

Supporting Information

High-Density Assembly of Gold Nanoparticles with Zwitterionic Carbon Nanotubes and Their Electrocatalytic Activity in Oxygen Reduction Reaction

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Contents

1. Instruments

2. Materials

2.1. Syntheses of Homopolymeric PolyZWION and PolyVBIM(Cl)

Scheme S1. Synthetic methods of materials

2-1-1. Synthesis of 1-butyl-3-vinylimidazolium chloride (**S1**)

2-1-2. Synthesis of 3-(1-vinyl-1*H*-imidazolium-3-yl)propane-1-sulfonate (**S2**)

2-1-3. Synthesis of homopolymeric PolyVBIM(Cl)

2-1-4. Synthesis of homopolymeric polyZWION

2.2. Preparation of Imidazolium salt-functionalized MWCNTs

2-2-1. Preparation of carboxylic acid functionalized MWCNTs

2-2-2. Preparation of PolyVBIM(Cl)-*f*-MWCNTs.

2-2-3. Preparation of PolyZWION-*f*-MWCNTs

Figure S1. TGA of Pristine MWCNTs, PolyZWION-*f*-MWCNTs, PolyVBIM(Cl)-*f*-MWCNTs

2.3. Synthesis of an aqueous AuNPs solution and assembly with imidazolium salt functionalized CNTs.

Figure S2. Photos for the aqueous solution of (1) AuNPs as prepared and (2)-(6) a mixture of AuNPs with (a) COOH-*f*-MWCNT, (b) PolyZWION-*f*-MWCNTs, and (c) PolyVBIM(Cl)-*f*-MWCNTs

Figure S3. XRD of AuNP@COOH-*f*-MWCNTs, AuNP@PolyVBIM(Cl)-*f*-MWCNTs, and AuNP@PolyZWION-*f*-MWCNTs

Figure S4. XPS of AuNP@COOH-*f*-MWCNTs, AuNP@PolyVBIM(Cl)-*f*-MWCNTs, and AuNP@PolyZWION-*f*-MWCNTs

3. Electrochemical measurements

Figure S5. RDE polarization curves obtained from (a) AuNP@COOH-*f*-MWCNTs, (b) AuNP@PolyVBIM(Cl)-*f*-MWCNTs, and (c) AuNP@PolyVIMPS-*f*-MWCNTs electrodes at different rpms.

Figure S6. ¹H NMR (DMSO-*d*₆) spectrum of 1-butyl-3-vinylimidazolium chloride

Figure S7. ¹³C NMR (DMSO-*d*₆) Spectrum of 1-Butyl-3-vinylimidazolium chloride

Figure S8. ¹H NMR (DMSO-*d*₆) Spectrum of *N*-vinylimidazolium-*N*-propylsulfonate

Figure S9. ¹³C NMR (DMSO-*d*₆) Spectrum of *N*-vinylimidazolium-*N*-propylsulfonate

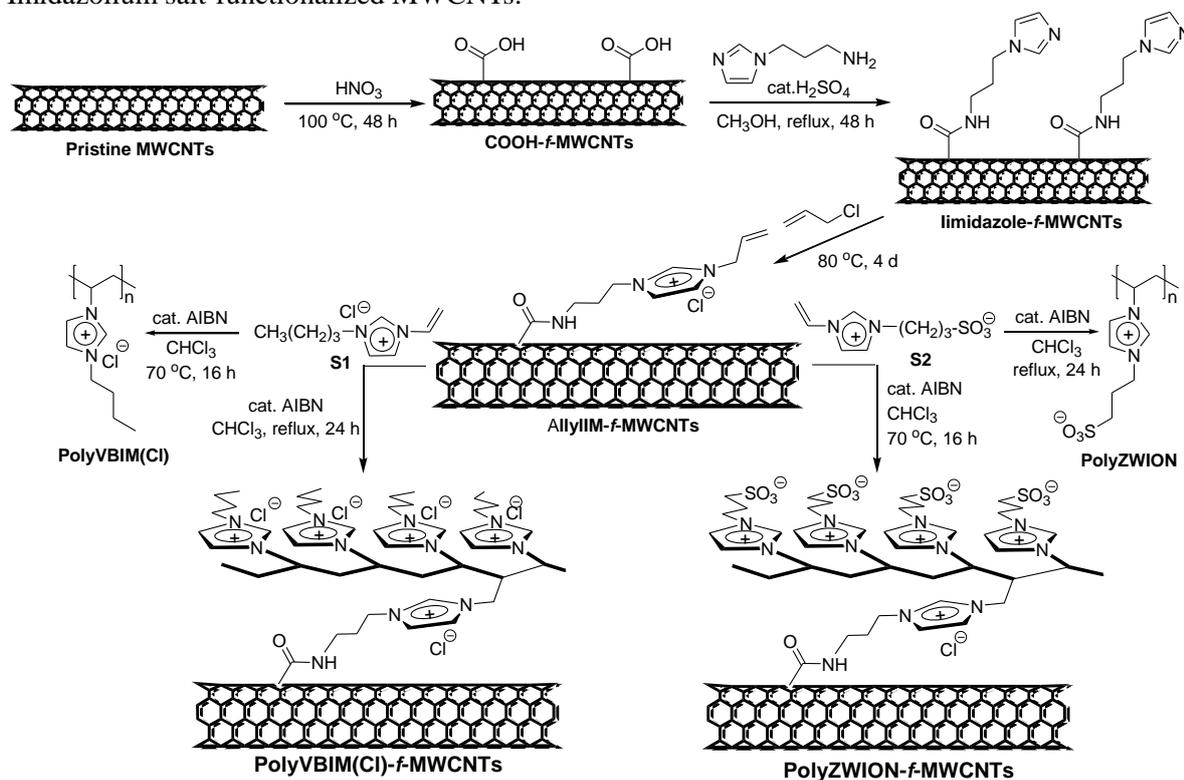
Figure S10. ¹H NMR (D₂O) spectrum of PolyVBIM(Cl)

Figure S11. ¹H NMR (D₂O) spectrum of PolyZWION.

1. Instruments: The pristine multi-walled carbon nanotubes (MWCNTs) were purchased from Hanwha Nanotech Co., Ltd. (purity: >95%, length: 10~50 pm, diameter: 10~15 nm). All chemicals were used as received. Double-distilled deionized H₂O was used. High Resolution TEM images were obtained using JEM-2100F (JEOL, 200 kV). Scanning Electron Microscope (SEM) images were obtained using Jeol JSM-6700F. X-ray diffraction (XRD) was obtained from Cu α radiation (0.02°/s) with 2 θ range from 20° to 90° using Siemens D500. X-ray photoelectron spectrometer (XPS) was measured using theta Probe AR-XPS system. TGA was performed on a SDT 2960 at a heating rate 10 °C in N₂ atmosphere. The UV-vis spectra were obtained with a HP-8452A spectrometer using quartz cell. The RDE measurements and cyclic voltammograms (CVs) were obtained using a RDE-1 of Bioanalytical Systems, Inc (BSA). The rotating ring-disk electrode (RRDE) was carried out on a MSR-X electrode rotator (Pine Instrument Co.) in conjunction with a CHI 760C (CH Instrument, USA) potentiostat. CV and RDE voltammetry were collected with a glassy carbon electrode (GCE, 3.0 mm diameter, BSA), while RRDE voltammetry using a GC disk electrode (6.0 mm diameter) surrounded by a Pt ring (6.5 mm inside diameter, Pine Instrument Co.).

2. Materials. The synthetic methods for all materials are depicted in Scheme S1.

Scheme S1. Synthetic methods for homopolymeric PolyVBIM(Cl), PolyZWION, and the Imidazolium salt-functionalized MWCNTs.



2.1. Syntheses of Homopolymeric PolyZWION and PolyVBIM(Cl). The homopolymeric poly[3-(1-vinyl-1*H*-imidazolium-3-yl)propane-1-sulfonate](PolyZWION)¹ and the poly(1-butyl-3-vinylimidazolium chloride)² were synthesized according to the reported procedure by polymerization of the corresponding *N*-vinylated imidazolium salts **S1** and **S2** in the presence of azobisisobutyronitrile (AIBN).

2-1-1. Synthesis of 1-butyl-3-vinylimidazolium chloride (S1). A mixture of 1-chlorobutane (11.11 g, 0.12 mol) and 1-vinylimidazole (2.82 g, 0.03 mol) was stirred at 70 °C for 50 h under nitrogen

¹ M. Yoshizawa, M. Hirao, K. Ito-Akita, H. Ohno, *J. Mater. Chem.* 2001, **11**, 1057.

² R. Marcilla, J. A. Blazquez, J. Rodriguez, J. A. Pomposo, D. Mecerreyes, *J. Polym. Sci. Part A: Polym. Chem.* 2004, **42**, 208.

atmosphere. The reaction mixture was cooled to room temperature, and the precipitate was washed with ethyl acetate (3 x 15 mL), and dried at 30 °C for 12 h under vacuum to give (3.19 g, 57%). ¹H NMR (250 MHz, CDCl₃) of [BVIM][I]: δ 10.51(s, 1H), 7.93(s, 1H), 7.72 (s, 1H), 7.45 (dd, *J* = 15.6, 8.7 Hz, 1H), 6.05 (dd, *J* = 15.6, 3.0 Hz, 1H), 5.44 (dd, *J* = 8.6, 3.2 Hz, 1H), 4.46 (t, *J* = 7.5 Hz, 2H), 1.96 (m, 2H), 1.43 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H) ppm; ¹³C NMR (63 MHz, CDCl₃) δ 134.8, 127.9, 123.0, 119.5, 110.3, 50.1, 31.9, 19.3, 13.4 ppm.

2-1-2. Synthesis of 3-(1-vinyl-1H-imidazolium-3-yl)propane-1-sulfonate (S2). To a stirred solution of 1-vinylimidazole (10.0 g, 0.106 mol) in toluene (50 mL) was added a solution of 1,3-propanesultone (10.0 g, 0.082 mol) in toluene (50 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 5 days. The resulting precipitate was filtered through a glass filter, and the filter-cake was washed with toluene and acetone successively, and then dried overnight under a vacuum at 30 °C to give the product (15.3g, 86%). ¹H NMR (300 MHz, DMSO) : δ 9.47 (s, 1H), 8.18 (s, 1H), 7.93 (s, 1H), 7.29 (dd, *J* = 15.9, 9.0 Hz, 1H), 5.94 (dd, *J* = 15.6, 2.1 Hz, 1H), 5.40 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.34 (t, *J* = 6.9 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.13 (m, 2H) ppm; ¹³C NMR (75 MHz, DMSO) δ 135.7, 129.0, 123.3, 119.1, 108.5, 48.2, 47.3, 25.9 ppm.

2-1-3. Synthesis of homopolymeric poly(vinylbutylimidazolium chloride) [PolyVBIM(Cl)]. The previously synthesized monomer 1-butyl-3-vinylimidazolium chloride (3.0 g) were diluted in chloroform (30 mL), then azobisisobutyronitrile (0.06 g, 2 wt%) was added. The solution was heated at 70 °C for 16 h. The unreacted monomers were removed by dialysis (cut-off molecular weight = 2000) in ethanol. The solution was concentrated with rotary evaporator and the final product was dried in vacuum at 30 °C to give 2.9 g of PolyVBIM(Cl). ¹H NMR spectrum indicated all vinyl protons were disappeared (Figure S10).

2-1-4. Synthesis of homopolymeric poly(vinylimidazoliumpropane sulfonate) (PolyZWION). The previously synthesized monomer 3-(1-vinyl-1H-imidazolium-3-yl)propane-1-sulfonate (3.0 g) were diluted in chloroform (30 mL), then azobisisobutyronitrile (0.06 g, 2 wt%) was added. The solution was refluxed for 24 h. The unreacted monomers were removed by dialysis (cut-off molecular weight = 2000) in ethanol. The solution was concentrated with rotary evaporator and the final product was dried in vacuum at 30 °C to give 2.6 g of PolyZWION. ¹H NMR spectrum indicated all vinyl protons were disappeared (Figure S11).

2.2. Preparation of Imidazolium Salt-Functionalized MWCNTs, PolyVBIM(Cl)-*f*-MWCNTs and PolyZWION-*f*-MWCNTs.

2-2-1. Preparation of carboxylic acid functionalized MWCNTs (COOH-*f*-MWCNTs). The carboxylic acid functionalized MWCNTs (COOH-*f*-MWCNTs) were prepared according to our reported procedure.³ The chemical oxidation of the pristine MWCNTs (5.0 g, purchased from Hanwha nanotech Co.,Ltd, purity:>95%, length: 10~50 μm, diameter:10~15 nm) was carried out by cutting them in 69-71% HNO₃ 300 mL under the sonication (Saehan, model SH-1070, 28 kHz) for 6 h at 60 °C, and the black mixture was stirred at 100 °C for 48 h. The reaction mixture was diluted with distilled water (1 L) and filtered by using polytetrafluoroethylene (PTFE) membrane filter (pore size 0.2 μm), the filter-cake was washed with distilled water several times, and dried under vacuum for 12 h at 60 °C. The 2nd chemical oxidation of the dried multi-walled CNTs was carried out in piranha solution (300 mL, H₂O₂ (30%)/H₂SO₄ (98%) = 3/7, v/v) under the sonication at 50 °C for 5 h. The mixture was poured into distilled water (1 L) and filtered and washed with distilled water several times until the filtrate pH = ~7, and then washed with methanol. The black filter cake was dried under vacuum for 24 h at 60 °C to give 4.9 g of COOH-*f*-MWCNTs.

2-2-2. Preparation of *N*-allylimidazolium chloride-functionalized MWCNTs. The poly(vinylbutylimidazolium chloride)-*f*-MWCNTs [PolyVBIM(Cl)] and carboxylic acid-functionalized MWCNTs were prepared according to our reported procedure.⁴ A suspension of COOH-*f*-MWCNTs (4.0 g) with several drops of H₂SO₄ in methanol (240 mL) was stirred at reflux under N₂ atmosphere for 48 h. The reaction mixture was diluted and washed several times with distilled water, and washed with acetone, and dried under vacuum for 12 h at 40 °C to give the methyl

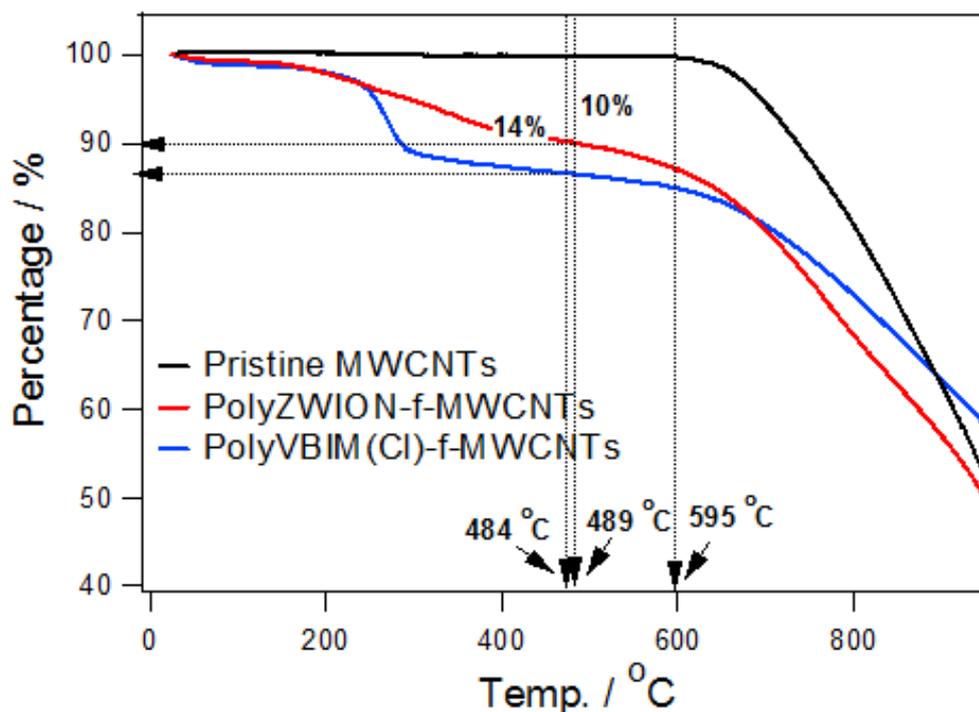
³ M. J. Park, J. K. Lee, B. S. Lee, Y.-W. Lee, I. S. Choi, S.-g. Lee, *Chem. Mater.* 2006, **18**, 1546-1551.

⁴ J. Y. Shin, Y. S. Kim, Y. Lee, J. H. Shim, C. Lee, S.-g. Lee, *Chem. Asian J.* 2011, **6**, 2016.

ester functionalized CNTs (3.9 g). A mixture of the methyl ester-functionalized CNTs (2.0 g) and 1-(3-aminopropyl)imidazole 60 mL was stirred in the presence of a few drops of H₂SO₄ at 120 °C for 4 days. The black solid was separated by filtration through a 0.2 μm PTFE membrane. The filter cake was washed successively with anhydrous tetrahydrofuran, followed by 1 N HCl solution, saturated NaHCO₃ solution, and distilled water until the filtrate pH = 7.0. The resulting solid was finally washed with acetone and dried overnight under vacuum at 50 °C to give IM-*f*-CNTs (2.0 g). Elemental analysis indicated 0.4 mmol/g of imidazole moiety was incorporated onto the CNTs. A mixture of imidazole functionalized (100 mg) and allylchloride (10 equiv based on the imidazole moiety of CNTs) was stirred at 80 °C for 4 days in acetonitrile 25 mL under N₂ atmosphere. The solid was separated by filtration through 0.2 μm PTFE membrane, and washed several times with acetonitrile, and then dried overnight under a vacuum at 30 °C to give PolyVBIM(Cl)-*f*-MWCNTs (106 mg). A mixture of N-allylimidazolium chloride-functionalized MWCNT (500 mg) and the pre-synthesized corresponding 1-butyl-3-vinylimidazolium chloride (500 mg) was stirred in chloroform (30 mL) at 70 °C for 16 h in the presence of azobisisobutyronitrile (10 mg, 2 wt%). The formed solid was filtered, and washed several times with methanol, and dried overnight under vacuum at 30 °C to give PolyVBIM(Cl)-*f*-MWCNTs (480 mg).

2-2-3. *Preparation of PolyZWION-f-MWCNTs.* A mixture of the N-allylimidazolium chloride-functionalized MWCNTs (AllylIM-*f*-MWCNTs) (500 mg, imidazolium chloride content: 0.4 mmol/g) and 3-(3-vinylimidazolium-1-yl)propane-1-sulfonate (500 mg) in chloroform (30 mL) at 70 °C for 16 h in the presence of azobisisobutyronitrile (AIBN, 10 mg, 2 wt%). The formed solid was filtered, and washed several times with methanol to remove unreacted monomers, and dried at 30 °C under vacuum for 12 h to give PolyZWION-*f*-MWCNTs (500 mg).

Figure S1. TGA of pristine MWCNTs, PolyZWION-*f*-MWCNTs, PolyVBIM(Cl)-*f*-MWCNTs.



2.3. Synthesis of an aqueous AuNPs solution and assembly with imidazolium salt-functionalized CNTs. An aqueous solution of citrate-coated AuNPs was synthesized according to the reported procedure.⁵ To an aqueous solution of HAuCl₄ (0.04 M, 0.5 mL), was diluted with 15 mL of deionized water, was added an aqueous solution of trisodium citrate (0.04 M, 0.5 mL) at room

⁵ Y. Shia, R. Yangb, P. K. Yueta, *Carbon* 2009, **44**, 3139.

temperature. After 5 min stirring, an aqueous solution of NaBH_4 (0.015 M, 4.0 mL) was added slowly, and the mixture was stirred for 20 min at room temperature to give deep pink AuNP solution (photo 1). To an aqueous solution of AuNPs (20 mL), prepared above, was added the functionalized MWCNTs (8.8 mg), COOH-*f*-MWCNT, PolyVBIM(Cl)-*f*-MWCNTs, PolyZWION-*f*-MWCNTs. After addition of 6.0 mL of ethanol, the solution was sonicated for 10 min (photos 2). The solution was stirred for 10 h at room temperature. To take the photos shown in Figure S2, the stirring was stopped (to take the photos 3 and 4, the solution was centrifuged at 1000 rpm because the solution was well-dispersed and no precipitates were observed). The black precipitates were corrected by centrifuge and washed thoroughly with distilled water and then dried in vacuum at room temperature. For TEM measurements, 200 L of aqueous solution of AuNPs (2.0 mg mL^{-1}) was diluted with 1.0 mL of ethanol, and one drop of sample on copper grid coated with carbon film. UV-vis measurements: The homopolymer, PolyZWION and PolyVBIM(Cl), (0.009 mg) was added to an aqueous solution of AuNPs (20 mL), prepared above. After 5 min sonication, 200 L of mixture solution was diluted with 1.0 mL of water to take the UV-vis spectrum.

Figure S2. Photos for the aqueous solution of (1) AuNPs as prepared and (2)-(6) a mixture of AuNPs with (a) COOH-*f*-MWCNT, (b) PolyZWION-*f*-MWCNTs, and (c) PolyVBIM(Cl)-*f*-MWCNTs.

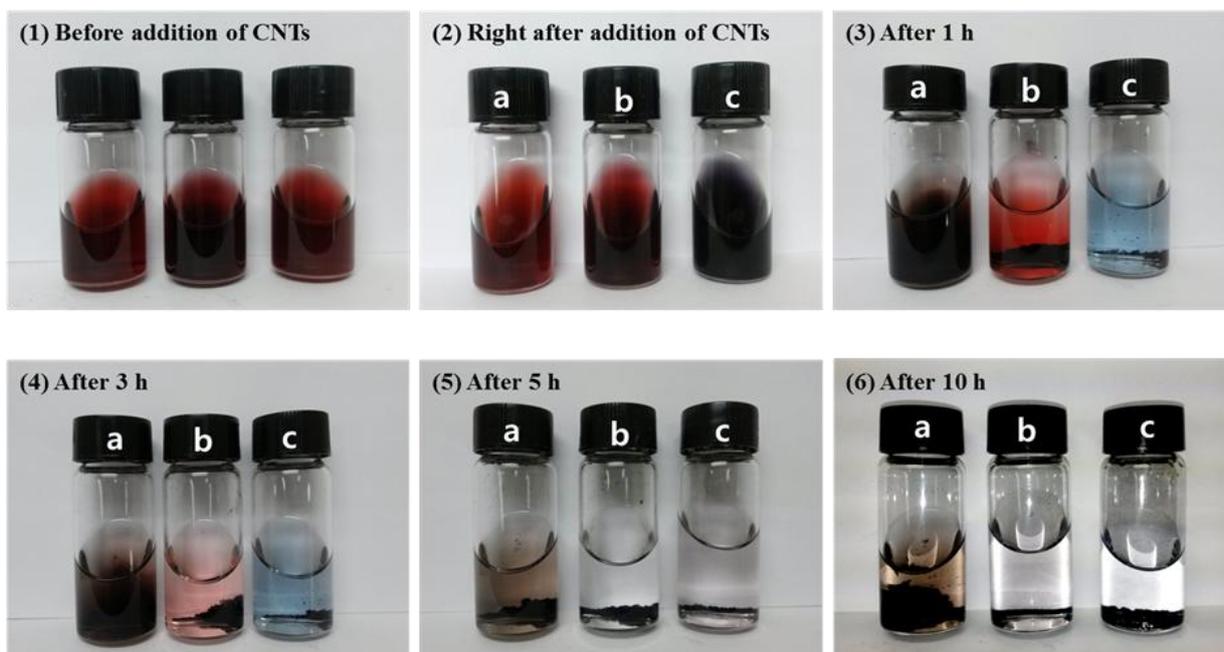


Figure S3. XRD of AuNP@COOH-*f*-MWCNTs, AuNP@PolyVBIM(Cl)-*f*-MWCNTs, and AuNP@PolyZWION-*f*-MWCNTs.

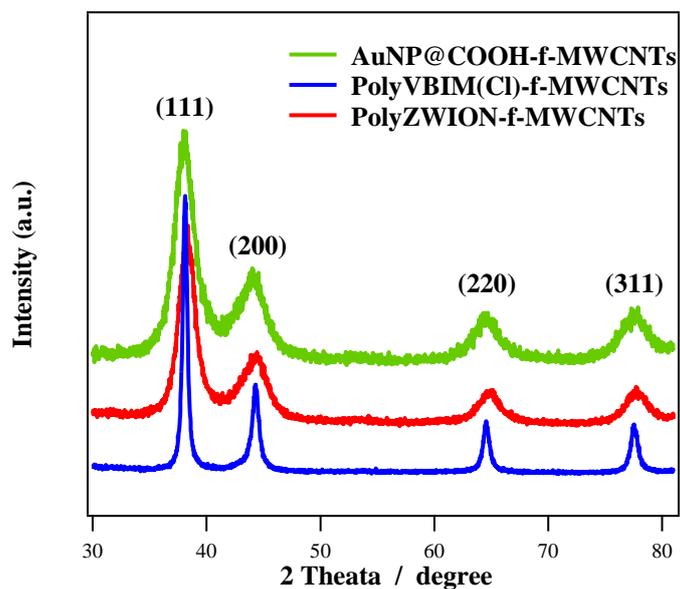
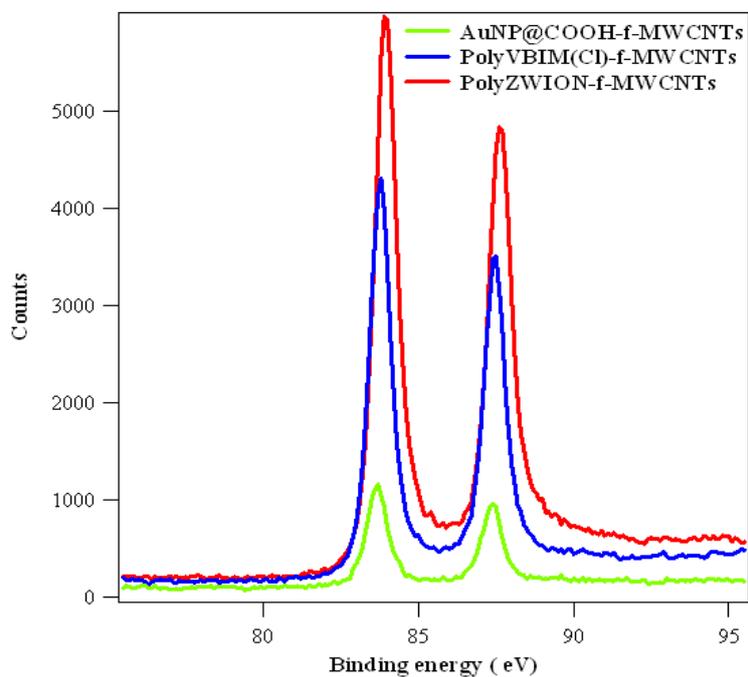


Figure S4. XPS of AuNP@COOH-*f*-MWCNT, AuNP@PolyVBIM(Cl)-*f*-MWCNTs, and AuNP@PolyZWION-*f*-MWCNTs.



3. Electrochemical measurements: The AuNP@MWCNT electrodes were prepared as follows: 20 μL of the aqueous suspension of AuNP/MWCNT hybrid (1 mg mL^{-1}) was dropped onto the surface of a pre-polished GCE, followed by dropping 10 μL of Nafion solution in ethanol (0.05 wt%) as a binder. The counter- and the reference electrodes were a platinum wire and saturated calomel electrode (SCE), respectively. All measurements were run at RT. The electrolyte solution was purged with either O_2 or N_2 for 30 min prior to each measurement and a flow of O_2 or N_2 was maintained over the electrolyte solution surface, respectively during the experiments to maintain constant concentration. When ORR was performed in O_2 saturated 0.1 M HClO_4 electrolyte solution, RDE and CV measurement were performed in the applied potential range from 0.6 to -0.4 V at a scan rate of 10 mV s^{-1} , and from 1.4 to -0.3 V at a scan rate of 50 mV s^{-1} , respectively. All the RDE currents were measured at rotating speeds from 100 to 3600 rpm and the measured current at each rpm in O_2 saturated solution was corrected by subtracting the background current measured in N_2 saturated solution. The corrected currents were then converted to the current densities.

One of the efficient methods to calculate the transferred electron number is the RRDE technique, where the peroxide produced at the disk electrode is detected by the ring electrode (Figure 4c) and the n value is calculated from the ratio of the ring current (j_R) and the disk current (j_D) using the following equation given below:⁶

$$n = \frac{4j_d}{j_d + \frac{j_R}{N}} \quad (1)$$

Where N is the collection efficiency (0.3) of the ring electrode. According to equation 3, the electron transferred number (n) of ORR on AuNP@COOH-*f*-MWCNTs, AuNP@PolyVBIM(Cl)-*f*-MWCNTs, and AuNP@PolyZWION-*f*-MWCNTs, estimated from the ring and disk currents at -0.2 V, are found to be around 2.9, 3.4, and 3.8, respectively, which are consistent with the n values obtained from the *K-L* results of RDE experiments (3.1, 3.5, and 3.7, respectively) shown in Figure 4d.

⁶ K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, *Science* 2009, **323**, 760.

Figure S5. RDE polarization curves obtained from (a) AuNP@COOH-*f*-MWCNTs, (b) AuNP@PolyVBIM(Cl)-*f*-MWCNTs, and (c) AuNP@PolyZWION-*f*-MWCNTs electrodes at different rpms.

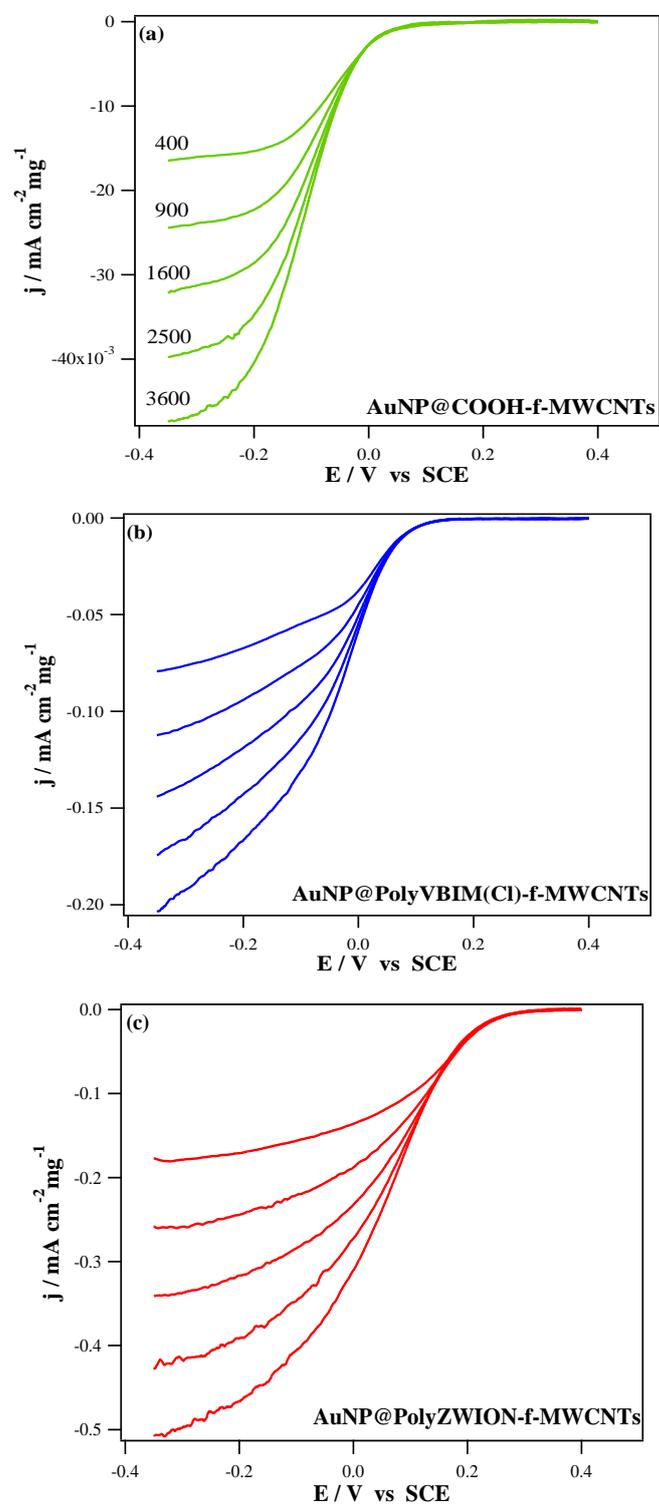


Figure S6. ^1H NMR ($\text{DMSO-}d_6$) spectrum of 1-butyl-3-vinylimidazolium chloride.

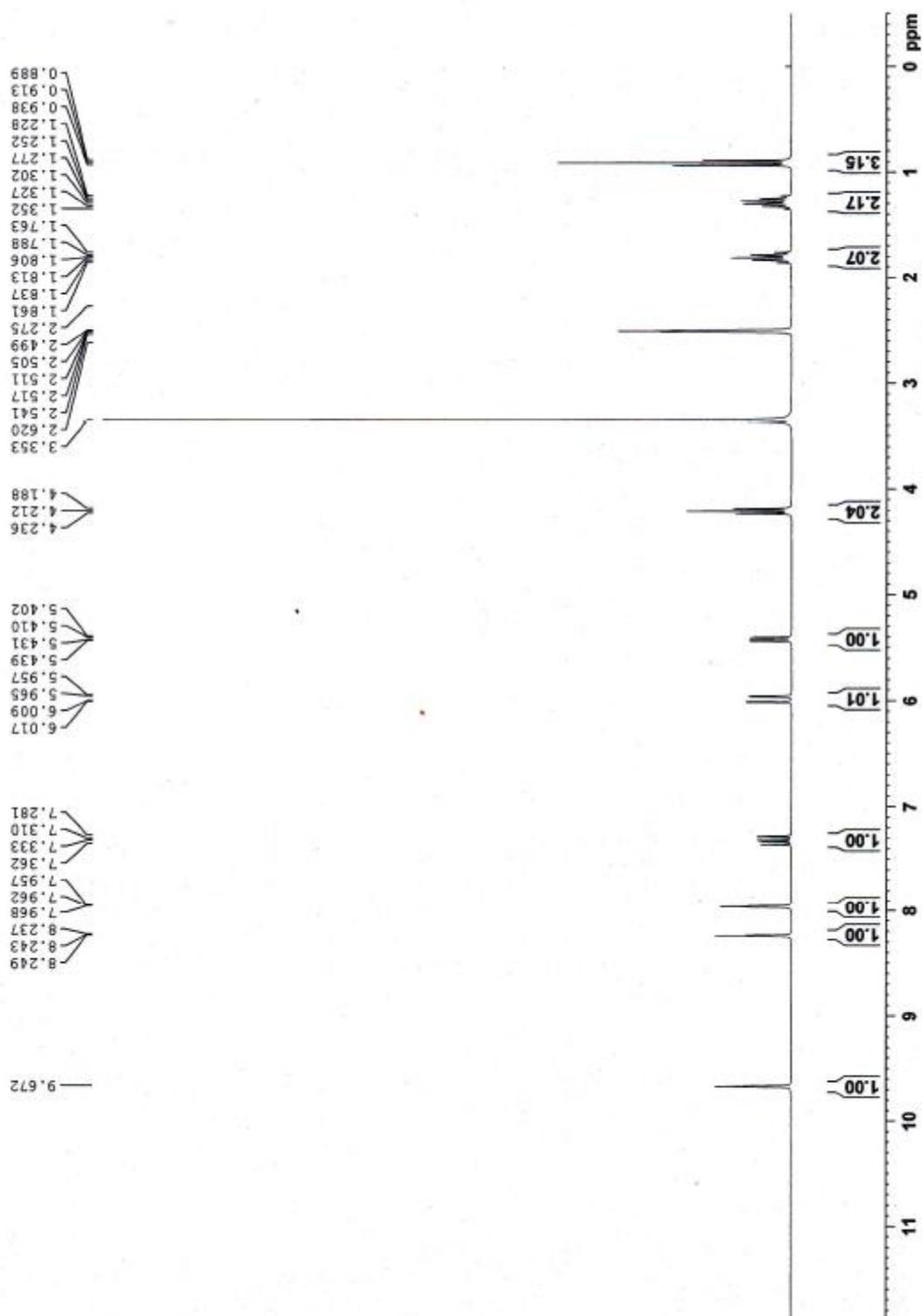


Figure S7. ^{13}C NMR ($\text{DMSO-}d_6$) Spectrum of 1-Butyl-3-vinylimidazolium chloride.

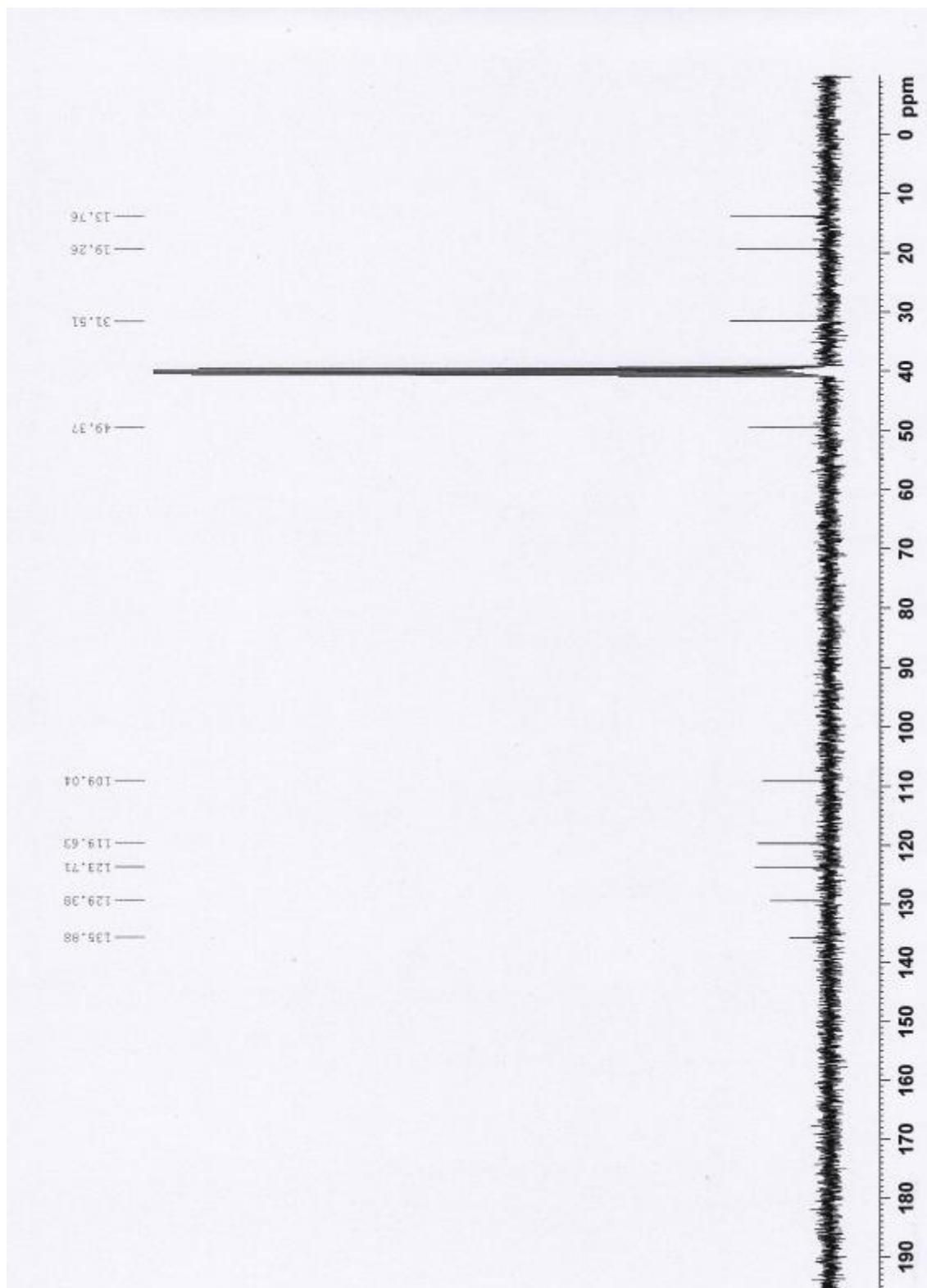


Figure S8. ^1H NMR ($\text{DMSO-}d_6$) Spectrum of N-vinylimidazolium-N-propylsulfonate.

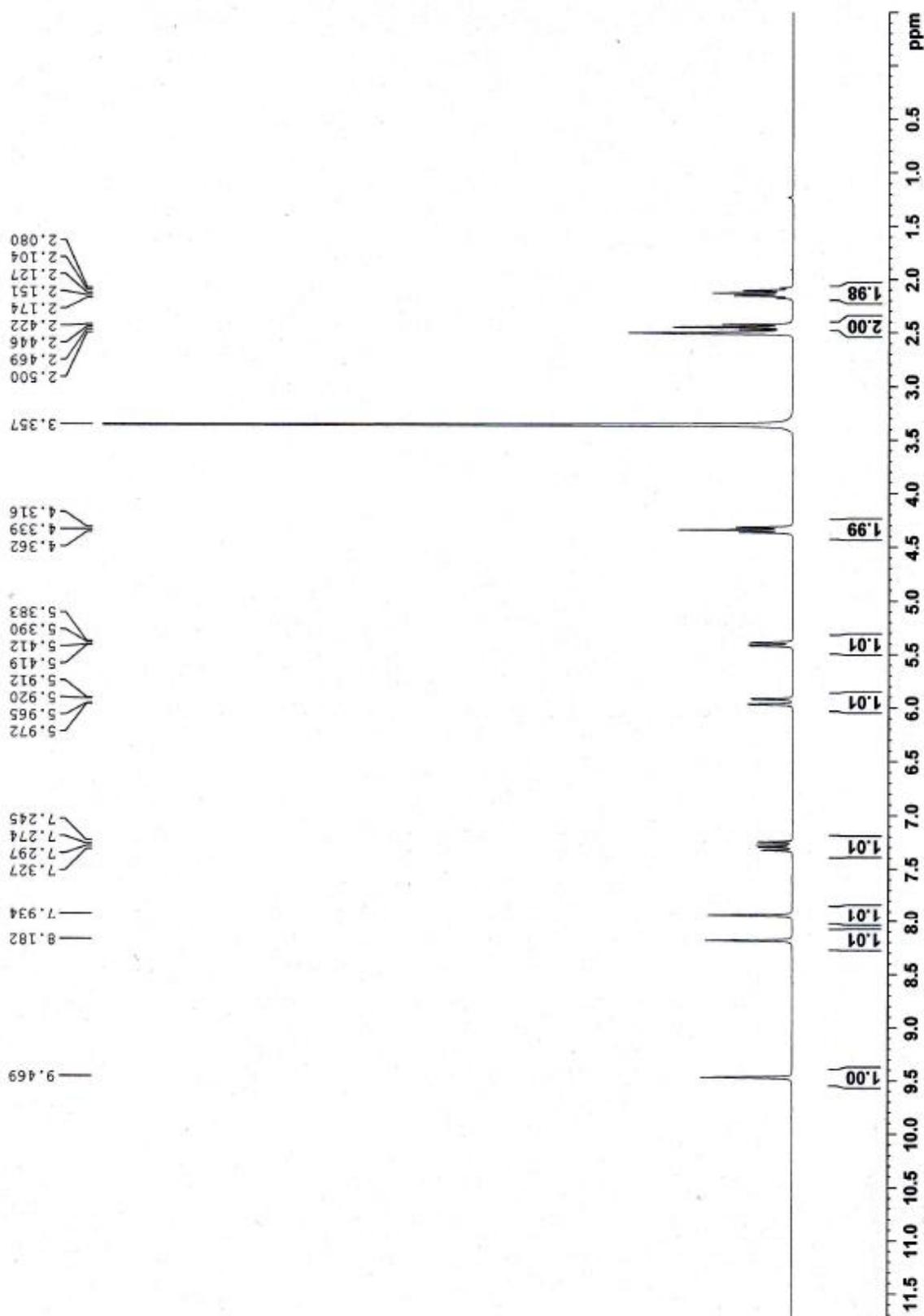


Figure S9. ^{13}C NMR ($\text{DMSO-}d_6$) Spectrum of N-vinylimidazolium-N-propylsulfonate.

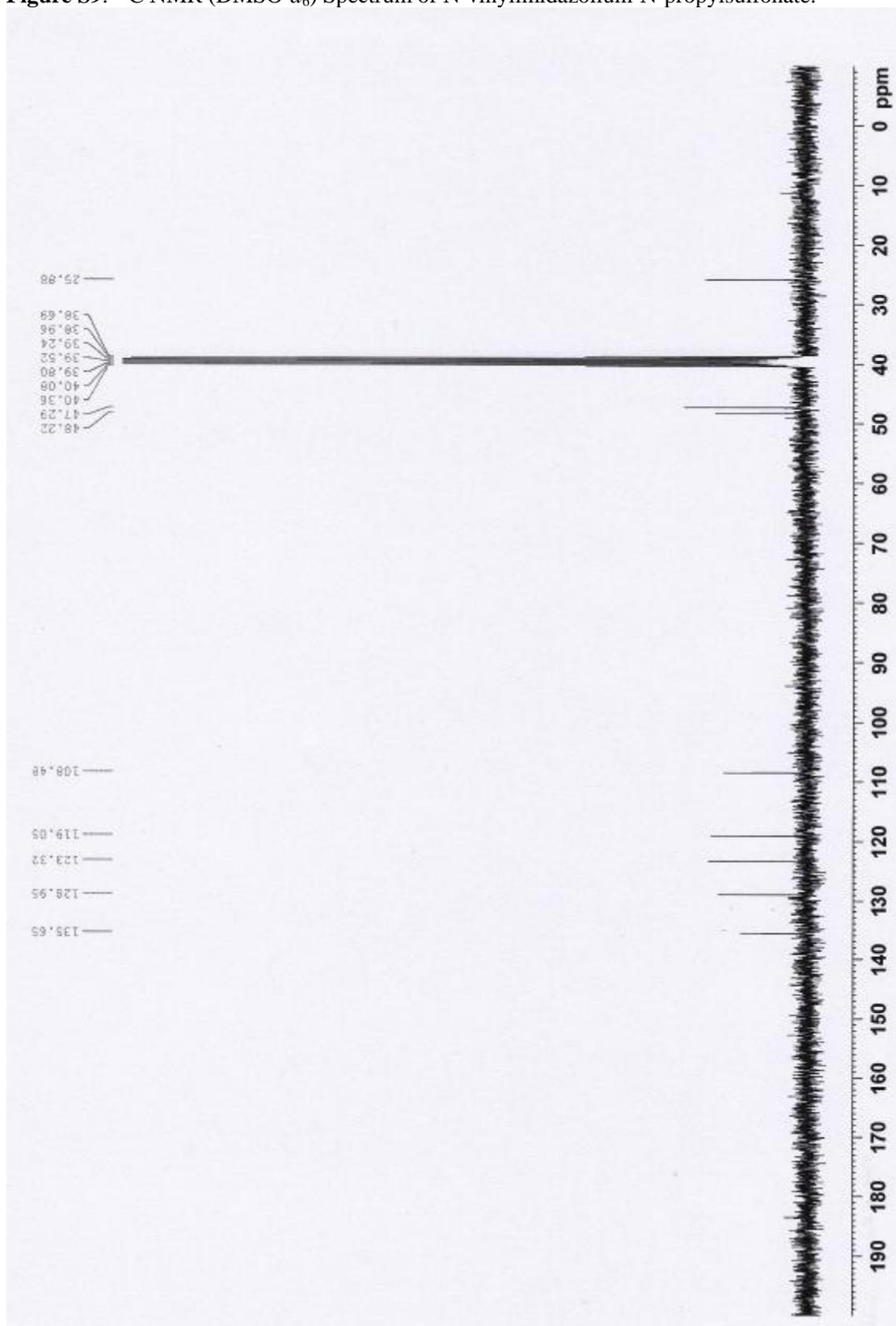


Figure S10. ^1H NMR (D_2O) spectrum of PolyVBIM(Cl).

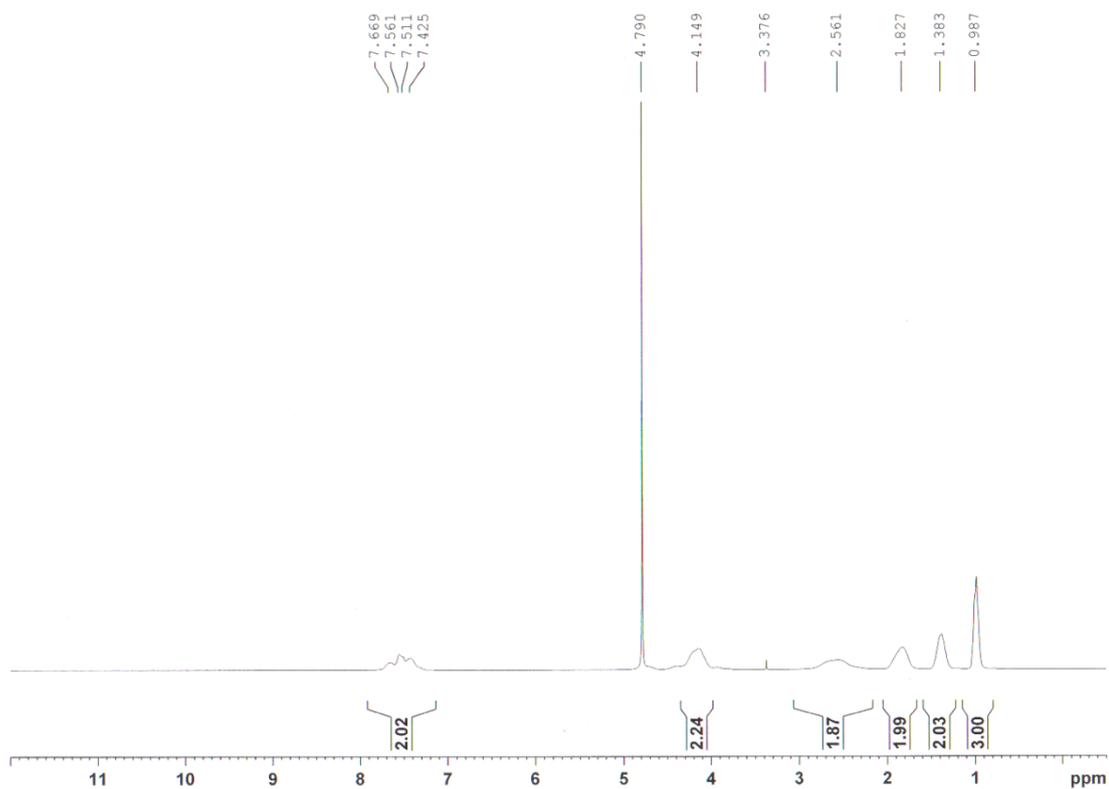


Figure S11. ^1H NMR (D_2O) spectrum of PolyZWION.

