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Further Investigations of Crystal-to-Crystal Phase Transition of a [2]Pseudorotaxane Composed of Ferrocene-terminated Dialkylammonium and Dibenzo[24]crown-8-ether

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Table 1 Crystal data

No	1	2	3	4
Formula by ICP	[**1**][PF_6]$_{0.68}$[AsF_6]$_{0.32}$	[**1**][PF_6]$_{0.48}$[AsF_6]$_{0.52}$	[**1**][PF_6]$_{0.27}$[AsF_6]$_{0.73}$	[**1**][PF_6]$_{0.17}$[AsF_6]$_{0.83}$
ccdc	2075188	2075193	2075185	2075191
Formula for X-ray	[**1**][PF_6]$_{0.84}$[AsF_6]$_{0.16}$	[**1**][PF_6]$_{0.64}$[AsF_6]$_{0.37}$	[**1**][PF_6]$_{0.46}$[AsF_6]$_{0.54}$	[**1**][PF_6]$_{0.36}$[AsF_6]$_{0.64}$
Temp/K	113	113	113	113
a/Å	10.204(2)	10.194(3)	10.188(4)	10.175(5)
b/Å	11.089(3)	11.112(3)	11.162(4)	11.163(6)
c/Å	19.442(4)	19.439(5)	19.431(7)	19.424(8)
α/°	86.955(6)	86.850(6)	86.926(9)	86.799(13)
β/°	77.616(4)	77.726(6)	77.759(9)	77.778(13)
γ/°	88.875(6)	88.805(7)	88.866(10)	88.65(2)
V/Å^3	2145.6	2148.3	2156.2	2152.7
crystal system	triclinic	triclinic	triclinic	triclinic
space group	P–1 (No. 2)	P–1 (No. 2)	P–1 (No. 2)	P–1 (No. 2)
Z	2	2	2	2
Mr	920.93	929.73	937.42	941.60
Dx/g cm^{-3}	1.425	1.437	1.444	1.453
μ/mm^{-1}	0.611	0.732	0.857	0.927
F(000)	962	969	975	979
Nref	9403	9432	9450	9351
R (reflections)	0.0411 (6248)	0.0387 (5746)	0.0399 (7047)	0.0504 (6274)
wR2 (reflections)	0.1098 (9043)	0.0925 (9432)	0.1002 (9450)	0.1364 (9351)
GOF	0.933	0.949	0.986	0.998
N_{par}	606	598	606	743

No	5	6	7	8
Formula by ICP	[**1**][PF_6]$_{0.04}$[AsF_6]$_{0.96}$	[**1**][PF_6]$_{0.94}$[SbF_6]$_{0.06}$	[**1**][PF_6]$_{0.89}$[SbF_6]$_{0.11}$	[**1**][PF_6]$_{0.76}$[SbF_6]$_{0.24}$
ccdc	2075186	2075187	2075189	2075194
Formula for X-ray	[**1**][PF_6]$_{0.28}$[AsF_6]$_{0.72}$	[**1**][PF_6]$_{1.00}$[SbF_6]$_{0.00}$	[**1**][PF_6]$_{0.93}$[SbF_6]$_{0.07}$	[**1**][PF_6]$_{0.84}$[SbF_6]$_{0.17}$
Temp/K	113	113	113	113
a/Å	10.1710(17)	10.1785(5)	10.203(3)	10.170(3)
b/Å	11.182(2)	11.0668(10)	11.091(3)	11.106(4)
c/Å	19.436(4)	19.4314(9)	19.440(5)	19.439(6)
α/°	86.722(56)	86.883(9)	86.950(6)	86.836(9)
β/°	77.689(5)	77.412(7)	77.515(5)	77.378(6)
γ/°	88.611(5)	88.969(10)	88.980(6)	88.730(9)
V/Å^3	2156.2	2133.0	2144.8	2139.2
crystal system	triclinic	triclinic	triclinic	triclinic
space group	P–1 (No. 2)	P–1 (No. 2)	P–1 (No. 2)	P–1 (No. 2)
Z	2	2	2	2
Mr	945.33	957.72	920.04	968.0
Dx/g cm^{-}3	1.456	1.423	1.425	1.442
μ/mm^{-1}	0.987	0.470	0.508	0.565
F(000)	982	957.4	961	968
Nref	9469	9367	9416	9383
R (reflections)	0.0361 (7554)	0.0614 (6065)	0.0429 (6820)	0.0605 (6282)
wR2 (reflections)	0.0976 (9469)	0.1732 (9367)	0.1277 (9416)	0.1807 (9383)
GOF	1.006	1.028	1.017	1.079
N_{par}	678	749	606	735

No	9	10	11
Formula by ICP	[**1**][PF_6]$_{0.65}$[SbF_6]$_{0.35}$	[**1**][SbF_6]	[**1**][PF_6] (α'-phase)
ccdc	2075195	2075192	2075508
Formula for X-ray	[**1**][PF_6]$_{0.64}$[SbF_6]$_{0.36}$	[**1**][PF_6]$_{0.35}$[SbF_6]$_{0.65}$	[**1**][PF_6]
Temp/K	113	113	293
a/Å	10.1390(18)	10.163(3)	21.497(5)
b/Å	11.679(2)	11.824(4)	9.893(2)
c/Å	17.971(3)	17.902(5)	22.324(5)
α/°	85.655(46)	85.765(74)	90.000
β/°	87.434(4)	86.936(6)	116.199(2)
γ/°	88.542(5)	87.915(7)	90.000
V/Å^3	2119.2	2141.2	4259.6
crystal system	triclinic	triclinic	triclinic
space group	P–1 (No. 2)	P–1 (No. 2)	P2/c (No. 13)
Z	2	2	4
Mr	945.92	972.70	913.69
Dx/g cm^{-3}	1.482	1.509	1.425
μ/mm^{-1}	0.681	0.846	0.471
F(000)	982	1003	1912
Nref	9054	9392	10485
R (reflections)	0.0449 (7718)	0.0407 (8017)	0.0758 (6632)
wR2 (reflections)	0.1433 (9054)	0.1089 (9392)	0.1623 (10485)
GOF	1.066	1.054	1.097
N_{par}	563	700	588

Table 2. IR spectra of [**1b**]$(PF_6)_{1-n}(Y)_n$ (Y = AsF_6, SbF_6)（KBr disk, r.t.）

Rotaxane[a)]	ν_{N-H} /cm^{-1} (rotaxane)	ν_{N-H} /cm^{-1} (axle)	$\Delta\nu$[b)]
[**1**]$(PF_6)_{0.90}(AsF_6)_{0.10}$	3186, 3066	3265, 3231	79, 165
[**1**]$(PF_6)_{0.83}(AsF_6)_{0.17}$	3186, 3068	3265, 3231	79, 163
[**1**]$(PF_6)_{0.68}(AsF_6)_{0.32}$	3186, 3068	3264, 3230	78, 162
[**1**]$(PF_6)_{0.46}(AsF_6)_{0.54}$	3186, 3068	3262, 3229	76, 161
[**1**]$(PF_6)_{0.48}(AsF_6)_{0.52}$	3187, 3068	3262, 3229	75, 161
[**1**]$(PF_6)_{0.37}(AsF_6)_{0.63}$	3187, 3068	3262, 3228	75, 160
[**1**]$(PF_6)_{0.27}(AsF_6)_{0.73}$	3187, 3068	3261, 3228	74, 160
[**1**]$(PF_6)_{0.17}(AsF_6)_{0.83}$	3187, 3068	3260, 3227	73, 159
[**1**]$(PF_6)_{0.04}(AsF_6)_{0.96}$	3187, 3068	3259, 3226	72, 158
[**1**]$(PF_6)_{0.00}(AsF_6)_{1.00}$	3188, 3068	3259, 3226	71, 158

Rotaxane[a)]	ν_{N-H} /cm^{-1} (rotaxane)	ν_{N-H} /cm^{-1} (axle)	$\Delta\nu$[b)]
[**1b**]$(PF_6)_{0.94}(SbF_6)_{0.06}$	3186, 3068	3264, 3231	78, 163
[**1b**]$(PF_6)_{0.89}(SbF_6)_{0.11}$	3187, 3067	3263, 3231	76, 164
[**1b**]$(PF_6)_{0.76}(SbF_6)_{0.24}$	3187, 3068	3259, 3229	72, 161
[**1b**]$(PF_6)_{0.65}(SbF_6)_{0.35}$	3187, 3067	3256, 3228	69, 161
[**1b**]$(PF_6)_{0.50}(SbF_6)_{0.50}$	3186, 3068	3252, 3227	66, 159
[**1b**]$(PF_6)_{0.41}(SbF_6)_{0.59}$	3188, 3068	3249, 3226	61, 158
[**1b**]$(PF_6)_{0.31}(SbF_6)_{0.69}$	3185, 3066	3247, 3224	62, 158
[**1b**]$(PF_6)_{0.14}(SbF_6)_{0.86}$	3188, 3068	3242, 3223	54, 155
[**1b**]$(PF_6)_{0.003}(SbF_6)_{0.997}$	3179, 3064	3238, 3221	59, 157
[**1b**]$(PF_6)_{0.00}(SbF_6)_{1.00}$	3188, 3068	3238, 3221	50, 153

a) Ratio of counter anions are determined by ICP measurements

c) $\Delta\nu = \nu_{N-H}$ (axle) $- \nu_{N-H}$ (rotaxane)

Figure 1 DSC results of the pseudorotaxanes with mixed counter anions [**1**][PF_6]$_{1-x}$[AsF_6]$_x$.

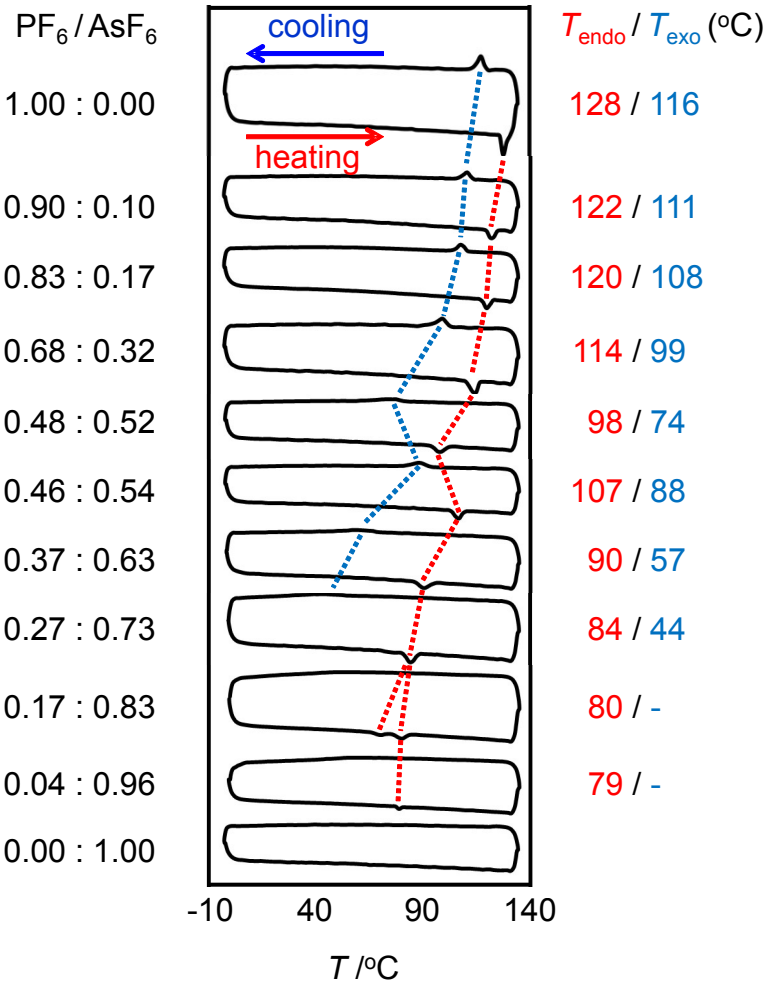


Figure 2 DSC results of the pseudorotaxanes with mixed counter anions [**1**][PF_6]$_{1-x}$[SbF_6]$_x$.

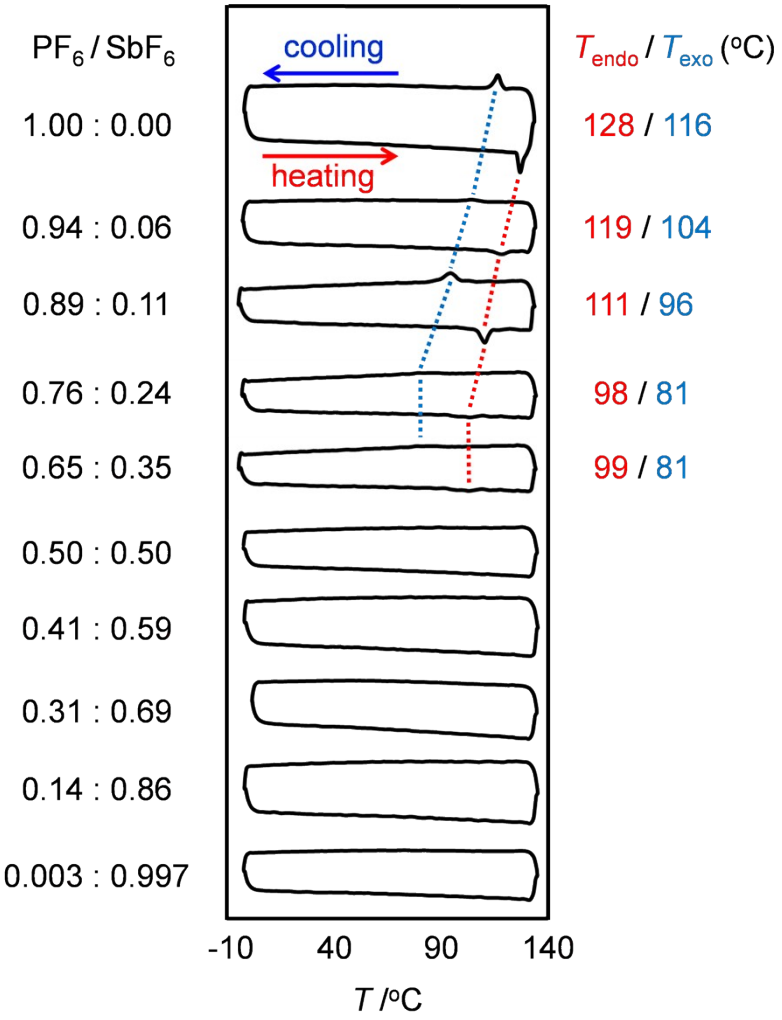


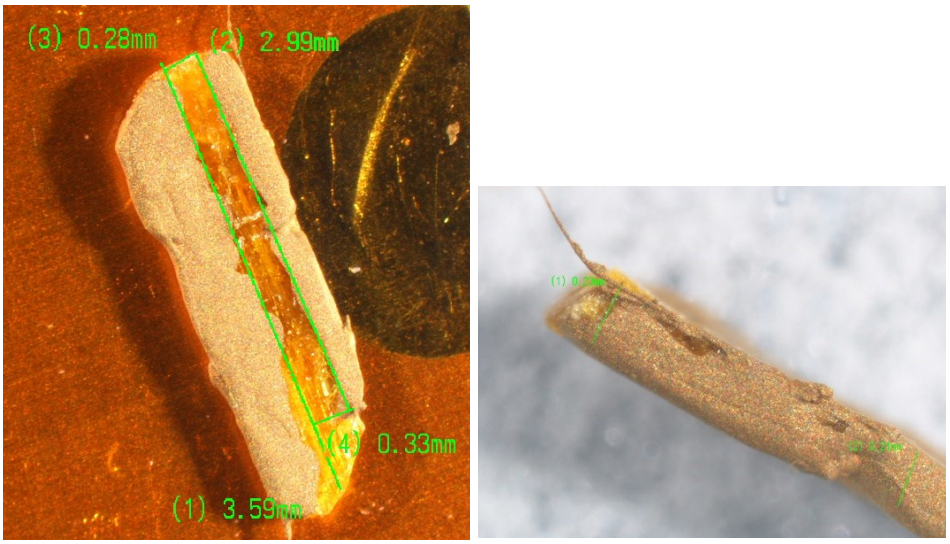
Table 3. DSC data of [**1**]$(PF_6)_{1-n}(AsF_6)_n$ (n = 0.10 - 0.96)

		Endo			Exo		
[**1**]$(PF_6)_{1-n}(AsF_6)_n$	Scan	T_{endo} /^{o}C	ΔH /kJ mol^{-1}	ΔS /J K^{-1} mol^{-1}	T_{exo} /^{o}C	ΔH /kJ mol^{-1}	ΔS /J K^{-1} mol^{-1}
n = 0.10	1st	123	8.5	21	110	-5.8	-15
	2nd	122	6.4	16	111	-5.8	-15
	3rd	122	6.5	17	110	-4.5	-12
n = 0.17	1st	121	8.7	22	107	-6.0	-16
	2nd	120	7.2	18	108	-6.6	-17
	3rd	120	7.2	18	108	-6.6	-17
n = 0.32	1st	115	8.3	21	99	-8.0	-21
	2nd	114	8.1	21	99	-8.8	-24
	3rd	114	8.0	21	98	-7.4	-20
n = 0.52	1st	101	7.9	21	74	-6.4	-18
	2nd	98	8.2	22	74	-5.7	-16
	3rd	98	8.4	23	72	-6.4	-19
n = 0.54	1st	108	8.0	21	87	-7.5	-21
	2nd	107	8.3	22	88	-7.6	-21
	3rd	107	7.5	20	88	-6.6	-18
n = 0.63	1st	95	7.9	21	61	-4.0	-12
	2nd	90	7.4	20	57	-4.6	-14
	3rd	91	6.5	18	60	-4.0	-12
n = 0.73	1st	89	4.8	13	43	-3.0	-9.3
	2nd	84	5.6	16	44	-2.4	-7.6
	3rd	85	5.1	14	42	-1.7	-5.5
n = 0.83	1st	84	2.9	8.2	-	-	-
	2nd	71	0.89	2.6	-	-	-
	3rd	80	2.3	6.5	-	-	-
n = 0.96	1st	79	0.44	1.2	-	-	-
	2-3	-	-	-	-	-	-

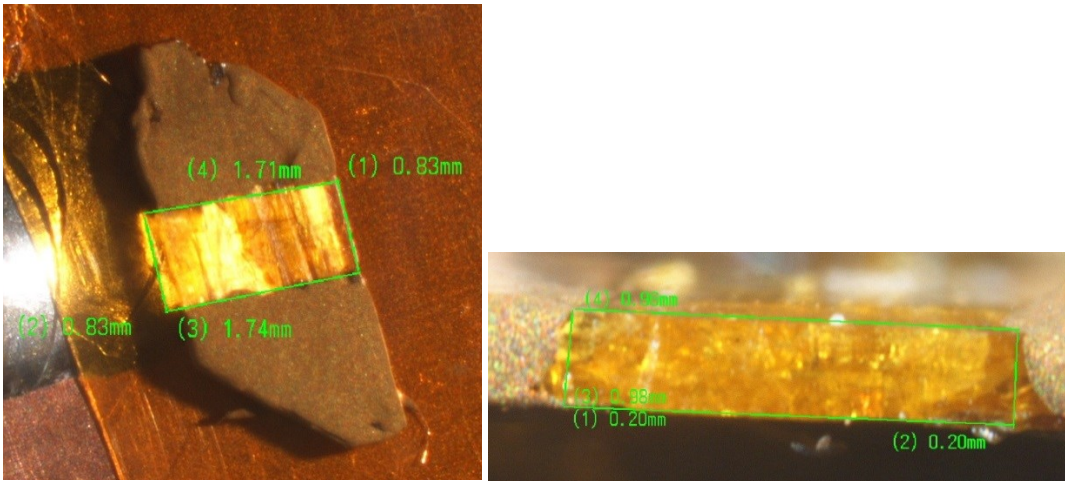
[**1**](PF$_6$)$_{1-n}$(SbF$_6$)$_n$	Scan	Endo			Exo		
		T_{endo} /^{o}C	ΔH /kJ mol^{-1}	ΔS /J K^{-1} mol^{-1}	T_{exo} /^{o}C	ΔH /kJ mol^{-1}	ΔS /J K^{-1} mol^{-1}
n = 0.06	1st	120	7.6	19	106	-3.7	-9.9
	2nd	119	4.1	10	104	-1.6	-4.2
	3rd	119	3.4	8.6	103	-1.1	-2.9
n = 0.11	1st	113	4.1	11	95	-3.8	-10
	2nd	111	5.0	13	96	-4.1	-11
	3rd	111	4.3	11	96	-5.0	-13
n = 0.24	1st	103	8.1	22	80	-3.2	-9.1
	2nd	98	7.6	20	81	-4.8	-14
	3rd	98	6.0	16	80	-3.6	-10
n = 0.35	1st	102	2.9	7.8	81	-1.7	-4.8
	2nd	99	2.0	5.3	81	-1.7	-4.9
	3rd	102	2.3	6.0	89	-1.5	-4.2
n = 0.50	1-3	-	-	-	-	-	-
n = 0.59	1-3	-	-	-	-	-	--
n = 0.69	1-3	-	-	-	-	-	-
n = 0.86	1-3	-	-	-	-	-	-
n = 0.997	1-3	-	-	-	-	-	-

Figure 3 Dielectric measurement

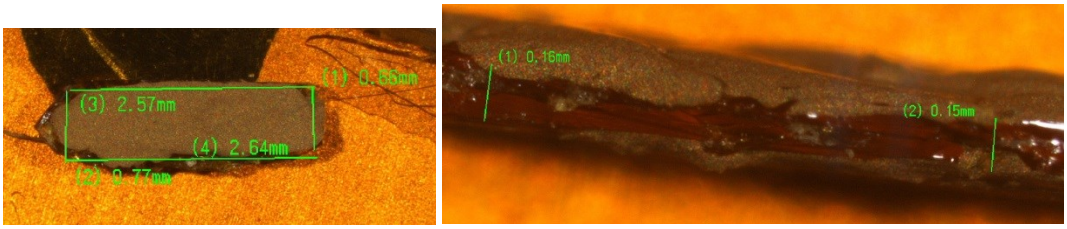
a-axis



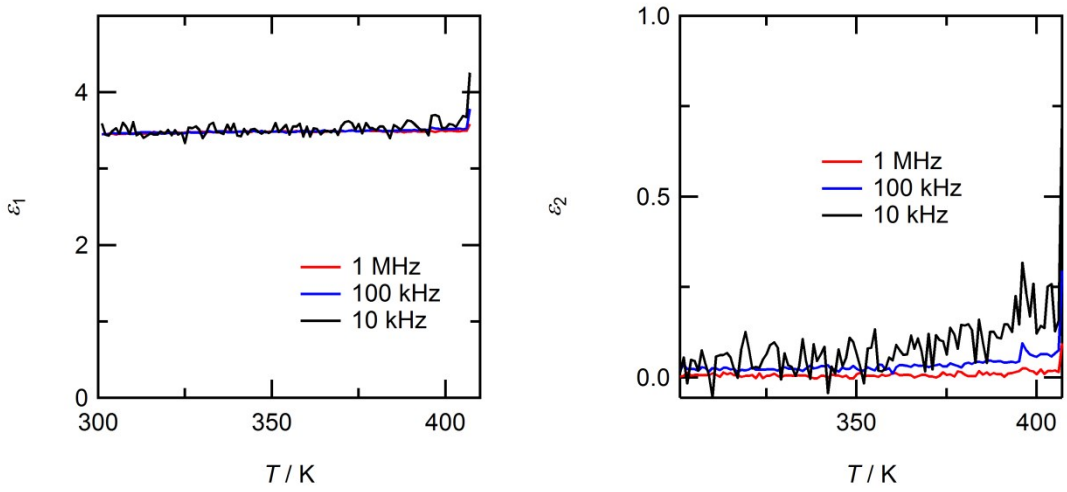
b-axis



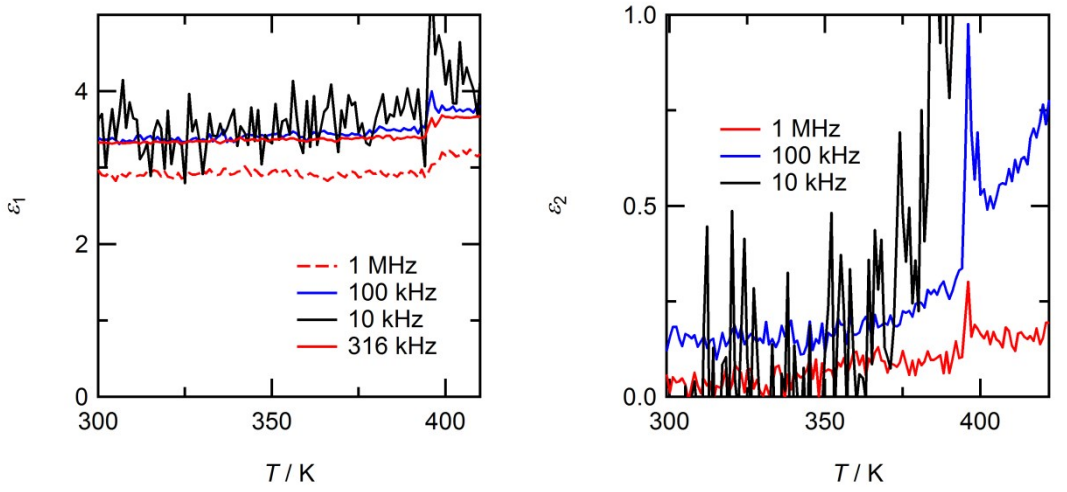
c-axis



a-axis



b-axis



c-axis