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Development of triarylamine mediator having ionic-tag and its application to electrocatalytic reaction in ionic liquid

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ABSTRACT

Novel triarylamine (Ar_3N) mediators bearing an ionic-tag moiety were synthesized from 4,4′-dibromotriphenylamine. Their electrochemical properties were investigated by cyclic voltammetry both in organic solvent and ionic liquid HF salt. The electrocatalytic reactions such as deprotection and fluorodesulfurization of dithioacetals were successfully carried out using these Ar_3N mediators in an undivided cell at room temperature.

1. Introduction

The development of efficient methods for selective fluorination of organic compounds is becoming increasingly important in order to produce novel medicines, agrochemicals and functional materials [1–6]. Electrochemical partial fluorination is a promising approach to introduce fluorine atoms into a specific position of organic compounds such as heteroatom compounds [7–10]. The reaction involves the electrochemical oxidation of substrates, followed by a nucleophilic attack of fluoride anion used as a supporting electrolyte. However, passivation that forms a non-conducting polymer film at anodic surface often occurs and suppresses anodic current, resulting in decrease of yield and current efficiency [11]. The indirect electrolysis using mediators can solve the problems [12,13]. One of the most promising anodic mediator, triarylamine (Ar_3N) has been widely used [14]. For example, anodic deprotection of dithioacetal [15], anodic *gem*-difluorodesulfurization of dithioacetal [16], anodic monofluorodesulfurization of phenylthio β-lactams [17] and arylthio esters [18] have been reported.

However, mediators are usually discarded after electrolysis, which is far from atom economy. Recent progress in reusable mediators is remarkable [19]. For example, polymer-supported system is one successful approach for reusable mediator [20]. We previously prepared a polystyrene-supported iodobenzene (PSIB) mediator which was effective in combination with chloride mediator for anodic fluorination [21]. 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 [22]. 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 [23–28]. 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 [29,30]. In our previous report, we prepared a reusable iodobenzene derivative, in which an imidazolium tag was introduced [31]. 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 paper, we report on 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.

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2. Experimental

2.1. Measurements

^{1}H, ^{13}C and ^{19}F NMR spectra were determined on a JEOL EX270 (^{1}H: 270.05 MHz, ^{13}C: 67.8 MHz ^{19}F: 254.05 MHz) spectrometer using $CDCl_3$ as a solvent. The chemical shifts for ^{1}H, ^{13}C and ^{19}F NMR were given in δ (ppm) from internal TMS, $CDCl_3$, and monofluorobenzene (−36.5 ppm), respectively. The product yields were determined by ^{19}F NMR using monofluorobenzene as an internal standard. Cyclic voltammetry measurements were carried out using ALS 600A Electrochemical Analyzer. The preparative electrolysis was performed using Metronix Corp. constant current power supply model 5944 monitored with coulomb/amperehour meter HF-201. High resolution mass spectra were recorded on JEOL The MStaion JMS-700. Melting points were determined using Yanako Micro Melting Point Apparatus MP-500P.

2.2. Materials

Unless otherwise stated, all reagents and chemicals were obtained from commercial sources and used without further purification. Dry solvents were perchased and used as received.

2.3. Synthesis of *4-[bis(4-bromophenyl)amino]benzyltriethylammonium trifluoromethanesulfonate (**Med-1**) and 1-{4-[bis(4-bromophenyl)amino]benzyl}-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (**Med-2**)*

2.3.1. Synthesis of 4-[bis(4-bromophenyl)amino]benzaldehyde (**2**) [32]

$POCl_3$ (14.0 mL, 155 mmol) in DMF (12.0 mL, 155 mmol) was added to the solution of 4,4′-dibromotriphenylamine (**1**) (2.50 g, 6.20 mmol). The mixture was stirred at 95 °C for 1 h and cooled to room temperature. Aqueous NaOH was then added to the mixture. After stirring for 30 min, the product was extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, and the solvent was evaporated. The residue was purified by column chromatography over silica gel with CH_2Cl_2/hexane (5:1) to give compound **2** (2.42 g, 5.61 mmol, 90%) as yellow solid. M.p. 155–156 °C; ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ = 9.84 (s, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 4H), 7.02 (d, J = 8.6 Hz, 6H), ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm): δ = 190.10, 152.09, 144.79, 132.73, 131.19, 129.92, 127.20, 120.24, 117.86.

2.3.2. Synthesis of 4-[bis(4-bromophenyl)amino]benzyl alcohol (**3**)

$NaBH_4$ (0.284 g, 6.88 mmol) in EtOH (13.0 mL) and 1.0 M NaOH solution (1.40 mL) were added to the solution of 4-[bis(4-bromophenyl)amino]benzaldehyde (**2**) (2.42 g, 5.61 mmol) in THF (16 mL). The mixture was stirred for 1 h at room temperature. Aqueous HCl was added to the mixture and the mixture was stirred for further 30 min. Then the product was extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, and the solvent was evaporated. The residue was purified by column chromatography over silica gel with $CHCl_3$ to give compound **3** (2.20 g, 5.07 mmol, 90%) as pale yellow solid. M.p. 90–91 °C; ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ = 7.34 (d, J = 8.9 Hz, 4H), 7.27 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.9 Hz, 4H), 4.66 (d, J = 5.7 Hz, 2H), 1.62 (t, J = 5.7 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm): δ = 146.38, 146.36, 136.04, 132.31, 128.44, 125.37, 124.47, 115.50, 64.84; IR (KBr): ν = 3214, 2934, 2871, 1574, 1493 cm^{-1}; HRMS Calcd for $C_{19}H_{15}NOBr_2$: 430.9520, found: 430.9529.

2.3.3. Synthesis of **Med-1**

To a stirred solution of 4-[bis(4-bromophenyl)amino]benzyl alcohol (**3**), (0.60 g, 1.4 mmol) and triethylamine (0.55 mL, 4.2 mmol) in CH_2Cl_2 (2.0 mL), trifluoromethanesulfonyl chloride (0.48 mL, 4.2 mmol) in CH_2Cl_2 (2 mL) was added at 0 °C and the mixture was stirred for 2 h. The mixture was washed with water and extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was washed with Et_2O (5× 30 mL) to give compound **Med-1** (0.65 g, 0.97 mmol, 71%) as white solid. M.p. 128–131 °C; ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ = 7.42 (d, J = 8.6 Hz, 4H), 7.21 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 4H), 4.25 (s, 2H), 3.23 (q, J = 8.1 Hz, 6H), 1.42 (t, J = 8.1 Hz, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm): δ = 150.24, 147.02, 134.64, 133.69, 127.74, 123.94, 121.94, 121.63 (q, J = 319 Hz), 117.81, 60.79, 53.31, 8.07; ^{19}F NMR (254 MHz, $CDCl_3$, ppm): δ = −1.70 (s, 3F); HRMS Calcd for $C_{25}H_{29}Br_2N_2^+$: 515.0697, found: 515.0710, $CF_3O_3S^-$: 148.9520, found: 148.9520.

2.3.4. Synthesis of 1-{4-[bis(4-bromophenyl)amino]benzyl}-3-methylimidazolium trifluorometanesulfonate (**4**)

Trifluoromethanesulfonyl chloride (1.17 mL, 11.1 mmol) in CH_2Cl_2 (8.0 mL) was added to the solution of 4-[bis(4-bromophenyl)amino]benzyl alcohol (**3**) (1.60 g, 3.69 mmol) and 1-methylimidazole (0.911 g, 11.1 mmol) in CH_2Cl_2 (8.0 mL) at 0 °C and the reaction mixture was stirred for 2 h. The mixture was washed with water and extracted with $CHCl_3$. The solvent was evaporated. The residue was washed with Et_2O (5× 30 mL) to give compound **4** (1.37 g, 2.17 mmol, 59%) as dark yellow solid. M.p. 101.1–103.7 °C; ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ = 10.64 (s, 1H), 7.39–7.28 (m, 4H), 7.15 (d, J = 5.7 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 4H), 5.45 (s, 2H), 4.07 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm): δ = 147.76, 145.78, 145.68, 133.57, 131.27, 127.14, 125.26, 124.80, 124.72, 122.33, 120.41 (q, J = 320 Hz), 116.23, 52.64, 35.47; ^{19}F NMR (254 MHz, $CDCl_3$): δ = −1.87 (s, 3F); HRMS Calcd for $C_{23}H_{20}Br_2N_3^+$: 496.0024, found: 496.0030, Calcd for $CF_3O_3S^-$: 148.9520, found: 148.9517.

2.3.5. Synthesis of **Med-2**

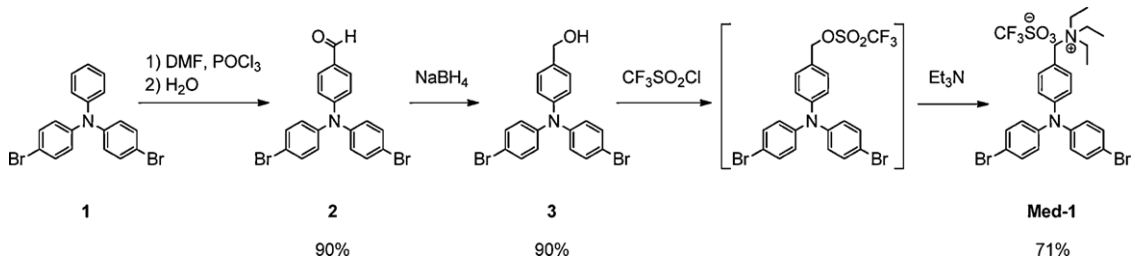
Lithium bis(trifluoromethanesulfonyl)amide (1.50 g, 5.23 mmol) in water (50 mL) was added to the solution of 3-{4-[bis(4-bromophenyl)amino]benzyl}-1-methyl-imidazolium trifluoromethanesulfonate (**4**) (1.10 g, 1.74 mmol) in $CHCl_3$ (3.0 mL), and the reaction mixture was stirred for 3 h at room temperature. Then the organic layer was washed with water, and the solvent was evaporated. The residue was washed with Et_2O (5× 30 mL) to give compound **Med-2** (0.860 g, 1.11 mmol, 64%) as yellow solid. M.p. 74.7–78.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ = 8.76 (s, 1H), 7.36–7.24 (m, 8H), 7.03 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 4H), 5.24 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm): δ = 147.56, 145.50, 145.42, 135.22, 132.16, 129.91, 126.50, 125.70, 123.58, 121.87, 119.37 (q, J = 320 Hz), 115.87, 52.49, 35.85; ^{19}F NMR (254 MHz, $CDCl_3$, ppm): δ = −2.32 (s, 6F); HRMS Calcd for $C_{23}H_{20}Br_2N_3^+$: 496.0024, found: 497.9987. Calcd for $C_2F_6NO_4S_2^-$: 279.9173, found: 279.9175.

2.3.6. Synthesis of dithioacetals (**7a**–**7c**)

Dithioacetals, **7a**–**7c** were prepared from the corresponding ketones and ethane dithiol in the presence of BF_3-2(AcOH) at room temperature [33].

2.4. Cyclic voltammetry

Cyclic voltammetry was carried out at 25 °C in anhydrous MeCN containing 0.6 M tetraethylammonium perchlorate (Et_4NClO_4, TEAP) using a platinum disk working electrode (ϕ = 0.16 cm) and



Scheme 1.

a platinum plate counter electrode (1 cm × 1 cm). Potentials were referred to a saturated calomel electrode (SCE) using saturated KCl salt bridge for the junction between SCE and the MeCN solution. In the case of measurement in ionic liquid HF salt, potentials were referred to Ag wire with external ferrocene/ferrocenium (Fc/Fc^+).

2.5. General procedure for indirect anodic deprotection of dithioacetal using *Med-1* and *Med-2*

Constant current electrolysis was carried out with platinum anode and cathode (1 cm × 1 cm) in 0.6 M TEAP/25 mM H_2O/$MeNO_2$ (3.0 mL) containing dithioacetal **7** (0.1 mmol) and Ar_3N mediator (10 mol%) using an undivided cell at room temperature. After the charge was passed, the solution was passed through a short column filled with silica gel using EtOAc as an eluent to remove salts. The product **8a** was identified by the comparison with ^{19}F NMR (−29.17 ppm) and mass spectra of the authentic sample. The yields were determined by ^{19}F NMR using monofluorobenzene (−36.50 ppm) as an internal standard.

2.6. General procedure for indirect anodic fluorodesulfurization of dithioacetal using *Med-1* and *Med-2*

Constant current electrolysis was carried out with platinum anode and cathode (1 cm × 1 cm) in 0.3 M Et_3N-5HF/$MeNO_2$ (3 mL) containing dithioacetal **7** (0.1 mmol) and Ar_3N mediator (10 mol%) using an undivided cell at room temperature. After the charge was passed, the solution was passed through a short column filled with silica gel using EtOAc as an eluent to remove HF salts. The difluorinated products **9a**–**9c** were identified by the comparison with ^{19}F NMR (**9a**: δ = −9.73, −34.01, **9b**: δ = −11.98, **9c**: δ = −12.21 ppm) and mass spectra of authentic samples [34]. The yields were determined by ^{19}F NMR using monofluorobenzene as an internal standard.

3. Results and discussion

3.1. Synthesis of *Med-1* and *Med-2*

Ar_3N mediator bearing ionic-tag was synthesized according to Schemes 1 and 2. First, a formyl group was introduced to 4,4′-dibromotriphenylamine (**1**) using Vilsmeier–Haack reaction. Next, 4-[bis(4-bromophenyl)amino]benzaldehyde (**2**) was reduced using $NaBH_4$ to form 4-[bis(4-bromophenyl)amino]benzyl alcohol (**3**). The compound **3** was reacted with trifluoromethanesulfonyl chloride in the presence of triethyamine (Et_3N) to form the corresponding sulfonyl ester, which was immediately reacted with Et_3N to provide 4-[bis(4-bromophenyl)amino] benzyltriethylammonium trifluoromethanesulfonate (**Med-1**). In a similar way, 1-{4-[bis(4-bromophenyl)amino]benzyl}-3-methylimidazolium trifluoromethanesulfonate (**4**) was synthesized by using 1-methylimidazole instead of triethylamine as cation part. Since **4** was too hygroscopic to handle under air, the anion part of **4** was changed to more hydrophobic anion like bis(trifluoromethanesulfonyl)amide anion. As expected, the obtained **Med-2** was easy to handle under air.

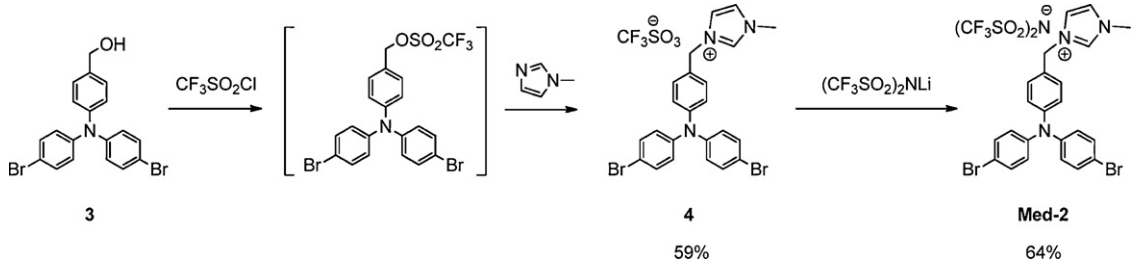
3.2. Cyclic voltammetry (CV) analysis for *Med-1* and *Med-2*

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, respectively as shown in Fig. 1. 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)) [35,36].

$$I_{pa} = 0.44nF\left(\frac{nF}{RT}\right)^{1/2} \times AC_0D^{1/2}\nu^{1/2} \quad (1)$$

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

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 (Fig. 3). Their estimated diffusion coefficients in Et_3N-5HF were 2.7×10^{-6} $cm^2\ s^{-1}$ and 2.6×10^{-6} $cm^2\ s^{-1}$, respectively. These values are less than half of those in MeCN (Fig. 4).



Scheme 2.

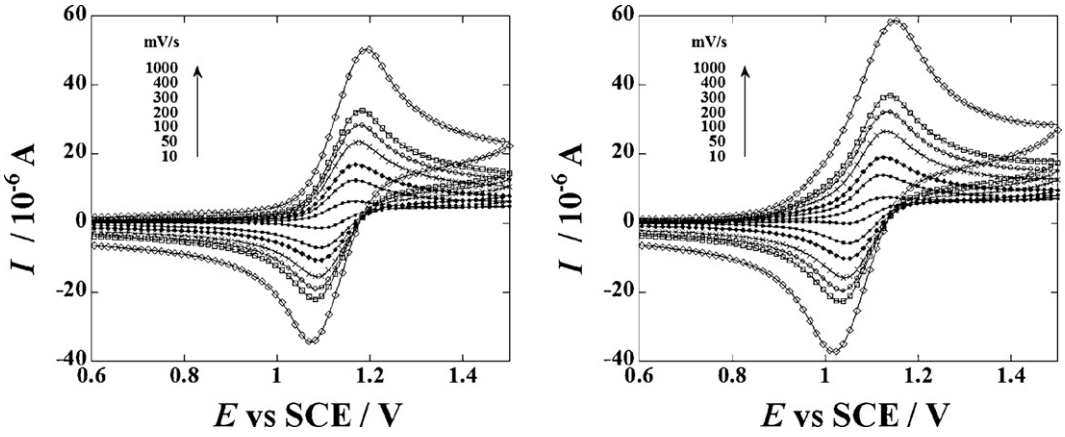


Fig. 1. Cyclic voltammograms of **Med-1** (left) and **Med-2** (right) (3 mM) in 0.6 M TEAP/MeCN (5 mL) at 25 °C at several scan rates; solid circle (●): 10 mV s^{-1}, solid square (■): 50 mV s^{-1}, solid diamond (♦): 100 mV s^{-1}, cross (**x**): 200 mV s^{-1}, circle (○): 300 mV s^{-1}, square (□): 400 mV s^{-1}, diamond (◊): 1000 mV s^{-1}.

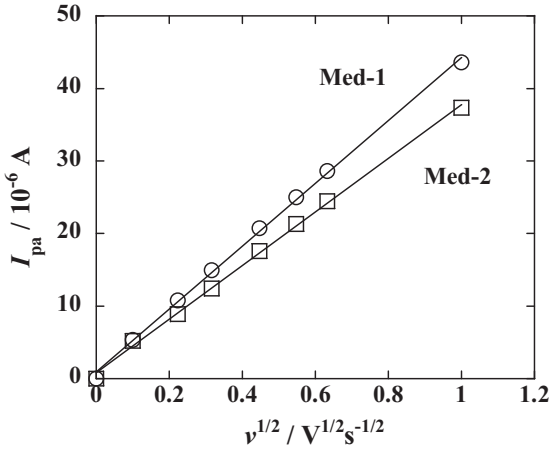


Fig. 2. Plots of I_{pa} (**Med-1**: circle; ○, **Med-2**: square; □) in 0.6 M TEAP/MeCN (5 mL) as a function of $v^{1/2}$.

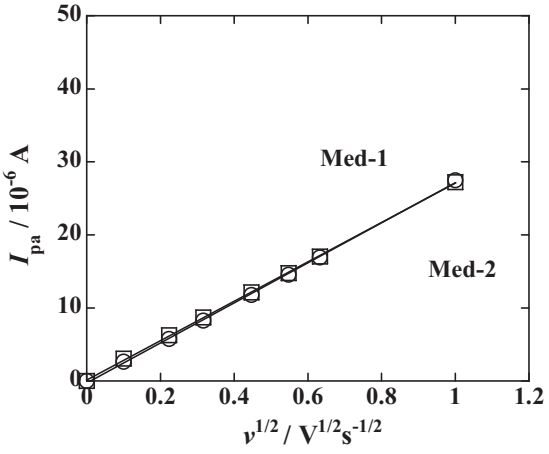


Fig. 4. Plots of I_{pa} (**Med-1**: circle; ○, **Med-2**: square; □) in Et_3N-5HF as a function of $v^{1/2}$.

Diffusion coefficient of tris(*p*-bromophenyl)amine in MeCN and ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF_6] were 1.3×10^{-5} cm^2 s^{-1} and 2.8×10^{-8} cm^2 s^{-1}, respectively [37]. In general, diffusion coefficient of organic molecules in ionic liquid is *ca.* 500–1000 times lower than that in MeCN due to the highly viscous nature of ionic liquid [38]. However, the diffusion coefficients of **Med-1** and **Med-2** in HF salt ionic liquid were little smaller than those of ordinary molecular solvents like MeCN. This is because of low viscosity of Et_3N-5HF (1.30 mPa s^{-1}) [39–41]. Therefore, it was found that such low viscous HF salt ionic liquids like Et_3N-5HF can be used as electrolytic reaction media similarly to molecular organic solvents.

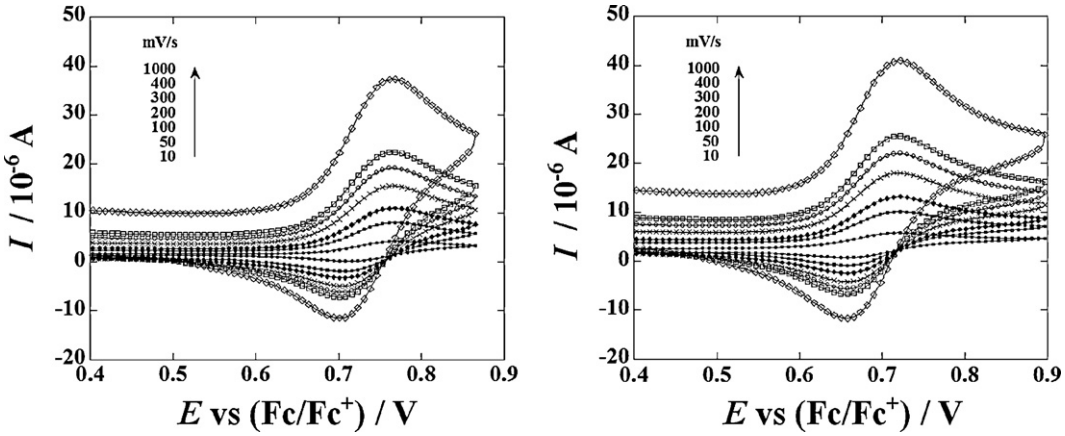


Fig. 3. Cyclic voltammograms of **Med-1** (left, 3 mM) and **Med-2** (right, 3 mM) in Et_3N-5HF (5 mL) at 25 °C referenced to Ag wire with external ferrocene/ferrocenium (Fc/Fc^+, 3 mM) at several scan rates; solid circle (●): 10 mV s^{-1}, solid square (■): 50 mV s^{-1}, solid diamond (♦): 100 mV s^{-1}, cross (**x**): 200 mV s^{-1}, circle (○): 300 mV s^{-1}, square (□): 400 mV s^{-1}, diamond (◊): 1000 mV s^{-1}.

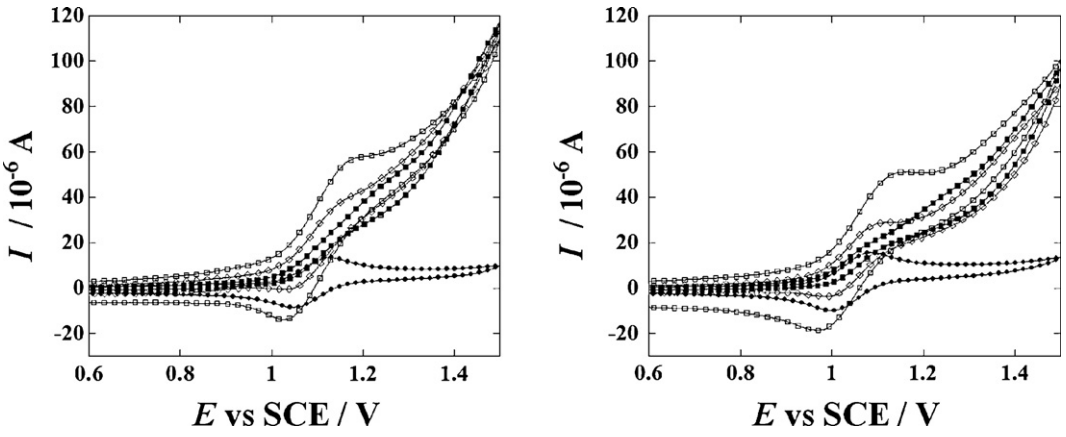


Fig. 5. Cyclic voltammgrams of **Med-1** (left, 3 mM) and **Med-2** (right, 3 mM) in 0.6 M TEAP/$MeNO_2$ (5 mL), (solid circle; ●) at 100 mV s^{-1}, (solid square; ■) in the presence of **7a** (15 mM) at 100 mV s^{-1}, (diamond; ◊) in the presence of **7a** (15 mM) at 300 mV s^{-1} (left) or 200 mV s^{-1} (right), (square; □) in the presence of **7a** (15 mmol) at 1000 mV s^{-1}.

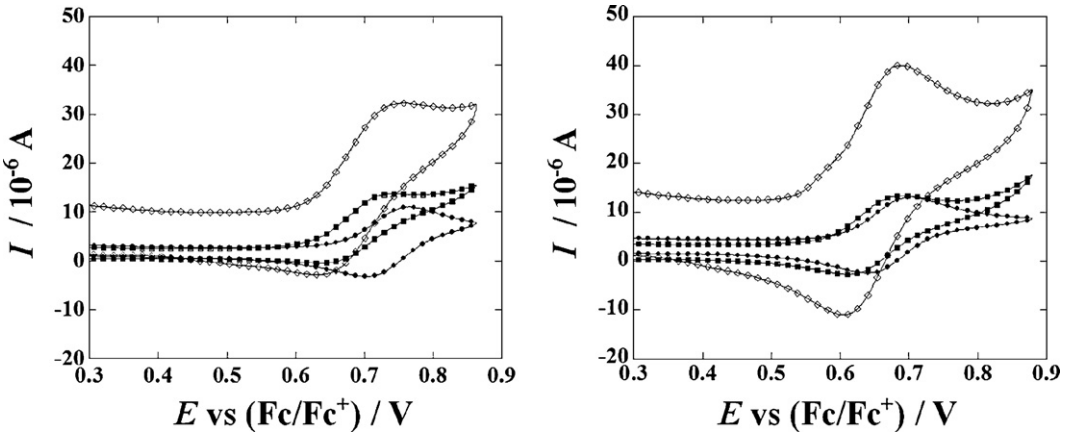


Fig. 6. Cyclic voltammgrams of **Med-1** (left, 3 mM) and **Med-2** (right, 3 mM) in Et_3N-5HF (5 mL) using Ag wire with external ferrocene/ferrocenium (Fc/Fc^+, 3 mM), (solid circle; ●) at 100 mV s^{-1}, (solid square; ■) in the presence of **7a** (15 mM) at 100 mV s^{-1}, (diamond; ◊) in the presence of **7a** (15 mM) at 1000 mV s^{-1}.

Ar_3N derivatives have been utilized as an electrocatalytic mediator for electrochemical oxidative deprotection of dithioacetal compounds [14,15]. Therefore, CV measurements for **Med-1** and **Med-2** were carried out in the absence and the presence of dithioacetal **7a** (15 mM) (E_{pa} = 2.30 V *vs.* SCE, 1.79 V *vs.* Fc/Fc^+) as a model substrate in $MeNO_2$ and Et_3N-5HF, respectively (Figs. 5 and 6). In both media, the oxidation peak currents for **Med-1** and **Med-2** were markedly increased in the presence of **7a**, while the re-reduction peaks completely disappeared at a scan rate of 100 mV s^{-1}. Even at a scan rate of 300 mV s^{-1}, the re-reduction peaks mostly disappeared. However, at extremely high scan rate like 1000 mV s^{-1}, the re-reduction peaks appeared. Therefore, the enhanced anodic currents seem to be typical catalytic currents.

3.3. *Mediatory use of **Med-1** and **Med-2** for electrocatalic reaction*

On the basis of the results of the CV measurements above, the macroscale electrocatalytic oxidative deprotection of dithioacetal **7a** was carried out using **Med-1** as a mediator. The results are summarized in Table 1.

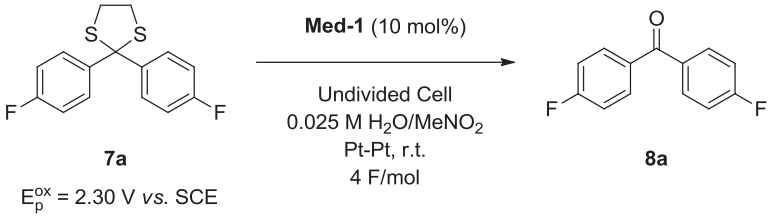
The deprotection reaction using **Med-1** in the absence of base did not proceed well (Entry 1), whereas the deprotection was achieved in the presence of base to give the corresponding ketone, **8a** in good yield (Entry 2). Interestingly, constant-potential electrolysis at 1.10 V *vs.* SCE provided **8a** in favorable yield even without base (Entry 3). In the presence of base, the yield of **8a** increased to *ca.* 80% (Entry 4). In sharp contrast, constant-potential electrolysis of **7a** at this potential did not proceed at all in the absence of **Med-1**.

Next, electrocatalytic oxidative fluorodesulfurization of dithioacetal **7a** using **Med-1** and **Med-2** in $MeNO_2$ containing ionic liquid HF salt, Et_3N-5HF was carried out. As shown in Table 2, fluorodesulfurization without mediator resulted in the fluorinated product **9a** in low yield (Entries 1–3). On the other hand, in the presence of a mediator, the yield of **9a** increased appreciably compared to the case without mediator (Entries 4–9). However, the yield of **9a** was up to 54% due to the formation of considerable amount of ketone **8a** as a by-product. According to the reaction mechanism previously proposed [15,42], the cation intermediate generated by the oxidation of **7a** is attacked by a fluoride anion to provide fluorinated product **9a**. However, the nucleophilic attack by contaminating water is also possible to give by-product **8a**.

In order to reduce the contaminating water from the reaction system, we conducted the electrolysis in neat ionic liquid HF salt, Et_3N-5HF without organic solvent. In this system, ionic liquid, Et_3N-5HF works not only as a fluorine source and electrolyte, but also as reaction media [43]. Due to the acidic nature of the HF salt, the contaminating water would be protonated to be less nucleophilic as reported previously [44]. Moreover, these mediators are well compatible with the ionic liquid HF salt. The results are shown in Table 3.

Although, the fluorodesulfurization of **7a** did not take place efficiently in the absence of a mediator, the desired fluorination using the mediators proceeded well (Entries 2–6). Especially, when

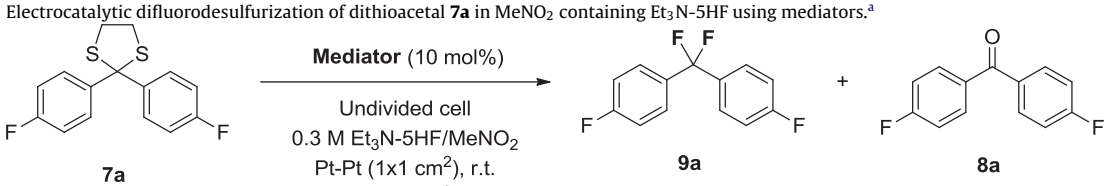
Table 1
Electrocatalytic oxidative deprotection of dithioacetal **7a** using mediator, **Med-1**.[a]



Entry	Base	Method[b]	Yield of **8a** (%)[c]	Recovery of **7a** (%)[c]
1	–	C. C.	42	29
2	$NaHCO_3$	C. C.	81	3
3	–	C. P.	71	22
4	$NaHCO_3$	C. P.	78	12

[a] Reaction conditions: **7a** (0.1 mmol) and base (0.5 mmol) in 0.6 M Et_4NClO_4/Solvent (3 mL)
[b] C. C. = constant current electrolysis at 5 mA/cm^2.
C. P. = constant potential electrolysis at 1.10 V *vs.* SCE.
[c] Determined by ^{19}F NMR.

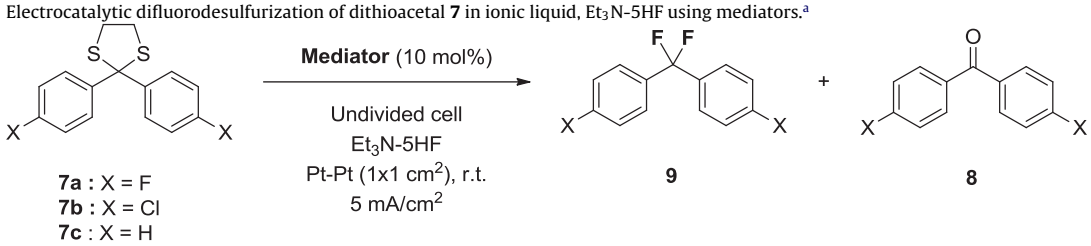
Table 2
Electrocatalytic difluorodesulfurization of dithioacetal **7a** in $MeNO_2$ containing Et_3N-5HF using mediators.[a]



Entry	Mediator	Electricity (F/mol)	Yield (%)[b]		Recovery of **7a** (%)[b]
			9a	**8a**	
1	–	2	27	10	21
2		4	35	8	3
3		6	39	12	0
4	**Med-1**	4	41	19	32
5		6	53	25	19
6		8	54	24	0
7	**Med-2**	2	35	16	41
8		3	44	15	30
9		4	52	16	19

[a] Reaction conditions: **7a** (0.1 mmol) in 0.3 M Et_3N-5HF/$MeNO_2$ (3 mL).
[b] Determined by ^{19}F NMR.

Table 3
Electrocatalytic difluorodesulfurization of dithioacetal **7** in ionic liquid, Et_3N-5HF using mediators.[a]



Entry	Substrate	Oxidation potential (V *vs.* SCE)	Mediator	Electricity (F/mol)	Yield (%)[b]		Recovery of **7** (%)[b]
					9	**8**	
1	**7a**: X = F	2.30	–	4	30	8	8
2	**7a**: X = F	2.30	**Med-1**	3	72	9	8
3	**7a**: X = F	2.30	**Med-1**	4	53	21	Trace
4	**7a**: X = F	2.30	**Med-2**	2	61	12	26
5	**7a**: X = F	2.30	**Med-2**	3	74	8	14
6	**7a**: X = F	2.30	**Med-2**	4	80	9	Trace
7	**7b**: X = Cl	2.30	**Med-2**	6	73	–[c]	–[c]
8	**7c**: X = H	2.20	**Med-2**	4	34 (45[d])	–[c]	–[c]

[a] Reaction conditions: **7** (0.1 mmol) in 0.3 M Et_3N-5HF (3 mL).
[b] Determined by ^{19}F NMR.
[c] Not determined.
[d] PEG (2.5%) was added.

Med-2 was used as mediator, desired **9a** was obtained in good yield suppressing the formation of **8a** (Entry 6).

Furthermore, **7b** having an electron-withdrawing Cl group at the para-position of the benzene ring underwent electrocatalytic fluorodesulfurization to provide the desired fluorinated product **9b** in good yield (Entry 7). On the other hand, non-substituted **7c** provided **9c** in moderate yield even in addition of PEG to enhance the nucleophilicity of fluoride anion (Entry 8) [45,46]. This suggested that the difluorodesulfurization of dithioacetal substrates was strongly affected by substituents on the benzene ring. Previously, we reported similar results, namely, that electron-withdrawing groups markedly promoted the anodic fluorodesulfurization due to the high electrophilic reactivity of the anodically generated benzyic cation intermediates [42].

The reusability of **Med-2** in anodic fluorodesulfurization of **7a** as a model substrate was investigated under the same conditions as Entry 6 in Table 3. The product 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 **9a** decreased from 80% to 51% and 48% for the second and the third electrolyses, respectively. The recovered mediator, **Med-2** showed a slightly less positive redox peaks in the cyclic voltammogram compared to the original one. However, the real structure of the recovered mediator could not be established. Therefore, the decrease of the yield seems to be as due to the partial modification of the mediator during the electrolysis. 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.

4. Conclusion

In conclusion, novel Ar_3N mediators containing ionic-tags such as ammonium and imidazolium moieties were synthesized from 4,4′-dibromotriphenylamine. The introduction of the ionic-tag enhanced the solubility of the mediators in ionic liquid HF salt, Et_3N-5HF. Electrocatalytic reaction such as deprotection and fluorodesulfurizaiton of dithioacetals using these mediators in molecular solvent, $MeNO_2$ and ionic liquid HF salt, Et_3N-5HF was successfully carried out to produce the desired deprotected and difluorinated products, respectively. Since the fixation of the mediators in ionic liquid HF salt was possible even after extraction with a less polar organic solvent like hexane, the recycle use of the mediators was successfully demonstrated to some extent.

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