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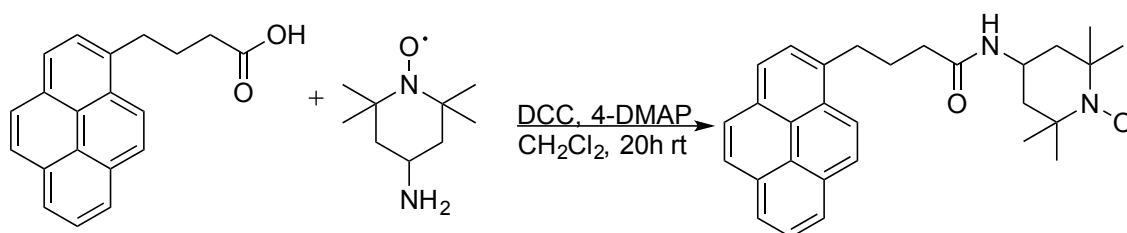
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I. Experimental section

1. General considerations

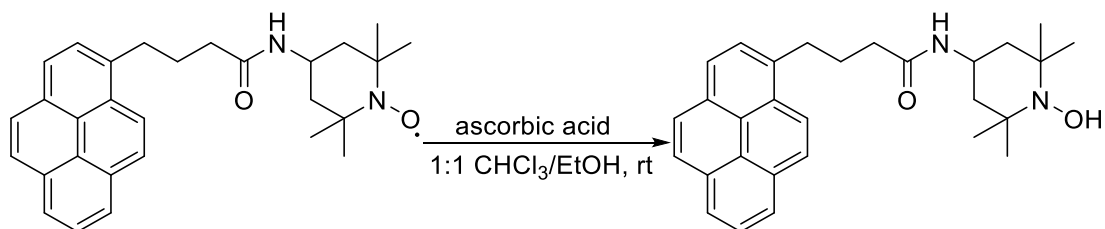
All chemicals and solvents were purchased from commercially available sources and used without further purification. MWCNTs were purchased from Cheaptubes.com. Plain carbon cloth was purchased from Fuel Cell Store. Dry solvents were obtained from a solvent purification system using columns of Al₂O₃ under argon. ¹H and ¹³C NMR spectra were obtained with Bruker Avance-400 MHz with residual solvent peaks or tetramethylsilane used as the internal reference. Multiplicities are described using the following abbreviations: s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, hept = heptet. ESI mass spectra were recorded using a Thermo Q Exactive™ Plus mass spectrometer. SEM images were collected using a LEO 1530 scanning electron microscope.

2. Synthesis of pyrene-TEMPO.



Pyrene-2-butanoic acid (864 mg, 3 mmol) was weighed into in a 3-necked flask under nitrogen atmosphere. A degassed solution of 4-amino-TEMPO (513 mg, 3 mmol in 60 mL dry DCM) was added to the flask and the mixture was stirred for 30 min at room temperature. At this point, a clear orange solution was observed. N,N'-Dicyclohexylcarbodiimide (DCC) (879 mg, 3 mmol) and 4-dimethylamino pyridine (36.6 mg, 0.3 mmol) were added to the above solution and stirred for an additional 20 h at room temperature.^[1] On progression of the reaction, a white precipitate of N,N'-dicyclohexylurea (DCU) was observed. The reaction mixture was filtered, and the solvent was evaporated under vacuum to obtain the crude product. The crude product was then purified by silica gel flash column chromatography (3:7 hexanes and ethyl acetate). The solid product was obtained by evaporation of the solvent under reduced pressure. Yield 1.198 g (90%). ESI-MS (M+H)⁺: 442.22 (Calcd. 442.26). IR (ν/cm⁻¹): 3322.10, 1643.66, 1535.29.

3. Reduction of pyrene-TEMPO.



The radical form of pyrene-TEMPO was reduced by using ascorbic acid as the reducing agent. In a typical procedure, 50 mg (0.11 mmol) of the pyrene-TEMPO was dissolved in 3 mL 1:1 chloroform/ethanol. After that, ascorbic acid solution (50 μ L solution containing 30 mg ascorbic acid) was added to the above solution under nitrogen and the mixture was stirred at room temperature for 30 min.^[2] The reaction mixture was then diluted with 20 mL nitrogen saturated deionized water and extracted with dichloromethane (2 x 5 mL). The combined organic mixture was then dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to afford the colorless crude product. The crude product was further purified by silica gel (60 mesh) column using a solvent mixture of 3:2 hexane/ethyl acetate. Yield: 43 mg (86%). ¹H NMR (400 MHz, CDCl₃): δ 8.30 (d, J = 9.2 Hz, 1H), 8.17 (dd, J = 7.7, 2.4 Hz, 2H), 8.12 (d, J = 7.8 Hz, 2H), 8.00 (t, J = 7.6 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 5.04 (bs, 1H), 4.17 (bs, 1H), 3.40 (s, 2H), 2.22 (s, 4H), 1.80 (dd, J = 12.2, 3.7 Hz, 2H), 1.19 (s, 6H), 1.14 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 171.84, 135.88, 131.48, 130.95, 130.01, 128.87, 127.55, 127.48, 126.81, 125.95, 125.16, 125.05, 125.02, 124.86, 123.45, 60.49, 59.03, 45.69, 41.03, 36.14, 32.73, 32.48, 27.38, 21.15, 19.71, 14.29.

4. Electrochemistry.

a) Cyclic voltammetry experiments. Electrochemical experiments were performed with a Pine WaveNow PGstat or a BASi epsilon potentiostat. Cyclic voltammetry (CV) experiments under homogeneous condition were performed using a three-electrode setup with glassy carbon (GC) working electrode (3 mm diameter), platinum wire auxiliary electrode and Ag/AgCl (3 M KCl) as the reference electrode (all electrodes from BASi). The GC electrode was polished with 0.05 micron alumina before each experiment.

b) Preparation of GC-MWCNTs electrodes. The MWCNT-functionalized GC electrode was prepared as follows: MWCNTs (1 mg) were suspended in ethanol (10 mL) containing 0.02 wt% Nafion® and sonicated for 30 minutes. 10 μ L of this suspension was drop-casted onto the GC electrode and then dried under vacuum.

c) Surface immobilization of pyrene-TEMPO. A solution of 5 mM pyrene-TEMPO was prepared in acetonitrile. To this solution, GC-MWCNTs electrode was dipped and kept for 15 min. The GC-MWCNTs electrode was then taken out and washed with water and acetonitrile (1

mL) and dried under vacuum. This GC-MWCNTs electrode with surface immobilized pyrene-TEMPO was used for CV experiments.

d) Preparation of CC-MWCNTs electrodes. Carbon-cloth (CC) electrode impregnated with MWCNTs was prepared by the following way. A suspension of MWCNTs (2 mg) was prepared 20 mL ethanol containing 0.02 wt% Nafion®. A 3 cm x 2 cm strip of CC was dipped into the suspension and soaked for 30 min. Then the CC was removed, washed with ethanol and dried at 80 °C.

e) Controlled potential electrolysis experiments. Controlled potential coulometry experiments were performed in a 20 mL undivided cell using a three-electrode setup with a 3 cm x 2 cm CC-MWCNT working electrode, a Pt-wire auxiliary electrode and a Ag/AgCl reference electrode. To the cell was added 9.9 mL solution of 0.2 M carbonate/bicarbonate buffer solution (1:1 mixture of Na₂CO₃ and NaHCO₃) followed by benzyl alcohol (1 mmol) and 0.1 mL acetonitrile solution of 5 mM pyrene-TEMPO. For certain substrates that are insoluble in water, a 4:1 water/acetonitrile mixture was used as the solvent. Upon addition of the pyrene-TEMPO solution, the mixture became slightly cloudy. The electrolysis was performed at an applied potential of 0.7 V vs Ag/AgCl. At the end of electrolysis (when current became <0.1 mA), the reaction mixture was extracted three times with diethyl ether or ethyl acetate. The combined organic layers were then washed with saturated sodium bicarbonate and dried over anhydrous sodium sulfate. Evaporation of the organic solvent under reduced pressure gave the product. For low boiling products, evaporation was performed at 0 °C in an ice-bath.

In case of 4-trifluoromethyl benzyl alcohol, the reaction mixture was extracted with chloroform-D. The organic layer was washed with saturated sodium bicarbonate, dried over anhydrous sodium sulfate and the NMR spectrum was recorded. The yield of the product was obtained using 1,3,5-trimethoxybenzene as the external standard.

In order to determine the amount of carboxylic by-product formed in the reactions, the reactions were repeated with a modified work-up at the end of the reaction. The crude reaction mixture was acidified with 2 M HCl until the pH was ~4. Then, 0.3 equiv of 1,3,5-trimethoxybenzene (with respect to substrate) was added, and the mixture was extracted three times with diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure (for low boiling products, evaporation was performed at 0 °C in an ice-bath) and NMR spectra were recorded using chloroform-D as solvent. Most of the substrates gave <5% carboxylic acid byproduct. An exception was 4-trifluoromethyl benzyl alcohol, which generated 10% of the corresponding benzoic acid byproduct.

f) Comparison of the activity between pyrene-TEMPO and 4-acetamido-TEMPO for oxidation of benzyl alcohol by CV (Figure 4). A glassy-carbon electrode with surface-immobilized pyrene-TEMPO was prepared following same method as described above (sections 4b and c). CV experiments were performed in 5 mL 0.2 M NaHCO₃/Na₂CO₃ (1:1) at a scan rate

of 20 mV s⁻¹, and then in presence of 0.1 M benzyl alcohol in the same buffer solution. In another experiment, 2.5 mM 4-acetamido-TEMPO in 5 mL 0.2 M NaHCO₃/Na₂CO₃ (1:1) was used. This 2.5 mM 4-acetamido-TEMPO gave similar anodic current as observed for surface immobilized pyrene-TEMPO when cyclic voltammograms were recorded by using glassy carbon working electrode at 20 mV s⁻¹ scan rate. Now to this solution 0.5 mmol was added and cyclic voltammogram was recorded at the same scan rate.

g) Comparison of the activity between pyrene-TEMPO and 4-acetamido-TEMPO for oxidation of benzyl alcohol by electrolysis (Figure 5). Electrolysis experiment using pyrene-TEMPO (0.05 mol%) was performed following the procedure as described above (section 4e) using 0.1 M benzyl alcohol in 10 mL 0.2 M NaHCO₃/Na₂CO₃ (1:1) and 3 cm x 2 cm CC-MWCNT working electrode. Another electrolysis experiment was performed using 4-acetamido-TEMPO in place of pyrene-TEMPO under same set of reaction conditions.

h) Oxidation of rosuvastatin precursor alcohol. Rosuvastatin precursor alcohol (353 mg, 1 mmol) was dissolved in 10 mL 0.2 M NaHCO₃/Na₂CO₃ (1:1) in acetonitrile/water (1:1). The electrolysis was performed using a 3-electrode setup as mentioned above (section 4e) at an applied potential of 0.7 V vs Ag/AgCl. At the end of the electrolysis, acetonitrile was evaporated and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The solvent was evaporated to afford a light yellow solid which was purified by using a silica gel column (30/70 EtOAc/hexanes mixture) to obtained white product. Yield: 320 mg (91%). ¹H NMR (400 MHz, CDCl₃) δ 9.96 (s, 1H), 7.64 - 7.60 (m, 2H), 7.22 (t, *J* = 8.6 Hz, 2H), 4.00 (hept, *J* = 6.7 Hz, 1H), 3.63 (s, 3H), 3.54 (s, 3H), 1.31 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 190.69, 179.24, 170.00, 164.66 (d, *J*_{C-F} = 252.7 Hz), 159.00, 132.83 (d, *J*_{C-F} = 8.8 Hz), 132.33 (d, *J*_{C-F} = 3.3 Hz), 119.71, 116.18 (d, *J*_{C-F} = 22.0 Hz), 42.73, 33.30, 32.20, 21.90. Spectral properties are consistent with literature values.^[3]

II. Characterization of aldehyde products.

Benzaldehyde. The electrolysis was performed in 99:1 water/acetonitrile mixture. The reaction mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 99.8 mg (91%) of the title compound as colorless oil. Faradaic yield: 87%. ¹H NMR (400 MHz, CDCl₃): δ 10.02 (s, 1 H), 7.88 (d, *J* = 7.9, 2H), 7.63 (t, *J* = 7.6, 1 H), 7.53 (t, *J* = 7.5, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 192.43, 136.44, 134.50, 129.78, 129.04. Spectral properties are consistent with literature values.^[4]

p-tolualdehyde. The electrolysis was performed in 99:1 water/acetonitrile mixture. The reaction mixture was extracted with diethyl ether (3x5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 112.6 mg (93%) of the title compound as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 9.95 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* =

7.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.18, 145.72, 134.34, 130.00, 129.84, 22.04. Spectral properties are consistent with literature values.^[5]

4-methoxy benzaldehyde. The electrolysis was performed in 99:1 water/acetonitrile mixture. The reaction mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 132.5 mg (97%) of the title compound as a light yellow oil. Faradaic yield: 92%. ^1H NMR (400 MHz, CDCl_3): δ 9.87 (s, 1H), 7.83 (d, $J = 8.8$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.03, 164.78, 132.17, 130.11, 114.49, 55.77. Spectral properties are consistent with literature values.^[6]

4-bromobenzaldehyde. The electrolysis was performed in 99:1 water/acetonitrile mixture. The reaction mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 168.4 mg (91%) of the title compound as a white solid. Faradaic yield: 91%. ^1H NMR (400 MHz, CDCl_3) δ 9.98 (s, 1H), 7.75 (d, $J = 8.5$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 191.13, 135.07, 132.47, 131.00, 129.81. Spectral properties are consistent with literature values.^[6]

4-chlorobenzaldehyde. The electrolysis was performed in 99:1 water/acetonitrile mixture. The reaction mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 134 mg (95%) of the title compound as a white solid. Faradaic yield: 85%. ^1H NMR (400 MHz, CDCl_3) δ 9.97 (s, 1H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.08, 141.13, 134.87, 131.09, 129.64. Spectral properties are consistent with literature values.^[6]

4-(methylthio)benzaldehyde. The electrolysis was performed in 99:1 water/acetonitrile mixture. The reaction mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure at 0 °C gave 145.6 mg (95%) of the title compound as pale yellow oil. Faradaic yield: 87%. ^1H NMR (400 MHz, CDCl_3) δ 9.91 (s, 1H), 7.76 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.40, 148.08, 133.11, 130.16, 125.35, 14.84. Spectral properties are consistent with literature values.^[3]

4-(trifluoromethyl)benzaldehyde. The electrolysis was performed in 99:1 water/acetonitrile mixture. At the end of electrolysis, it was extracted with CDCl_3 . The CDCl_3 layer was then washed with saturated sodium bicarbonate and dried over dry sodium sulfate and NMR spectra were recorded. The yield of the product was determined by NMR spectroscopy using 1,3,5-trimethoxy benzene as an external standard. Yield: 85% (based on NMR). Faradaic yield: 87%.

^1H NMR (400 MHz, CDCl_3): δ 10.10 (s, 1H), 8.01 (d, $J = 7.7$ Hz, 2H), 7.80 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 191.32, 138.83, 135.81 (q, $J_{\text{C-F}} = 32.8$ Hz), 130.12, 126.32 (q, $J_{\text{C-F}} = 3.8$ Hz), 123.63 (d, $J_{\text{C-F}} = 272.9$ Hz). Spectral properties are consistent with literature values.^[5]

4-Nitrobenzaldehyde. The electrolysis was performed in 4:1 water/acetonitrile mixture. The reaction mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 113.6 mg (74%) of the title compound as a pale yellow solid. Faradaic yield: 78%. ^1H NMR (400 MHz, CDCl_3) δ 10.15 (s, 1H), 8.39 (d, $J = 8.6$ Hz, 2H), 8.07 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.52, 151.30, 140.22, 130.68, 124.50. Spectral properties are consistent with literature values.^[6]

Piperonaldehyde. The electrolysis was performed in 4:1 water/acetonitrile mixture. The reaction mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 141.4 mg (94%) of the title compound as a pale yellow liquid. Faradaic yield: 85%. ^1H NMR (400 MHz, CDCl_3) δ 9.81 (s, 1H), 7.41 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.33 (d, $J = 1.6$ Hz, 1H), 6.93 (d, $J = 7.9$ Hz, 1H), 6.08 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.32, 153.10, 148.69, 131.85, 128.69, 108.35, 106.89, 102.14. Spectral properties are consistent with commercially available compound.

2-chloro-6-fluoro-benzaldehyde. The electrolysis was performed in 4:1 water/acetonitrile mixture. The reaction mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 162 mg (1.02 mmol, >98% y) of the title compound as light yellow oil. Faradaic yield: 88%. ^1H NMR (400 MHz, CDCl_3): δ 10.46 (s, 1H), 7.50 (td, $J = 8.2, 5.7$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 1H), 7.11 (t, $J = 9.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 186.88 (d, $J_{\text{C-F}} = 2.9$ Hz), 163.17 (d, $J_{\text{C-F}} = 264.9$ Hz), 137.03 (d, $J_{\text{C-F}} = 3.7$ Hz), 135.13 (d, $J_{\text{C-F}} = 10.7$ Hz), 126.73 (d, $J_{\text{C-F}} = 3.9$ Hz), 121.73 (d, $J_{\text{C-F}} = 9.7$ Hz), 115.60 (d, $J_{\text{C-F}} = 21.6$ Hz). Spectral properties are consistent with literature values.^[4]

2,4,6-Trimethylbenzaldehyde. The electrolysis was performed in 4:1 water/acetonitrile mixture. The reaction mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 135.7 mg (91%) of the title compound as a pale yellow liquid. Faradaic yield: 87%. ^1H NMR (400 MHz, CDCl_3): δ 10.56 (s, 1H), 6.90 (s, 2H), 2.58 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 193.19, 144.03, 141.68, 130.71, 130.14, 21.66, 20.70. Spectral properties are consistent with literature values.^[6]

2-iodobenzaldehyde. The electrolysis was performed in 4:1 water/acetonitrile mixture. The reaction mixture was extracted with ethyl acetate (3x5 mL). The combined organic layers were

then washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave 205.2 mg (88%) of the title compound as yellow oil. Faradaic yield: 82%. ¹H NMR (400 MHz, CDCl₃): δ 10.07 (d, *J* = 0.8 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.47 (t, *J* = 7.5, 1H), 7.29 (td, *J* = 7.6, 1.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ = 195.80, 140.65, 135.50, 135.10, 130.26, 128.73, 100.74. Spectral properties are consistent with literature values.^[3]

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III. Figures

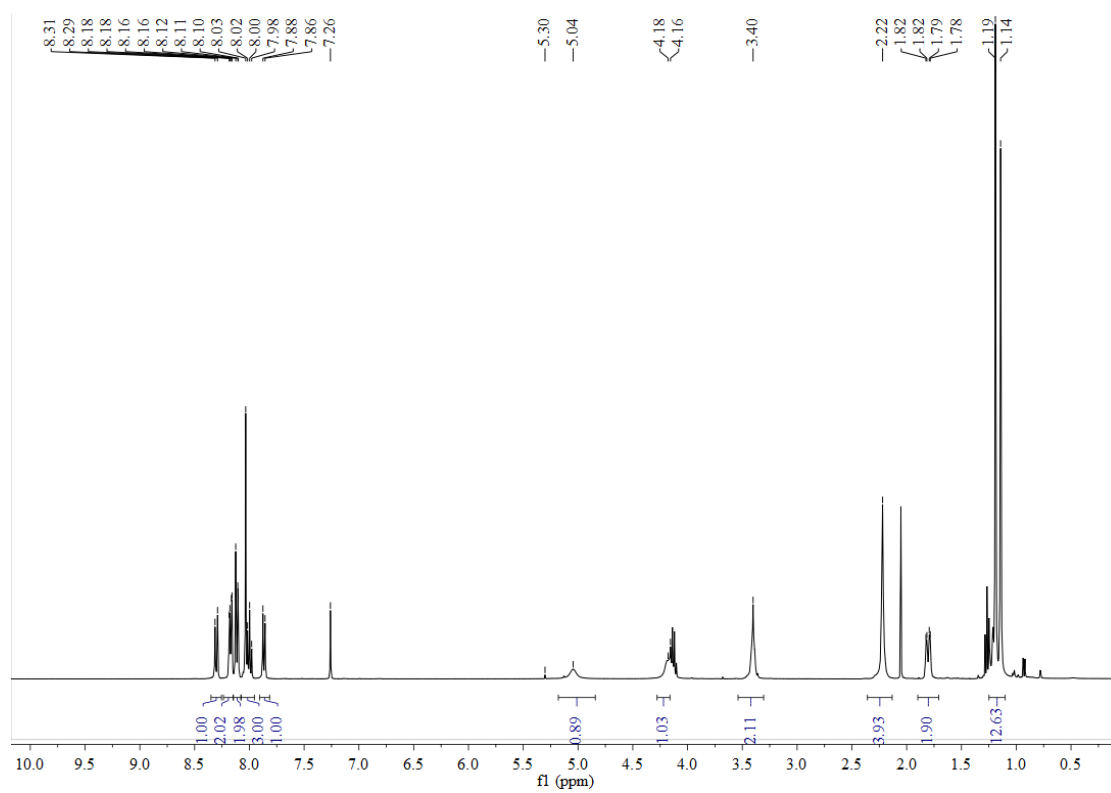


Figure S1. ^1H NMR of pyrene-TEMPOH in CDCl_3 .

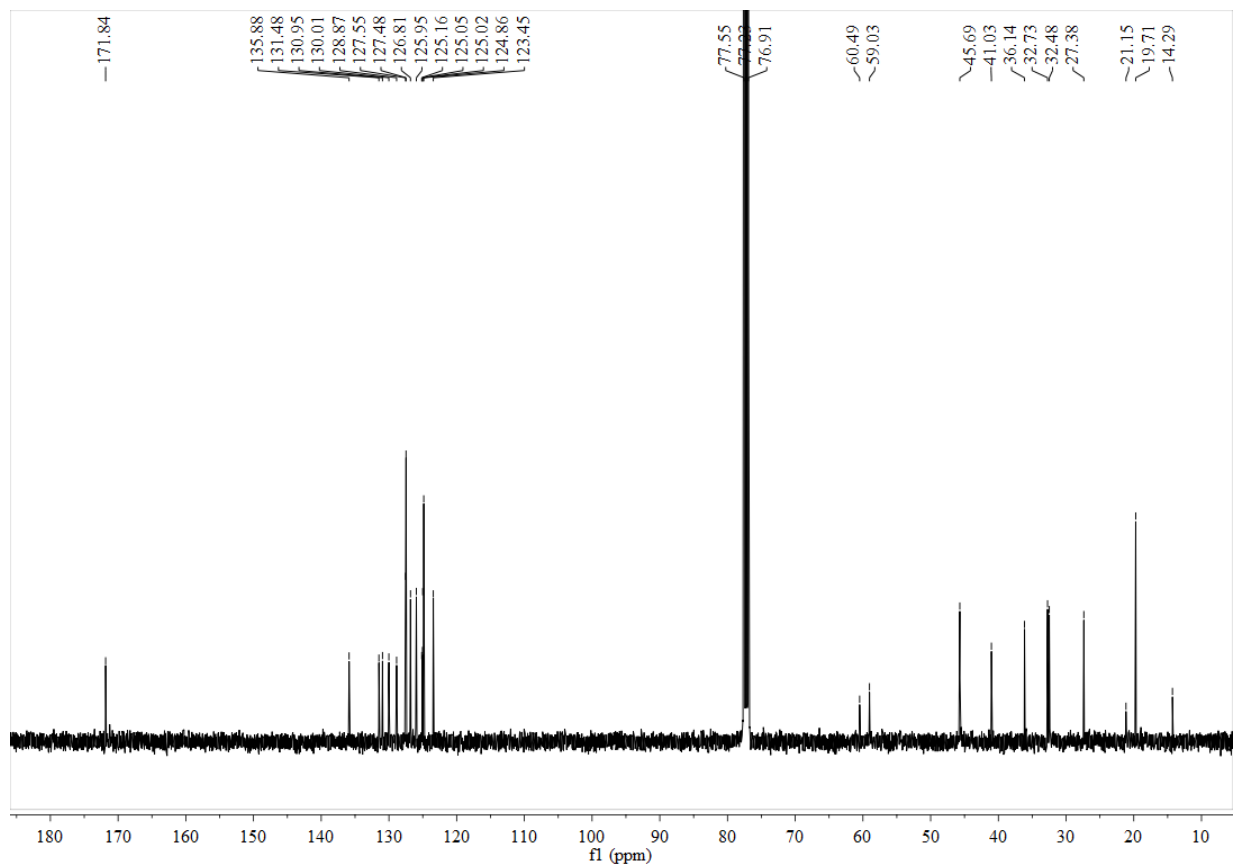


Figure S2. ^{13}C NMR of pyrene-TEMPOH in CDCl_3 .

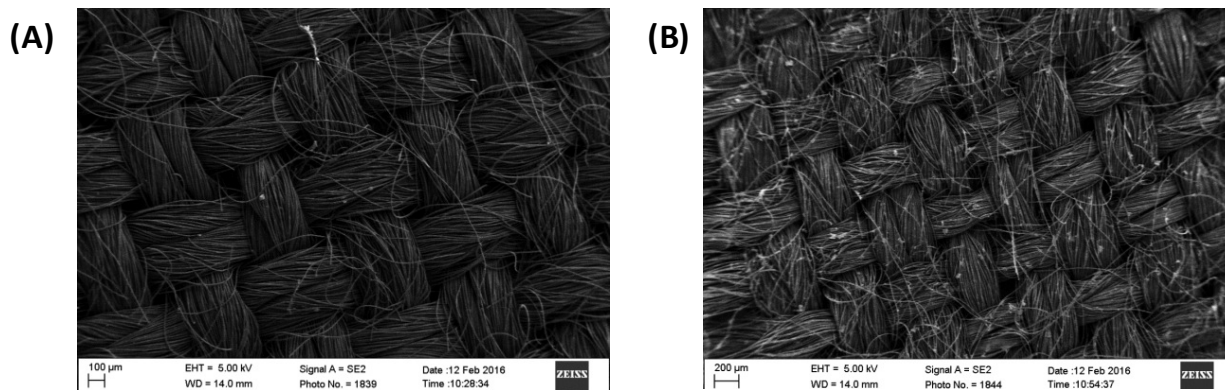


Figure S3. SEM images of (A) bare carbon cloth electrode and (B) carbon cloth with MWCNTs.

IV. ^1H and ^{13}C NMR spectra of the products

