Development of Triarylamine Mediator Having Ionic-Tag and Its Application to Electrocatalytic Reaction in Ionic Liquid

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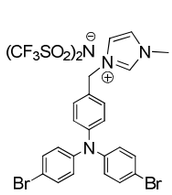
Mediators are highly useful for organic electrosynthesis. However, mediators are usually discarded after electrolysis, which is far from atom economy. Recent progress in reusable mediators is remarkable [1]. For example, polymer-supported system is one successful approach for reusable mediator [2]. We previously prepared a polystyrene-supported iodobenzene (PSIB) mediator which was effective in combination with chloride mediator for anodic fluorination [3]. The PSIB mediator could be recovered with a simple filtration after electrolysis. As for Ar_3N, Steckhan and co-workers reported a polymer electrolyte-supported Ar_3N used as both electrolyte and mediator [4]. However, this polymer electrolyte-supported Ar_3N mediator was decomposed by the elimination of Ar_3N moiety from polymer chain during electrolysis.

Mediators bearing ionic-tag show good compatibility to polar solvents especially ionic liquid [5]. For example, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) derivative having ionic-tag could be used repeatedly for chemical oxidation of alcohols in ionic liquid [6,7]. In our previous report, we prepared a reusable iodobenzene derivative, in which an imidazolium tag was introduced [8]. The ionic-tag strategy makes the mediators stay in polar solvent even after extraction of products with non-polar organic solvents; therefore this is still promising for development of practical mediators.

In this work, we have developed novel Ar_3N-based mediators (**Med-1** and **Med-2**) bearing ionic-tag moiety, which imparts compatibility to ionic liquid. Electrochemical properties of the mediators in organic solvent and ionic liquid HF salts and their mediatory use for electrocatalytic reaction such as deprotection and difluorodesulfurization of dithioacetal compounds were investigated [9].

Med-1



Med-2

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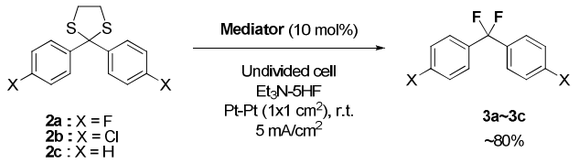
Cyclic voltammograms of **Med-1** and **Med-2** in 0.6 M TEAP/MeCN showed a reversible redox wave, and their oxidation peak potentials were 1.16 V and 1.13 V *vs.* SCE, respectively. Their diffusion coefficients could be estimated from the gradient of the linear plot of anodic peak current vs. square root of scan rate based on the Randles-Sevcik formula for a reversible process (Eq. 1) [10,11].

$$I_{pa} = 0.44nF\left(\frac{nF}{RT}\right)^{\frac{1}{2}} \times AC_0 D^{\frac{1}{2}} v^{\frac{1}{2}} \quad \text{(Eq. 1)}$$

I_{pa} is oxidation peak current [A], n is the number of reaction electrons, A is the square of electrode [cm^2], C_0 is concentration of substance [mol cm^{-3}], D is diffusion coefficient [cm^2 s^{-1}] and v is scan rate [mV s^{-1}]. The estimated diffusion coefficients of **Med-1** and **Med-2** in MeCN were 7.4 x 10^{-6} cm^2 s^{-1} and 5.5 x 10^{-6} cm^2 s^{-1}, respectively.

Med-1 and **Med-2** were easily soluble in ionic liquid HF salt due to the introduction of ionic-tag. CV analysis for **Med-1** and **Med-2** was also carried out in neat ionic liquid HF salt. Cyclic voltammograms of **Med-1** and **Med-2** in Et_3N-5HF showed a reversible redox wave, and their oxidation peak potentials were 0.77 V and 0.73 V *vs.* Fc/Fc^+, respectively. Their estimated diffusion coefficients in Et_3N-5HF were 2.7 x 10^{-6} cm^2 s^{-1} and 2.6 x 10^{-6} cm^2 s^{-1}, respectively. These values are less than half of those in MeCN.

Next, we have successfully carried out electrocatalytic fluorodesulfurization of dithioacetals (**2**) using mediators as follows.



Furthermore, the reusability of **Med-2** in anodic fluorodesulfurization of **2a** as a model substrate was investigated. The product **3a** in the ionic liquid Et_3N-5HF was readily extracted with hexane, and the ionic liquid containing **Med-2** was reused for next runs. However, the yield of **3a** decreased from 80% to 51% and 48% at the second and the third electrolyses, respectively. Although the yield of the fluorination product decreased when **Med-2** was reused, it was demonstrated that the mediator having an ionic-tag moiety could be recyclable to some extent.

References

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