

Preparation and Electrochemical Investigation of 4-Amino-TEMPO Derivatives

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Nitroxides as stable free radicals are widely used as owing to their interesting redox behavior.¹ They are applied to radical batteries,² spin probes,³ antioxidants,⁴ magnetoactive materials,⁵ and radiation protective agents.⁶ Recently these nitroxides are interesting to organic electrolyte in redox flow batteries(RFBs) for offering the possibility of wide potential windows.⁷

In this study, we have investigated the relationship between electrochemical properties of 4-amino-TEMPO derivatives which are different electronic effects. To do this we prepared 4-amino-TEMPO derivatives **1-6** (Fig. 1) and investigated cyclic voltammetry (CV) results depending on their different functional group. Ultimately these materials will be applied for Fiber-Shaped Dye-Sensitized Solar Cells (FDSSCs) to improve efficiency and stability.⁸

Preparation of 4-Amino-TEMPO Derivatives 2-6⁹

4-Acetamide-TEMPO **2** in 98% yield was prepared by treatment of acetyl chloride and 4-amino-TEMPO **1** with N,N'-diisopropylethylamine (DIPEA) at 0 °C for 2 hours. 4-Acetamide-TEMPO **2** was characterized by IR at 3293 cm⁻¹ (NH stretching), 1697 cm⁻¹ (C=O stretching) (Scheme 1).

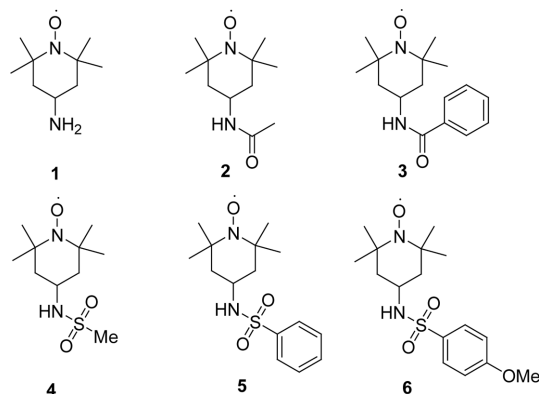
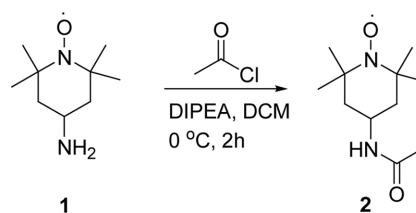
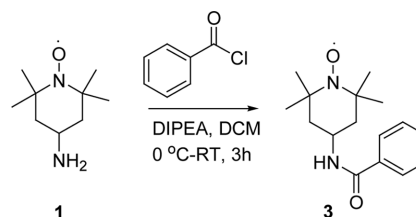


Figure 1. 4-Amino-TEMPO and 4-Amino-TEMPO Derivatives.



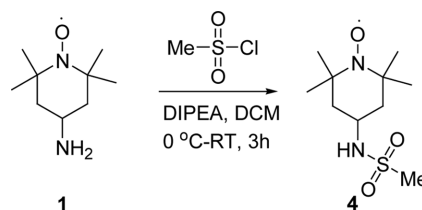
Scheme 1. Preparation of 4-Acetamide-TEMPO **2**.



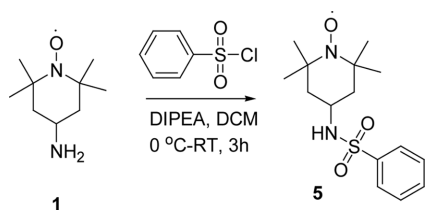
Scheme 2. Preparation of 4-Benzamide-TEMPO **3**.

4-Benzamide-TEMPO **3** in 96% yield was prepared by treatment of benzoyl chloride and 4-amino-TEMPO **1** with DIPEA at 0 °C to room temperature. 4-Benzamide-TEMPO **3** was characterized by IR at 3308 cm⁻¹ (NH stretching), 1634 cm⁻¹ (C=O stretching) (Scheme 2).

4-Methanesulfonamide-TEMPO **4** in 94% yield was prepared by treatment of methanesulfonyl chloride and 4-amino-TEMPO **1** with N,N'-diisopropylethylamine (DIPEA) at 0 °C to room temperature for 3 hours. 4-Methanesulfonamide-TEMPO **4** was characterized by IR at 3249 cm⁻¹ (NH stretching), 1326 cm⁻¹ (S=O asymmetric stretching),



Scheme 3. Preparation of 4-Methanesulfonamide-TEMPO **4**.



Scheme 4. Preparation of 4-Benzenesulfonamide-TEMPO 5.

1150 cm^{-1} (S=O symmetric stretching) (Scheme 3).

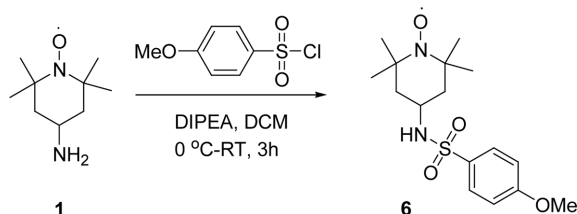
4-*p*-Methoxybenzenesulfonamide-TEMPO 5 in 58% yield was prepared by treatment of benzenesulfonyl chloride and 4-amino-TEMPO 1 with *N,N'*-diisopropylethylamine (DIPEA) at 0 °C to room temperature for 3 hours. 4-Benzenesulfonamide-TEMPO 5 was characterized by IR at 3293 cm^{-1} (NH stretching), 1330 cm^{-1} (S=O asymmetric stretching), 1162 cm^{-1} (S=O symmetric stretching) (Scheme 4).

4-*p*-Methoxybenzenesulfonamide-TEMPO 6 in 80% yield was prepared by treatment of *p*-methoxybenzenesulfonyl chloride and 4-amino-TEMPO 1 with *N,N'*-diisopropylethylamine (DIPEA) at 0 °C to room temperature for 3 hours. 4-*p*-Methoxybenzenesulfonamide-TEMPO 6 was characterized by IR at 3293 cm^{-1} (NH stretching), 1331 cm^{-1} (S=O asymmetric stretching), 1153 cm^{-1} (S=O symmetric stretching) (Scheme 5).

Electrochemical Properties of 4-Amino-TEMPO Derivatives 1-6

Electrochemical Measurement

All electrochemical measurements were conducted on WPG100e potentiostat/Galvanostat (WonTech). The glassy carbon rotating disk electrode, Pt foil and saturated calomel electrode were used as the working electrode, counter electrode and reference electrode, respectively. The potential was reported relative to the standard hydrogen electrode. The 4-amino-TEMPO derivatives were dissolved in 0.1 M TEABF₄ with acetonitrile solution, served as electrolyte solution.



Scheme 5. Preparation of 4-*p*-Methoxybenzenesulfonamide-TEMPO 6.

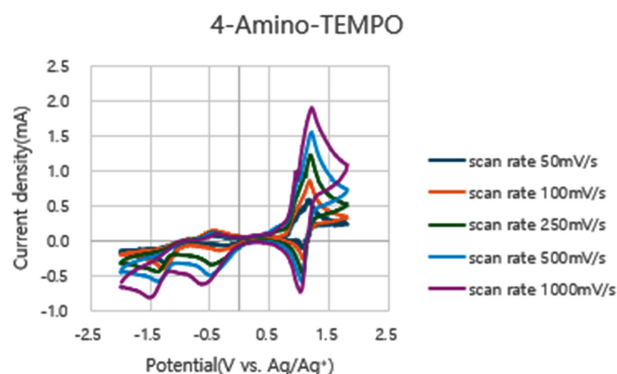


Figure 2. Cyclic Voltammogram of 4-amino-TEMPO 1 in 0.1 M TEA·BF₄ in acetonitrile solution.

Electrochemical Properties

To compare the CV results of functionalized 4-amino-TEMPO derivatives 2-6, commercially available 4-amino-TEMPO 1 is determined by CV in 0.1 M TEABF₄ with acetonitrile solution using glassy carbon electrode (GC). Cyclic voltammogram of 4-amino-TEMPO 1 shows the half-wave potential ($E_{1/2}$) in potential range -0.05 V and I_{pa}/I_{pc} : 0.98 vs Ag/Ag⁺ reference electrode at 50 mV/s (Fig. 2).

4-Acetamide-TEMPO 2 was determined by CV in 0.1 M TEABF₄ with acetonitrile solution using glassy carbon electrode (GC). Cyclic voltammogram of 4-acetamide-TEMPO 2 shows the half-wave potential ($E_{1/2}$) in the potential range 0.94 V and I_{pa}/I_{pc} : 0.96 vs Ag/Ag⁺ reference electrode at 50 mV/s (Fig. 3).

4-Benzamide-TEMPO 3 was determined by CV in 0.1 M TEABF₄ with acetonitrile solution using glassy carbon electrode (GC). Cyclic voltammogram of 4-benzamide-TEMPO 3 shows the half-wave potential ($E_{1/2}$) in the potential range 0.97 V and I_{pa}/I_{pc} : 0.97 vs Ag/Ag⁺ reference electrode at 50 mV/s (Fig. 4).

4-Methanesulfonamide-TEMPO 4 was determined by CV in 0.1 M TEABF₄ with acetonitrile solution using

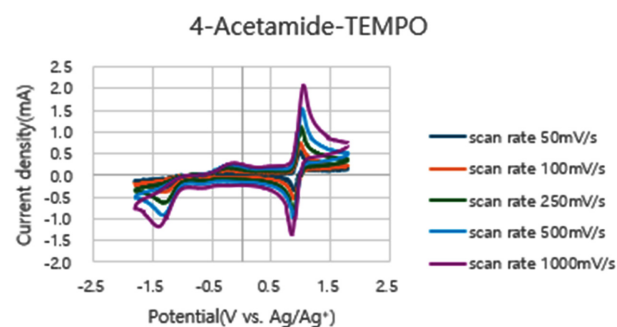


Figure 3. The CV of 4-Acetamide-TEMPO 2.

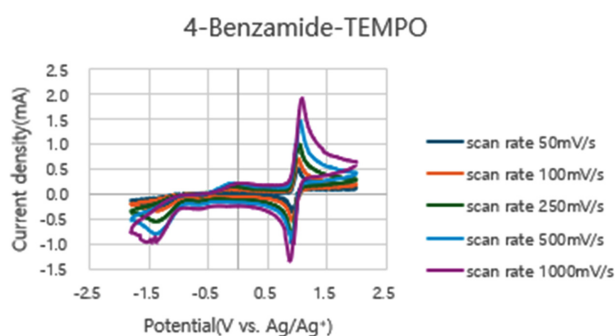


Figure 4. The CV of 4-Benzamide-TEMPO 3.

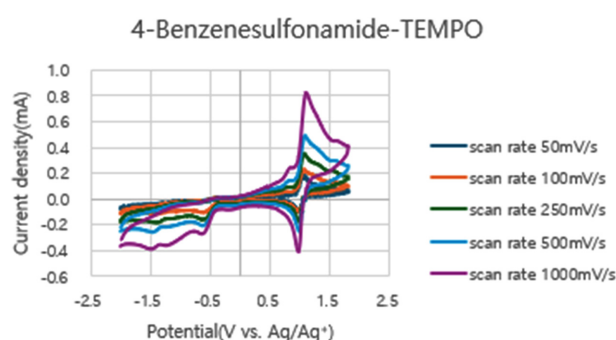


Figure 6. The CV of Benzenesulfonamide-TEMPO 5.

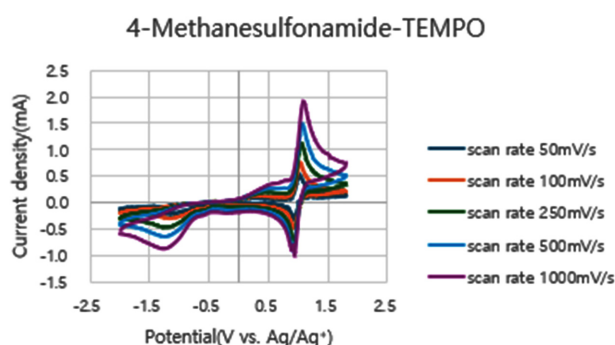


Figure 5. The CV of 4-Methanesulfonamide-TEMPO 4.

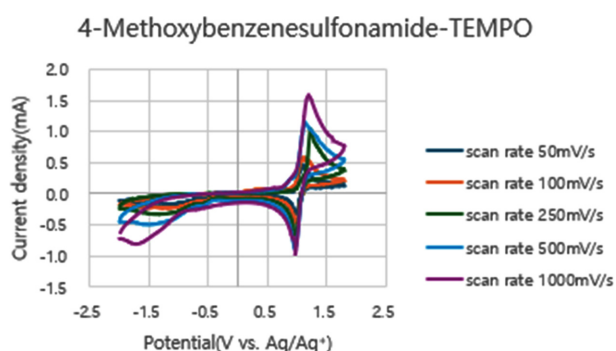


Figure 7. The CV of 4-*p*-Methoxybenzenesulfonamide-TEMPO 6.

glassy carbon electrode (GC). Cyclic voltammogram of 4-Methanesulfonamide-TEMPO 4 shows the half-wave potential ($E_{1/2}$) in the potential range 0.98 V and I_{pa}/I_{pc} : 0.76 vs Ag/Ag⁺ reference electrode at 50 mV/s (Fig. 5).

4-Benzenesulfonamide-TEMPO 5 was determined by CV in 0.1 M TEABF₄ with acetonitrile solution using glassy carbon electrode (GC). Cyclic voltammogram of 4-benzenesulfonamide-TEMPO 5 shows the half-wave potential ($E_{1/2}$) in potential range 1.01 V and I_{pa}/I_{pc} : 0.85 vs Ag/Ag⁺ reference electrode at 50 mV/s (Fig. 6).

4-*p*-Methoxybenzenesulfonamide-TEMPO 6 was determined by CV in 0.1 M TEABF₄ with acetonitrile solution using glassy carbon electrode (GC). Cyclic voltammogram of 4-*p*-Methoxybenzenesulfonamide-TEMPO 6 shows the half-wave potential ($E_{1/2}$) in the potential range 1.04 V and

I_{pa}/I_{pc} : 0.77 vs Ag/Ag⁺ reference electrode at 50 mV/s (Fig. 7).

Comparing to CV results of 4-amino-TEMPO derivatives 1-6, 4-amino-TEMPO derivatives 2-6 are better than 4-amino-TEMPO 1 in half-wave potential ($E_{1/2}$), but the value of I_{pa}/I_{pc} is not improved. Also comparing to CV results of 4-amino-TEMPO derivatives 2-6, 4-*p*-methoxybenzenesulfonamide-TEMPO 6 is best in half-wave potential ($E_{1/2}$) in 4-amino-TEMPO derivatives 2-6.

In these results, we investigated the sulfonyl functional group is better than the carbonyl functional group in half-wave potential ($E_{1/2}$) by some different electronic effects.

In 4-amino-TEMPO derivatives 4-6 which has the sulfonyl functional group, *p*-methoxybenzenesulfonyl functional group is better than methyl and benzenesulfonyl

Table 1. 4-Amino-TEMPO 1 and 4-Amino-TEMPO Derivatives 2-6

Compound name	E_{pa} (V)	E_{pc1} (V)	E_{pc2} (V)	$\Delta E/n$ (V)	$E_{1/2}$ (V)	I_{pa} (V)	I_{pc1} (V)	I_{pc2} (V)	$I_{pa}/I_{pc(1+2)}$
1	1.1560	-1.2533	-	2.4093	-0.0487	0.5436	0.5507	-	0.9871
2	0.9862	0.8948	-1.2824	0.0915	0.9405	0.5096	0.3492	0.1795	0.9640
3	1.0184	0.9278	-1.1426	0.0906	0.9731	0.4741	0.3517	0.1368	0.9704
4	1.0220	0.9361	-1.1178	0.0859	0.9790	0.4436	0.3989	0.1848	0.7600
5	1.0526	0.9771	-1.3109	0.0755	1.0148	0.1387	0.1081	0.0543	0.8541
6	1.0988	0.9881	-1.1138	0.1107	1.0434	0.4121	0.3928	0.1435	0.7684

0.025 M 4-Amino-TEMPO derivatives and 1 M TEABF₄ in ACN at scan rate 50 mV/s

functional group. In our laboratories, we are continuing study the reason of different half-wave potential ($E_{1/2}$) and I_{pa}/I_{pc} depending on functional group (Table 1).

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