Studies on Metal Complexes as Active Materials in Redox-flow Battery Using Ionic Liquids as Electrolyte: Electrochemical Properties of $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ (L: Multidentate Ligands, $x = 2$ or 3) in 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)Imide, $[\text{BMI}][\text{Tf}_2\text{N}]$

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ABSTRACT

As part of studies for finding active materials in the redox-flow battery system using ionic liquids (ILs) as electrolyte, we have synthesized $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ (L = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), or 2,2':6',2''-terpyridine (terpy)); Tf_2N = bis(trifluoromethylsulfonyl)imide, $x = 3$ for bpy and phen; $x = 2$ for terpy), and examined their electrochemical properties in $[\text{BMI}][\text{Tf}_2\text{N}]$ (BMI = 1-butyl-3-methylimidazolium). From ^1H -NMR and UV-vis absorption spectra, it was confirmed that three Fe(II) species exist as $[\text{Fe}(\text{L})_x]^{2+}$ in $[\text{BMI}][\text{Tf}_2\text{N}]$ solution. Cyclic voltammograms (CVs) and chronoamperograms (CAs) of the $[\text{Fe}(\text{L})_x]^{2+}$ species in $[\text{BMI}][\text{Tf}_2\text{N}]$ solution were measured at 25°C. In the CVs, two peaks corresponding to the redox couples of Fe(II)/Fe(III) were observed around 1 V vs. Ag/AgCl, and their redox reactions were found to be quasi-reversible. The diffusion coefficients of $[\text{Fe}(\text{L})_x]^{2+}$ were estimated to be $(3\text{--}9) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ by chronoamperometry. The standard rate constants for the redox reactions were estimated to be $(2\text{--}6) \times 10^{-3} \text{ cm s}^{-1}$ at 25°C. Furthermore, the present Fe(II)/Fe(III) redox systems were found to be cycled stably. From these results, the $[\text{Fe}(\text{L})_x]^{2+}$ species are expected to be used as cathode active materials for the redox-flow batteries using $[\text{BMI}][\text{Tf}_2\text{N}]$ as the electrolyte.

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1. Introduction

As one of promising battery systems for electric power storage, the redox-flow batteries (RFBs) have been developed, because of their long cycle life and large theoretical capacity.^{1,2} Especially, vanadium RFB has been investigated widely and expected to be used commercially.³ In the vanadium RFB, however, concentrated sulfuric acid solution has been used as the electrolyte. Thus, electrolysis of solvent water and corrosion of materials used in the battery system are subjects for improving.^{1,3} From these viewpoints, organic solvents have been examined as alternative electrolytes.^{2,4–7} However, flammability or pollution problems have been still remained.

Recently, ionic liquids (ILs) have been known as a “green solvent” and paid attention as alternative media to the conventional organic solvents, because of their unique properties, such as thermal stability, non-flammability, high ionic conductivity, low vapor pressure, wide electrochemical potential windows, and so on.^{8–15} If ILs can be used as electrolyte in the RFBs, the disadvantageous points of conventional RFBs are expected to be overcome.

From above viewpoints, electrochemical properties of metal ions and complexes in ILs have been studied.^{16–27} Especially, diffusion coefficients and standard rate constants for Fe(II) and Ru(II) complexes with 2,2'-bipyridine (bpy) in ILs have been investigated in detail, and these complexes were proposed to be candidates of active materials of RFBs.^{19–23,25,26} In these studies, however, the sample solutions were prepared by dissolving $\text{Fe}(\text{Tf}_2\text{N})_2$ and bpy into 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[\text{BMP}][\text{Tf}_2\text{N}]$), and hence the chemical forms of Fe(II) species are not strictly assigned.

In this study, we have prepared $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ [L = bpy ($x = 3$), 1,10-phenanthroline (phen, $x = 3$), 2,2':6',2''-terpyridine (terpy, $x = 2$)], and investigated electrochemical properties of the $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ complexes dissolved in $[\text{BMI}][\text{Tf}_2\text{N}]$ to examine whether the present complexes are applicable as the active materials of RFBs.

2. Experimental

2.1 Materials

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{BMI}][\text{Tf}_2\text{N}]$, Tokyo Chemical Industry Co., Ltd.) was kept under molecular sieve 3A to remove water and used without further purification. Iron(II) sulfate heptahydrate ($\geq 99\%$ Kanto Chemical Co., Inc.), 1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl] methane-sulfonamide ($\geq 99\%$, Kanto), sodium perchlorate ($\geq 96.0\%$, Kanto), bpy ($\geq 99\%$, SIGMA-ALDRICH), phen ($\geq 99\%$, ACRS), terpy ($\geq 98\%$, SIGMA-ALDRICH) were used as received. Structural formulae of bpy, phen, and terpy are shown in Fig. 1.

2.2 Instrumentation

All electrochemical experiments were carried out using BAS CV-50W voltammetric analyzer with provision for iR compensation and BAS CV cell at 25°C in a glove-box filled with N_2 gas. A three-electrode system was utilized, that is, a BAS 002012 as GC working electrode (electrode surface area 0.0707 cm^2), a BAS 012961 as Pt counter electrode, and a BAS 012167 RE-1B as Ag/AgCl reference electrode jointed to CV cell by the salt bridge filled with $[\text{BMI}][\text{Tf}_2\text{N}]$. All potentials reported here are vs. Ag/AgCl. The formal

Figure 1. Structural formulae of bpy, phen, and terpy.

potential of Fc/Fc^+ (6 mM, $M = \text{mol dm}^{-3}$) in $[\text{BMI}][\text{Tf}_2\text{N}]$ was 0.266 V vs. Ag/AgCl reference electrode. The sample solutions were deoxygenated by passing N_2 gas into the solution for at least 10 min before starting measurements.

Elemental analyses were performed by MICRO CORDER MJ10 (J-SCIENCE). ^1H -NMR spectra were recorded at 400 MHz on a JEOL ECX-400P spectrometer. UV-vis absorption spectra were measured by Shimadzu UV-vis 2400PC spectrophotometer. Water content of ILs was measured by Karl fisher moisture content meter (Metrohm 831 Coulometer) and confirmed to be less than 35 ppm.

2.3 Syntheses of Fe(II) complexes

The $[\text{Fe}(\text{bpy})_3](\text{SO}_4)$, $[\text{Fe}(\text{phen})_3](\text{SO}_4)$ ^{28–30} and $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$ ^{31,32} complexes were synthesized according to the literature procedures. The $[\text{Fe}(\text{bpy})_3][\text{Tf}_2\text{N}]_2$, $[\text{Fe}(\text{phen})_3][\text{Tf}_2\text{N}]_2$, and $[\text{Fe}(\text{terpy})_2][\text{Tf}_2\text{N}]_2$ complexes were synthesized by adding HTf_2N aqueous solution to the aqueous solutions dissolving above each Fe(II) complex. Details are described as follows.

2.3.1 $[\text{Fe}(\text{bpy})_3][\text{Tf}_2\text{N}]_2$

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (5.0 g, 18 mmol) was dissolved in water (20 mL), followed by addition of bpy (8.4 g, 54 mmol) under stirring for 30 min. The mixture was filtered and the filtrate was condensed to 26 mL using rotary evaporator. Dark red colored $[\text{Fe}(\text{bpy})_3]\text{SO}_4$ was precipitated after keeping for 24 h at 5°C . The precipitate $[\text{Fe}(\text{bpy})_3]\text{SO}_4$ was filtered off and dried under vacuum. Yield: 3.6 g (36%). The resulting $[\text{Fe}(\text{bpy})_3]\text{SO}_4$ (2.5 g, 4 mmol) was dissolved in water (30 mL). To this solution, 25 wt% HTf_2N aqueous solution (6.4 g, 5.7 mmol) was added under vigorous stirring. Dark red colored $[\text{Fe}(\text{bpy})_3][\text{Tf}_2\text{N}]_2$ was precipitated instantly. The precipitates were filtered off and dried under vacuum. Yield: 2.9 g (67%). Elemental anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{N}_8\text{FeF}_{12}\text{S}_4\text{O}_8$ (M.W. = 1084.70): C, 37.65; H, 2.23; N, 10.33%. Found: C, 37.41; H, 2.11; N, 10.49%. ^1H NMR (400 MHz, CD_3CN): δ 7.60 (dd, 2H, H(3)), 7.66 (dd, 2H, H(2)), 8.26 (s, 2H, H(5)), 8.62 (d, 2H, H(4)) ppm. UV-vis absorption spectra ($\lambda_{\text{max}}/\text{nm}$, ($\log[\epsilon/(\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1})]$): 348 (3.89), 519 (4.02).

2.3.2 $[\text{Fe}(\text{phen})_3][\text{Tf}_2\text{N}]_2$

To aqueous solution (20 mL) dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (5.0 g, 18 mmol), phen (9.8 g, 54 mmol) was added, followed by stirring for 30 min. The mixture was filtered and the filtrate was condensed to 15 mL by rotary evaporator. Dark red $[\text{Fe}(\text{phen})_3]\text{SO}_4$ was precipitated after keeping for 24 h at 5°C . The precipitate $[\text{Fe}(\text{phen})_3]\text{SO}_4$ was filtered off and dried in vacuo. Yield: 3.3 g (26%). The resulting $[\text{Fe}(\text{phen})_3]\text{SO}_4$ (1.5 g, 2.2 mmol) was dissolved in water (100 mL), followed by addition of 25 wt% HTf_2N aqueous solution (3.4 g, 3 mmol) under vigorous stirring. Dark red $[\text{Fe}(\text{phen})_3][\text{Tf}_2\text{N}]_2$ was precipitated instantly, and was filtrated and dried under vacuum. Yield: 1.2 g (47%). Elemental anal. Calcd for $\text{C}_{40}\text{H}_{24}\text{N}_8\text{FeF}_{12}\text{S}_4\text{O}_8$ (M.W. = 1156.76): C, 41.53; H, 2.09; N, 9.69%. Found: C, 41.19; H, 2.46; N, 9.58%. ^1H NMR (400 MHz, CD_3CN): δ 7.60 (dd, 2H, H(3)), 7.66 (dd, 2H, H(2)), 8.26 (s, 2H, H(5)), 8.62 (d, 2H, H(4)) ppm. UV-vis absorption spectra ($\lambda_{\text{max}}/\text{nm}$, ($\log[\epsilon/(\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1})]$): 508 (4.09).

2.3.3 $[\text{Fe}(\text{terpy})_2][\text{Tf}_2\text{N}]_2$

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.2 g, 4.1 mmol) was dissolved in water (35 mL), followed by addition of terpy (1.7 g, 7.3 mmol) under stirring. The mixture was filtered, and then the aqueous solution of 25 wt% NaClO_4 (4 g, 8.2 mmol) was added to the filtrate under vigorous stirring. Deep purple $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$ was precipitated after keeping for 24 h at 5°C . The precipitate $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$ was filtrated and dried under vacuum. Yield: 2.5 g (85%). The resulting $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$ (0.35 g, 0.46 mmol) was dissolved in water (400 mL), followed by addition of 25 wt% HTf_2N aqueous solution (0.76 g, 0.68 mmol) under vigorous stirring. Deep purple $[\text{Fe}(\text{terpy})_2][\text{Tf}_2\text{N}]_2$ was precipitated instantly. The precipitates were filtered off and dried under vacuum. Yield: 0.34 g (67%). Elemental anal. Calcd for $\text{C}_{34}\text{H}_{22}\text{N}_8\text{FeF}_{12}\text{S}_4\text{O}_8$ (M.W. = 1082.68): C, 37.72; H, 2.05; N, 10.35%. Found: C, 37.81; H, 2.23%; N, 10.38%. ^1H NMR (400 MHz, CD_3CN): δ 7.06 (m, 4H, H(5), H(6)), 7.87 (m, 2H, H(4)), 8.45 (dt, 2H, H(3)), 8.67 (m, 1H, H(4')), 8.90 (d, 2H, H(3')) ppm. UV-vis absorption spectra ($\lambda_{\text{max}}/\text{nm}$, ($\log[\epsilon/(\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1})]$): 550 (4.10).

3. Results and Discussion

3.1 Chemical forms of Fe(II) complexes in $[\text{BMI}][\text{Tf}_2\text{N}]$

In order to examine the chemical forms of Fe(II) species in the solutions prepared by dissolving $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ ($\text{L} = \text{bpy}$, phen, or terpy, $x = 3$ or 2) complexes into $[\text{BMI}][\text{Tf}_2\text{N}]$, we measured ^1H -NMR spectra of CD_3CN solutions dissolving these Fe(II) complexes. As a result, ^1H -NMR spectra were found to be consistent with those of the solutions prepared by dissolving $[\text{Fe}(\text{L})_x]\text{Cl}_2$ into CD_3CN .^{33,34} Furthermore, UV-vis absorption spectra of the CH_3CN and $[\text{BMI}][\text{Tf}_2\text{N}]$ solutions dissolving $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ complexes were found to be consistent with each other and also to be in agreement with those of CH_3CN solutions dissolving $[\text{Fe}(\text{L})_x](\text{BF}_4)_2$.^{35,36} From these results, it was concluded that in the dissolution of $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ complexes into $[\text{BMI}][\text{Tf}_2\text{N}]$ the Fe(II) species are not oxidized to Fe(III) and exist as $[\text{Fe}(\text{bpy})_3]^{2+}$, $[\text{Fe}(\text{phen})_3]^{2+}$, and $[\text{Fe}(\text{terpy})_2]^{2+}$, respectively.

3.2 Electrochemical measurements

As a preliminary experiment, the saturation concentrations of $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ complexes in $[\text{BMI}][\text{Tf}_2\text{N}]$ were examined before carrying out electrochemical experiments. Adding excess amounts of each $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ complex into $[\text{BMI}][\text{Tf}_2\text{N}]$ and then the solutions were centrifuged. From the UV-vis absorption spectra of supernatants, we estimated the solubility of these complexes in $[\text{BMI}][\text{Tf}_2\text{N}]$. The saturation concentrations of $[\text{Fe}(\text{L})_x][\text{Tf}_2\text{N}]_2$ were ca. 45, 15, and 8 mM for $\text{L} = \text{bpy}$, phen, and terpy, respectively. From these results, the concentrations of sample solutions for electrochemical experiments were fixed to ca. 10 mM for $\text{L} = \text{bpy}$, phen, and 5 mM for $\text{L} = \text{terpy}$.

3.2.1 Electrochemical properties of $[\text{Fe}(\text{bpy})_3][\text{Tf}_2\text{N}]_2$

Cyclic voltammograms (CVs) of $[\text{BMI}][\text{Tf}_2\text{N}]$ solution dissolving $[\text{Fe}(\text{bpy})_3][\text{Tf}_2\text{N}]_2$ (10 mM) were measured in the potential range

Table 1. Cyclic voltammetric data for solutions prepared by dissolving complexes into [BMI][Tf₂N].

Complex	Scan rate /(mV s ⁻¹)	<i>E</i> _{pa} /mV	<i>E</i> _{pc} /mV	(<i>E</i> _{pa} + <i>E</i> _{pc})/2 /mV	(<i>E</i> _{pa} – <i>E</i> _{pc}) /mV	<i>I</i> _{pa} /μA	<i>I</i> _{pc} /μA
[Fe(bpy) ₃][Tf ₂ N] ₂ 10 mM	50	1010	936	973	74	14.3	–15.3
	100	1013	936	975	77	20.5	–19.8
	250	1023	929	976	94	31.7	–30.3
	500	1031	921	976	110	43.4	–42.7
	750	1036	922	979	114	55.8	–52.1
[Fe(phen) ₃][Tf ₂ N] ₂ 9.8 mM	50	1031	963	997	68	13.0	–12.6
	100	1045	959	1002	86	19.1	–17.3
	250	1048	949	999	99	28.8	–24.8
	500	1063	939	1001	124	38.0	–34.4
	750	1065	938	1002	127	48.0	–42.8
[Fe(terpy) ₂][Tf ₂ N] ₂ 5.2 mM	100	1062	988	1025	74	16.5	–9.6
	300	1064	984	1024	80	17.2	–15.2
	500	1063	980	1022	83	20.4	–19.5
	700	1066	973	1020	93	25.5	–23.9
	900	1070	979	1025	91	30.3	–27.1

Figure 2. Cyclic voltammograms of the [BMI][Tf₂N] solution dissolving [Fe(bpy)₃][Tf₂N]₂ (10 mM) measured in the potential range from 500 to 1500 mV at different scan rates ($\nu = 50$ –750 mV s⁻¹). Temp. = 25°C. Initial scan direction: anodic.

of 500 to 1500 mV at various scan rate ($\nu = 50$ –750 mV s⁻¹). The results are shown in Fig. 2. Two peaks corresponding to one redox couple are observed around 930 (*E*_{pc}) and 1020 mV (*E*_{pa}). Cyclic voltammetric data are listed in Table 1. With increasing the scan rate, two peaks shift to anodic and cathodic directions, respectively. The potential differences (ΔE_p) between two peaks are 74 and 114 mV at 50 and 750 mV s⁻¹, respectively. The (*E*_{pa} + *E*_{pc})/2 values are constant, 0.976 ± 0.002 V regardless of ν (Table 1). In addition, the CVs were measured at $\nu = 100$ mV s⁻¹ by 100 cycles. The results are shown in Fig. 3. The CVs are found to be almost same. This means that the present redox reaction has no side chemical reactions. These results strongly suggest that the [Fe(bpy)₃]²⁺ is oxidized to [Fe(bpy)₃]³⁺ quasi-reversibly and its formal redox potential (*E*^o)³⁷ is 0.976 ± 0.002 V as shown in Eq. (1).

This is consistent with the results reported for the electrochemical reactions of Fe(II)-bpy complex in [BMP][Tf₂N].¹⁹

Figure 3. Steady state cyclic voltammograms of the [BMI][Tf₂N] solution dissolving [Fe(bpy)₃][Tf₂N]₂ (10 mM) measured in the potential range from 500 to 1500 mV at $\nu = 100$ mV s⁻¹. Temp. = 25°C. Initial scan direction: anodic.

Furthermore, in order to estimate the diffusion coefficient (*D*, cm² s⁻¹) of [Fe(bpy)₃]²⁺ species in [BMI][Tf₂N], we performed chronoamperometry experiments. The potentials were stepped from 500 mV to 900–1300 mV. The resulting chronoamperograms (CAs) are shown in Fig. 4. The *D* value was determined from a plot of currents (*I*_t) vs. $t^{-1/2}$ (*t*: the elapse time after stepping the potential) (see Fig. 5) based on the following Cottrell equation,³⁷

$$I_t = \frac{nFA D^{1/2} C^b}{\pi^{1/2} t^{1/2}} \quad (2)$$

where *C*^b is the bulk concentration of the reactant, *A* is the electrode surface area, *n* is the number of electrons transferred in the redox reaction, and *F* is the Faraday constant. The result is listed in Table 2. Our data is twelve times larger than the reported one.¹⁹ This difference may be due to the differences in the experimental conditions, that is, the concentrations of [Fe(bpy)₃]²⁺ (10, 25 mM),¹⁹ the viscosity of ILs ([BMI][Tf₂N]: $\eta = 52$ mPa s at 20°C, [BMP][Tf₂N]: $\eta = 89$ mPa s at 20°C),¹⁴ and the sample compositions (the [BMI]-[Tf₂N] solution dissolving [Fe(bpy)₃][Tf₂N]₂, the [BMP][Tf₂N] solution dissolving Fe(Tf₂N)₂ and bpy¹⁹).

Table 2. Diffusion coefficients (D) of Fe(II) species and standard rate constants (k^0) for reactions (1), (3), and (4).

Complex	conc. /mM	solvent	D / $(10^{-8} \text{ cm}^2 \text{ s}^{-1})$	ν / (mV s^{-1})	ΔE /mV	ψ	k^0 / $(10^{-4} \text{ cm s}^{-1})$	
$[\text{Fe}(\text{bpy})_3]^{2+}$	10	[BMI][Tf ₂ N]	86	50	74	1.83	42	This study
				750	114	0.4	35	
$[\text{Fe}(\text{phen})_3]^{2+}$	9.8	[BMI][Tf ₂ N]	33	50	68	3	43	This study
				750	127	0.32	18	
$[\text{Fe}(\text{terpy})_2]^{2+}$	5.2	[BMI][Tf ₂ N]	51	100	74	1.82	45	This study
				900	91	0.79	59	
$[\text{Fe}(\text{bpy})_3]^{2+}$	25	[BMP][Tf ₂ N]	7.1	—	—	—	9	(19)

Figure 4. Chronoamperograms of the [BMI][Tf₂N] solution dissolving $[\text{Fe}(\text{bpy})_3][\text{Tf}_2\text{N}]_2$ (10 mM). The potential was stepped from 500 to 900–1300 mV. Temp. = 25°C. **Figure 5.** A Cottrell plot of I_t against $t^{-1/2}$ for the chronoamperometry experiments in the [BMI][Tf₂N] solution dissolving $[\text{Fe}(\text{bpy})_3][\text{Tf}_2\text{N}]_2$. The potential was stepped from 500 to 1200 mV.

3.2.2 Electrochemical properties of $[\text{Fe}(\text{phen})_3][\text{Tf}_2\text{N}]_2$

The CVs of [BMI][Tf₂N] solution dissolving $[\text{Fe}(\text{phen})_3][\text{Tf}_2\text{N}]_2$ were also measured in a similar manner as above. The results are shown in Fig. 6. One redox couple is also observed in the present system. The cyclic voltammetric data are shown in Table 1. As seen from this table, the ΔE_p values increase with an increase in ν , while the $(E_{pa} + E_{pc})/2$ values are constant without depending on ν , 1.000 ± 0.002 V. Furthermore, the CVs repeated 100 times at $\nu = 100 \text{ mV s}^{-1}$ were almost unchanged (see Fig. 7). These phenomena are very similar to those observed in the [BMI][Tf₂N] solution dissolving $[\text{Fe}(\text{bpy})_3][\text{Tf}_2\text{N}]_2$. This indicates that the

Figure 6. Cyclic voltammograms of the [BMI][Tf₂N] solution dissolving $[\text{Fe}(\text{phen})_3][\text{Tf}_2\text{N}]_2$ (9.8 mM) measured in the potential range from 500 to 1500 mV at different scan rates ($\nu = 50$ – 750 mV s^{-1}). Temp. = 25°C. Initial scan direction: anodic. **Figure 7.** Steady state cyclic voltammograms of the [BMI][Tf₂N] solution dissolving $[\text{Fe}(\text{phen})_3][\text{Tf}_2\text{N}]_2$ (9.8 mM) measured in the potential range from 500 to 1500 mV at scan rates 100 mV s^{-1} . Temp. = 25°C. Initial scan direction: anodic.

$[\text{Fe}(\text{phen})_3]^{2+}$ species are oxidized to $[\text{Fe}(\text{phen})_3]^{3+}$ quasi-reversibly under the present conditions, that is,

The D value for $[\text{Fe}(\text{phen})_3]^{2+}$ species in [BMI][Tf₂N] was determined by chronoamperometry in the same way as mentioned above. The results are shown in Fig. 8 and also the Cottrell plots are shown in Fig. 9. The D value was estimated from the slope in Fig. 9

Figure 8. Chronoamperograms of the [BMI][Tf₂N] solution dissolving [Fe(phen)₃][Tf₂N]₂ (9.8 mM). The potential was stepped from 500 to 900–1300 mV. Temp. = 25°C.

Figure 9. A Cottrell plot of I_t against $t^{-1/2}$ for the chronoamperometry experiments in the [BMI][Tf₂N] solution dissolving [Fe(phen)₃][Tf₂N]₂. The potential was stepped from 500 to 1200 mV.

and is listed in Table 2. The D value is found to be almost consistent with that for [Fe(bpy)₃]²⁺ species.

3.2.3 [Fe(terpy)₂][Tf₂N]₂

The CVs of sample solution prepared by dissolving [Fe(terpy)₂][Tf₂N]₂ into [BMI][Tf₂N] are shown in Fig. 10. The cyclic voltammetric data are listed in Table 1. The phenomena in this system are almost consistent with those observed in the [Fe(bpy)₃][Tf₂N]₂ and [Fe(phen)₃][Tf₂N]₂ systems, that is, the ΔE_p values increase with increasing ν , the $(E_{pa} + E_{pc})/2$ values are constant regardless of ν , 1.023 ± 0.002 V, and the CVs repeated 100 cycles at 100 mV s⁻¹ are almost constant (see Fig. 11). These results strongly support that the following oxidation reaction takes place quasi-reversibly.

The D value of [Fe(terpy)₂]²⁺ in [BMI][Tf₂N] was also determined by chronoamperometry experiments. The CAs and the corresponding Cottrell plots are shown in Figs. 12 and 13. The evaluated D value is listed in Table 2.

As expected, the D values in the [Fe(L)_x]²⁺ (L = bpy, phen, and terpy) species are almost same.

3.3 Estimation of standard rate constants

In order to evaluate the validity of assignment that the electrochemical reactions (1), (3), and (4) are quasi-reversible, the

Figure 10. Cyclic voltammograms of the [BMI][Tf₂N] solution dissolving [Fe(terpy)₂][Tf₂N]₂ (5.2 mM) measured in the potential range from 500 to 1500 mV at different scan rates (ν = 100–900 mV s⁻¹). Temp. = 25°C. Initial scan direction: anodic.

Figure 11. Steady state cyclic voltammograms of the [BMI]-[Tf₂N] solution dissolving [Fe(terpy)₂][Tf₂N]₂ (5.3 mM) measured in the potential range from 500 to 1500 mV at scan rates 100 mV s⁻¹. Temp. = 25°C. Initial scan direction: anodic.

Figure 12. Chronoamperograms of the [BMI][Tf₂N] solution dissolving [Fe(terpy)₂][Tf₂N]₂ (5.2 mM). The potential was stepped from 500 to 900–1400 mV. Temp. = 25°C.

standard rate constants (k^0) were estimated by Nicholson's equation [Eq. (5)] derived from the assumption that the D values of Fe(II) and Fe(III) species are equal, $n = 1$, and the transfer coefficient (α) = 0.5,^{36,37}

$$\psi = k^0 / \{D\pi(nF/RT)\nu\}^{1/2} \quad (5)$$

Figure 13. A Cottrell plot of I_p against $t^{-1/2}$ for the chronoamperometry experiments in the [BMI][Tf₂N] solution dissolving [Fe(terpy)₂][Tf₂N]₂. The potential was stepped from 500 to 1300 mV.

where ψ is the kinetic parameter defined by Nicholson. The ΔE_p values at slow and fast scan rates in each system, the corresponding ψ values, and the estimated k^0 values are summarized in Table 2.

If the (1), (3), and (4) reactions are quasi-reversible, the reversibility factor (Λ) proposed by Matsuda et al.,³⁹ $\Lambda = k^0 / (DnFv/RT)^{1/2}$, must be in the range, $15 > \Lambda > 10^{-3}$. In the present experimental conditions, the above relationships are described as follows.

$$(1.9\text{--}7.5) \times 10^{-2} > k^0 > (1.3\text{--}5.0) \times 10^{-6} \quad \text{for the reaction (1)}$$

$$(1.2\text{--}4.7) \times 10^{-2} > k^0 > (0.8\text{--}3.1) \times 10^{-6} \quad \text{for the reaction (3)}$$

$$(2.1\text{--}6.4) \times 10^{-2} > k^0 > (1.4\text{--}4.3) \times 10^{-6} \quad \text{for the reaction (4)}$$

The k^0 values listed in Table 2 are $(3.5\text{--}4.2) \times 10^{-3}$, $(1.8\text{--}4.3) \times 10^{-3}$, and $(4.5\text{--}5.9) \times 10^{-3} \text{ cm s}^{-1}$ for the reactions (1), (3), and (4), respectively and fall in the ranges shown above. These results support our proposal that the electrochemical reactions (1), (3), and (4) occur quasi-reversibly.

3.4 Effect of ligands on the Fe(II)/Fe(III) redox potentials

Kirgan and Rillema have performed the density functional theory (DFT) calculations for low spin Fe(II) complexes ([Fe(bpy)₃]²⁺, [Fe(phen)₃]²⁺, [Fe(bpz)₃]²⁺ (bpz = 2,2'-bipyrazine), and [Fe(terpy)₂]²⁺), whose redox potentials have known to correlate with Fe(II) centered HOMO energy level.⁴⁰ They found out that the HOMO energy levels of [Fe(bpy)₃]²⁺, [Fe(phen)₃]²⁺, and [Fe(terpy)₂]²⁺ are almost same. This expects that the redox potentials of three Fe(II) complexes do not show large differences. In fact, the experimental $E_{1/2}$ (half-wave potential) values for oxidation reactions of [Fe(bpy)₃]²⁺, [Fe(phen)₃]²⁺, and [Fe(terpy)₂]²⁺ are 0.80, 0.79, and 0.90 V vs. Fe/Fc⁺, respectively.⁴¹ This supports our experimental results that the potentials for [Fe(L)_x]²⁺/[Fe(L)_x]³⁺ (L = bpy, phen, terpy, x = 3 or 2) are almost consistent with each other.

Furthermore, Lever has proposed that the Fe(II)/Fe(III) redox potentials of six-coordinated Fe(II) complexes are estimated by the following equation.⁴²

$$E_{\text{obs}} (\text{V}) = 1.11[\Sigma E_L] - 0.43 \quad (6)$$

where E_L is the ligand electrochemical parameter. The estimated potentials for [Fe(L)_x]²⁺/[Fe(L)_x]³⁺ (L = bpy, phen, terpy) are 1.30, 1.29, and 1.26 V vs. NHE in aqueous system, and 1.28, 1.29, and 1.23 V vs. NHE in organic solvent system, respectively. These data are almost consistent with each other, and also support our experimental results.

Consequently, it is said that the redox potentials of [Fe(L)_x]²⁺ (L = bpy, phen, terpy) are not strongly affected by the coordinated ligands.

4. Conclusions

The Fe(II) complexes with same anion as that of [BMI][Tf₂N], i.e., [Fe(bpy)₃][Tf₂N]₂, [Fe(phen)₃][Tf₂N]₂, and [Fe(terpy)₂][Tf₂N]₂ were synthesized. From ¹H-NMR and UV-vis absorption spectra of the [BMI][Tf₂N] solutions dissolving these Fe(II) complexes, the Fe(II) species were found to exist as [Fe(bpy)₃]²⁺, [Fe(phen)₃]²⁺, and [Fe(terpy)₂]²⁺ in [BMI][Tf₂N]. From the CVs and CAs for the [BMI][Tf₂N] solutions dissolving [Fe(bpy)₃][Tf₂N]₂, [Fe(phen)₃][Tf₂N]₂, and [Fe(terpy)₂][Tf₂N]₂, it was found that the [Fe(bpy)₃]²⁺, [Fe(phen)₃]²⁺, and [Fe(terpy)₂]²⁺ species are oxidized to the corresponding Fe(III) species quasi-reversibly and that the k^0 and D values of three Fe(II) species are almost same. These results indicate that the Fe(II)/Fe(III) redox reactions take place through the same mechanism. In addition, the CVs measured at $v = 100 \text{ mV s}^{-1}$ by 100 cycles were found to be almost same. This indicates that the Fe(II)/Fe(III) redox reactions are relatively stable.

As mentioned above, the [Fe(L)_x]²⁺ (L = bpy, phen, terpy) species satisfy the requirements that the RFB active materials undergo the reversible redox reaction and have no side-reactions. Hence, it is expected that the [Fe(L)_x][Tf₂N]₂ (L = bpy, phen, terpy, x = 3 or 2) complexes are the candidate compounds as the cathode active material of RFB. However, the low solubility of these Fe(II) complexes is not suitable for the practical application. This matter should be improved by selecting the appropriate ligands, because the solubility of Fe(II) complexes is found to largely depend on the ligands as mentioned above.

In addition, in order to find out the more outstanding RFB active materials, it is necessary to examine optimal combinations of the metal complexes and ILs for bringing about the high solubility and energy density.

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