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Reactive Oxygen Species Accelerate Degradation of Anion Exchange Membranes Based on Polyphenylene Oxide in Alkaline Environments

Electronic Supplementary Information

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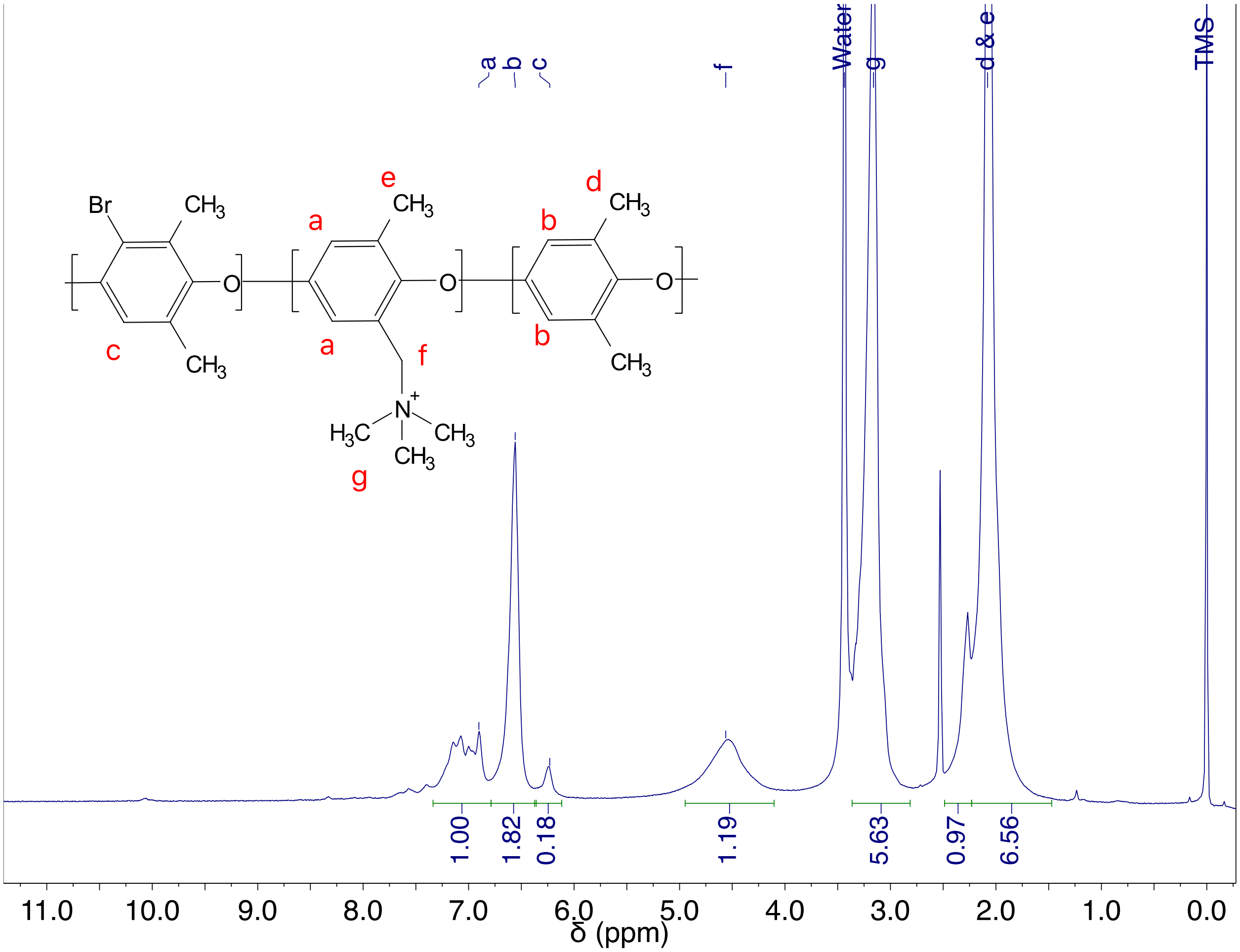

Figure S1. ^{1}H NMR spectrum of TMA-PPO AEM. The AEM polymer had a degree of functionalization in the benzyl position (DF_{benzyl}; mol of ammonium groups per polymer repeat unit) of 0.31 mol/mol and a degree of functionalization in the aryl position (mol of bromide in the backbone position per polymer repeat unit) of 0.11 mol/mol. The theoretical ion exchange capacity (IEC) was 1.9 mmol chloride/g; The actual IEC was approx. 1.8 mmol chloride/g (see **Figure 3** in the main manuscript). The NMR experiment was done in dimethylsulfoxide-d6 with tetramethylsilane (TMS) used as the internal standard for calibrating the chemical shift for ^{1}H.

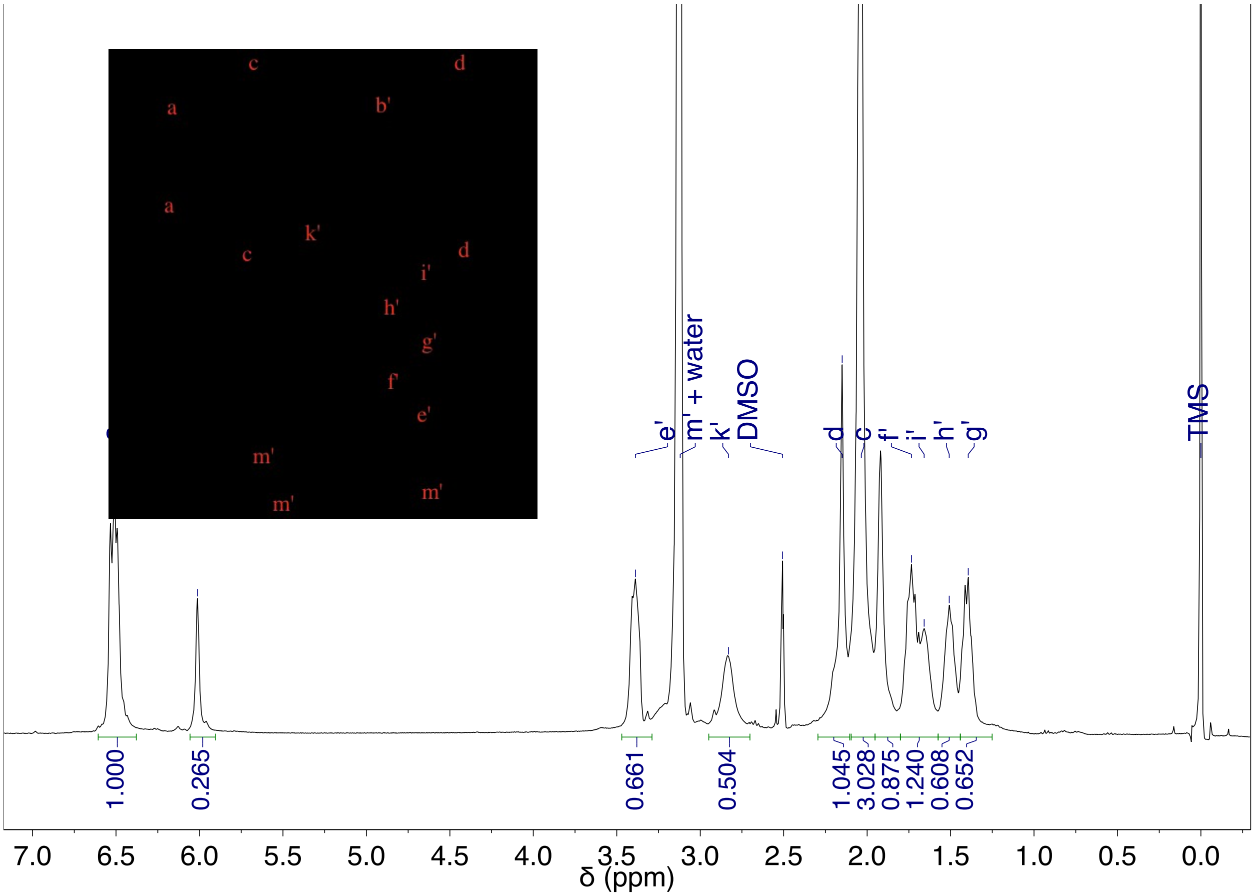

Figure S2. ^{1}H NMR spectrum of TMA-C6-PPO AEM. The AEM had a DF of 0.35 mol of quaternary ammonium per polymer repeat unit and a theoretical ion exchange capacity (IEC) of 1.9 mmol chloride/g; The actual IEC was approx. 1.8 mmol chloride/g (see **Figure 3** in the main manuscript). The NMR experiment was done in dimethylsulfoxide-d6 with tetramethylsilane (TMS) used as the internal standard for calibrating the chemical shift for ^{1}H.

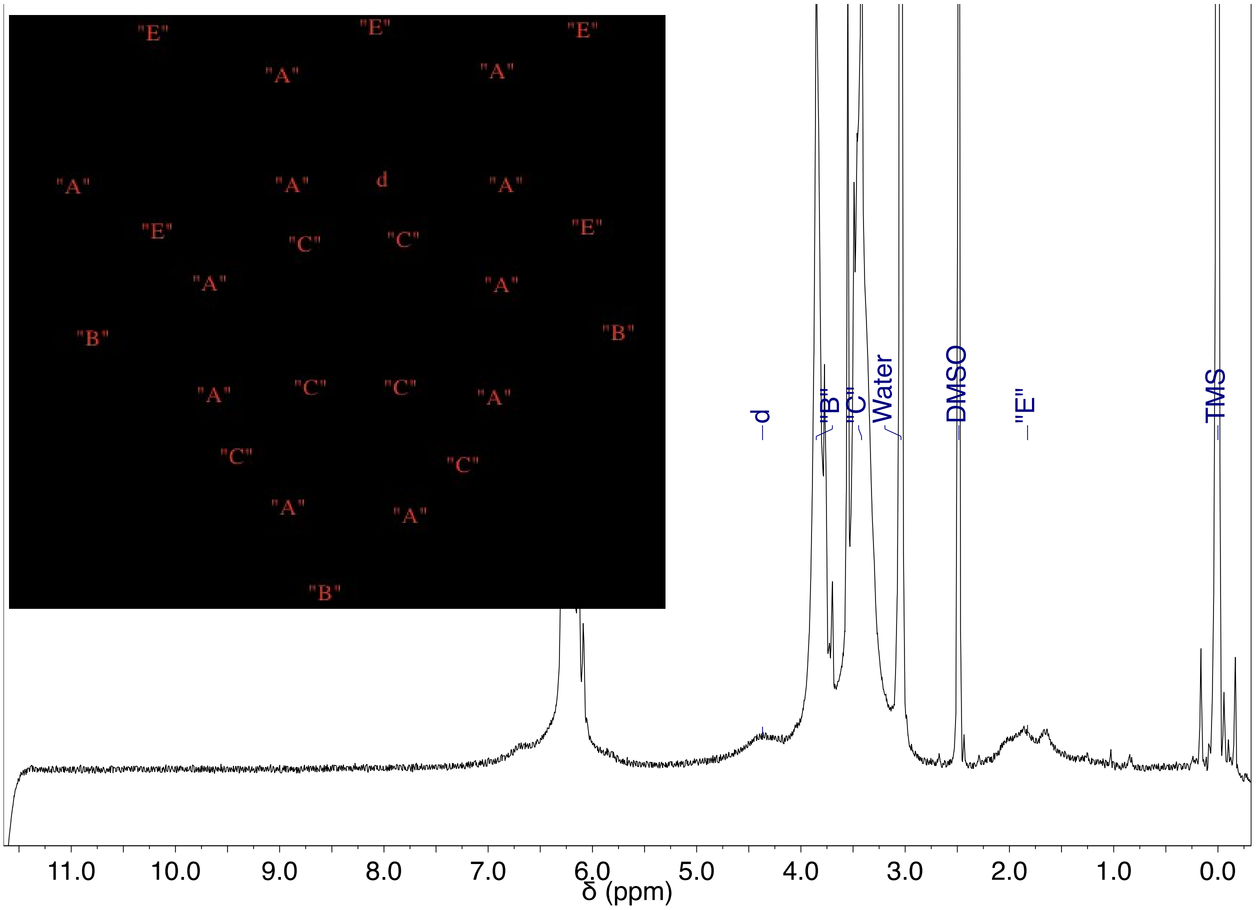

Figure S3. ^{1}H NMR spectrum of TTMPP-C6-PPO AEM. The AEM had a DF of approx. 1 mol of quaternary ammonium per polymer repeat unit and a theoretical ion exchange capacity (IEC) of 1.4 mmol chloride/g; The actual IEC was 1.1 mmol chloride/g (see **Figure 4** in the main manuscript). The NMR experiment was done in dimethylsulfoxide-d6 with tetramethylsilane (TMS) used as the internal standard for calibrating the chemical shift for ^{1}H.

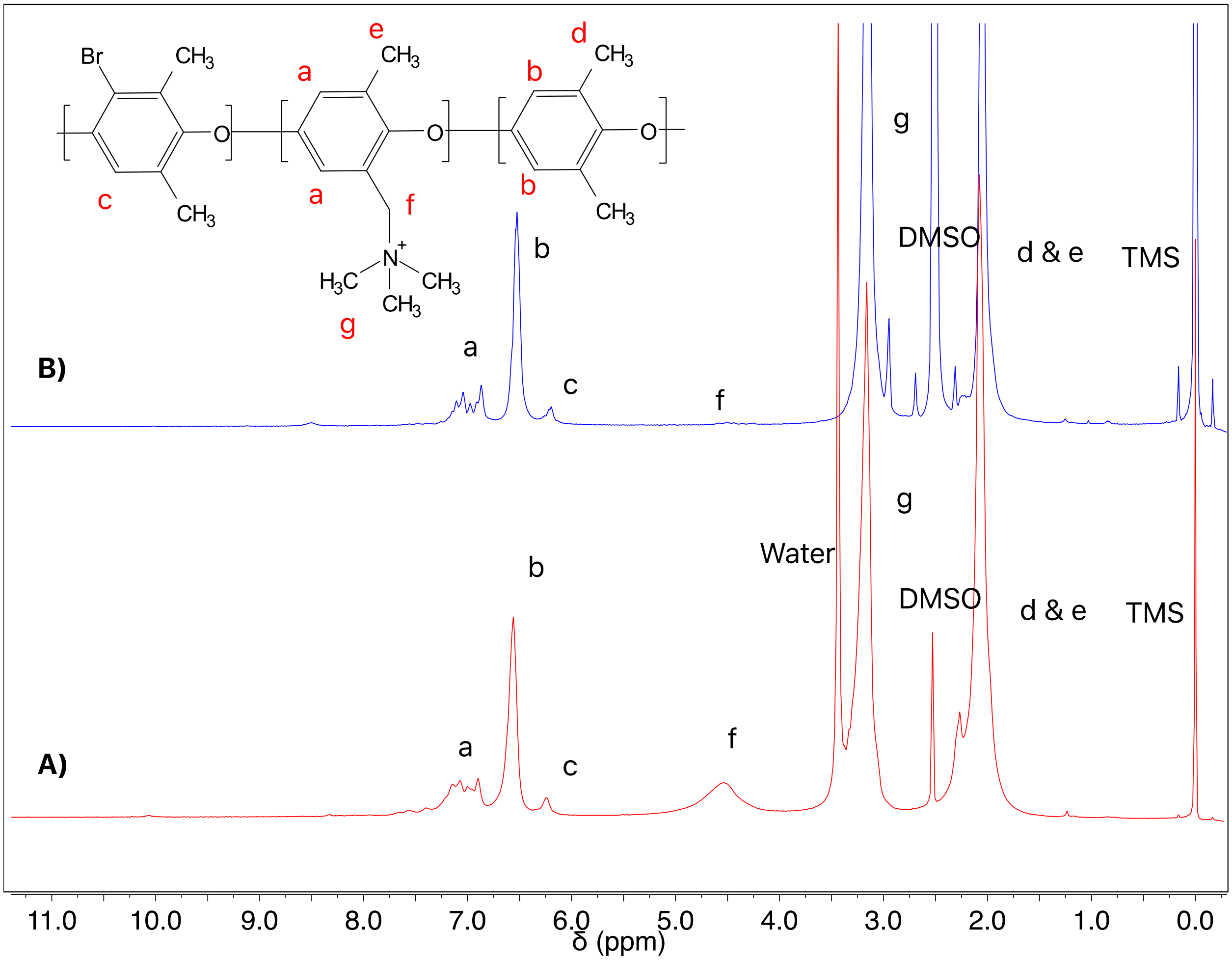

Figure S4. ^{1}H NMR of anion exchange membranes (TMA-PPO, structure shown in the figure insert) before (**A**) and after (**B**) the deuterium exchange experiment. The deuterium exchange experiments were performed with the anion exchange membranes dissolved in 1M NaOD in DMSO-d6+ D_2O (1:1 Vol). The solution was kept in an oven at 60°C for 2 days. Peak "f" almost disappeared due to the replacement of the protons in the methylene bridge by deuterium. This is a direct proof of the acidity of the protons in the methylene bridge and confirms the formation of ylide intermediates.

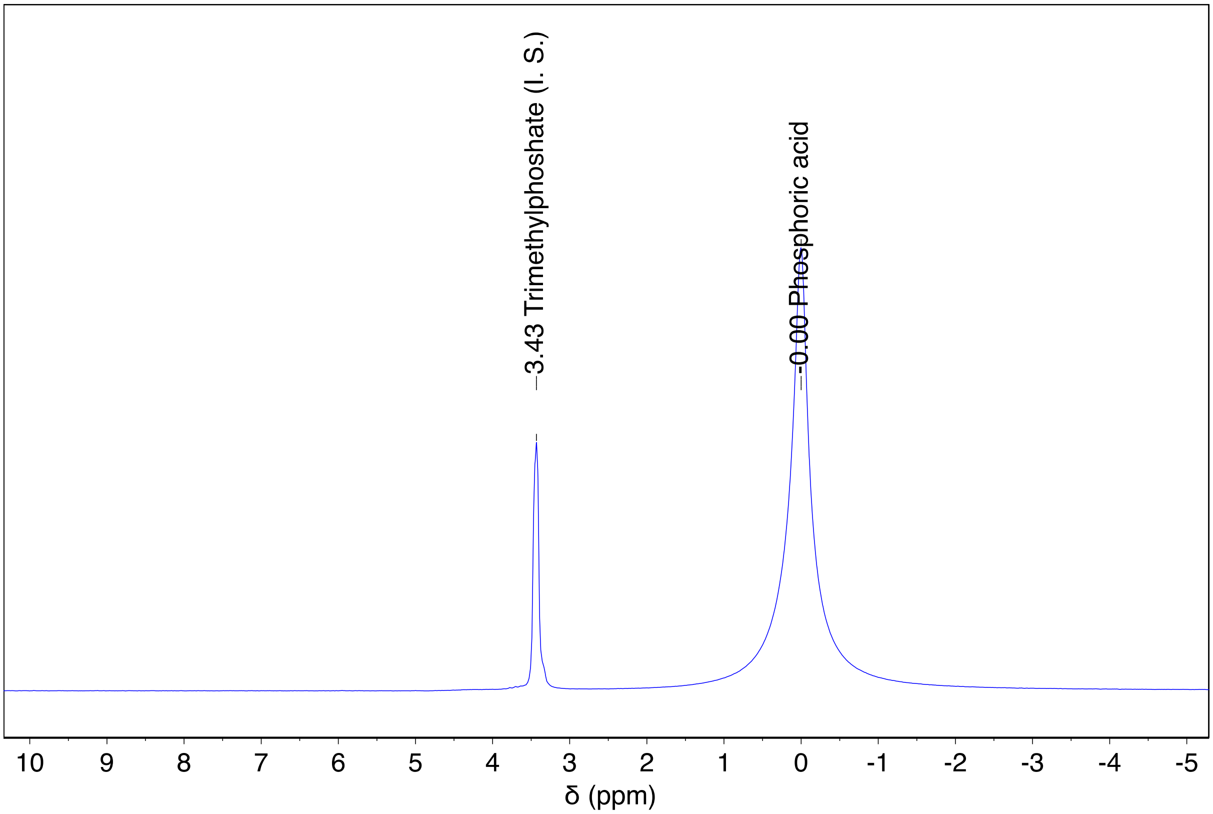

Figure S5. Calibration of trimethylphosphate chemical shift (^{31}P NMR) by using 85% H_3PO_4 as external standard (0 ppm). Trimethylphosphate was added to all the samples containing the spin-trap and used as internal standard for the quantification of the free radicals trapped.

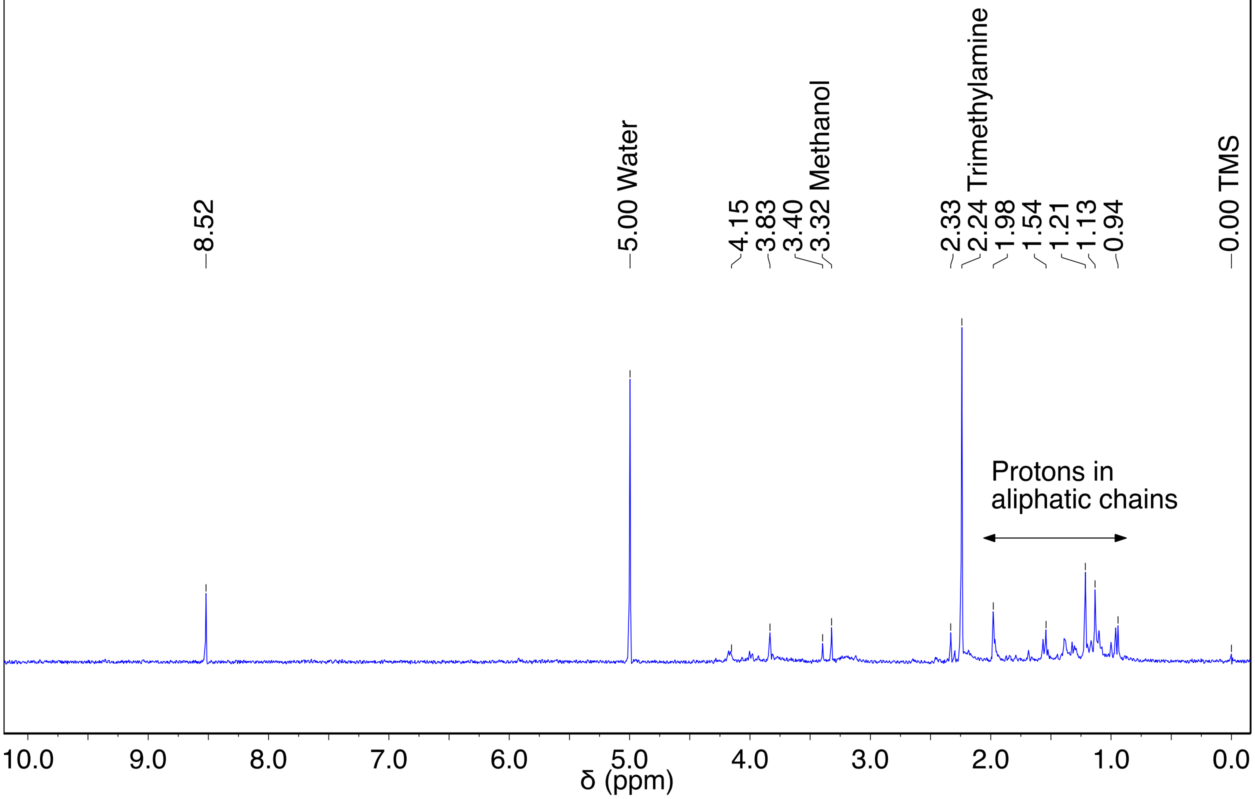

Figure S6. ^{1}H NMR of the supernatant (1M NaOD in D_2O) in contact with the anion exchange membrane (TMA-PPO) for 30 days. The experiment was performed in oxygen saturated 1M NaOD in D_2O at 60°C. We have identified the presence of water, methanol and trimethylamine, the typical products expected from direct nucleophilic substitutions. The other peaks were not identified, but point in the direction of polymer chain scission reactions. Some of the ^{1}H NMR peaks in the region 1-2 ppm are typically ascribed to aliphatic protons.

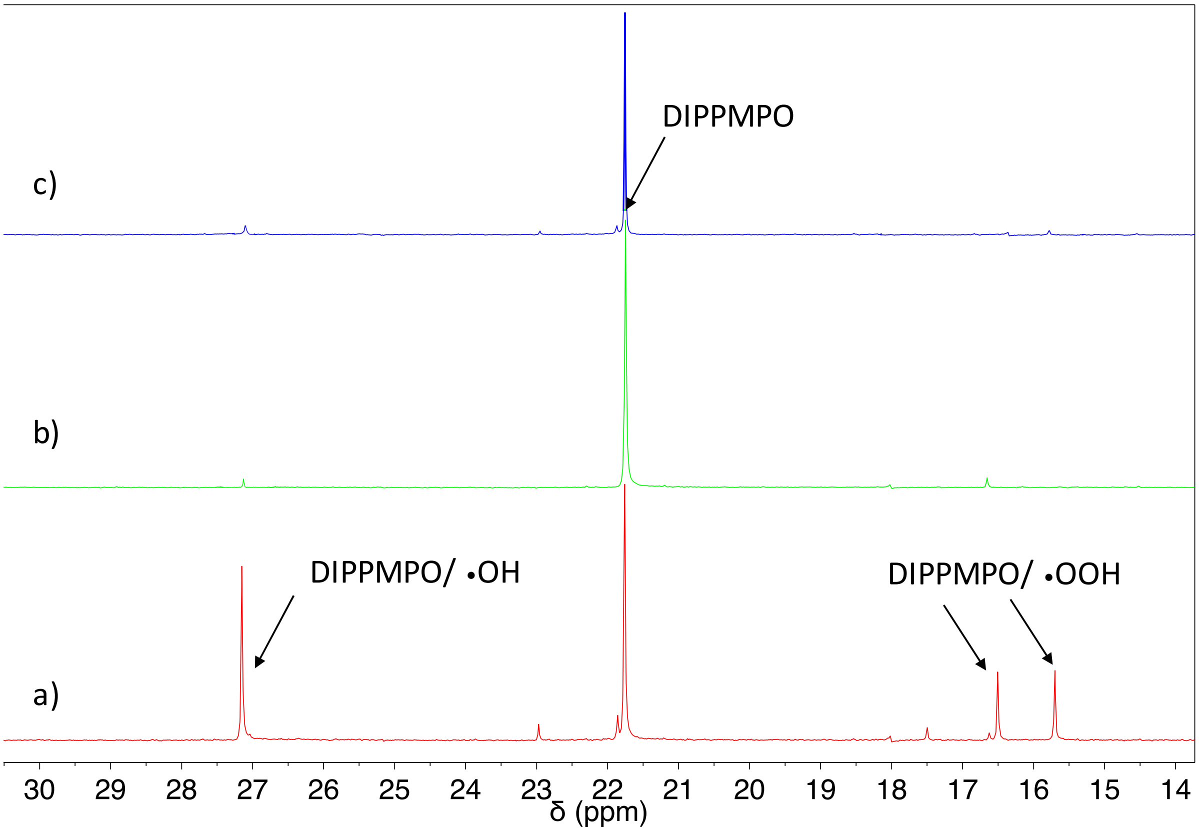

Figure S7. ^{31}P NMR spectra of **a)** O_2 and **b)** Ar filled NMR tubes containing 5-diisopropoxy-phosphoryl-5-methyl-1-pyrroline-N-oxide (DIPPMPO, 124 mM), potassium hydroxide (0.5 M), isopropanol/water (1:1 Vol. containing 10% D_2O) and the solubilized AEM (TMA-PPO, 2.6 g/100mL); **c)** blank experiment where the NMR tube (filled with O_2) was loaded with the same solution except the solubilized AEM. The chemical shift was calibrated by using the signal corresponding to DIPPMPO (21.76 ppm), obtained from previous experiments.