Supporting Information for

Four-Step Thermosensitive Dielectric Response Arising from Motionable Low-Symmetry Ammonium Confined in Deformable Supramolecular Cages

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Fig. S15 Local snapshots of NVT dynamic simulation at 180 K for N5-containing Me$_2$EtNH$^+$ ion in **1β** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h)

Fig. S16 Local snapshots of NVT dynamic simulation at 180 K for N6-containing Me$_2$EtNH$^+$ ion in **1β** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h)

Fig. S17 Local snapshots of NVT dynamic simulation at 180 K for N7-containing Me$_2$EtNH$^+$ ion in **1β** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h)

Fig. S18 Local snapshots of NVT dynamic simulation at 300 K for N3-containing Me$_2$EtNH$^+$ ion in **1γ** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h)

Fig. S19 Local snapshots of NVT dynamic simulation at 300 K for N4-containing Me$_2$EtNH$^+$ ion in **1γ** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h)

Fig. S20 Overlapping maps of the snapshots for one [Ni(NCS)$_6$]$^{4-}$ anion (a) and two N3-containing Me$_2$EtNH$^+$ ions (b, c), respectively, by first-principles NVT dynamic simulation of **1λ** phase at simulation temperature of 573 K, showing orientation changes and short-range displacements over the simulation time of 0, 2, 4, 6, 8, and 10 ps

Fig. S21 The variable-temperature Cole–Cole plots as a series of arcs shown the relationship between ε' and ε''. Based on the obtained fitting parameters, the fitted Cole–Cole diagrams of two separated relaxation processes 1 and 2 are illustrated in the inset map

Fig. S22 Variable-temperature impedance spectra for the polycrystalline pellet of **1**

Fig. S23 Variable-temperature infrared spectra of **1**

Table S1 Summary of crystal data and structural refinement for 1 at three phases

Temperature (K)	120(2)	180(2)	296(2)
Empirical formula		$C_{22}H_{48}N_{10}S_6Ni_1$	
Formula weight		703.77	
Phase	**α**	**β**	**γ**
Space group[a]	$P2_1/n$	$Pbnm$	$Acam$
a (Å)	12.783(3)	12.8756(3)	12.9430(7)
b (Å)	14.478(3)	14.5845(3)	15.0014(8)
c (Å)	19.285(4)	19.1455(4)	19.3631(11)
β/deg	90.207(6)	90	90
V/Å^3	3569.0(14)	3595.22(13)	3759.6(4)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.310	1.300	1.243
μ/mm^{-1}	0.924	0.917	0.877
GOF on F^2	1.069	1.044	1.050
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.0508, 0.1026	0.0484, 0.1280	0.0569, 0.1624
R_1, wR_2 (all data)	0.0699, 0.1150	0.0540, 0.1309	0.0816, 0.1836

[a]To straightly compare the corresponding cell parameters, non-standard space groups for them were adopted here.

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

Table S2 Selected bond lengths (Å) for **1** at three phases

	α phase at 120 K		
Ni(1)–N(6)	2.064(4)	Ni(1)–N(5)	2.070(4)
Ni(1)–N(3)	2.081(4)	Ni(1)–N(4)	2.086(4)
Ni(1)–N(6)	2.094(3)	Ni(1)–N(6)	2.115(3)
	β phase at 180 K		
Ni(1)–N(2)	2.064(2)	Ni(1)–N(1)	2.083(2)
Ni(1)–N(3)	2.093(2)	Ni(1)–N(4)	2.106(2)
γ phase at 296 K			
Ni(1)–N(2)	2.078(3)	Ni(1)–N(1)	2.113(4)

Table S3 The S···S contacts (Å) in **1** at three phases

α phase at 120 K			
S(3)···S(6)#1	3.462(2)	S(4)···S(5)#2	3.536(2)
S(1)···S(2)#3	3.594(2)		
β phase at 180 K			
S(2)···S(3)#4	3.553(1)	S(1)···S(4)#3	3.611(1)
γ phase at 296 K			
S(2)···S(2)#5	3.573(2)	S(1)···S(1)#6	3.632(2)

Symmetry code: #1. 1/2 + x, 3/2 − y, −1/2 + z; #2. 1/2 + x, 3/2 − y, 1/2 + z; #3. 1 + x, y, z; #4. x, 1 + y, z; #5. 3/2 − x, y, 1/2 − z; #6. 2 − x, 1 − y, 1 − z.

Table S4 The fitting parameters of the doubly superimposed Havriliak–Negami equation for **1** at specific temperatures

T (K)	ε_∞	α_1	β_1	$\Delta\varepsilon_1$	$\tau_{0,1}$ (s)	α_2	β_2	$\Delta\varepsilon_2$	$\tau_{0,2}$ (s)	σ_{dc}
263	4.78	0	0.79	3.00	7.0×10^{-7}	-		-	-	-
273	4.71	0	0.73	3.04	4.2×10^{-7}	0	0.67	0.53	1.2×10^{-2}	4.4×10^{-11}
283	4.64	0	0.68	3.10	2.4×10^{-7}	0	0.66	0.76	8.6×10^{-3}	5.5×10^{-10}
293	4.54	0	0.63	3.21	1.6×10^{-7}	0	0.65	1.08	6.4×10^{-3}	1.5×10^{-9}
303	4.42	0	0.57	3.34	1.0×10^{-7}	0	0.65	1.63	4.5×10^{-3}	3.8×10^{-9}
313	4.30	0	0.49	3.49	7.0×10^{-8}	0	0.64	2.49	3.3×10^{-3}	9.5×10^{-9}

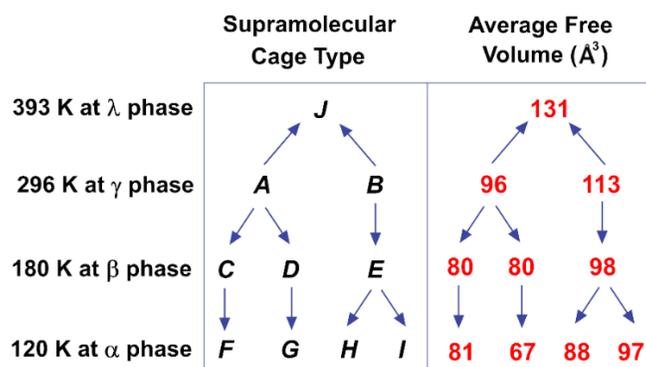|	Supramolecular Cage Type	Average Free Volume (Å³)
393 K at λ phase	J	131
296 K at γ phase	A B	96 113
180 K at β phase	C D E	80 80 98
120 K at α phase	F G H I	81 67 88 97

Chart S1 Evolution of the supramolecular cage types with variable free volumes (using a probe radius set as 2.4 Å) in the four phases of **1**.
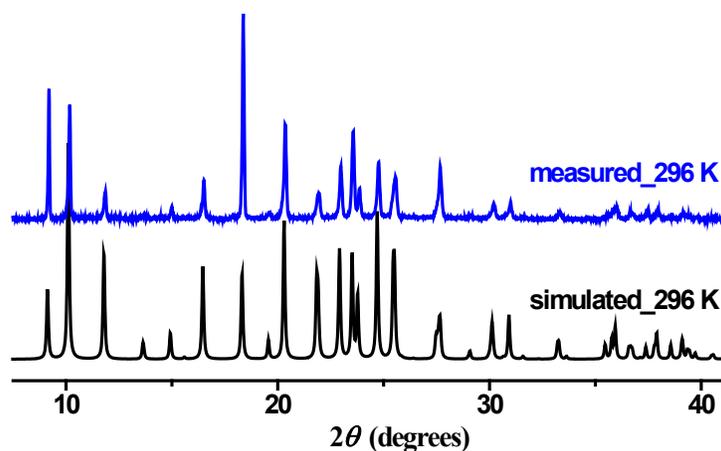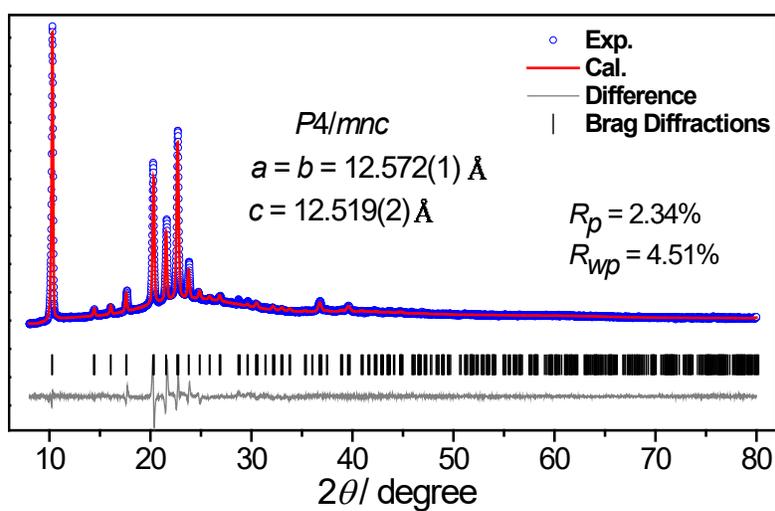

Fig. S1 Room-temperature powder XRD patterns of **1**.

$P4/mnc$

$a = b = 12.572(1)$ Å

$c = 12.519(2)$ Å

$R_p = 2.34\%$

$R_{wp} = 4.51\%$

- ○ Exp.
- ── Cal.
- ── Difference
- | Brag Diffractions

Fig. S2 Final Rietveld refinement result for **1λ** phase at 393 K.
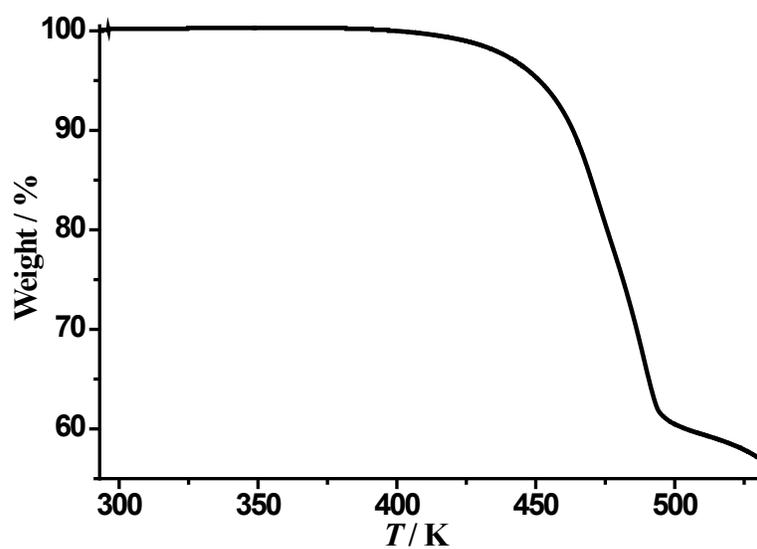
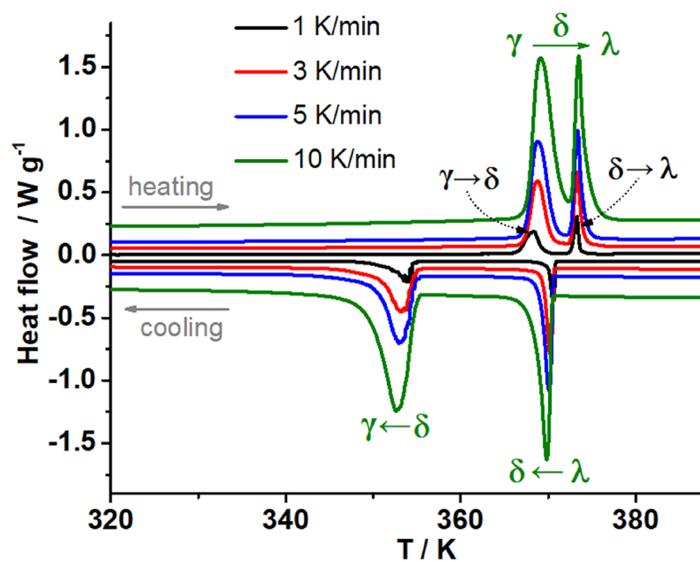**Fig. S3** Thermogravimetric curve of **1**.

Fig. S4 In situ above-room-temperature DSC measurement for **1** recorded on variable heating/cooling rates of 1, 3, 5 and 10 K/min, respectively.
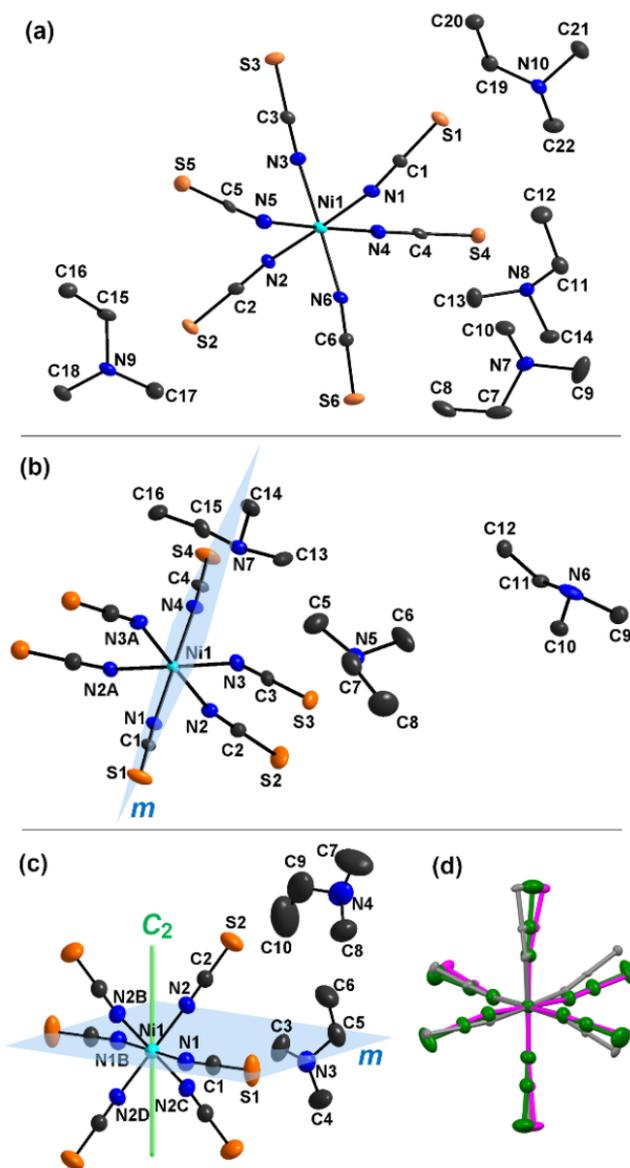
Fig. S5 ORTEP representations of the selected unit of **1** at 120 K (a), 180 K (b), and 296 K (c), respectively, with symmetry breaking and increasing thermal vibration amplitude. For the disordered Me$_2$EtNH$^+$ ions in (b) and (c), only one orientation is shown for clarity. For comparison, the overlay map of the [Ni(NCS)$_6$]$^{4-}$ anions in three phases is shown in (d), shaded in grey (120 K), purple (180 K), and green (296 K), respectively. Symmetry codes: A) x, y, 1/2 − z; B) 1 − x, 1 − y, z; C) x, y, 1 − z; D) 1 − x, 1 − y, 1 − z.
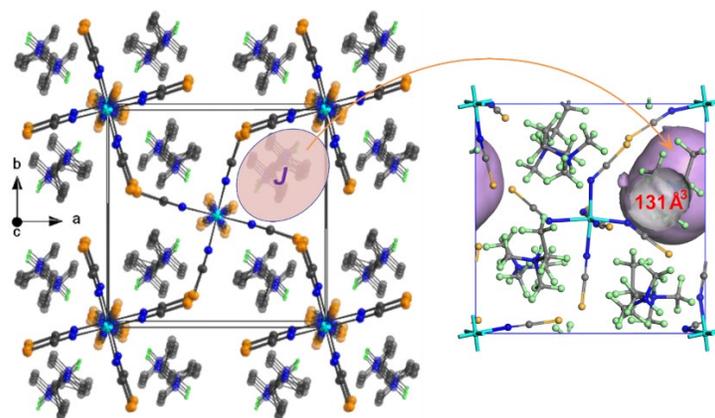
Fig. S6 View of the overall stacking in **1λ** phase. The disordered Me_2EtNH^+/$[Ni(NCS)_6]^{4-}$ ions are shaded in transparent. The N4-containing Me_2EtNH^+ ions reside in the supramolecular cage **J**. For display details, see Fig. 2.
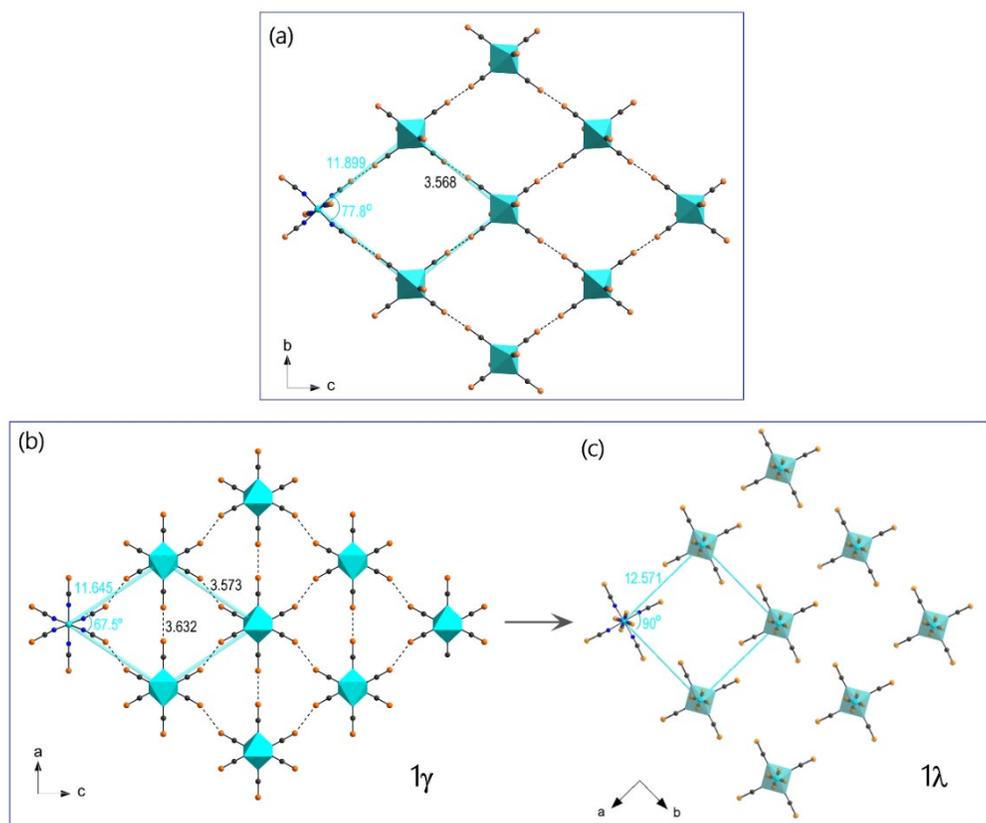

Fig. S7 Comparison of the room-temperature supramolecular $\{[Ni(NCS)_6]^{4-}\}_\infty$ layers in $(Me_3NH)_4[Ni(NCS)_6]$ (a) and **γ** (b). The S⋯S contacts are represented by dashes. From **1γ** to **1λ**, the supramolecular $\{[Ni(NCS)_6]^{4-}\}_\infty$ layer is broken and the $[Ni(NCS)_6]^{4-}$ anions turn disordered dynamically. The significantly changed geometric arrangement of the $[Ni(NCS)_6]^{4-}$ anions is shown in (c).
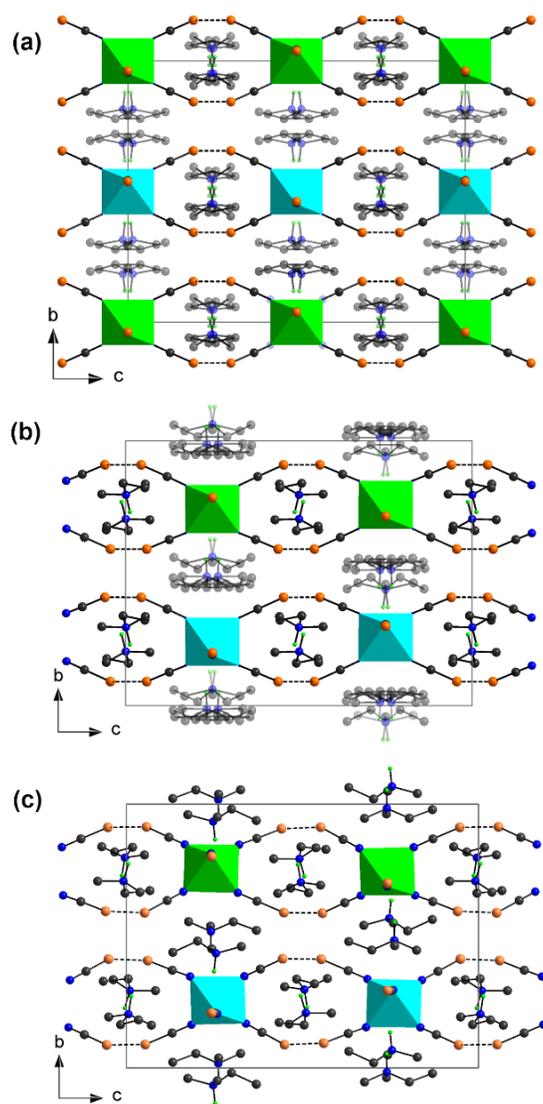
Fig. S8 Views of the overall stacking of **1γ** (a), **1β** (b) and **1α** phases (c), respectively. The disordered Me_2EtNH^+ ions are shaded in transparent.
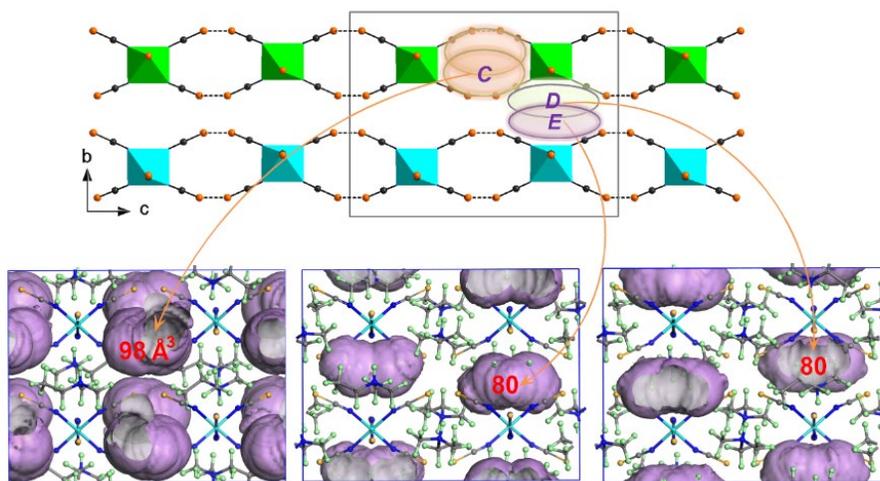
Fig. S9 Views of the stacking of the supramolecular layers of $[Ni(NCS)_6]^{4-}$ anions in **1β** phase (180 K) down the a-axis. The N5-, N6- and N7-containing Me_2EtNH^+ ions reside in the supramolecular cages **C**, **D** and **E**, respectively. For display details, see Fig. 2.
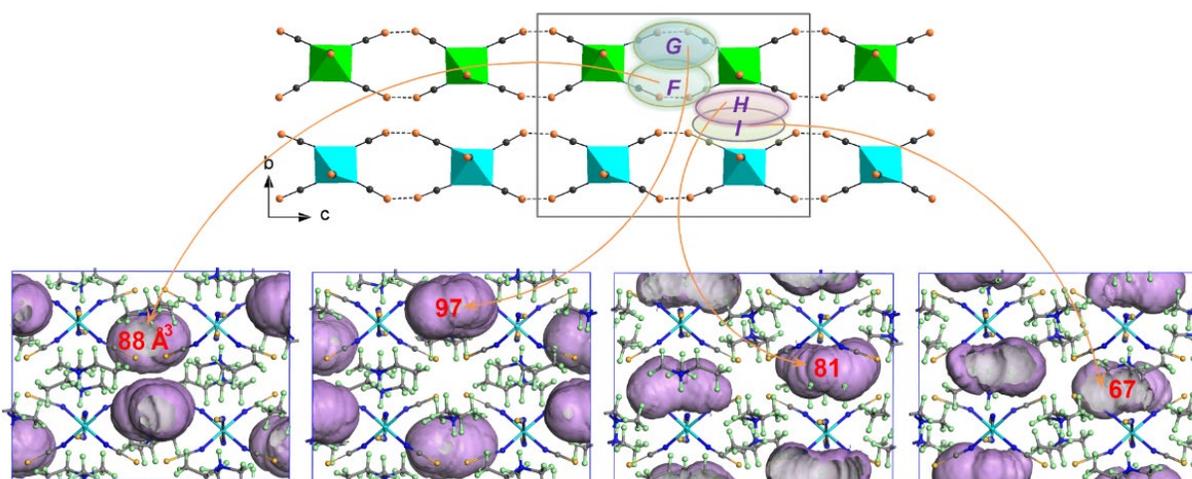

Fig. S10 Views of the stacking of the supramolecular layers of $[Ni(NCS)_6]^{4-}$ anions in **1α** phase (120 K) down the a-axis. The N7-, N8-, N9- and N10-containing Me_2EtNH^+ ions reside in the supramolecular cages **F**, **G**, **H** and **I**, respectively. For display details, see Fig. 2.
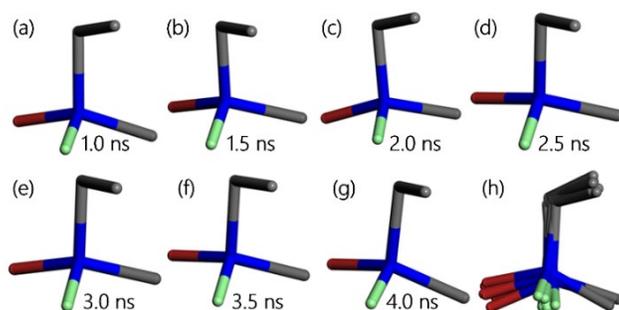
Fig. S11 Local snapshots of NVT dynamic simulation at 120 K for N7-containing Me_2EtNH^+ ion in **1α** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h). All C-bound H atoms are omitted for clarity.
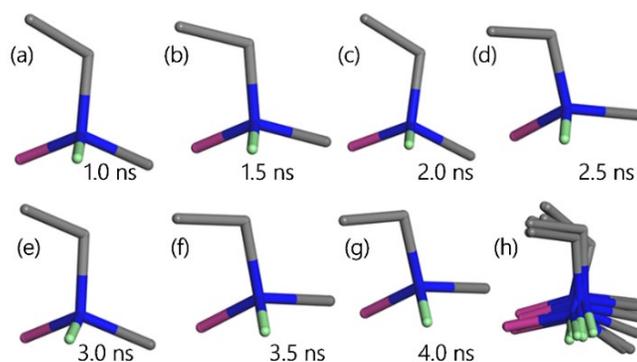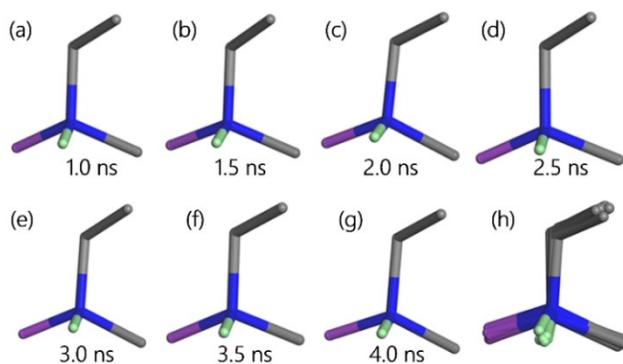

Fig. S12 Local snapshots of NVT dynamic simulation at 120 K for N8-containing Me_2EtNH^+ ion in **1α** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h).
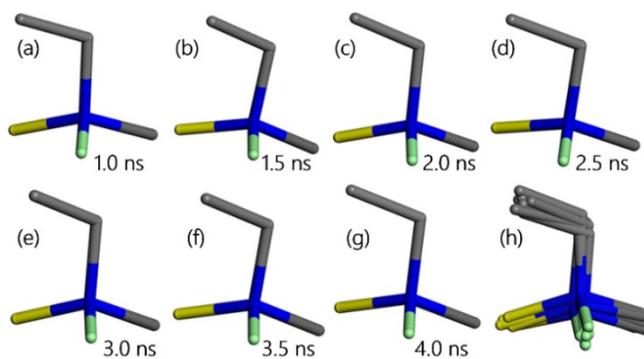

Fig. S13 Local snapshots of NVT dynamic simulation at 120 K for N9-containing Me_2EtNH^+ ion in **1α** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h).
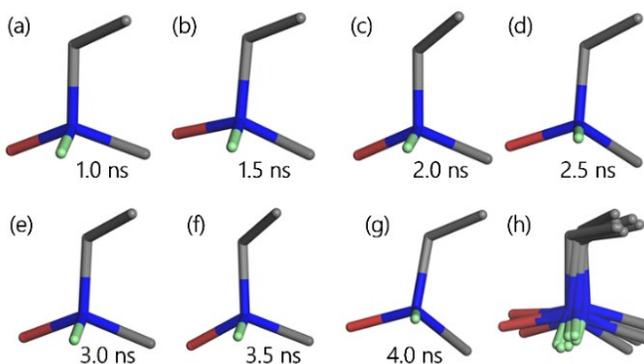
Fig. S14 Local snapshots of NVT dynamic simulation at 120 K for N10-containing Me$_2$EtNH$^+$ ion in **1α** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h).

Fig. S15 Local snapshots of NVT dynamic simulation at 180 K for N5-containing Me$_2$EtNH$^+$ ion in **1β** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h).
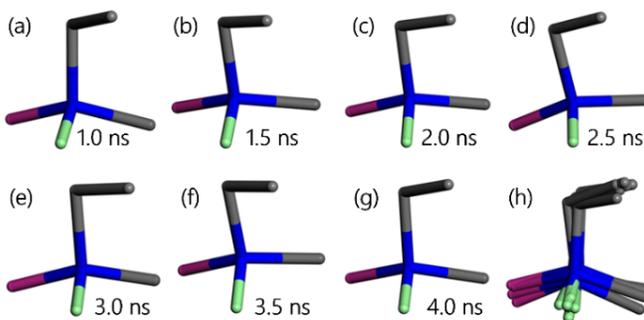

Fig. S16 Local snapshots of NVT dynamic simulation at 180 K for N6-containing Me$_2$EtNH$^+$ ion in **1β** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h).
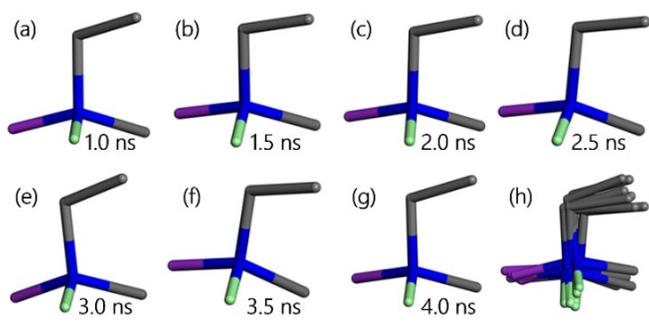
Fig. S17 Local snapshots of NVT dynamic simulation at 180 K for N7-containing Me$_2$EtNH$^+$ ion in **1β** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h).
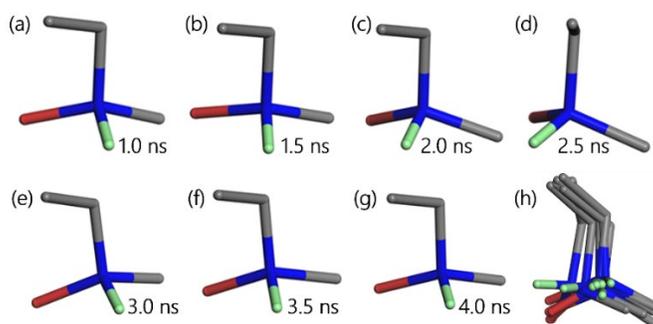

Fig. S18 Local snapshots of NVT dynamic simulation at 300 K for N3-containing Me$_2$EtNH$^+$ ion in **1γ** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h).
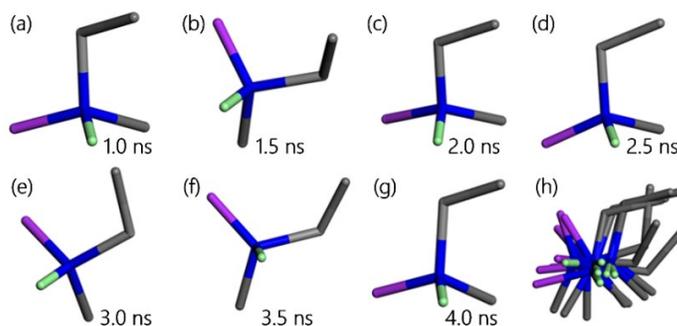

Fig. S19 Local snapshots of NVT dynamic simulation at 300 K for N4-containing Me$_2$EtNH$^+$ ion in **1γ** phase over the simulation time (a-g), and the overlapping maps of these snapshots (h).
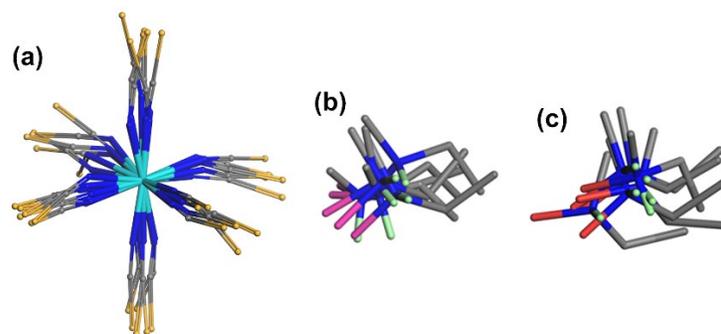
Fig. S20 Overlapping maps of the snapshots for one $[Ni(NCS)_6]^{4-}$ anion (a) and two N3-containing Me_2EtNH^+ ions (b, c), respectively, by first-principles NVT dynamic simulation of **1λ** phase at simulation temperature of 573 K, showing orientation changes and short-range displacements over the simulation time of 0, 2, 4, 6, 8, and 10 ps.
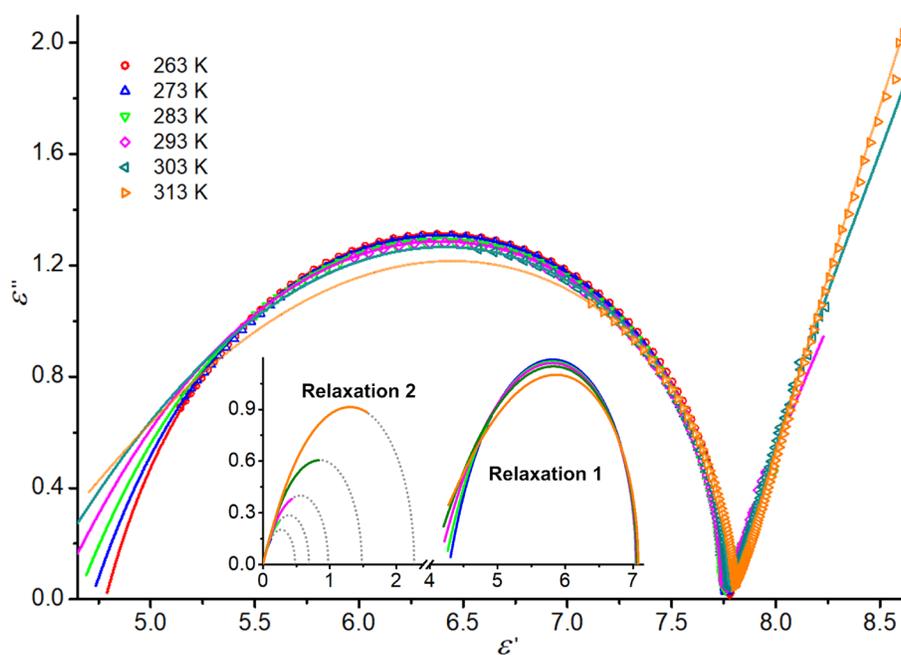

Fig. S21 The variable-temperature Cole–Cole plots as a series of arcs shown the relationship between ε' and ε''. Based on the obtained fitting parameters, the fitted Cole–Cole diagrams of two separated relaxation processes 1 and 2 are illustrated in the inset map.
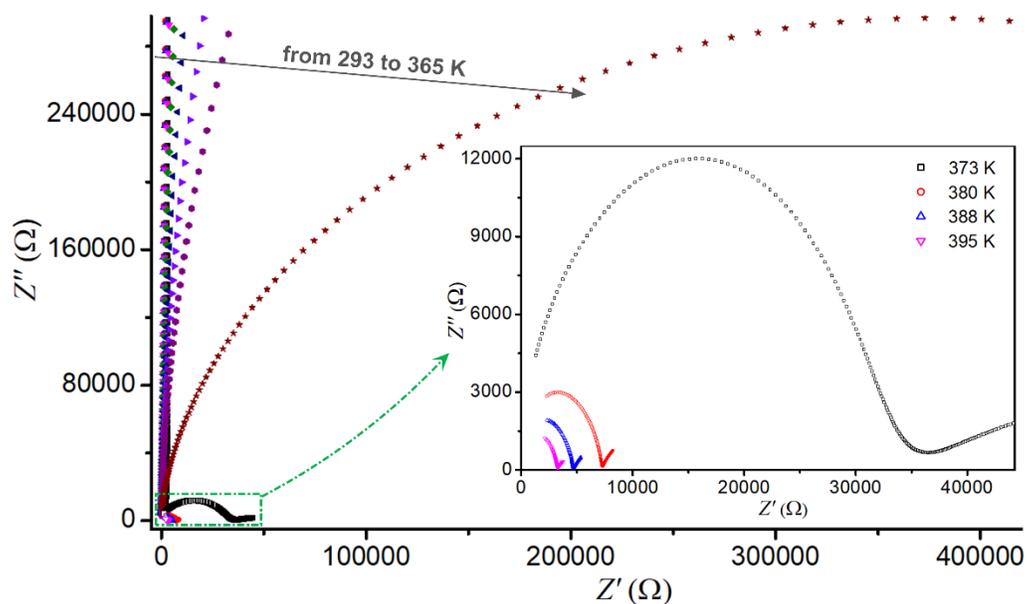
Fig. S22 Variable-temperature impedance spectra for the polycrystalline pellet of **1** in the temperature range from 293 to 395 K.
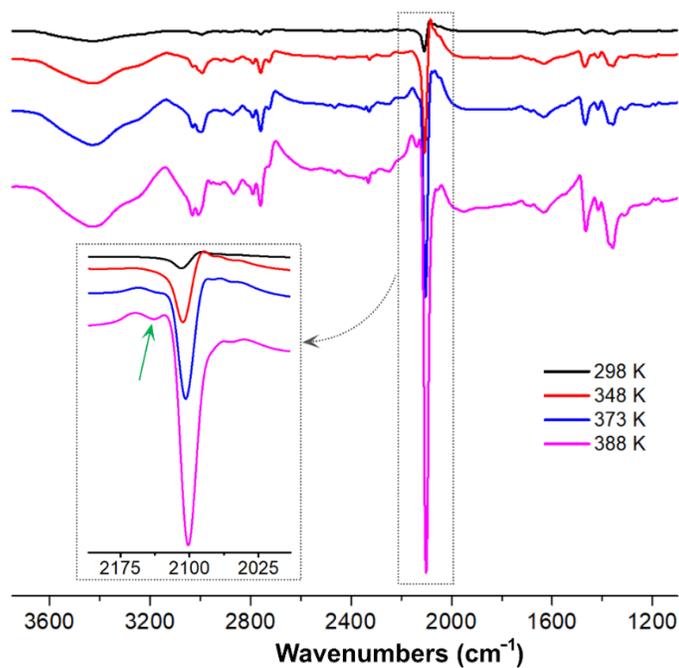

Fig. S23 Variable-temperature infrared spectra of **1** in the temperature range from 298 to 388 K.