Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Effects of Substituents and Anions on the Phase Behavior of Ru(II) Sandwich Complexes: Exploring the Boundaries between Ionic Liquids and Ionic Plastic Crystals

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Table S1 Volumes and radii of anions estimated by DFT calculations.

anion	V (Å^3)	r_{anion} (Å)
PF_6^-	74.9	2.61
$C(CN)_3^-$	90.8	2.79
FSA^-	98.7	2.87
$B(CN)_4^-$	117.2	3.04
Tf_2N^-	157.5	3.35

Table S2 Volumes and radii of cations estimated by DFT calculations.

cation	V (Å^3)	r_{cation} (Å)
[**C0**]$^+$	186.6	3.54
[**C1**]$^+$	204.9	3.66
[**C2**]$^+$	223.1	3.76
[**C4**]$^+$	260.0	3.96

Table S3 Phase transition data of the salts investigated herein.[a]

	Phase transition	T_c (°C)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
[**C0**][PF_6] [b]	I → II	59.3	4.16	12.5
[**C0**][FSA]	I → II	159.8	9.7	22.2
	II → III*	182.7	6.5	14.2
[**C0**][$B(CN)_4$]	I → II	55.8	7.6	22.9
	II → III*	67.1	8.8	25.6
[**C0**][$C(CN)_3$]	I → II	48.9	10.2	31.6
	II → liq.	90.2	10.1	27.5
[**C1**][PF_6]	I → II*	14.8	8.6	29.0
[**C1**][FSA]	I → II	–8.6	7.7	28.6
	II → III*	45.7	2.5	7.6
[**C1**][$B(CN)_4$]	I → II*	14.2	26.5	91.2
[**C1**][$C(CN)_3$]	liq. → I	–58.6	10.0	45.4
	I → II	–29.7	0.9	3.6
	II → liq.	–1.3	20.4 [d]	73.7 [d]
[**C2**][PF_6]	I → II*	88.3	10.3	28.1
	II* → liq.	161.3	5.8	13.2
[**C2**][FSA]	I → liq.	16.9	18.9	64.6
[**C2**][$B(CN)_4$]	I → II*	15.7		
	II* → liq.	22.6	15.2 [e]	52.2 [e]
[**C4**][PF_6] [c]	I → II	62.8	8.7	26.3
	II → III	73.0	5.6	16.6
	III → liq.	87.0	7.8	22.8

[a]Asterisk symbols (*) denote plastic phases. [b]Data from Ref 8. [c]Data from Ref 7. [d]Including the contribution of a solid phase transition near the melting point that appeared as a shoulder. [e]Including the contribution of the solid phase transition from I to II*.

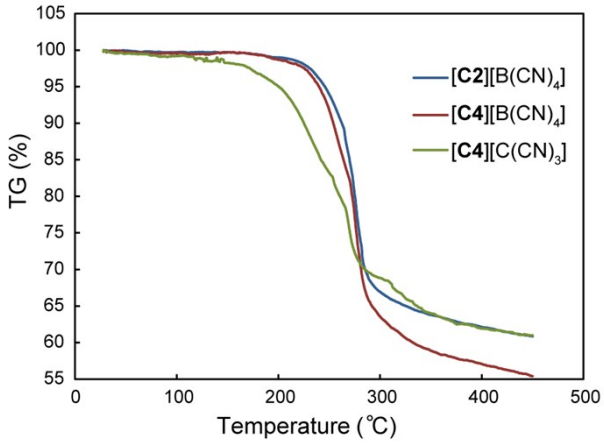

Fig. S1 Thermogravimetric traces of (a) [**C2**][$B(CN)_4$], (b) [**C4**][$B(CN)_4$], and (c) [**C4**][$C(CN)_3$] (10 K min^{-1}).

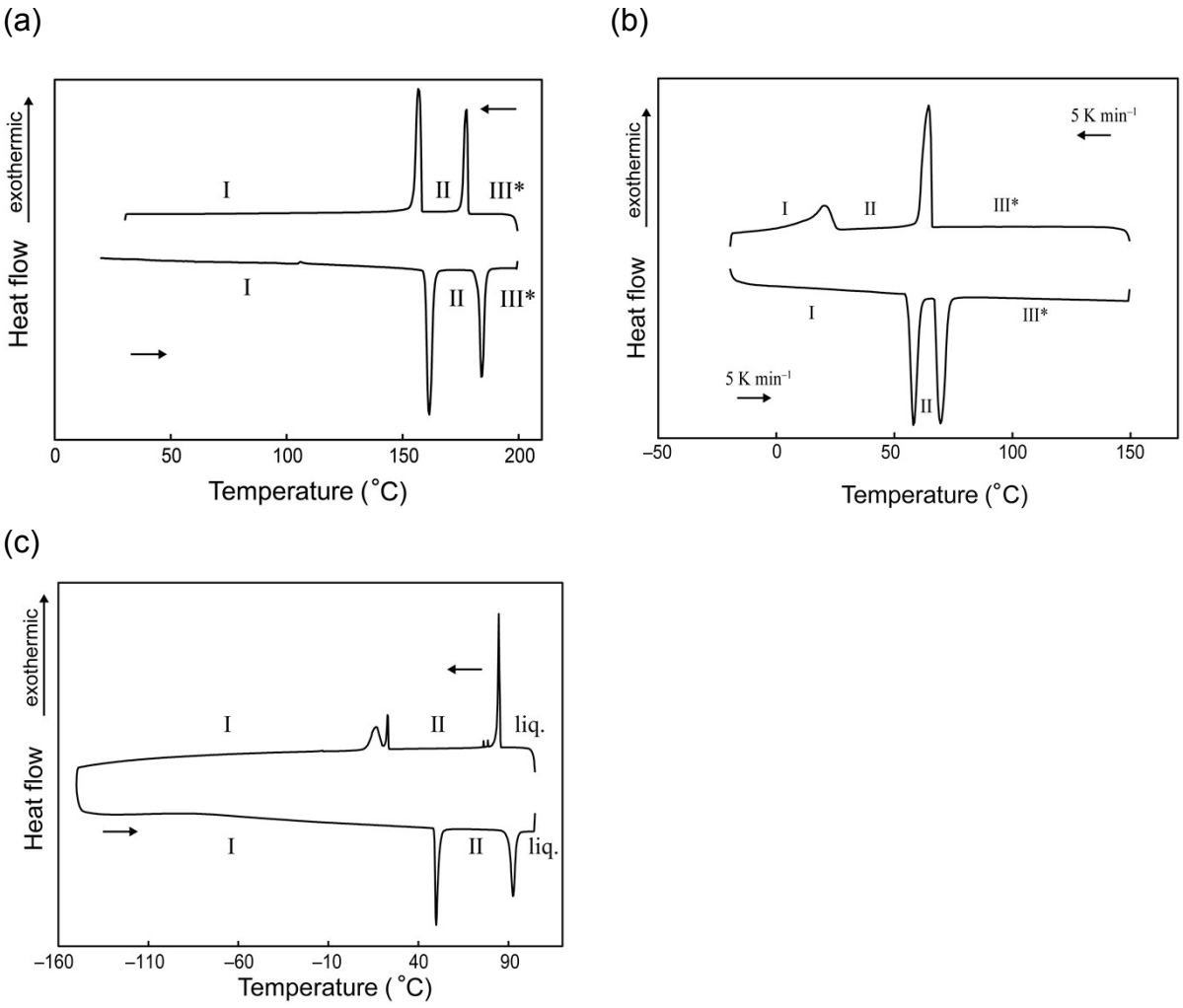

Fig. S2 DSC traces of (a) [**C0**][FSA], (b) [**C0**][$B(CN)_4$], and (c) [**C0**][$C(CN)_3$] (*liq*.: liquid phase). Asterisk symbols (*) denote plastic phases.

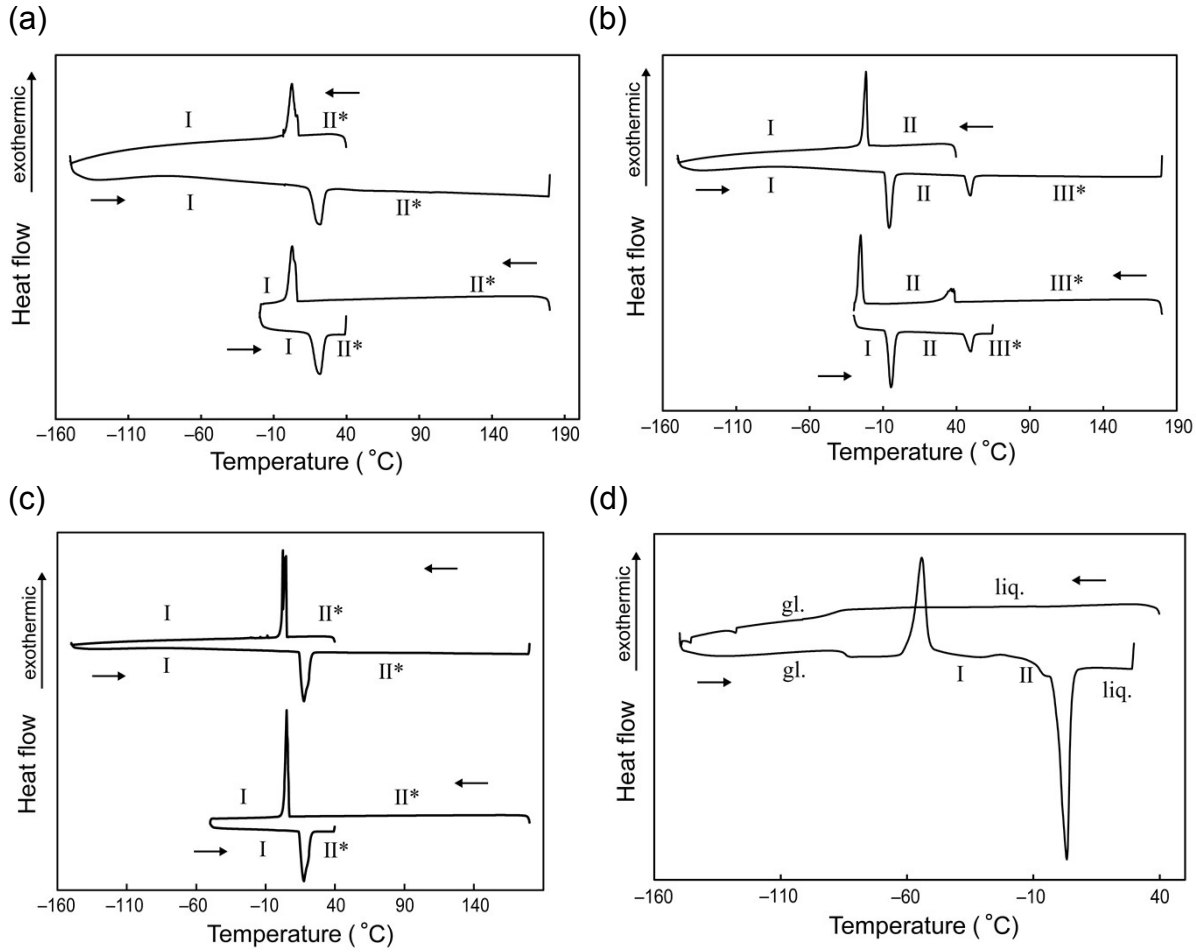

Fig. S3 DSC traces of (a) [**C1**][PF_6], (b) [**C1**][FSA], (c) [**C1**][$B(CN)_4$], and (d) [**C1**][$C(CN)_3$] (*gl.*: glassy phase, *liq.*: liquid phase). Asterisk symbols (*) denote plastic phases.

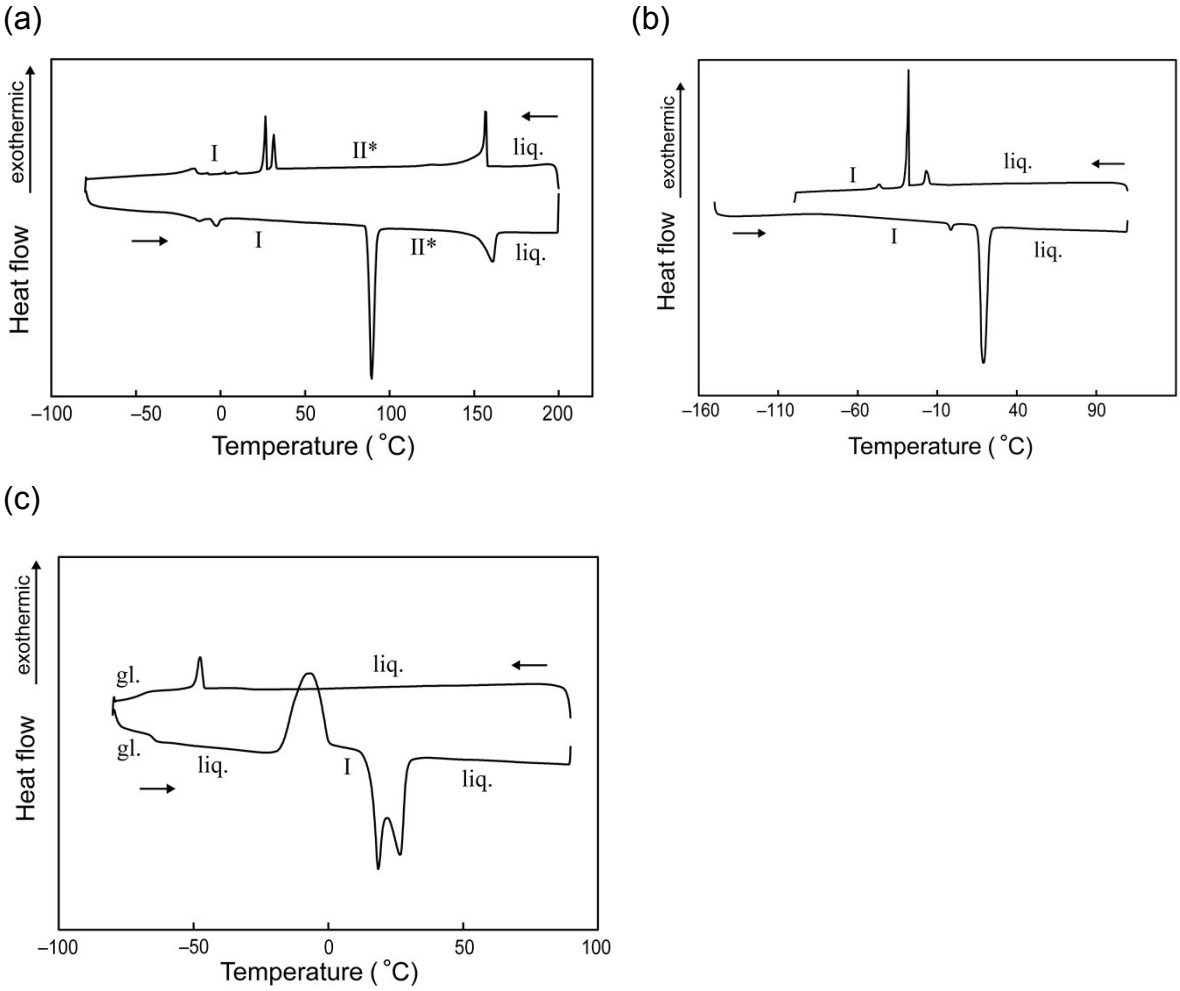

Fig. S4 DSC traces of (a) [**C2**][PF_6], (b) [**C2**][FSA], and (c) [**C2**][$B(CN)_4$] (*gl*.: glassy phase, *liq*.: liquid phase).

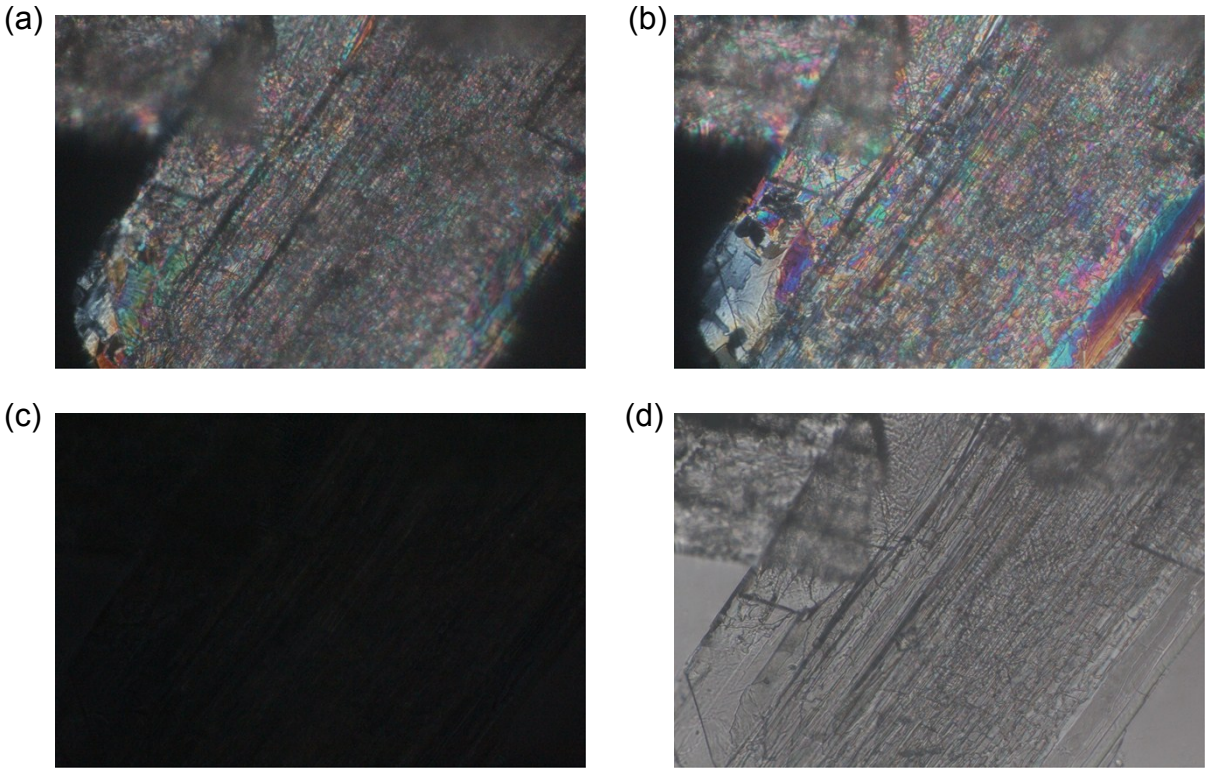

Fig. S5 Polarizing microscope images of [**C0**][FSA] at (a) 25 °C, (b) 170 °C, (c) 200 °C (crossed nicols), and (d) 200 °C (open nicol).

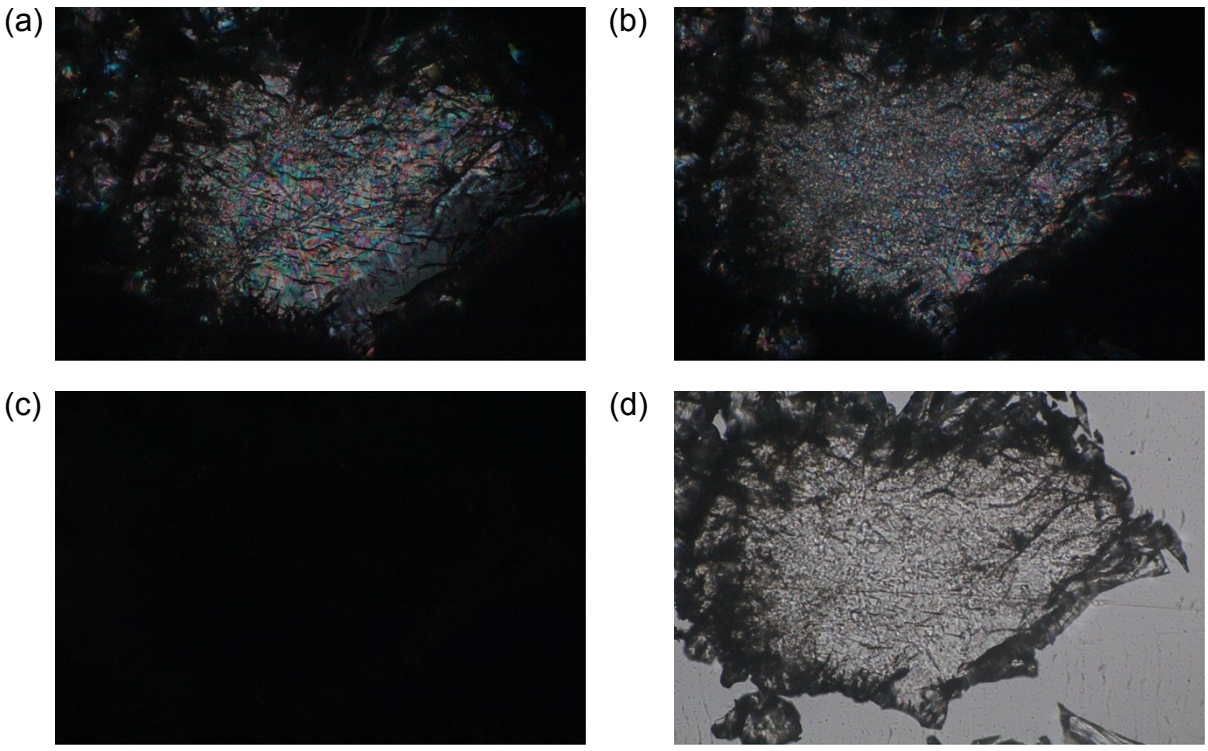

Fig. S6 Polarizing microscope images of [**C0**][$B(CN)_4$] at (a) 25 °C, (b) 60 °C, (c) 80 °C (crossed nicols), and (d) 80 °C (open nicol).

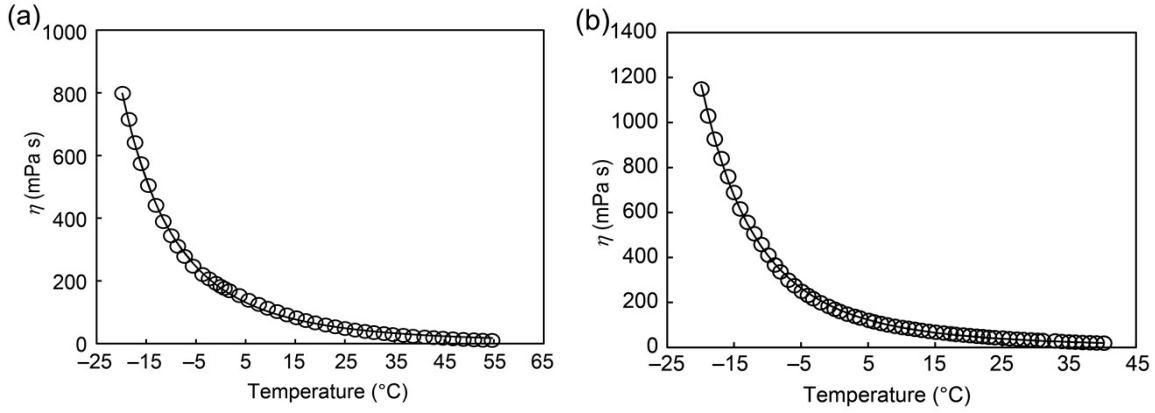

Fig. S7 Temperature dependence of the viscosities of (a) [**C2**][$B(CN)_4$] and (b) [**C4**][$B(CN)_4$]. Solid lines are fitted from the VFT equation.

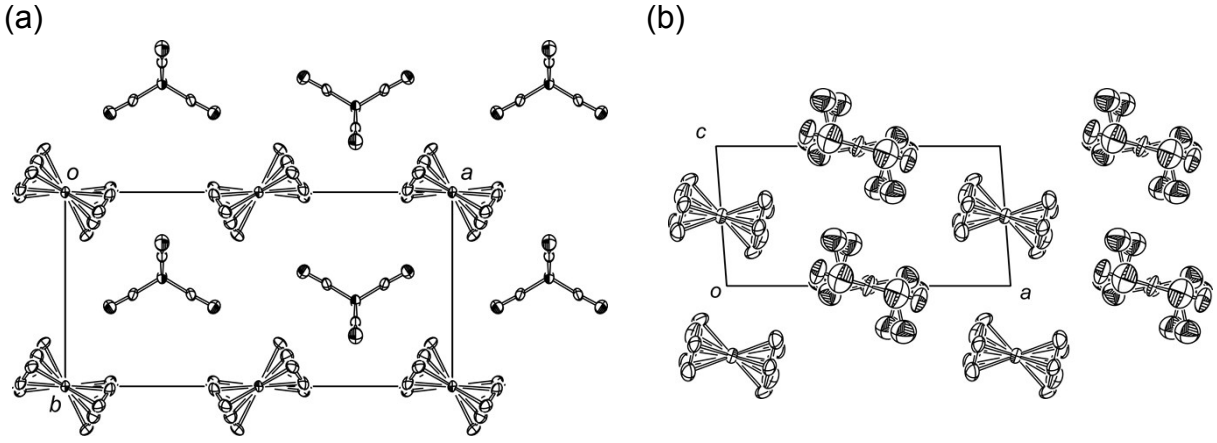

Fig. S8 Packing diagrams of (a) [**C0**][FSA] (296 K) and (b) [**C0**][$B(CN)_4$] (173 K). Hydrogen atoms have been omitted for clarity. Refinements were performed by tentatively assuming the space groups to be *A*ma2 and *C*2, respectively (See text).

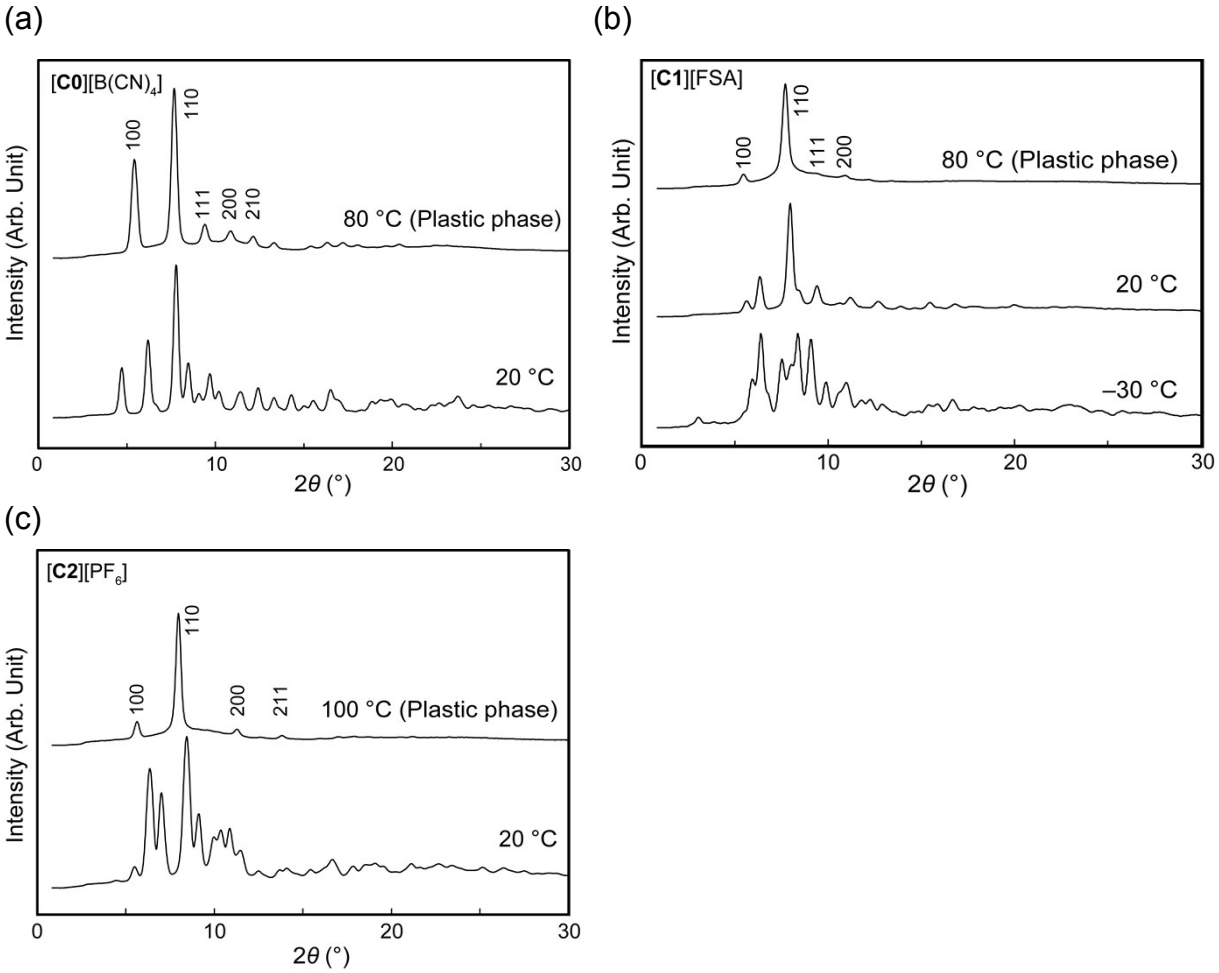

Fig. S9 Powder XRD patterns of (a) [**C0**][$B(CN)_4$], (b) [**C1**][FSA] and (c) [**C2**][PF_6] (MoKα radiation, $\lambda = 0.71073$ Å).

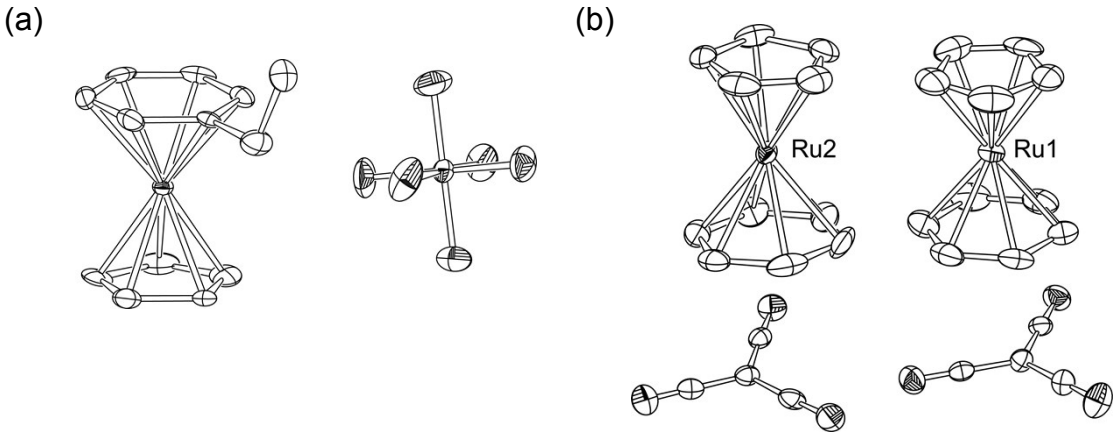

Fig. S10 ORTEP drawings of the molecular structures of (a) [**C2**][PF_6] and (b) [**C0**][$C(CN)_3$]. Hydrogen atoms have been omitted for clarity.

Table S4 Cell parameters of [**C0**][FSA] and [**C0**][$B(CN)_4$]

	[**C0**][FSA]	[**C0**][$B(CN)_4$]
Empirical formula	$C_{11}H_{11}F_2NO_4RuS$	$C_{15}H_{11}N_4BRu$
Formula weight	424.40	359.16
Crystal system	Monoclinic	Orthorhombic
a (Å)	12.856(6)	17.530(10)
b (Å)	8.925(4)	8.791(5)
c (Å)	6.333(3)	9.499(6)
α (°)	69.578(5)	90
β (°)	86.466(6)	90
γ (°)	86.334(5)	90
V (Å^3)	724.5(6)	1463.9(15)
Z	2	4
$d_{\text{calcd.}}$ (mg m^{-3})	1.945	1.630
T (K)	296	173