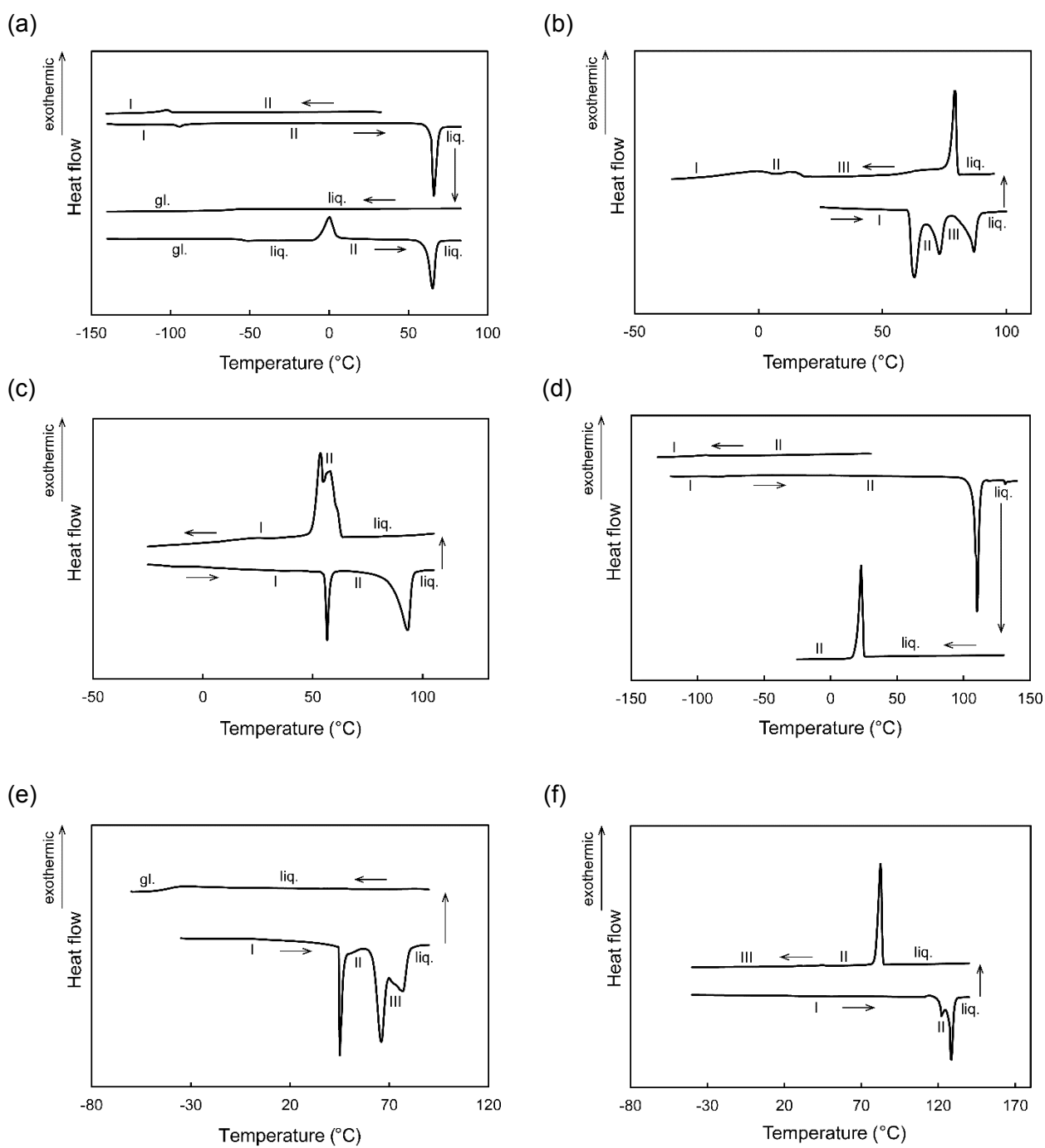


## Electronic supporting information

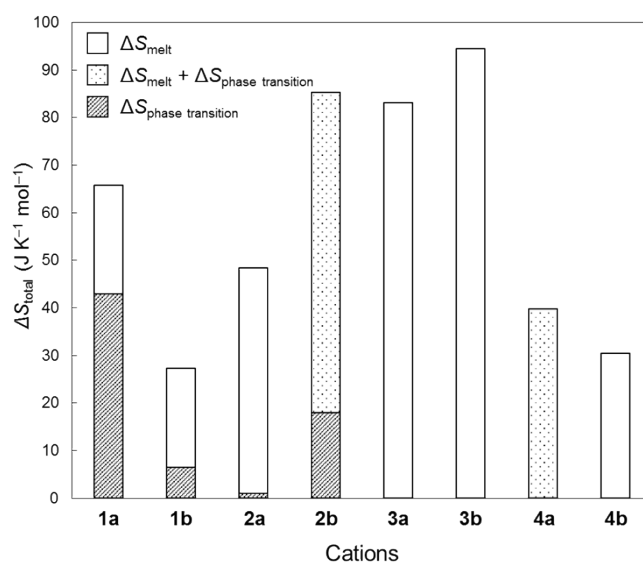
Colorless Organometallic Ionic Liquids from Cationic Ruthenium Sandwich  
Complexes: Thermal Properties, Liquid Properties, and Crystal Structures of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_5\text{R})][\text{X}]$  ( $\text{X} = \text{N}(\text{SO}_2\text{CF}_3)_2, \text{N}(\text{SO}_2\text{F})_2, \text{PF}_6$ )

**Aina Komurasaki, Yusuke Funasako, Tomoyuki Mochida\***

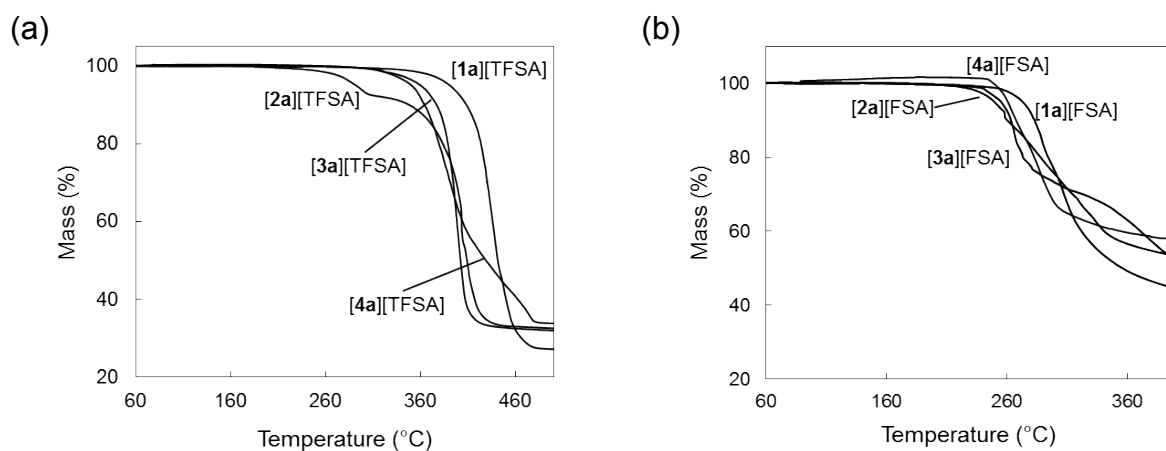
*Department of Chemistry, Graduate School of Science, Kobe University, Rokkodai, Nada, Hyogo 657-8501, Japan*



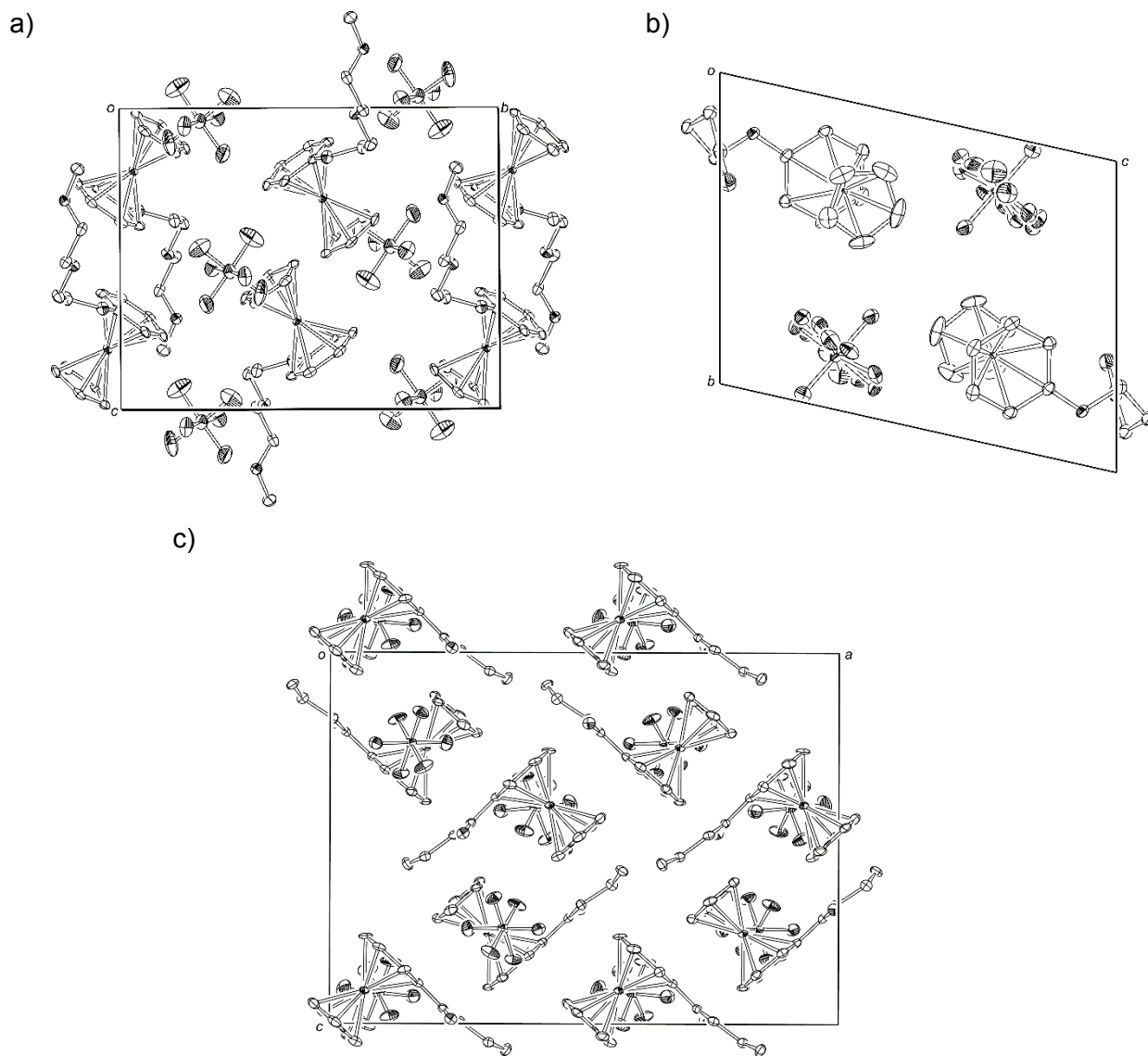
**Fig. S1.** DSC traces of (a) [4a][FSA], (b) [1a][PF<sub>6</sub>], (c) [1b][PF<sub>6</sub>], (d) [2a][PF<sub>6</sub>], (e) [2b][PF<sub>6</sub>], and (f) [4a][PF<sub>6</sub>]. Glassy state and liquid phase are indicated as gl. and liq., respectively.



**Fig. S2.** Sum of the phase transition entropies of the PF<sub>6</sub> salts.



**Fig. S3.** Thermogravimetric traces of (a) [1a][TFSA]–[4a][TFSA] and (b) [1a][FSA]–[4a][FSA] (10 K min<sup>-1</sup>).



**Fig. S4.** Packing diagrams of (a)  $[2b][PF_6]$ , (b)  $[3a][PF_6]$ , and (c)  $[4a][PF_6]$ .

**Table S1.** Crystallographic parameters.

	[1a][PF <sub>6</sub> ]	[2a][PF <sub>6</sub> ] (100 K)	[2a][PF <sub>6</sub> ] (293 K)	[2b][PF <sub>6</sub> ]
Empirical formula	C <sub>15</sub> H <sub>19</sub> F <sub>6</sub> PRu	C <sub>13</sub> H <sub>15</sub> F <sub>6</sub> O <sub>2</sub> PRu		C <sub>16</sub> H <sub>21</sub> F <sub>6</sub> O <sub>3</sub> PRu
Formula weight	445.34	449.29		507.37
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> nma	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	7.6403(10)	18.367(4)	12.742(4)	10.573(3)
<i>b</i> (Å)	9.1602(12)	8.8317(18)	9.035(3)	14.685(4)
<i>c</i> (Å)	23.401(3)	25.123(4)	13.613(4)	14.804(3)
$\beta$ (°)	108.800(4)	133.146(10)	90.0	128.135(12)
Volume (Å <sup>3</sup> )	1550.4(3)	2973.4(10)	1567.3(9)	1807.9(8)
<i>Z</i>	4	8	4	4
<i>d</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.908	2.007	1.908	1.864
<i>T</i> (K)	100	100	293	100
$\mu$ (mm <sup>-1</sup> )	1.172	1.233	1.17	1.03
Reflections collected	8011	14283	8253	8506
Independent reflections	3166 ( <i>R</i> <sub>int</sub> = 0.0118)	5246 ( <i>R</i> <sub>int</sub> = 0.0742)	1775 ( <i>R</i> <sub>int</sub> = 0.0211)	3193 ( <i>R</i> <sub>int</sub> = 0.0204)
<i>F</i> (000)	888	1776	888	1016
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0281, 0.0634	0.0286, 0.0741	0.0307, 0.0786	0.0421, 0.1110
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.0305, 0.0649	0.0292, 0.0752	0.0330, 0.0803	0.0440, 0.1128
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.139	1.079	1.083	1.069
Completeness to $\theta$ (%)	99.5	99.7	99.8	99.8
Parameters	209	418	203	246
Largest diff. peak and hole	1.112 and -0.570	0.724 and -0.727	0.450 and -0.463	2.576 and 0.891

a)  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , b)  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

(Continued)

	[3a][PF <sub>6</sub> ]	[3b][PF <sub>6</sub> ]	[4a][PF <sub>6</sub> ]
Empirical formula	C <sub>15</sub> H <sub>16</sub> F <sub>6</sub> NOPRu	C <sub>18</sub> H <sub>22</sub> F <sub>6</sub> NOPRu	C <sub>15</sub> H <sub>17</sub> F <sub>6</sub> OPRu
Formula weight	472.33	514.41	459.33
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/c	<i>P</i> ca2 <sub>1</sub>
<i>a</i> (Å)	7.2737(14)	9.871 (2)	20.886(3)
<i>b</i> (Å)	10.0402(19)	19.268(5)	10.4222(13)
<i>c</i> (Å)	12.517(2)	20.870(5)	15.2449(19)
$\beta$ (°)	85.737(2)	96.111 (4)	90.0
Volume (Å <sup>3</sup> )	845.8(3)	2973.4(10)	3318.5(7)
<i>Z</i>	2	8	8
<i>d</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.855	1.731	1.839
<i>T</i> (K)	100	100	100
$\mu$ (mm <sup>-1</sup> )	1.086	0.939	1.103
Reflections collected	4167	8906	17705
Independent reflections	3013 ( <i>R</i> <sub>int</sub> = 0.0137)	3380 ( <i>R</i> <sub>int</sub> = 0.0647)	6457 ( <i>R</i> <sub>int</sub> = 0.0579)
<i>F</i> (000)	468	2064	1824
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0179, 0.0478	0.0414, 0.0930	0.0389, 0.1086
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.0183, 0.0481	0.0594, 0.1003	0.0411, 0.1111
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.068	1.015	1.042
Completeness to $\theta$ (%)	97.6	97.0	100.0
Parameters	301	308	436
Largest diff. peak and hole	0.353 and -0.389	0.910 and -0.889	1.363 and -1.133

a)  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , b)  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$