum of compound 1 in CDCl₃ (400 MHz, 298 K)



Figure S8. ¹H NMR spectrum of compound **2** in CD₂Cl₂ (400 MHz, 298 K)



Figure S9. ¹³C NMR spectrum of compound **2** in CD₂Cl₂ (600 MHz, 298 K)





Figure S10. ¹H NMR spectrum of compound **3** in CDCl₃ (600 MHz, 298 K)



Figure S11. ¹³C NMR spectrum of compound **3** in CDCl₃ (600 MHz, 298 K)





Figure S12. ¹H NMR spectrum of compound (P,P,M,M,M)-4_ in CDCl₃ (600 MHz, 298 K)



Figure S13. ¹³C NMR spectrum of compound (P,P,M,M,M)-4 in CDCl₃ (600 MHz, 298 K)





Figure S14. ¹H NMR spectrum of compound (**P**,**P**,**M**,**P**,**M**)-4 and (**P**,**P**,**M**,**M**,**M**)-4 (80/20) in CDCl₃ (400 MHz, 298 K)







Figure S16. ¹H-¹H NEOSY spectrum of compound **2Re** in CD₂Cl₂ (400 MHz, 298 K)





Figure S17. ¹³C NMR spectrum of compound **2Re** in CD₂Cl₂ (400 MHz, 298 K)





Figure S18. ¹H NMR spectrum of compound **3Re1** in CD₂Cl₂ (600 MHz, 298 K).



Figure S19. ¹H-¹H COSY spectrum of compound **3Re1** in CD₂Cl₂ (600 MHz, 298 K).





Figure S20. ¹H-¹H REOSY spectrum of compound **3Re1** in CD₂Cl₂ (600 MHz, 298 K).





Figure S21. ¹³C NMR spectrum of compound **3Re1** in CD₂Cl₂ (600 MHz, 298 K).







Figure S22. ¹H NMR spectrum of compound **3Re2** in CD₂Cl₂ (600 MHz, 298 K).



Figure S23. ¹H-¹H COSY spectrum of compound **3Re2** in CD₂Cl₂ (600 MHz, 298 K).





Figure S24. ¹H-¹H REOSY spectrum of compound **3Re2** in CD₂Cl₂ (600 MHz, 298 K).





Figure S25. ¹³C NMR spectrum of compound **3Re2** in CD₂Cl₂ (600 MHz, 298 K).





Figure S26. ¹H NMR spectrum of compound **4Re1** in CD₂Cl₂ (600 MHz, 298 K).


Figure S27. ¹H-¹H REOSY spectrum of compound **4Re1** in CD₂Cl₂ (600 MHz, 298 K).





Figure S28. ¹H NMR spectrum of compound **4Re2** in CD₂Cl₂ (600 MHz, 298 K).



Figure S29. ¹H-¹H REOSY spectrum of compound 4Re2 in CD₂Cl₂ (600 MHz, 298 K).





Figure S30. ¹³C NMR spectrum of compound **4Re2** in CD₂Cl₂ (600 MHz, 298 K).





Figure S31. Comparison of NMR spectrum nanographene (**P**,**P**,**M**,**P**,**M**)-4 with the compound 4Re2 in CDCl₃ (400 MHz, 298 K).





Figure S32. Comparison of NMR spectrum of compound **2Re** synthesized at a) 110° C and b) 40° C in CDCl₃ (400 MHz, 298 K).





Figure S33. Comparison of NMR spectrum of compound **4Re1** synthesized at a) 110° C and b) 40° C in CDCl₃ (400 MHz, 298 K).

b)





Figure S34. Comparison of NMR spectrum of compound **4Re2** synthesized at a) 110° C and b) 40° C in CDCl₃ (400 MHz, 298 K).



Figure S35.Conversion of **4Re1** to **4Re2** monitored by ¹H NMR. The red dots represent the peaks corresponding to **4Re1**, and the black triangles represent the peaks corresponding to **4Re2**. [**4Re**] represent the molar ratio of compound **4Re1** at $H_{10.46ppm}$.



Figure S36. Conversion of **4Re2** to **4Re1** monitored by ¹H NMR. The red dots represent the peaks corresponding to **4Re**, and the black triangles represent the peaks corresponding to **4Re2**. [**4Re2**] represent the molar ratio of compound **4Re2** at $H_{10.47ppm}$.

Similar to compounds **4Re1** and **4Re2**, compounds **3Re1** and **3Re2** were also challenging to isolate via chromatography due to their rapid interconversion at room temperature in solution. The interconversions of **3Re1** to **3Re2** and **3Re2** to **3Re1** reached a 1:1 ratio within 34 hours, with no additional changes noted over an extended period (Figures S28 and S29). The racemization rates of the ligands (**4a** and **4b**) were experimentally determined using ¹H NMR spectroscopy. However, in the metal complexes (**4Re1**, **4Re2**, **3Re1**, and **3Re2**), each band consists of multiple isomers, making it challenging to accurately calculate the isomerization barrier for the nanographene-based metal complexes.



Figure S37. Conversion of **3Re1**, to **3Re2** monitored by ¹H NMR. The red dots represent peaks corresponding to **3Re1**, and the black triangles represent peaks corresponding to **3Re2**. [**3Re1**] represent the molar ratio of compound **3Re1** at $H_{8.66ppm}$.



Figure S38. Conversion of **3Re2** to **3Re1** monitored by ¹H NMR. The red dots represent peaks corresponding to **3Re1**, and the black triangles represent peaks corresponding to **3Re2**. [**3Re2**] represent the molar ratio of compound **3Re2** at $H_{8.62ppm}$

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msa 2 re 1 (-85 C) single_pulse									JJ	N				





Figure S39. Variable temperature ¹H NMR spectrum of the mixture of compound **4Re1** and **4Re2** (50/50) in CD₂Cl₂(400 MHz). The red dots represent peak corresponding to **4Re1**, and black triangles represent peak corresponding to **4Re2**. At lower temperatures, the peaks of compound **4Re2** marked H^{h/k}, H^{c/p}, H^{d/o}, H^{f/m}, H^{e/n}, H^{s/x}, H^{t/w} and H^{u/v}that appeared broad at room temperature are split into two separate peaks.

4. Mass Spectra



Figure S40. High resolution mass spectrum of compound 1



Figure S41. High-resolution mass spectrum of compound 2



Figure S42. High-resolution mass spectrum of compound 3



Figure S43. High resolution mass spectrum of compound (P,P,M,M,M)-4



Figure S44. High-resolution mass spectrum of 2Re



Figure S45. High-resolution mass spectrum of 3Re1



Figure S46. High-resolution mass spectrum of 3Re2



Figure S47. High-resolution mass spectrum of 4Re1



Figure S48. High-resolution mass spectrum of 4Re2

5. Optical properties

Table S1: Characterization of the absorption spectra of compounds 4Re1, 4Re2, 3Re1, 3Re2, and 2Re.

Compound	$\lambda_{abs}^{max}/nm (\mathcal{E}/M^{-1}cm^{-1})$
4Re1	233(67300), 281(50400), 328(32500), 373(30600), 423(45300), 450(32800),
	510(12200), 590(7500), 636(9200)
4Re2	233(65900), 275(50600), 325(35100), 389(35000), 418(43700), 470(23200),
	502(13200), 590(6800), 636(8700)
3Re1	233(64100), 266(52900), 309(36200), 367(31000), 414(39000), 458(22200),
	490(13700), 585(7100), 629(9160)
3Re2	233(70400), 265(57600), 310(39600), 370(33800), 414(44100), 459(24300),
	490(14900), 585(7600), 629(10100)
2Re	233(65400), 255(56100), 307(31100), 354(31200), 394(43200), 451(20500),
	481(15800), 576(8200), 619(10200)

6. Electrochemical study



Figure S49. CVs of a) **2Re**, b) **3Re** and c) **4Re**, recorded at 100 mV/s, under N_2 in THF with 0.1 M TBAPF₆ supporting electrolyte.



Figure S50. CV of Re(bpy)(CO)₃Cl, recorded at 100 mV/s, under N_2 in THF with 0.1 M TBAPF₆ supporting electrolyte.



Figure S51. CV of nanographene 2, recorded at 100 mV/s, under N_2 in THF with 0.1 M TBAPF₆ supporting electrolyte.



Figure S52. CV of nanographene **3**, recorded at 100 mV/s, under N_2 in THF with 0.1 M TBAPF₆ supporting electrolyte.



Figure S53. CV of nanographene 4, recorded at 100 mV/s, under N_2 in THF with 0.1 M TBAPF₆ supporting electrolyte.

Under electrochemical conditions that were both acid-saturated and scan rate-independent, the rate constant for H₂ evolution (k_{obs} or TOF_{max}) was determined using the following equation 1.^{2, 3}

$$\frac{I_{cat}}{I_P} = \frac{2}{0.4463} \sqrt{\frac{RTk_{obs}}{Fv}}$$
(1)

where v is the scan rate, i_{cat} is the catalytic peak current, i_p is the non-catalytic peak current, n is the number of electrons transferred (two for hydrogen evolution), R is the universal gas constant, T is the temperature, and F is Faraday's constant.

The overpotential can be calculated using the following equation $2.^4$ The calculation of overpotential was performed according to the reported methods. The following equation was used for the determination of the reaction standard potential in V with respect to the Fc⁺/Fc couple:

$$E_{\rm H^+/H^2} = -0.440 \ \rm V - 0.059 \ \rm Pk_a \tag{2}$$

using $E^{\circ}_{H^+/H^2} = -0.440 \text{ V}$ (vs Fc⁺/Fc)) in THF,⁵ pK_a of 22.48 for acetic acid in THF.⁶

$$E_{H^{+}/H^{2}}(CH_{3}COOH) = -1.76V \text{ vs Fc}^{+}/Fc$$
overpotential is $\eta = \left| E_{cat/2} - E_{H^{+}/H^{2}} \right|$
(2)

Faradaic efficiency (FE), also referred to as faradaic yield, is a measure of the actual product obtained compared to the theoretical product that could have been generated based on the charge passed during the experiment. This calculation was determined using a specific equation 3.⁷

$$FE = \frac{2Fn}{Q} \times 100 \tag{3}$$

Within this equation, the variable n represents the moles of H_2 produced, which was determined through the gas chromatograph analysis. F stands for Faraday's constant, while Q represents the total charge passed during the experiment. Similarly, the Total turnover numbers (TON) resulting from the experiment were calculated using a specific equation 4.8





Figure S54. CVs of a) **2Re**, b) **3Re** and c) **4Re**, recorded at variable scan rate under argon in THF with 0.1 M TBAPF₆ supporting electrolyte.



Figure S55.CVs of **2Re** (a), **3Re** (b) and **4Re** (c) under N_2 saturation without AcOH (black) and with 1.5 mM AcOH (red).



Figure S56. Linear sweep voltammograms of 2Re (red), 3Re (green), 4Re (blue), and blank (black) underN2saturationwith1.5mMAcOH.



Figure S57. CV current enhancement effects on a) **2Re**, b) **3Re** and c) **4Re** induced by the incremental addition of AcOH, were recorded at 100 mV/s.



Concentration of AcOH (mM) Figure S58. Plot of i_{cat}/i_p versus acetic acid concentration for compound a) **2Re**, b) **3Re** and c) **4Re**. Currents were extracted from voltammogram such as those shown in Figure S43

Under electrochemical conditions that were both acid-saturated and scan rate-independent, the rate constant for H_2 evolution (k_{obs} or TOF_{max}) was calculated.

$$k_{obs} = \left(\frac{I_{cat}}{I_p}\right)^2 \frac{0.4463^2 \times F \times \nu}{2^2 \times R \times T}$$

For compound 2Re

$$k_{obs} = (4.70)^2 \frac{0.4463^2 \times 96485 \times 0.1}{2^2 \times 8.314 \times 298}$$
$$= 4.28 \text{ s}^{-1}$$

For compound **3Re**

$$k_{obs} = (3.80)^2 \frac{0.4463^2 \times 96485 \times 0.1}{2^2 \times 8.314 \times 298}$$
$$= 2.8 \text{ s}^{-1}$$

For compound 4Re (-1.85 V)

$$k_{obs} = (1.99)^2 \frac{0.4463^2 \times 96485 \times 0.1}{2^2 \times 8.314 \times 298}$$
$$= 0.77 \text{ s}^{-1}$$

For compound 4Re (-2.03 V)

$$k_{obs} = (2.19)^2 \frac{0.4463^2 \times 96485 \times 0.1}{2^2 \times 8.314 \times 298}$$

 $= 0.93 \text{ s}^{-1}$

For compound 4Re (-2.25 V)

$$k_{obs} = (2.52)^2 \frac{0.4463^2 \times 96485 \times 0.1}{2^2 \times 8.314 \times 298}$$
$$= 1.23 \text{ s}^{-1}$$



Figure S59. CV current enhancement effects as a function of a) 2Re, b) 3Re and c) 4Re concentration. Under an atmosphere of N₂, CVs of 2Re, 3Re and 4Re at 0.1 mM (black), 0.2 mM (red), 0.3 mM (blue), 0.4mM (pink) and 0.5 mM (green) were recorded at 100 mV/s. inset, linear relationship of catalytic current with respect to catalyst concentration.

Compound	E _{applied} (V)	Time (hr)	Charge (coulombs)	Moles of H ₂	FE _{H2} (%)	TON
2Re	-2.13	6	4.5143	1.03E-05	44	6.05
3Re	-2.03	6	5.16	5.94E-6	22	3.4
4 D a	-1.93	6	3.99	5.72E-06	28	3.3
4Ke	-2.13	6	10.48	3.83E-06	7	2.3

Table S2. Summary of results from CPE experiment

Catalyst	Solvent	Acid Source	Overpotential	TOF	Faradaic	References
			η		Efficiency	
					(%)	
А	MeCN/H ₂ O	$DMF(H)^+$	1200 mV	$1.6 \times 10^{6} \text{ s}^{-1}$	90	9
В	DMF	HBF ₄	580 mV	110 s ⁻¹	77	10
С	MeCN	CH ₃ COOH	530 mV	4200 s ⁻¹	87	11
D	DMF	Trifluoroacetic	580 mV	1.54 h ⁻¹	58	12
F	DMF/H ₂ O	СН.СООН	360 mV	652 s ⁻¹	86	13
E F	MeCN	СН.СООН	500 mV	5400 s^{-1}	93	14
G	MeCN	p-cyanoanilinium tetrafluoroborate	400 mV	5.3 ×10 ³ s ⁻¹		15
Н	MeCN	CH ₃ COOH	590 mV	200 s ⁻¹		16
Ι	MeCN	Bromoanilinium	160 mV	160 s ⁻¹	96	17
		tetrafluoroborate				
J	MeCN	CF ₃ COOH	770 mV	$102 \ s^{-1}$		18
K	CH ₃ CN	CH ₃ COOH	20 mV		50	19
L	DMF	CH ₃ COOH	838 mV	450 h ⁻¹		20
М	MeCN	CH ₃ COOH	394 mV	$5.07 \ s^{-1}$	19	21
N	MeCN	CH ₃ COOH	270 mV	155 s ⁻¹	85	22
О	THF	<i>para</i> - toluenesulfonic acid monohydrate	390 mV	4640 s ⁻¹	91.7	23
Р	MeCN	CH ₃ COOH	670 mV	414 s ⁻¹		24
Q	MeCN	CH ₃ COOH	260 mV	1200 s ⁻¹		25
R	MeCN	CH ₃ COOH	300 mV	14.2 s ⁻¹	95	26
S	DMF	pentafluorophenol	1170 mV	$103 \ s^{-1}$	94	4
Т	MeCN	CH ₃ COOH	130 mV	$4 \times 10^2 \text{ s}^{-1}$	80	27
U	THF	CH ₃ COOH	265 mV	1240 s ⁻¹	99	28
V	THF	CH ₃ COOH	133 mV	1.23 s ⁻¹	28	This work

Table S3. Comparison of the catalytic HER performances of Nanographene Re complexes with other reported Catalyst

A: [Ni(P₄N₂)(CH₃CN)]²⁺

B: [Co(bapbpy)Cl]⁺ (bapbpy: 6,6 ' -bis(2-aminopyridyl)-2,2 ' -bipyridine)

C: Ni (diacetyl-bis(*N*-4-methyl-3-thiosemicarabzone)

D: [Ni(bpy)(mp)] (mp = 2-hydroxythiophenol)

 $E: [Co(4-tolyl-tpy)_2]^{2+} (4-tolyl-tpy=2, 6-di(pyridin-2-yl)-4-p-tolylpyridine)$

 $F: Co^{-NHC}U$

G: $[Co(N_4H)Cl_2]^+$

H: $[Co(HBMIM^{Ph2})_2]^{2+}$ (HBMIM^{Ph2} = bis(1-methyl-4,5-diphenyl-1H-imidazol-2-yl)methane)

I: $[Co(P^{tBu}_2N^{Ph}_2)(CH_3CN)_3](BF_4)_2$

J: $[Mn_2(CO)_7(\mu - S_2NC_7H_4)_2]$

K: $[Co^{III}(L^2)MeOH]$ (H₃L²=6,6 ' -(((2-((3,5-di-tert-butyl-2- hydroxybenzyl)amino)-4,5 dinitrophenyl)azanediyl) bis(methylene)) bis(2,4-di-tert-butylphenol)

L: Co-BPNC-PPh₃ (BPNC=5,15-bis(pentafluorophenyl)-10-(4-N-(triphenylphosphoranylidene)- 2,3,5,6-tetrafluorophenyl) corrole).

 $M: [Co(bpaq)(OH_2)](ClO_4)_2 \quad (bpaq = 2 - (bis(pyridin - 2 - ylmethyl)amino) - N - (quinolin - 8 - yl)acetamide).$

N: cobalt-protic-NHC complexes (*NHC*= 6-(*1H-imidazol-1-yl*) pyridin-2-amine)

O: bimetallic palladium salixpyrrole complex

P: $[Fe_2(\mu-9-fluorenethiol)_2(CO)_6]$

Q: Diacetyl-2-(4-methyl-3 -thiosemicarbazato)-3-(2-pyridinehydrazonato))palladium(II)

R: $[Co(L_2)_2](ClO_4)_2$, $2CH_3CN$, $0.5H_2O$ ($L_2= 2$, 6-bis-(1-methoxycarbonylmethyl-1H-1, 2, 3-triazol-4-

yl)isonicotinate methyl ester)

S: Ni($^{p-tbu}$ dhbpy) ($^{p-tbu}$ dhbpy(H2)=2,2'-([2,2'-bipyridine]-6,6'-diyl)bis(4-(tert-butyl)phenol))

T: $[Cp*CoL^1Cl](PF_6)$ (Cp*=1,2,3,4,5-Pentamethylcyclopentadienyl, $HL^1[BF_4]=1$ -Ethyl-3-methyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium tetrafluoroborate)

U: [Ni(bdt)(dppf)] (bdt = 1,2-benzenedithiolate, dppf = 1,1' -bis(diphenylphosphino)ferrocene)

V: Nanographene-Re

7. Gas Chromatography



Figure S60. Gas chromatogram of bulk electrolysis catalyzed by compound **2Re** at an applied potential of -2.13 V.



Figure S61. Gas chromatogram of bulk electrolysis catalyzed by compound **3Re** at an applied potential of -2.03 V.



Figure S62. Gas chromatogram of bulk electrolysis catalyzed by compound **4Re** at an applied potential of -1.93 V.



Figure S63. Gas chromatogram of bulk electrolysis catalyzed by compound **4Re** at an applied potential of -2.13 V.

8. FT-IR Spectroscopy



Figure S64. FT-IR Spectrum of Compound 4Re1 (black), 4Re2 (red), 3Re1 (green), 3Re2 (blue) and 2Re (magenta) measured in CH_2Cl_2 .
9. X-ray crystallography



Figure S65. Crystal structures of compounds **4Re1-a** (a, b), **4Re1-a**' (c, d), **4Re1-b** (e, f), and **4Re1-b**' (g, h) with 50% thermal ellipsoids. Color code: carbon atoms, gray ellipsoids; chlorine atoms, green ellipsoids; nitrogen atoms, blue ellipsoids; oxygen atoms, red ellipsoids; ruthenium atoms, cyan ellipsoids. The hydrogen atomswere omitted for clarity.



Figure S66. Crystal structure of compound **4Re1** (a), nanographene (**P**,**P**,**M**,**M**,**H**)-**4** (b).



Figure S67. Crystal structure of compound 2Re (a), nanographene 2 (b).

	Compound 2Re	Compound 4Re1
Identification code	Ic22236_sq	ic21912_tw_sq
Empirical formula	C98 H88 Cl3 N8 O3 Re	C91 H72 Cl N8 O3 Re
Formula weight	1718.31	1547.21
Temperature/K	100(2)	100(2)
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
a/Å	24.5780(7)	20.0184(6)
b/Å	35.7337(9)	21.3728(7)
c/Å	21.4113(6)	22.6375(8)
a/°	90	83.5455(17)
β/°	102.6239(14)	74.0558(17)
γ/°	90	79.7460(17)
Volume/Å ³	18350.2(9)	9143.4(5)
Z	8	4
Pcalc	1.244 Mg/m ³	1.124 Mg/m ³
μ/mm ⁻¹	3.797	3.236
F(000)	7056	3160
Crystal size/mm ³	0.020 x 0.015 x 0.010	0.100 x 0.050 x 0.010
Θ range for data collection/°	2.22 to 69.92	2.034 to 79.791
Reflections collected	200105	65624
Independent reflections	17365 [R(int) = 0.1162]	65624 [R(int) = ?]
Data/restraints/parameters	17365/504/1068	65624/349/1994
eGoodness-of-fit on F ²	1.021	0.868
Final R indexes [I>=2 σ (I)]	R1 = 0.0620, wR2 = 0.1594	R1 = 0.0761, wR2 = 0.2091
Final R indexes [all data]	R1 = 0.0967, wR2 = 0.1799	R1 = 0.1458, wR2 = 0.2756
Largest diff. peak/hole / e Å-3	3.054 and -1.218	1.898 and -1.623
CCDC number	2422960	2422959

Table S4: Crystal data and experimental details for compound **2Re** and **4Re**.

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