Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Uniaxial Negative Thermal Expansion Induced by Molecular Rotation in One-Dimensional Supramolecular Assembly with Associated Peculiar Magnetic Behavior

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§1. Crystal data, Crystal Data, Data Collection, and Reduction Parameter.

The Flack parameter analyzed for $P2_1$ was 0.320(11) at 118 K. Relatively large Flack parameter suggests that the inverted domain, where dipole moment of **PD2** are aligned anti-parallel to the first domain, are included in the crystal **1**. It is because crystal structure of **1** can be refined by assuming inversion twin and BASF commands in shelx refinement, where volume ratio of twin domains were 0.680(11):0.320(11) at 118 K.

Table S1. Crystal Data, Data Collection, and Reduction Parameter for crystal **1**.

	1			
Temperature / K	118	135	151	169
Crystal Dimensions / mm^3	0.6×0.6×0.6			
Chemical formula	$C_{92}H_{106}N_4Ni_2O_{24}S_{20}$			
Formula weight	2410.42			
Crystal System	Monoclinic			
Space group	$P2_1$			
a / Å	13.0944(2)	13.1146(2)	13.1390(2)	13.1620(3)
b / Å	21.8192(3)	21.8149(3)	21.8050(3)	21.7862(3)
c / Å	18.0486(3)	18.0621(3)	18.0856(3)	18.1119(3)
β / deg	94.6070(15)	94.502(2)	94.4155(16)	94.3187(16)
V / Å^3	5139.99(14)	5151.51(14)	5166.08(15)	5178.82(15)
Z	2	2	2	2
D_{calc} / g·cm^{-3}	1.557	1.554	1.550	1.546
μ(Mo Kα) / cm^{-1}	0.847	0.845	0.843	0.840
$2\theta_{max}$ / deg	62.5200	61.8940	62.1320	61.586
Reflections measured	77144	78128	77762	80139
Independent reflections	26132	25961	25989	26243
Reflections used	26132	25961	25989	26243
R_1 [a]	0.0350	0.0357	0.0364	0.0374
$R_w(F^2)$ [a]	0.0803	0.0833	0.0861	0.0888
GOF	1.026	1.034	1.041	1.039
Flack Parameter	0.320(11)	0.334(11)	0.318(11)	0.315(11)
CCDC No.	2163119	2163120	2163121	2163122

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

	1				
Temperature / K	177	186	194	202	221
Crystal Dimensions / mm^3	0.6×0.6×0.6				
Chemical formula	$C_{92}H_{106}N_4Ni_2O_{24}S_{20}$				
Formula weight	2410.42				
Crystal System	Monoclinic				
Space group	$P2_1$				
a / Å	13.19743(18)	13.1936(3)	13.2130(3)	13.2325(3)	13.2688(3)
b / Å	21.7622(2)	21.7511(3)	21.7297(3)	21.7185(3)	21.6763(3)
c / Å	18.1487(2)	18.1553(3)	18.1815(3)	18.1943(3)	18.2309(3)
β / deg	94.1520(11)	94.2038(17)	94.1495(18)	94.039(2)	93.8703(18)
V / Å^3	5198.74(11)	5196.10(16)	5206.48(17)	5215.87(16)	5231.59(17)
Z	2	2	2	2	2
D_{calc} / g·cm^{-3}	1.540	1.541	1.538	1.535	1.530
μ(Mo Kα) / cm^{-1}	0.837	0.838	0.836	0.834	0.832
$2\theta_{max}$ / deg	62.3520	61.878	60.702	61.526	61.938
Reflections measured	97567	83480	79833	82353	87510
Independent reflections	26744	26486	26365	26375	26468
Reflections used	26744	26486	26365	26375	26468
R_1 [a]	0.0333	0.0381	0.0390	0.0379	0.0369
$R_w(F^2)$ [a]	0.0806	0.0900	0.0913	0.0895	0.0851
GOF	1.018	1.042	1.031	1.021	1.027
Flack Parameter	0.356(10)	0.319(11)	0.309(12)	0.323(11)	0.276(11)
CCDC No.	2163123	2163124	2163125	2163126	2163127

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

	1			
Temperature / K	237	254	272	282
Crystal Dimensions / mm^3	0.6×0.6×0.6			
Chemical formula	$C_{92}H_{106}N_4Ni_2O_{24}S_{20}$			
Formula weight	2410.42			
Crystal System	Monoclinic			
Space group	$P2_1$			
a / Å	13.3027(3)	13.3375(3)	13.3760(3)	13.3988(3)
b / Å	21.6453(4)	21.6167(4)	21.5994(4)	21.5792(4)
c / Å	18.2686(4)	18.3081(4)	18.3362(4)	18.3596(4)
β / deg	93.655(2)	93.505(2)	93.373(2)	93.338(2)
V / $Å^3$	5249.58(19)	5268.58(19)	5288.40(19)	5299.40(19)
Z	2	2	2	2
D_{calc} / $g·cm^{-3}$	1.525	1.519	1.514	1.511
μ(Mo Kα) / cm^{-1}	0.829	0.826	0.823	0.821
$2\theta_{max}$ / deg	61.4080	61.8740	61.9860	62.5520
Reflections measured	82444	85675	84884	70798
Independent reflections	26609	26960	26919	21627
Reflections used	26609	26960	26919	21627
R_1 [a]	0.0382	0.0383	0.0391	0.0350
$R_w(F^2)$ [a]	0.0903	0.0879	0.1171	0.0839
GOF	0.934	1.018	0.902	1.018
Flack Parameter	0.321(12)	0.337(11)	0.299(12)	0.248(13)
	2163128	2163129	2163130	2163131

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

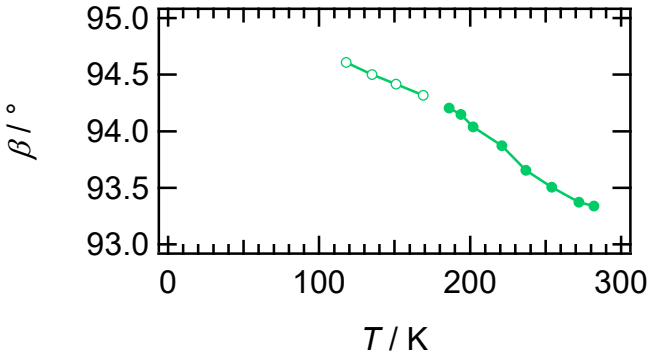

Figure S1. Temperature-dependence of β in unit cell.

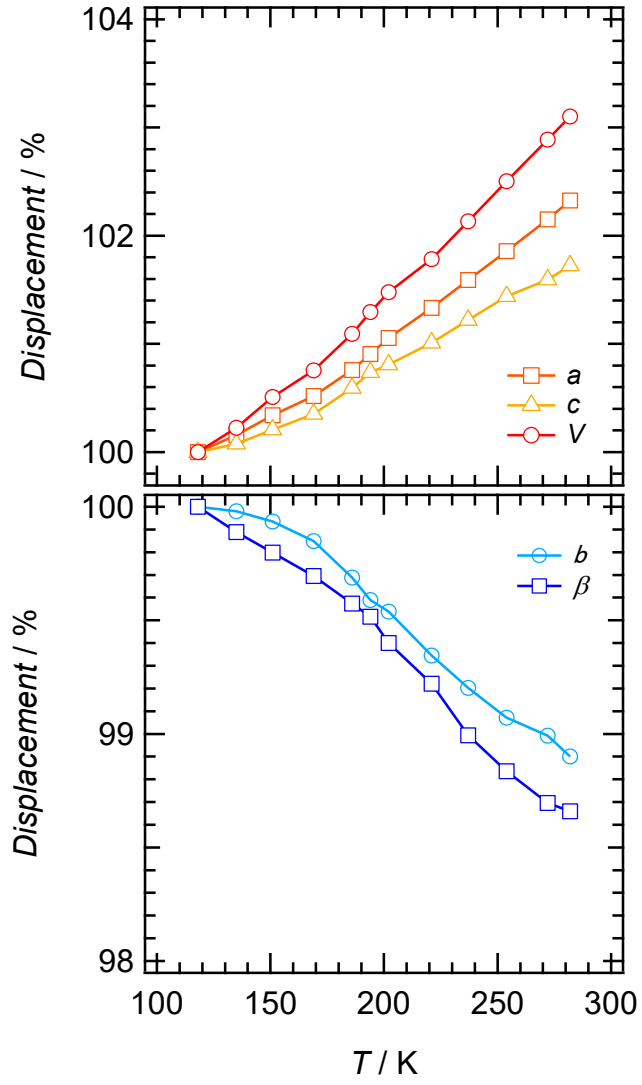

Figure S2. Temperature dependence of cell parameters normalized at 118 K.

§2. Crystallographically independent molecules with atom numbering

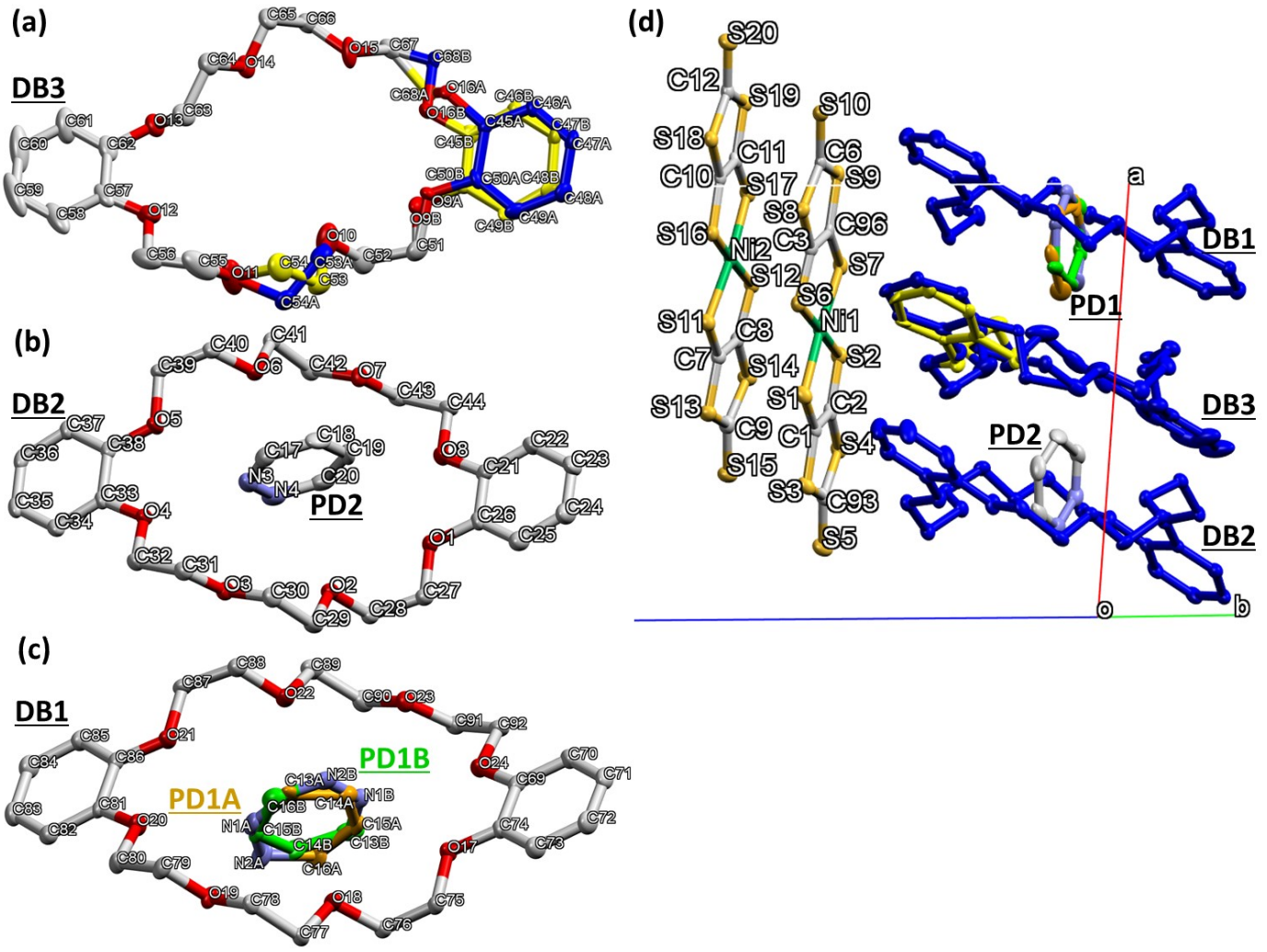

Figure S3. Crystallographically independent molecular structure in the crystal **1** at 118 K with atomic number. (a) Molecular structure of **DB3**. Disordered carbon atoms depicted as yellow and blue colors. (b) molecular structures of **PD2** and **DB2**. (c) Molecular structures of **DB1**, **PD1A**, and **PD1B**. (d) Atom numbering for $[Ni(dmit)_2]$ in the packing with crystallographically independent supramolecular cations.

The length of covalent bonds between the nitrogen atoms in the typical $pdazH^+$ cations are longer than those between the nitrogen and carbon atoms. We could not assign nitrogen atoms next to N1A and N1B from the lengths of C-C and C-N bond within **PD1A** and **PD1B** due to the disorder of $pdazH^+$. However, if we place the nitrogen atoms other than N2A and N2B, as described in Figure 2b, we could not solve the structure without using restrained commands for bond distance on Shelx refinement. On the other hand, the distance between N3 and N4 atoms in **PD2** was 1.307(5) Å whereas those between N3 or N4 and adjacent carbon atoms were 1.302(6) and 1.276(6) Å, respectively. Therefore, we could safely assign the position of N4

atom of the **PD2** in crystal **1**. The assignment of N4 atom in **PD2** is reasonable because N4 atom in **PD2** contacts C-H bond in **PD1A** and **PD1B** and forms a C-H•••N interaction (Figure 2c, see also Table S3 for the details of C-H•••N4 interactions).

Table S2. Temperature-dependent C•••O distance and C-H•••O angles between **PD1A•••DB3A**, and **PD1B•••DB3B**.

	PD1A•••DB3A		**PD1B•••DB3B**	
	C15A•••O16A	C15A-H@•••O16A	C13B•••O16B	C13B•••O16B
T / K	distance / Å	angle / °	distance / Å	angle / °
118	3.154	134.16	3.322	153.76
135	3.126	136.24	3.418	152.91
151	3.132	134.01	3.409	154.05
169	3.101	135.80	3.392	155.84
186	3.089	133.53	3.410	152.97
194	3.037	135.47	3.445	153.81
202	3.031	134.52	3.451	154.01
221	3.031	132.98	3.438	151.70
237	3.035	132.29	3.364	141.17
254	3.025	131.19	3.400	142.78
272	3.084	130.60	3.380	139.94
282	3.047	128.51	3.337	139.23

Table S3. Temperature-dependent C•••N distances, and C-H•••N angles between **PD1A•••PD2**, and **PD1B•••PD2**.

	PD1A•••PD2		**PD1B•••PD2**	
	C13A•••N4	C13A-H@•••N4	C16B•••N4	C16B-H•••N4
T / K	distance / Å	angle / °	distance / Å	angle / °
118	3.426	165.05	3.430	120.16
135	3.415	166.59	3.462	120.05
151	3.439	166.13	3.463	120.30
169	3.536	163.54	3.431	120.90
186	3.532	166.32	3.472	120.34
194	3.531	166.09	3.487	120.81
202	3.578	165.91	3.467	122.87
221	3.588	165.89	3.541	120.80
237	3.621	165.86	3.557	119.83
254	3.600	164.95	3.790	118.94
272	3.640	162.61	3.843	116.02
282	3.684	164.80	3.719	118.41

Table S3. Temperature dependence of the parameters for N-H•••O hydrogen bonds (N•••O distance and N-H•••O angle) between **PD1A•••DB1**, **PD1B•••DB1**, and **PD2•••DB2**.

	N-H•••O hydrogen bond					
	PD1A•••DB1		**PD1B•••DB1**		**PD2•••DB2**	
T / K	N1A•••O20 distance / Å	N1A-H1A•••O16 angle / °	N1B-O24 distance / Å	N1B-H1B•••O24 angle / °	N3•••O4 distance / Å	N3-H3•••O4 angle / °
118	2.806	172.03	2.932	170.89	2.814	170.45
135	2.804	171.12	2.914	171.28	2.814	169.79
151	2.831	171.57	2.911	171	2.816	169.85
169	2.793	168.83	2.912	172.16	2.818	168.57
186	2.798	169.97	2.912	170.83	2.827	167.07
194	2.806	169.38	2.92	168.51	2.83	166.68
202	2.81	167.66	2.916	174.45	2.832	165.48
221	2.81	168.14	2.922	172.7	2.847	164.54
237	2.806	168.41	2.919	166.59	2.853	163.28
254	2.817	169.19	2.983	171.32	2.865	161.69
272	2.813	169.66	2.955	166.01	2.884	161.11
282	2.824	168.64	2.907	166.33	2.88	160.99

Table S5. Temperature dependence of O•••π distances between **DB1•••PD1A** and **DB2•••PD2**.

	DB1•••PD1A			
	Interatomic Distance / Å			
T / K	O18•••C13A	O18•••C14A	O22•••C13A	O22•••C14A
118	2.999	3.022	2.908	3.057
135	2.969	3.038	2.941	3.036
151	2.984	3.038	2.936	3.048
169	2.979	3.039	2.929	3.058
186	3.021	3.054	2.902	3.054
194	3.027	3.016	2.901	3.112
202	3.026	3.045	2.901	3.083
221	3.048	3.053	2.894	3.081
237	3.031	3.019	2.92	3.124
254	3.052	3.022	2.93	3.132
272	3.091	3.019	2.91	3.143
282	3.055	3.028	2.937	3.125

	DB2•••PD2.			
	Interatomic Distance / Å			
T / K	O6•••C17	O6•••N3	O2•••C20	O7•••C20
118	3.192	3.092	3.057	3.192
135	3.202	3.096	3.055	3.194
151	3.19	3.092	3.054	3.197
169	3.202	3.083	3.049	3.195
186	3.212	3.075	3.047	3.19
194	3.22	3.073	3.041	3.188
202	3.224	3.068	3.045	3.187
221	3.237	3.059	3.046	3.174
237	3.241	3.054	3.045	3.177
254	3.247	3.042	3.05	3.17
272	3.25	3.038	3.048	3.176
282	3.259	3.038	3.053	3.17

§3. Input and output file of PASCal Calculation, and indicatrix plots

Table S6. Input and output file of PASCal Calculation for structural data of **1** between 118 and 169 K.

input	T / K	σ_T	a / Å	b / Å	c / Å	α / °	β / °	γ / °
	169	5	13.162	21.7862	18.1119	90	94.3187	90
	151	5	13.139	21.805	18.0856	90	94.4155	90
	135	5	13.1146	21.8149	18.0621	90	94.502	90
	118	5	13.0944	21.8192	18.0486	90	94.607	90

output				Direction		
	Axes	α / MK^{-1}	σ_α / MK^{-1}	a	b	c
	X_1	-29.6503	4.1985	0	1	0
	X_2	38.0421	3.9509	-0.6675	0	0.7446
	X_2	142.2858	1.4664	0.8931	0	0.4499
	V	151.2583	2.7976			

	% change in length					
	T / K	X_1	X_2	X_2	$X_{1,calc}$	$X_{2,calc}$	$X_{3,calc}$
	118	0	0	0	0.0159	-0.0179	-0.0069
	135	-0.0197	0.0215	0.2221	-0.0345	0.0468	0.235
	151	-0.0651	0.1047	0.4674	-0.082	0.1077	0.4626
	169	-0.1512	0.1865	0.72	-0.1354	0.1761	0.7188

	Volume		
	T / K	V / Å^3	Vlin / Å^3
	118	5139.993	5139.4723
	135	5151.509	5152.6892
	151	5166.071	5165.1287
	169	5178.84	5179.1231

Table S7. Input and output file of PASCal Calculation for structural data of **1** between 186 and 282 K.

input

T / K	σ_T	a / Å	b / Å	c / Å	α / °	β / °	γ / °
282	5	13.3988	21.5792	18.3596	90	93.338	90
272	5	13.376	21.5994	18.3362	90	93.373	90
254	5	13.3375	21.6167	18.3081	90	93.505	90
237	5	13.3027	21.6453	18.2686	90	93.655	90
221	5	13.2688	21.6763	18.2309	90	93.8703	90
202	5	13.2325	21.7185	18.1943	90	94.039	90
194	5	13.213	21.7297	18.1815	90	94.1495	90
186	5	13.1936	21.7511	18.1553	90	94.2038	90

output

			Direction		
Axes	α / MK^{-1}	σ_α / MK^{-1}	a	b	c
X_1	-81.2513	2.7	0	1	0
X_2	55.4528	3.149	-0.738	0	0.6749
X_2	230.0634	3.3742	0.859	0	0.512
V	204.178	1.9955			

% change in length

T / K	X_1	X_2	X_2	$X_{1,calc}$	$X_{2,calc}$	$X_{3,calc}$
186	0	0	0	-0.0324	0.018	0.028
194	-0.0984	0.1015	0.1967	-0.0974	0.0624	0.2121
202	-0.1499	0.1152	0.4153	-0.1624	0.1068	0.3961
221	-0.3439	0.2107	0.817	-0.3168	0.2121	0.8333
237	-0.4864	0.2644	1.2529	-0.4468	0.3008	1.2014
254	-0.6179	0.3778	1.6376	-0.5849	0.3951	1.5925
272	-0.6974	0.4775	1.9988	-0.7312	0.4949	2.0066
282	-0.7903	0.5935	2.1883	-0.8124	0.5504	2.2367

Volume

T / K	V / Å^3	Vlin / Å^3
186	5196.1057	5196.7608
194	5206.4888	5205.2482
202	5215.8741	5213.7356
221	5231.5855	5233.8933
237	5249.5783	5250.8682
254	5268.5849	5268.904
272	5288.3999	5288.0008
282	5299.4039	5298.6101

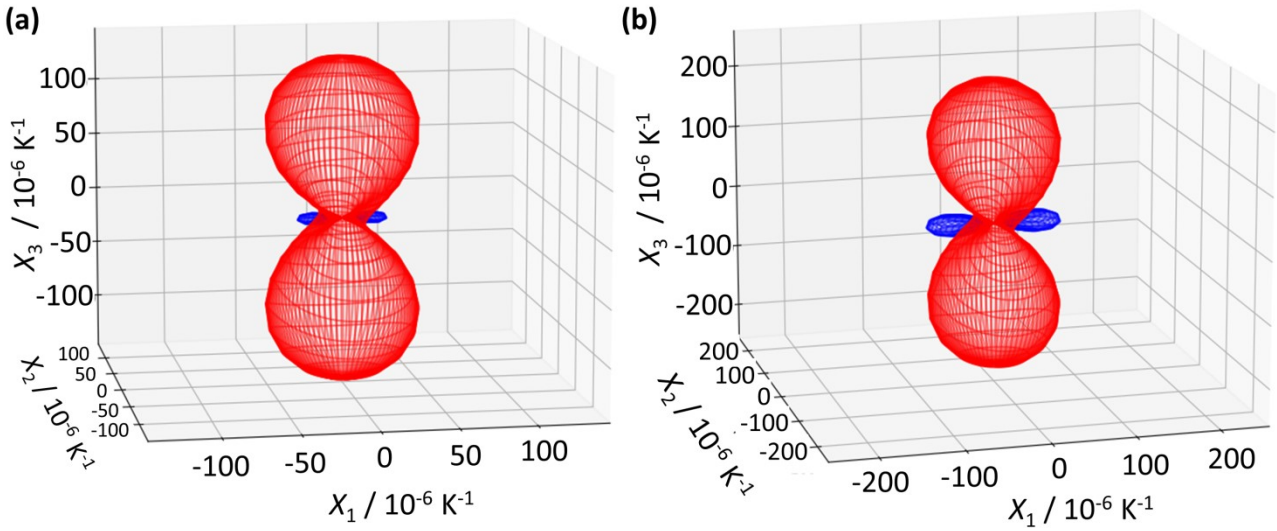

Figure S4. Indicatrix plots for structural data of **1** between (a) 118 and 169 K and (b) 186 and 282 K.

PASCal Indicatrix Plotter was used to plot the data. The software was obtained from the web site: https://cliffe.nottingham.ac.uk/programs/

§4 Differential scanning calorimetry (DSC) for crystal 1

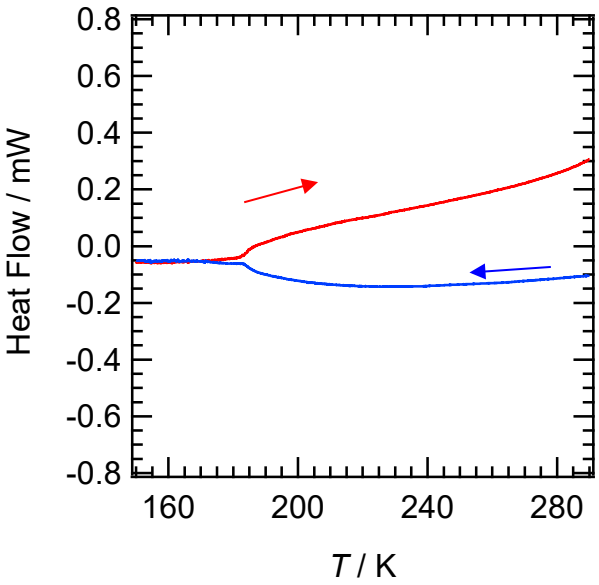

Figure S5. Differential scanning calorimetry from 150 to 290 K. Red and blue allows indicate the heating and cooling processes, respectively.

§5 Temperature-dependence of structural change between PD1B•••DB3B and PD1B•••PD2.

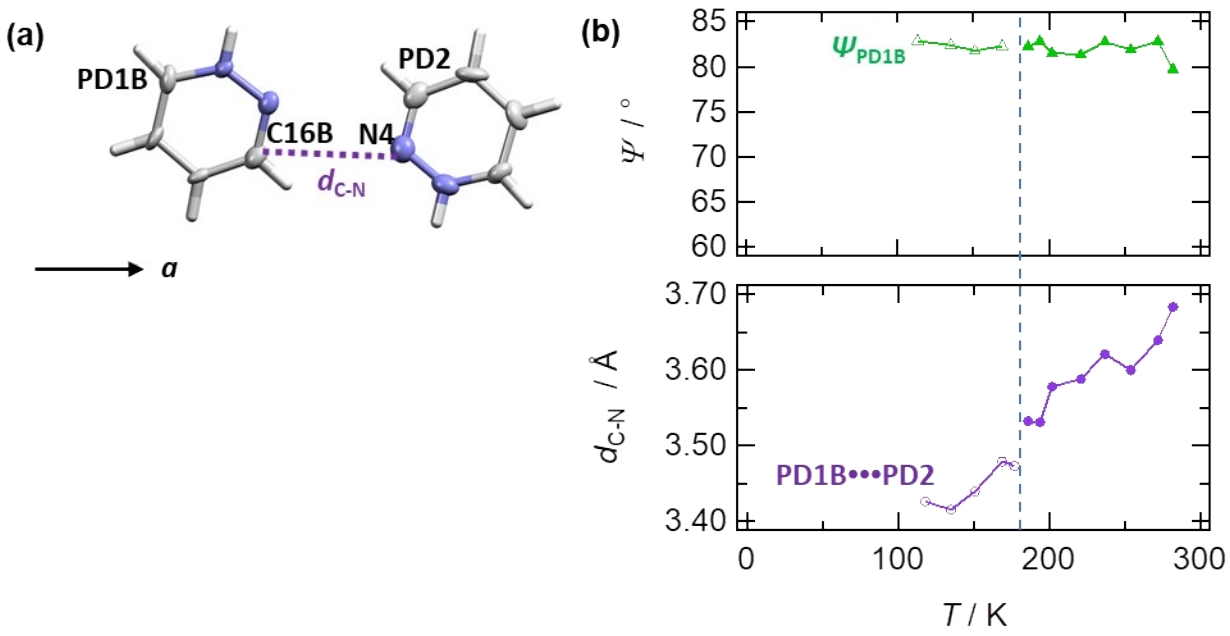

Figure S6. Schematic of selected parameters in supramolecular cation structure. The atoms are displayed using the thermal ellipsoid model. (a) Schematic of the interaction (purple) between C16B in **PD1B** and N4 in **PD2** ($d_{C\text{-}N}$). (b) Temperature dependences of Ψ_{PD1B} (Green), and $d_{C\text{-}N}$ (purple). The dashed line corresponds to the phase transition temperature of 183 K.

§6 Transfer integrals (t) between $[Ni(dmit)_2]^-$ anions and their temperature dependence.

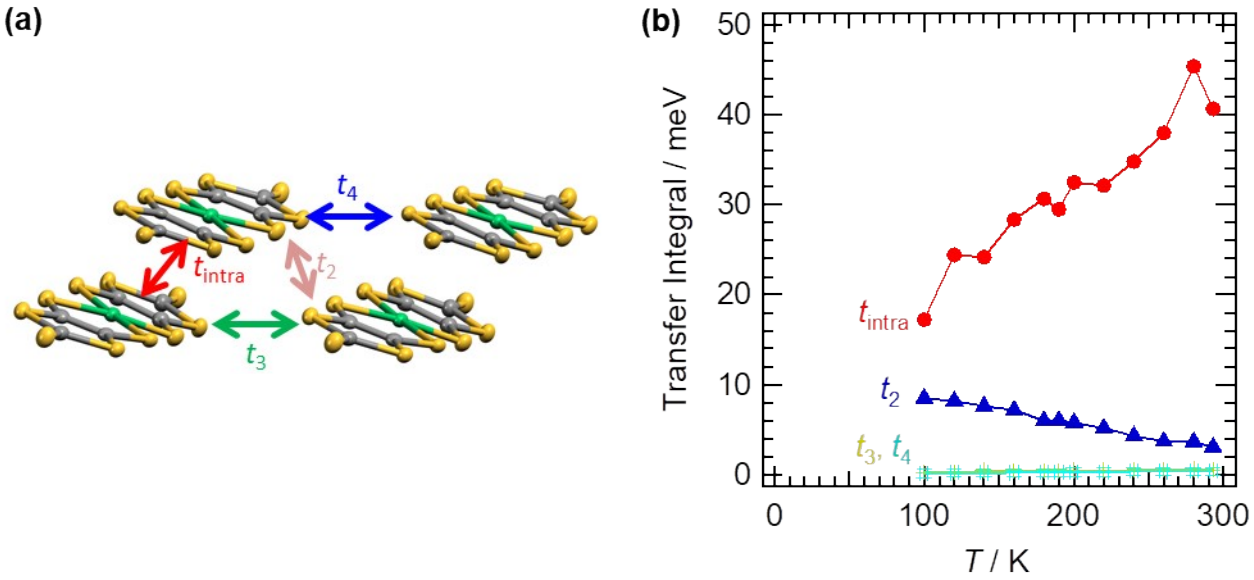

Figure S7. Transfer integrals (t) between $[Ni(dmit)_2]^-$ anions and their temperature dependence. (a) Arrangement of $[Ni(dmit)_2]^-$ and corresponding t (t_{intra}, t_2, t_3, and t_4), where t_{intra} represents t in intradimer. (b) Temperature-dependent t. Each t corresponds to those in (a).

§6 Expanded $\chi_m T$ versus T plot of Figure 5.

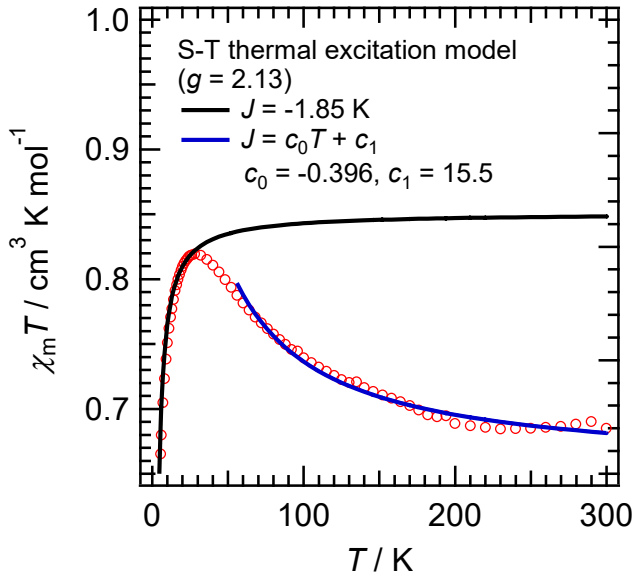

Figure S8. Expanded $\chi_m T$ *versus* T plot of Figure 5 with the left axis expanded from 0.65 to 1.0 cm^3 K mol^{-1}. Black and blue lines represent the singlet-triplet (S-T) thermal excitation models explained in the main text.

Singlet-triplet (S-T) thermal excitation model is described as follows [S1]:

$$\chi_m = \frac{2N_A{\mu_B}^2 g^2}{k_B T} \frac{1}{[3 + exp(-2J/k_B T)]}$$

where N_A, μ_B, g, and k_B are Avogadro number, Bohr magneton, Landé g-factor, and Boltzmann constant, respectively. In the modified model, $J/k_B = c_0 T + c_1$ are used, where c_0 and c_1 are constant.

References

[S1] B. Bleaney, K. D. Bowers, *Proc. R. Soc. Lond. A*, **1952**, *214*, 451–465.