Supporting Information

The Dramatic Acceleration Effect of Imidazolium Ionic Liquids on Electron Transfer Reactions

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General Remarks. $(C_5Me_5)_2Fe(II)$, $(C_5Me_5)_2Co(II)$, Et_4NCl, thiazole, and 1-bromobutane were purchased from Aldrich and used without further purification. The ILs, [bmim]X (bmim = 1-butyl-3-methylimidazolium cation; X = SbF_6, PF_6, NTf_2, BF_4 and Cl), were purchased from C-Tri Co., Ltd., Korea, www.c-tri.co.kr) and used without further purification. [bmim]X (X = SbF_6, PF_6, NTf_2, and BF_4) were spectrometrically pure, nearly chloride-free (<5 ppm) and their water content was <100 ppm (determined by Karl-Fisher titration). $[NBu_4][SbF_6]$ and *N*-buthylthiazolium hexafluoroantimonate were prepared by the reaction of $[NBu_4]Cl$ and *N*-buthylthiazolium bromide, respectively, with $KSbF_6$.

$[NBu_4][SbF_6]$:
^{19}F NMR (282 MHz, d_6-DMSO, $CFCl_3$ as an external standard): δ -120.1 (sextet, $J_{(F-Sb(I=5/2))}$ = 1963 Hz, octet, $J_{(F-Sb(I=7/2))}$ = 1061 Hz).

***N*-buthylthiazolium hexafluoroantimonate:**
^1H NMR (300 MHz, d_6-DMSO, $CFCl_3$ as an external standard): δ 0.90 (t, *J* = 7.3 Hz, 3H), 1.26 (m, *J* = 7.3 Hz, 2H), 1.86 (m, *J* = 7.3 Hz, 2H), 4.5 (t, *J* = 7.3 Hz, 2H), 8.33 (d, *J* = 3.7 Hz, 1H), 8.56 (d, *J* = 3.7 Hz , 1H), 10.19 (s, 1H); ^{13}C NMR (75 MHz, d_6-DMSO): δ 13.0, 18.6, 31.3, 54.1, 126.6, 136.8, 158.9; ^{19}F NMR (282 MHz, d_6-DMSO): δ -119.8 ppm (sextet, $J_{(F-Sb(I=5/2))}$ = 1954 Hz, octet, $J_{(F-Sb(I=7/2))}$ = 1079 Hz).

(a) Bis(pentamethylcyclodienyl)Co(III) PF$_6$
(b) [N-Butylthiazolium][SbF$_6$]
(c) [bmim][PF$_6$]
(d) [bmim][NTf$_2$]
(e) [bmim][OTf]
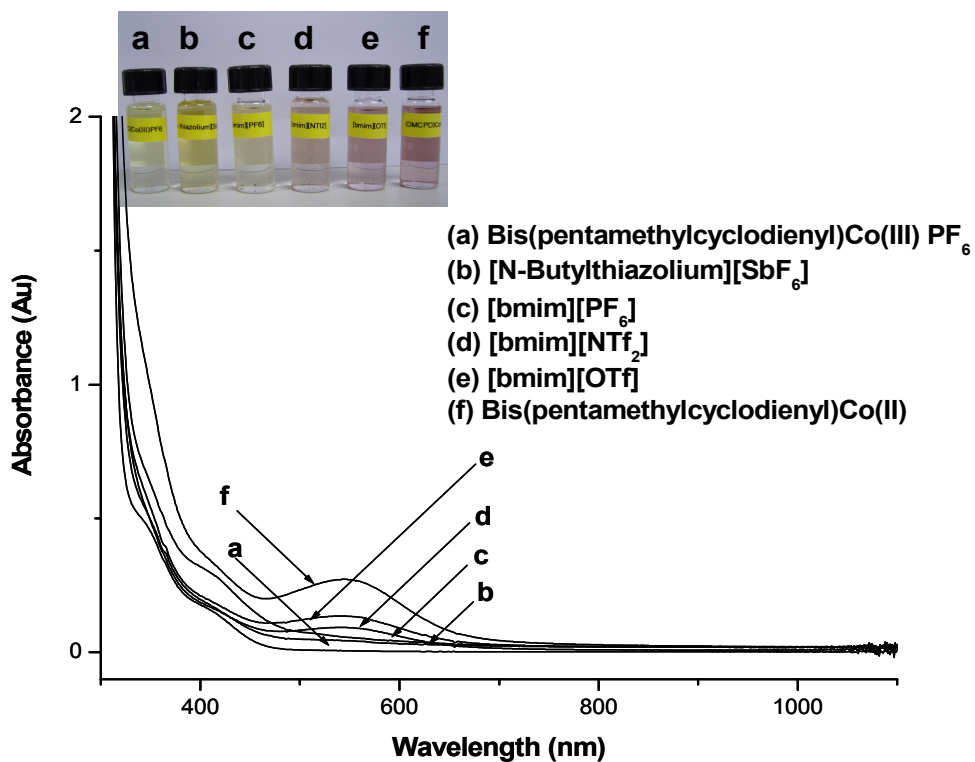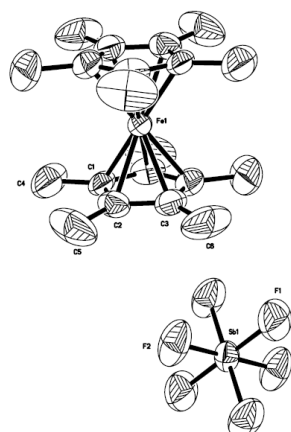(f) Bis(pentamethylcyclodienyl)Co(II)

Figure. UV-Vis spectra of a mixture of bis(pentamethylcyclopentadienyl)Co(II) (2 mg) with ILs (0.92 mmol) in CH$_2$Cl$_2$ (10 mL) (after 5 min).

Crystal X-ray crystallography data of 3-SbF$_6$

Single X ray crystal structure of (C$_5$Me$_5$)$_2$Fe(III)-SbF$_6$ (3-SbF$_6$)

Crystal data. C$_{20}$H$_{30}$F$_6$F$_1$Sb$_1$, M = 562.04, Orthorhombic, a = 8.414(2), b = 10.307(3), c = 13.192(3) Å, U = 1144.0(5) Å^3, T = 293(2) K, space group $Pnnm$, Z = 2, μ(Mo-Kα) = 1.865 mm^{-1}, 977 reflections collected, 620 unique (R_{int} = 0.0000) which were used in all calculations. The final $wR(F_2)$ was 0.1197.

Table 1. Crystal data and structure refinement for Fenew.

Identification code	fenew
Empirical formula	C$_{20}$H$_{30}$F$_6$F$_1$Sb$_1$
Formula weight	562.04
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pnnm$
Unit cell dimensions	a = 8.414(2) Å $\quad$. = 90°.
	b = 10.307(3) Å $\quad$. = 90°.
	c = 13.192(3) Å $\quad$ = 90°.
Volume	1144.0(5) Å^3
Z	2
Density (calculated)	1.632 Mg/m^3
Absorption coefficient	1.865 mm^{-1}
$F(000)$	562
Crystal size	0.34 × 0.28 × 0.14 mm^3
Theta range for data collection	2.51 to 24.98°.
Index ranges	$0 \le h \le 10, 0 \le k \le 12, -15 \le l \le 0$
Reflections collected	977
Independent reflections	977 [R(int) = 0.0000]
Completeness to theta = 24.98°	93.0 %
Absorption correction	Empirical
Max. and min. transmission	0.4967 and 0.1954
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	977 / 0 / 76
Goodness-of-fit on F^2	1.124
Final R indices [I>2sigma(I)]	$R1 = 0.0449$, $wR2 = 0.1197$
R indices (all data)	$R1 = 0.0785$, $wR2 = 0.1624$
Extinction coefficient	0.0007(7)
Largest diff. peak and hole	0.585 and -0.724 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2x 10^3) for FE.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sb(1)	0	0	5000	57(1)
Fe(1)	5000	-5000	5000	36(1)
F(1)	2136(9)	449(8)	5000	128(3)
F(2)	364(7)	-1251(4)	4002(3)	107(2)
C(1)	2519(12)	-5071(8)	5000	63(3)
C(2)	3049(8)	-4372(7)	4129(5)	64(2)
C(3)	3927(8)	-3281(6)	4454(5)	64(2)
C(4)	1541(15)	-6287(11)	5000	127(6)
C(5)	2693(12)	-4717(11)	3041(6)	122(4)
C(6)	4667(12)	-2235(9)	3793(8)	119(4)

Table 3.   Bond lengths [Å] and angles [°] for FE.

Sb(1)-F(1)#1	1.856(8)
Sb(1)-F(1)	1.856(8)
Sb(1)-F(2)	1.868(4)
Sb(1)-F(2)#2	1.868(4)
Sb(1)-F(2)#1	1.868(4)
Sb(1)-F(2)#3	1.868(4)
Fe(1)-C(1)#4	2.089(10)
Fe(1)-C(1)	2.089(10)
Fe(1)-C(2)	2.106(6)
Fe(1)-C(2)#5	2.106(6)
Fe(1)-C(2)#4	2.106(6)
Fe(1)-C(2)#2	2.106(6)
Fe(1)-C(3)#5	2.115(6)
Fe(1)-C(3)#4	2.115(6)
Fe(1)-C(3)	2.115(6)
Fe(1)-C(3)#2	2.115(6)
C(1)-C(2)#2	1.428(8)
C(1)-C(2)	1.428(8)
C(1)-C(4)	1.499(14)
C(2)-C(3)	1.412(9)
C(2)-C(5)	1.509(9)
C(3)-C(3)#2	1.439(13)
C(3)-C(6)	1.521(10)
C(4)-H(4A)	0.9600
C(4)-H(4B)	0.9600
C(4)-H(4C)	0.9600
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
F(1)#1-Sb(1)-F(1)	180.000(1)
F(1)#1-Sb(1)-F(2)	89.2(3)
F(1)-Sb(1)-F(2)	90.8(3)
F(1)#1-Sb(1)-F(2)#2	89.2(3)
F(1)-Sb(1)-F(2)#2	90.8(3)
F(2)-Sb(1)-F(2)#2	89.6(3)
F(1)#1-Sb(1)-F(2)#1	90.8(3)
F(1)-Sb(1)-F(2)#1	89.2(3)
F(2)-Sb(1)-F(2)#1	180.000(1)
F(2)#2-Sb(1)-F(2)#1	90.4(3)
F(1)#1-Sb(1)-F(2)#3	90.8(3)
F(1)-Sb(1)-F(2)#3	89.2(3)
F(2)-Sb(1)-F(2)#3	90.4(3)
F(2)#2-Sb(1)-F(2)#3	180.000(1)
F(2)#1-Sb(1)-F(2)#3	89.6(3)

C(1)#4-Fe(1)-C(1)	180.000(1)
C(1)#4-Fe(1)-C(2)	140.2(2)
C(1)-Fe(1)-C(2)	39.8(2)
C(1)#4-Fe(1)-C(2)#5	39.8(2)
C(1)-Fe(1)-C(2)#5	140.2(2)
C(2)-Fe(1)-C(2)#5	113.8(4)
C(1)#4-Fe(1)-C(2)#4	39.8(2)
C(1)-Fe(1)-C(2)#4	140.2(2)
C(2)-Fe(1)-C(2)#4	180.0(3)
C(2)#5-Fe(1)-C(2)#4	66.2(4)
C(1)#4-Fe(1)-C(2)#2	140.2(2)
C(1)-Fe(1)-C(2)#2	39.8(2)
C(2)-Fe(1)-C(2)#2	66.2(4)
C(2)#5-Fe(1)-C(2)#2	180.0(3)
C(2)#4-Fe(1)-C(2)#2	113.8(4)
C(1)#4-Fe(1)-C(3)#5	66.6(3)
C(1)-Fe(1)-C(3)#5	113.4(3)
C(2)-Fe(1)-C(3)#5	113.9(2)
C(2)#5-Fe(1)-C(3)#5	39.1(3)
C(2)#4-Fe(1)-C(3)#5	66.1(2)
C(2)#2-Fe(1)-C(3)#5	140.9(3)
C(1)#4-Fe(1)-C(3)#4	66.6(3)
C(1)-Fe(1)-C(3)#4	113.4(3)
C(2)-Fe(1)-C(3)#4	140.9(3)
C(2)#5-Fe(1)-C(3)#4	66.1(2)
C(2)#4-Fe(1)-C(3)#4	39.1(3)
C(2)#2-Fe(1)-C(3)#4	113.9(2)
C(3)#5-Fe(1)-C(3)#4	39.8(4)
C(1)#4-Fe(1)-C(3)	113.4(3)
C(1)-Fe(1)-C(3)	66.6(3)
C(2)-Fe(1)-C(3)	39.1(3)
C(2)#5-Fe(1)-C(3)	113.9(2)
C(2)#4-Fe(1)-C(3)	140.9(3)
C(2)#2-Fe(1)-C(3)	66.1(2)
C(3)#5-Fe(1)-C(3)	140.2(4)
C(3)#4-Fe(1)-C(3)	180.000(1)
C(1)#4-Fe(1)-C(3)#2	113.4(3)
C(1)-Fe(1)-C(3)#2	66.6(3)
C(2)-Fe(1)-C(3)#2	66.1(2)
C(2)#5-Fe(1)-C(3)#2	140.9(3)
C(2)#4-Fe(1)-C(3)#2	113.9(2)
C(2)#2-Fe(1)-C(3)#2	39.1(3)
C(3)#5-Fe(1)-C(3)#2	180.000(1)
C(3)#4-Fe(1)-C(3)#2	140.2(4)
C(3)-Fe(1)-C(3)#2	39.8(4)
C(2)#2-C(1)-C(2)	107.2(8)
C(2)#2-C(1)-C(4)	126.4(4)
C(2)-C(1)-C(4)	126.4(4)
C(2)#2-C(1)-Fe(1)	70.8(5)
C(2)-C(1)-Fe(1)	70.8(5)

C(4)-C(1)-Fe(1)	125.3(7)
C(3)-C(2)-C(1)	108.7(6)
C(3)-C(2)-C(5)	125.5(8)
C(1)-C(2)-C(5)	125.8(8)
C(3)-C(2)-Fe(1)	70.8(3)
C(1)-C(2)-Fe(1)	69.4(5)
C(5)-C(2)-Fe(1)	127.0(5)
C(2)-C(3)-C(3)#2	107.7(4)
C(2)-C(3)-C(6)	127.2(7)
C(3)#2-C(3)-C(6)	125.0(5)
C(2)-C(3)-Fe(1)	70.1(3)
C(3)#2-C(3)-Fe(1)	70.10(18)
C(6)-C(3)-Fe(1)	127.9(5)
C(1)-C(4)-H(4A)	109.5
C(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(3)-C(6)-H(6A)	109.5
C(3)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(3)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1   #2 x,y,-z+1   #3 -x,-y,z   #4 -x+1,-y-1,-z+1
#5 -x+1,-y-1,z

Table 4. Anisotropic displacement parameters ($\text{Å}^2\text{x } 10^3$) for FE.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sb(1)	71(1)	65(1)	35(1)	0	0	-12(1)
Fe(1)	39(1)	49(1)	20(1)	0	0	2(1)
F(1)	85(5)	100(5)	199(9)	0	0	-22(4)
F(2)	182(5)	83(3)	56(3)	-18(2)	14(3)	-15(3)
C(1)	41(5)	52(5)	96(8)	0	0	9(3)
C(2)	71(4)	82(4)	38(3)	-6(3)	-16(3)	25(4)
C(3)	77(4)	56(3)	59(4)	16(3)	1(3)	10(3)
C(4)	66(7)	72(7)	243(19)	0	0	-7(6)
C(5)	105(8)	211(12)	50(5)	-39(6)	-33(5)	43(7)
C(6)	134(8)	92(6)	130(9)	68(6)	25(7)	17(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($\text{Å}^2\text{x } 10^3$) for FE.

	x	y	z	U(eq)
H(4A)	1499	-6636	4326	191
H(4B)	484	-6092	5227	191
H(4C)	2015	-6912	5447	191
H(5A)	2555	-5639	2982	183
H(5B)	3559	-4445	2618	183
H(5C)	1736	-4287	2830	183
H(6A)	3954	-1512	3743	178
H(6B)	4865	-2579	3128	178
H(6C)	5651	-1955	4089	178