Supporting Information

Molecular motion of halogenated ethylammonium / [18]crown-6 supramolecular ions in nickel dithiolate magnetic crystals

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§1. Crystal data, crystal data, data collection, and reduction parameter.

Table S1. Crystal data, data collection, and reduction parameter for crystals **1**, **2**, **3** and **4** at the lowest temperatures.

	1@113K	**2@93K**	**3@93K**	**4@106K**
Temperature / K	113	93	93	106
Crystal Dimensions / mm^3	0.724×0.378×0.207	0.507×0.211×0.090	0.69×0.60×0.18	0.40×0.11×0.07
Chemical formula	$C_{20}H_{32}NNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}BrNNiO_6S_{10}$
Formula weight	761.77	779.77	796.22	840.73
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	11.1765(4)	10.3645(3)	11.2107(3)	10.9869(3)
b / Å	12.2812(3)	12.6254(5)	12.3150(2)	12.0485(4)
c / Å	12.6527(4)	12.9123(4)	12.7451(3)	13.7559(5)
α / deg	87.364(2)	69.835(3)	92.2792(18)	115.833(4)
β / deg	68.465(3)	79.972(3)	112.126(2)	91.587(3)
γ / deg	80.094(2)	79.948(3)	96.0601(18)	100.906(3)
V / $Å^3$	1591.12(9)	1549.82(10)	1614.83(7)	1596.83(10)
Z	2	2	2	2
D_{calc} / $g·cm^{-3}$	1.590	1.671	1.638	1.748
μ(Mo Kα) / cm^{-1}	1.302	1.343	1.366	2.549
$2\theta_{max}$ / deg	61.784	61.986	61.838	61.140
Reflections measured	22773	18605	45358	19669
Independent reflections	7934	7679	8651	7891
Reflections used	7934	7679	8651	7891
R_1 [a]	0.0357	0.0324	0.0495	0.0356
R_w (F^2) [b]	0.0980	0.0792	0.1395	0.0703
GOF	1.051	1.070	1.098	0.995
CCDC number	2053279	2053282	2053390	2053298

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

Table S2. Crystal data, data collection, and reduction parameter for crystal **1**.

Temperature / K	293
Crystal Dimensions / mm^3	0.724×0.378×0.207
Chemical formula	$C_{20}H_{32}NNiO_6S_{10}$
Formula weight	761.77
Crystal System	Triclinic
Space group	*P*-1
a / Å	11.2486(6)
b / Å	12.3540(8)
c / Å	12.7375(8)
α / deg	87.498(5)
β / deg	69.343(6)
γ / deg	80.758(5)
V / $Å^3$	1634.62(18)
Z	2
D_{calc} / $g \cdot cm^{-3}$	1.548
μ(Mo Kα) / cm^{-1}	1.267
$2\theta_{max}$ / deg	62.114
Reflections measured	20189
Independent reflections	8034
Reflections used	8034
R_1 [a]	0.0365
R_w (F^2) [b]	0.0945
GOF	1.051
CCDC number	2053280

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

Table S3. Crystal data, data collection, and reduction parameter for crystal **2** at different temperatures.

	2			
Temperature / K	113	133	153	173
Crystal Dimensions / mm^3	0.507×0.211×0.090	0.507×0.211×0.090	0.507×0.211×0.090	0.507×0.211×0.090
Chemical formula	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$
Formula weight	779.77	779.77	779.77	779.77
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	10.3864(2)	10.3884(3)	10.3994(3)	10.4067(3)
b / Å	12.6343(5)	12.6271(4)	12.6286(5)	12.6314(5)
c / Å	12.9338(5)	12.9344(4)	12.9431(4)	12.9479(4)
α / deg	69.944(3)	70.113(3)	70.317(3)	70.517(3)
β / deg	79.973(3)	79.966(2)	79.956(2)	79.892(2)
γ / deg	79.970(3)	80.068(2)	80.078(3)	80.138(3)
V / $Å^3$	1557.90(10)	1559.30(9)	1564.10(9)	1567.96(9)
Z	2	2	2	2
D_{calc} / $g \cdot cm^{-3}$	1.662	1.661	1.656	1.650
μ(Mo Kα) / cm^{-1}	1.336	1.335	1.331	1.327
$2\theta_{max}$ / deg	62.114	61.916	61.652	61.248
Reflections measured	19702	19502	19288	19026
Independent reflections	7645	7689	7694	7718
Reflections used	7645	7689	7694	7718
R_1 [a]	0.0329	0.0386	0.0340	0.0366
R_w (F^2) [b]	0.0806	0.0941	0.0865	0.0925
GOF	1.054	0.990	1.075	1.075
CCDC number	2053283	2053284	2053285	2053286

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

	2			
Temperature / K	193	213	233	253
Crystal Dimensions / mm^3	0.507×0.211×0.090	0.507×0.211×0.090	0.507×0.211×0.090	0.507×0.211×0.090
Chemical formula	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$
Formula weight	779.77	779.77	779.77	779.77
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	10.4204(3)	10.4363(3)	10.4520(3)	10.4754(3)
b / Å	12.6319(4)	12.6370(4)	12.6374(4)	12.6503(4)
c / Å	12.9511(4)	12.9511(4)	12.9527(4)	12.9637(4)
α / deg	70.735(3)	70.974(3)	71.178(3)	71.385(3)
β / deg	79.898(2)	79.852(2)	79.806(2)	79.802(2)
γ / deg	80.250(2)	80.316(2)	80.408(2)	80.550(2)
V / Å^3	1572.90(9)	1578.17(8)	1582.77(9)	1591.61(9)
Z	2	2	2	2
D_{calc} / g·cm^{-3}	1.646	1.641	1.636	1.627
μ(Mo Kα) / cm^{-1}	1.323	1.319	1.315	1.308
$2\theta_{max}$ / deg	61.70	61.50	62.07	61.34
Reflections measured	19734	19305	19876	19688
Independent reflections	7797	7814	7847	7844
Reflections used	7797	7814	7847	7844
R_1 [a]	0.0414	0.0336	0.0335	0.0343
R_w (F^2) [b]	0.1011	0.0838	0.0864	0.0810
GOF	1.016	1.050	1.044	1.047
CCDC number	2053287	2053288	2053289	2053290

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

	2			
Temperature / K	273	293	313	333
Crystal Dimensions / mm^3	0.507×0.211×0.090	0.507×0.211×0.090	0.507×0.211×0.090	0.507×0.211×0.090
Chemical formula	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$
Formula weight	779.77	779.77	779.77	779.77
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	10.4883(2)	10.5115(3)	10.5377(3)	10.5475(3)
b / Å	12.6467(3)	12.6531(4)	12.6697(3)	12.6632(3)
c / Å	12.9675(3)	12.9821(3)	13.0079(4)	13.0124(4)
α / deg	71.543(2)	71.701(2)	71.903(2)	72.091(3)
β / deg	79.792(2)	79.787(2)	79.822(2)	79.842(3)
γ / deg	80.656(2)	80.782(2)	80.956(2)	81.154(2)
V / Å^3	1595.30(6)	1603.24(8)	1615.05(8)	1618.65(8)
Z	2	2	2	2
D_{calc} / g·cm^{-3}	1.623	1.615	1.603	1.600
μ(Mo Kα) / cm^{-1}	1.305	1.298	1.289	1.286
$2\theta_{max}$ / deg	61.89	61.438	58.006	57.812
Reflections measured	39570	20112	17913	19117
Independent reflections	8451	7909	7336	7320
Reflections used	8451	7909	7336	7320
R_1 [a]	0.0357	0.0336	0.0354	0.0383
R_w (F^2) [b]	0.1327	0.0801	0.0855	0.0986
GOF	0.870	1.055	1.042	1.077
CCDC number	2053291	2053292	2053293	2053294

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

	2	
Temperature / K	353	373
Crystal Dimensions / mm^3	0.507×0.211×0.090	0.507×0.211×0.090
Chemical formula	$C_{20}H_{31}FNNiO_6S_{10}$	$C_{20}H_{31}FNNiO_6S_{10}$
Formula weight	779.77	779.77
Crystal System	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a / Å	10.5673(4)	10.5742(7)
b / Å	12.6724(4)	12.6426(7)
c / Å	13.0358(6)	13.0305(11)
α / deg	72.219(4)	72.446(6)
β / deg	79.801(4)	79.808(6)
γ / deg	81.293(3)	81.420(5)
V / Å^3	1627.17(12)	1626.1(2)
Z	2	2
D_{calc} / g·cm^{-3}	1.592	1.593
μ(Mo Kα) / cm^{-1}	1.279	1.280
$2\theta_{max}$ / deg	58.162	58.054
Reflections measured	18534	18911
Independent reflections	7331	7413
Reflections used	7331	7413
R_1 [a]	0.0459	0.0514
R_w (F^2) [b]	0.1373	0.1505
GOF	0.911	0.911
CCDC number	2053295	2053296

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

Table S4. Crystal data, data collection, and reduction parameter for crystal **3** at different temperatures.

	3			
Temperature / K	113	133	153	173
Crystal Dimensions / mm^3	0.69×0.60×0.18	0.69×0.60×0.18	0.69×0.60×0.18	0.290×0.249×0.157
Chemical formula	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$
Formula weight	796.22	796.22	796.22	796.22
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	11.2193(3)	11.2216(3)	11.2185(3)	11.2452(2)
b / Å	12.3191(2)	12.3162(3)	12.3084(3)	12.3442(2)
c / Å	12.7473(3)	12.7541(3)	12.7536(3)	12.8113(2)
α / deg	92.239(2)	92.155(2)	92.083(2)	91.8320(10)
β / deg	111.956(2)	111.864(2)	111.733(2)	111.4310(10)
γ / deg	96.066(2)	96.100(2)	96.128(2)	96.2430(10)
V / $Å^3$	1618.98(7)	1620.96(7)	1621.02(7)	1640.65(5)
Z	2	2	2	2
D_{calc} / $g·cm^{-3}$	1.633	1.631	1.631	1.612
μ(Mo Kα) / cm^{-1}	1.363	1.361	1.361	7.865
$2\theta_{max}$ / deg	52.742	52.744	61.84	144.97
Reflections measured	37298	35045	41879	39675
Independent reflections	6613	6623	8598	6266
Reflections used	6613	6623	8598	6266
R_1 [a]	0.0446	0.0419	0.0438	0.0385
R_w (F^2) [b]	0.1268	0.1168	0.1217	0.1156
GOF	1.077	1.056	1.068	1.020
CCDC number	2053392	2053393	2053394	2053395

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

	3			
Temperature / K	193	213	233	253
Crystal Dimensions / mm^3	0.371×0.624×0.961	0.290×0.249×0.157	0.290×0.249×0.157	0.290×0.249×0.157
Chemical formula	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$
Formula weight	796.22	796.22	796.22	796.22
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	11.25474(18)	11.2637(2)	11.27140(10)	11.27840(10)
b / Å	12.34881(18)	12.34200(10)	12.34060(10)	12.34600(10)
c / Å	12.82304(17)	12.8337(2)	12.84520(10)	12.86190(10)
α / deg	91.7415(11)	91.3720(10)	91.2410(10)	91.1450(10)
β / deg	111.2915(14)	110.9960(10)	110.8230(10)	110.6780(10)
γ / deg	96.3016(12)	96.4500(10)	96.4520(10)	96.4220(10)
V / Å^3	1645.75(4)	1651.13(4)	1655.78(3)	1661.63(3)
Z	2	2	2	2
D_{calc} / g·cm^{-3}	1.607	1.602	1.597	1.591
μ(Mo Kα) / cm^{-1}	1.341	7.815	7.793	7.765
$2\theta_{max}$ / deg	58.252	145.476	146.17	144.498
Reflections measured	33190	42270	41408	41385
Independent reflections	7803	6349	6351	6340
Reflections used	7803	6349	6351	6340
R_1 [a]	0.0347	0.0310	0.0321	0.0271
R_w (F^2) [b]	0.0910	0.0815	0.0845	0.0763
GOF	1.084	1.034	1.052	1.053
CCDC number	2053396	2053397	2053398	2053399

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

	3			
Temperature / K	273	293	313	333
Crystal Dimensions / mm^3	0.69×0.60×0.18	0.371×0.624×0.961	0.371×0.624×0.961	0.69×0.60×0.18
Chemical formula	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$
Formula weight	796.22	796.22	796.22	796.22
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	11.2803(3)	11.2892(3)	11.3149(3)	11.3046(5)
b / Å	12.3375(2)	12.3438(3)	12.3589(3)	12.3319(4)
c / Å	12.8611(3)	12.8805(3)	12.9090(3)	12.9008(6)
α / deg	91.103(2)	91.047(2)	90.9686(19)	90.991(3)
β / deg	110.634(2)	110.467(2)	110.340(2)	110.208(4)
γ / deg	96.375(2)	96.326(2)	96.269(2)	96.173(3)
V / $Å^3$	1661.43(7)	1668.26(7)	1679.59(8)	1675.11(13)
Z	2	2	2	2
D_{calc} / $g·cm^{-3}$	1.592	1.583	1.574	1.579
μ(Mo Kα) / cm^{-1}	1.328	1.322	1.314	1.317
$2\theta_{max}$ / deg	62.142	58.016	58.032	52.744
Reflections measured	49247	32304	32926	27105
Independent reflections	8848	7906	7989	6845
Reflections used	8848	7906	7989	6845
R_1 [a]	0.0389	0.0366	0.0389	0.0516
R_w (F^2) [b]	0.1292	0.1064	0.1150	0.1420
GOF	1.015	1.015	0.996	0.986
CCDC number	2053391	2053400	2053401	2053402

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

	3	
Temperature / K	353	373
Crystal Dimensions / mm^3	0.69×0.60×0.18	0.371×0.624×0.961
Chemical formula	$C_{20}H_{31}ClNNiO_6S_{10}$	$C_{20}H_{31}ClNNiO_6S_{10}$
Formula weight	796.22	796.22
Crystal System	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a / Å	11.3244(5)	11.3571(2)
b / Å	12.3495(4)	12.3603(2)
c / Å	12.9385(6)	12.9511(3)
α / deg	90.918(3)	90.864(2)
β / deg	110.128(4)	109.988(2)
γ / deg	96.018(3)	95.958(2)
V / $Å^3$	1686.95(13)	1696.81(6)
Z	2	2
D_{calc} / $g·cm^{-3}$	1.568	1.558
μ(Mo Kα) / cm^{-1}	1.308	1.300
$2\theta_{max}$ / deg	58.424	58.26
Reflections measured	30129	33505
Independent reflections	8054	8059
Reflections used	8054	8059
R_1 [a]	0.0559	0.0396
R_w (F^2) [b]	0.1553	0.1222
GOF	0.916	0.968
CCDC number	2053403	2053404

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

Table S5. Crystal data, data collection, and reduction parameter for crystal **4** at different temperatures.

	4			
Temperature / K	113	133	153	173
Crystal Dimensions / mm^3	0.40×0.11×0.07	0.40×0.11×0.07	0.40×0.11×0.07	0.40×0.11×0.07
Chemical formula	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$
	0	0	0	0
Formula weight	840.68	840.68	840.68	840.68
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	10.9810(3)	11.0117(3)	11.0165(3)	11.0374(3)
b / Å	12.0448(3)	12.0652(3)	12.0569(4)	12.0627(3)
c / Å	13.7409(4)	13.7791(4)	13.7786(4)	13.7656(4)
α / deg	115.825(3)	115.895(3)	64.116(3)	64.349(3)
β / deg	91.535(2)	91.351(2)	79.239(3)	79.574(2)
γ / deg	100.927(2)	101.004(2)	78.965(2)	78.920(2)
V / $Å^3$	1593.91(8)	1604.68(8)	1605.03(9)	1611.42(9)
Z	2	2	2	2
D_{calc} / $g·cm^{-3}$	1.747	1.740	1.739	1.733
μ(Mo Kα) / cm^{-1}	2.554	2.537	2.536	2.526
$2\theta_{max}$ / deg	62.086	61.834	62.064	62.062
Reflections measured	38281	38326	39974	40700
Independent reflections	8378	8423	8484	8560
Reflections used	8378	8423	8484	8560
R_1 [a]	0.0315	0.0325	0.0337	0.0333
R_w (F^2) [b]	0.0677	0.0677	0.0706	0.0690
GOF	1.016	1.026	1.032	1.039
CCDC number	2053299	2053300	2053301	2053302

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

	4			
Temperature / K	193	213	233	253
Crystal Dimensions / mm^3	0.40×0.11×0.07	0.40×0.11×0.07	0.40×0.11×0.07	0.40×0.11×0.07
Chemical formula	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$
	0	0	0	0
Formula weight	840.68	840.68	840.68	840.68
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	11.0467(3)	11.0537(3)	11.0760(3)	11.0864(3)
b / Å	12.0603(3)	12.0557(3)	12.0662(3)	12.0734(3)
c / Å	13.7505(4)	13.7262(4)	13.7164(5)	13.7103(4)
α / deg	64.635(3)	64.890(3)	65.106(3)	65.253(3)
β / deg	79.967(2)	80.331(2)	80.573(3)	80.773(3)
γ / deg	78.865(2)	78.815(2)	78.719(2)	78.660(2)
V / $Å^3$	1615.49(8)	1617.26(9)	1623.84(9)	1627.77(9)
Z	2	2	2	2
D_{calc} / $g \cdot cm^{-3}$	1.728	1.726	1.719	1.715
μ(Mo Kα) / cm^{-1}	2.520	2.517	2.507	2.501
$2\theta_{max}$ / deg	62.048	62.122	62.116	62.16
Reflections measured	40000	40716	40270	42066
Independent reflections	8603	8593	8614	8660
Reflections used	8603	8593	8614	8660
R_1 [a]	0.0375	0.0391	0.0405	0.0377
R_w (F^2) [b]	0.0851	0.0818	0.0923	0.0875
GOF	1.073	1.039	1.019	1.039
CCDC number	2053303	2053304	2053305	2053306

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

	4			
Temperature / K	273	293	313	333
Crystal Dimensions / mm^3	0.40×0.11×0.07	0.40×0.11×0.07	0.40×0.11×0.07	0.40×0.11×0.07
Chemical formula	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$	$C_{20}H_{31}BrNNiO_6S_1$
	0	0	0	0
Formula weight	840.68	840.68	840.68	840.68
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a / Å	11.1022(4)	11.1201(5)	11.1694(4)	11.1865(5)
b / Å	12.0838(4)	12.1021(5)	12.1413(4)	12.1459(5)
c / Å	13.7055(5)	13.7058(7)	13.7408(6)	13.7395(6)
α / deg	65.348(3)	65.393(5)	65.543(4)	65.630(4)
β / deg	80.897(3)	80.958(4)	81.123(3)	81.204(4)
γ / deg	78.557(3)	78.454(4)	78.362(3)	78.269(4)
V / $Å^3$	1632.00(11)	1637.40(15)	1656.09(12)	1659.95(14)
Z	2	2	2	2
D_{calc} / $g \cdot cm^{-3}$	1.709	1.705	1.686	1.682
μ(Mo Kα) / cm^{-1}	2.494	2.486	2.458	2.452
$2\theta_{max}$ / deg	62.156	62.106	58.064	58.072
Reflections measured	41574	42141	33146	34340
Independent reflections	8724	8744	7890	7868
Reflections used	8724	8744	7890	7868
R_1 [a]	0.0413	0.0431	0.0416	0.0879
R_w (F^2) [b]	0.0922	0.0958	0.0958	0.1086
GOF	1.020	1.031	1.049	1.027
CCDC number	2053307	2053308	2053309	2053310

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

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	4	
Temperature / K	353	373
Crystal Dimensions / mm^3	0.40×0.11×0.07	0.40×0.11×0.07
Chemical formula	$C_{20}H_{31}BrNNiO_6S_{10}$	$C_{20}H_{31}BrNNiO_6S_{10}$
Formula weight	840.68	840.68
Crystal System	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a / Å	11.2110(4)	11.2167(4)
b / Å	12.1703(4)	12.1808(4)
c / Å	13.7456(5)	13.7373(5)
α / deg	65.635(3)	65.696(3)
β / deg	81.252(3)	81.308(3)
γ / deg	78.145(3)	78.012(3)
V / $Å^3$	1667.21(10)	1668.72(11)
Z	2	2
D_{calc} / $g·cm^{-3}$	1.675	1.673
μ(Mo Kα) / cm^{-1}	2.442	2.439
$2\theta_{max}$ / deg	58.086	58.11
Reflections measured	34600	35265
Independent reflections	7944	7932
Reflections used	7944	7932
R_1 [a]	0.0522	0.0470
R_w (F^2) [b]	0.1284	0.1118
GOF	1.016	1.008
CCDC number	2053311	2053312

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

§2. Crystallographically independent molecules with atom numbering

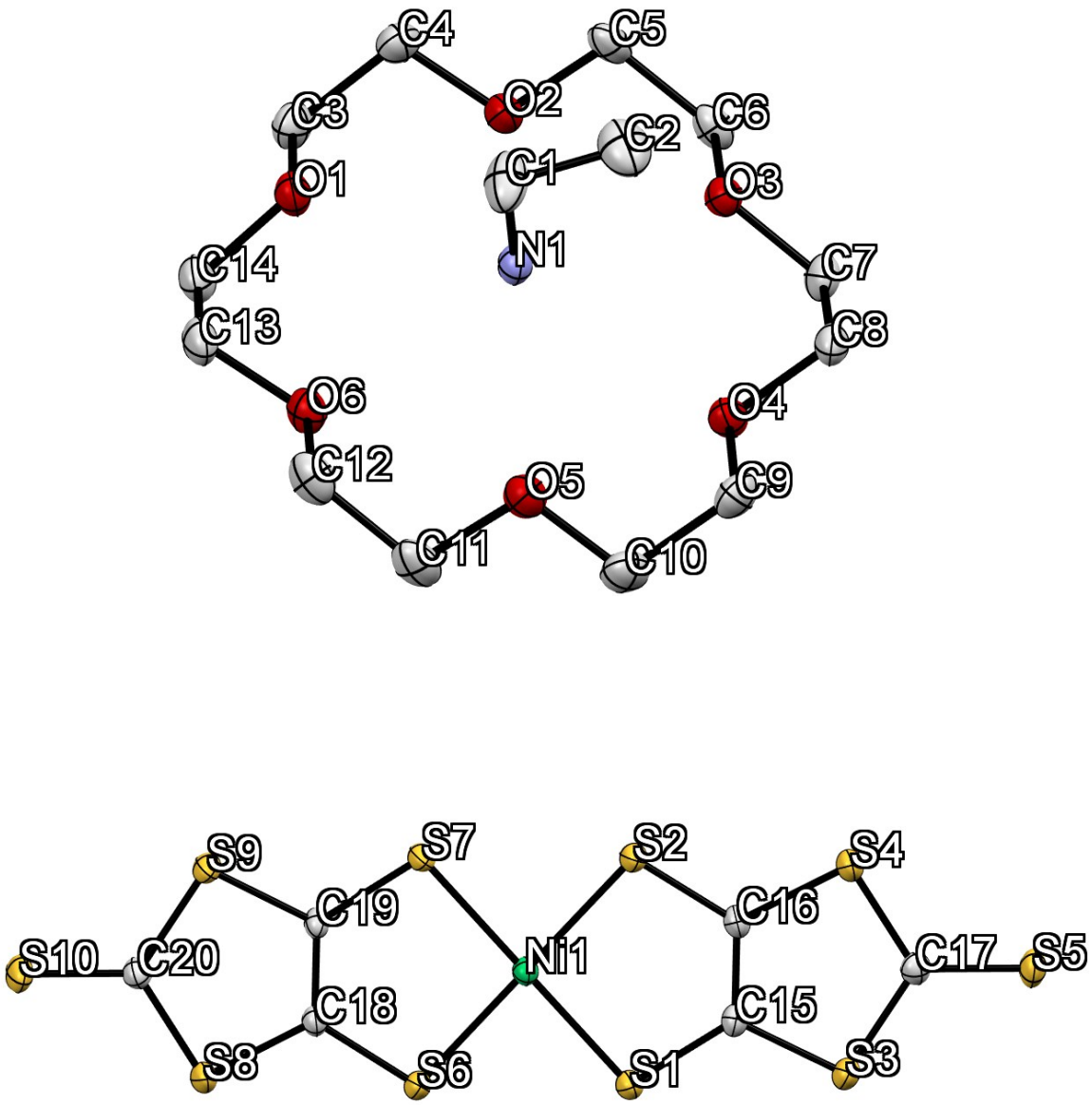

Figure S1. Crystallographically independent molecules in the crystal **1** at 113 K with atomic numbers. Crystallographically independent molecular structure is depicted as ORTEP with 50% thermal ellipsoids probability level. Hydrogen atoms are omitted for clarity.

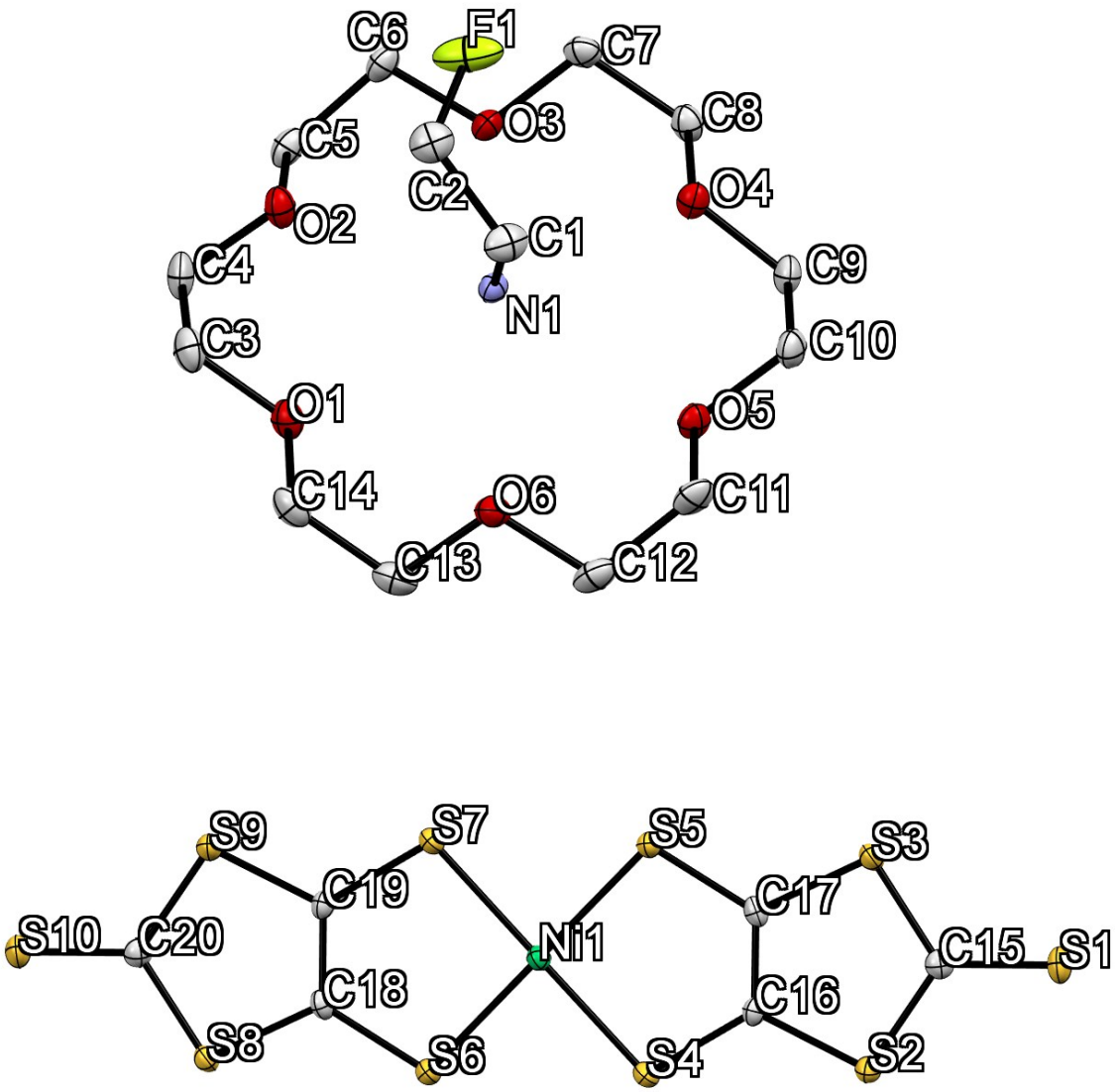

Figure S2. Crystallographically independent molecules in the crystal **2** at 93 K with atomic numbers. The structure is depicted as ORTEP with 50% probability. Hydrogen atoms are omitted for clarity.

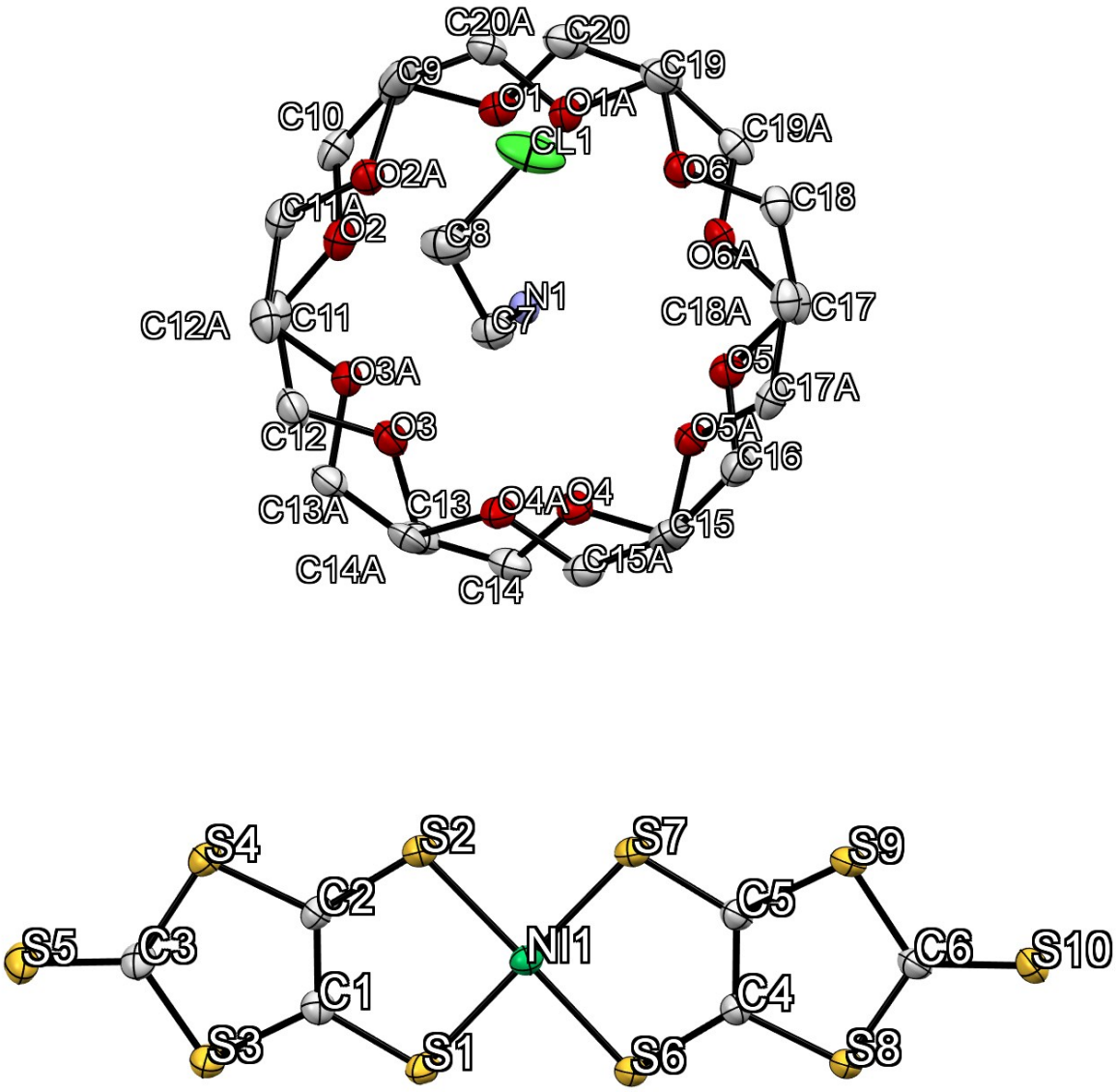

Figure S3. Crystallographically independent molecules in the crystal **3** at 93 K with atomic numbers. The structure is depicted as ORTEP with 50% probability. Hydrogen atoms are omitted for clarity.

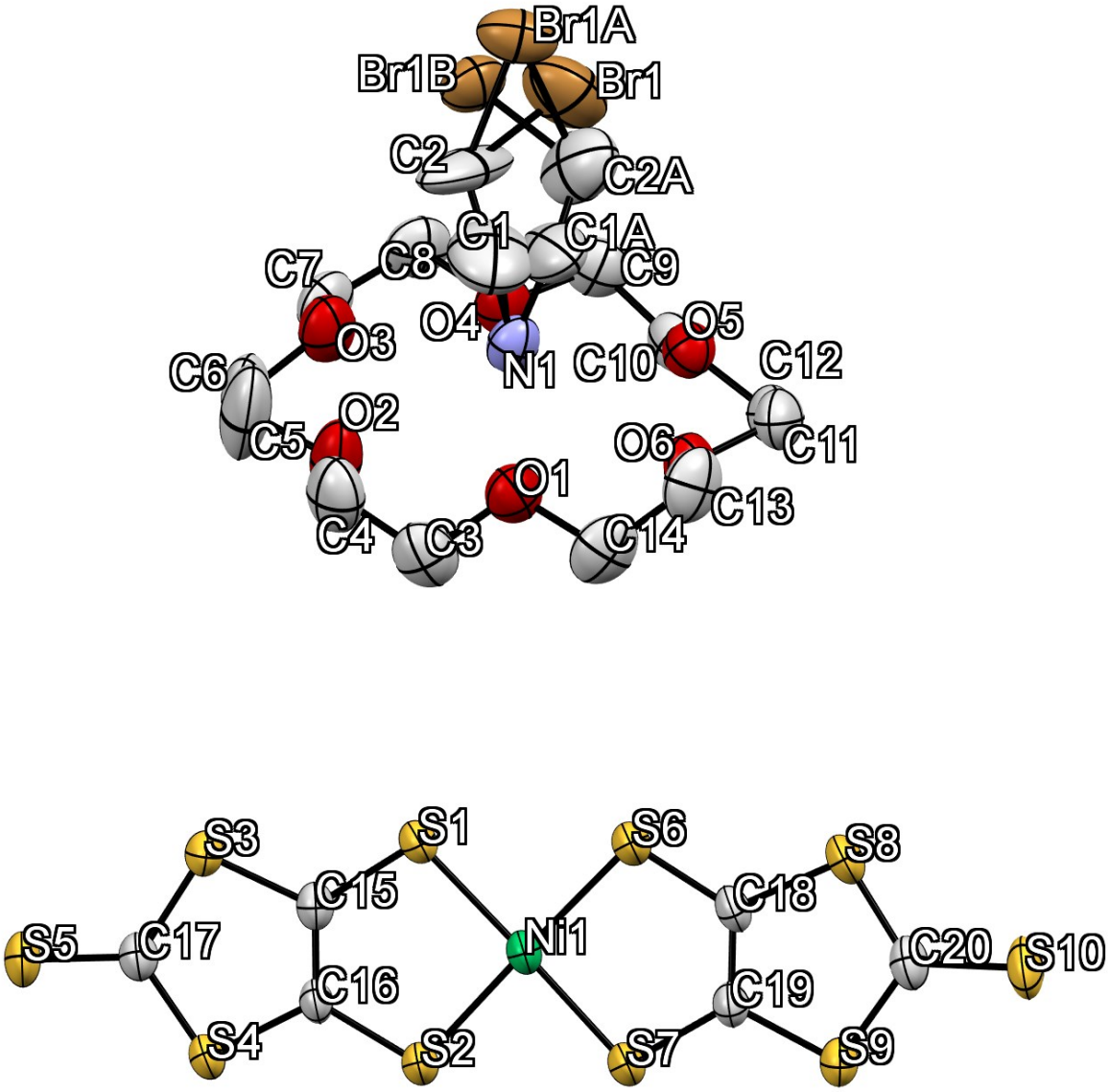

Figure S4. Crystallographically independent molecules in the crystal **4** at 293 K with atomic numbers. The structure is depicted as ORTEP with 50% probability. Hydrogen atoms are omitted for clarity.

§3. Packing structures of crystals 2-4.

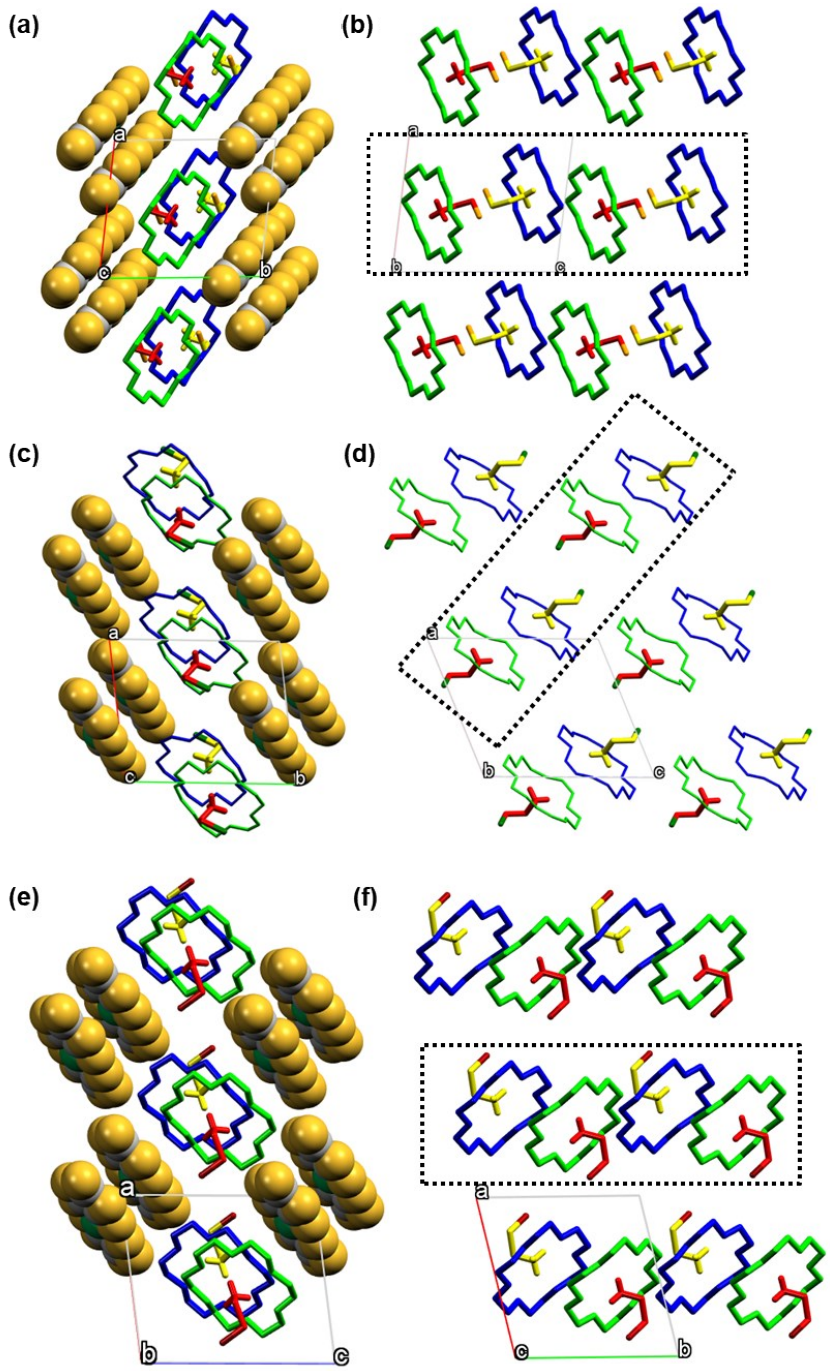

Figure S5. Packing structures of crystals **2**, **3** and **4** viewed along the (a) *c*, (c) c and (e) *b* axis, respectively. 2D arrangement of supramolecular cations for crystals **2**, **3** and **4** viewed along the (b) *b*, (d) b and (f) *c* axis, respectively. Dotted square encircles the 1D arrangement of supramolecular cations. Hydrogen atoms are omitted for clarity except the atoms connected to nitrogen atom. Sulfur, carbon, and nickel atoms in $[Ni(dmit)_2]$ colored as yellow, grey, and green, respectively. Yellow X-C_2-NH_3 and blue [18]crown-6, and red X-C_2-NH_3 and green [18]crown-6 is supramolecular cation unit and the two unit form supramolecular cation pair.

§4. Detailed analysis of structures of crystal 1-4.

Table S6. Intermolecular interaction between supramolecular cations and density of the crystals at the lowest temperatures.

Crystals	[a]Interaction	Å	[b]$d_{c\cdots c}$ / Å	D_{calc} / g cm^3
1	C-H•••O	3.595(2)	3.726	1.590
2	C-H•••O	3.633(2)	3.745	1.671
3			3.782	1.638
4	C-H•••O	3.468(3), 3.477(4)	3.635	1.748

[a] Intermolecular interaction between the neighboring supramolecular cations. Instead of H•••O distance, distance of C•••O was used for C-H•••O interaction. Distance of weak hydrogen bonding is in the range of 3.2-4.0 Å between hydrogen-bonded donor•••acceptor atoms.

[b] Distance between two plane of neighboring [18]crown-6. The plane of [18]crown-6 used by six oxygen atom in [18]crown-6.

§5. Temperature- and frequency-dependent dielectric constants for crystals 1-4

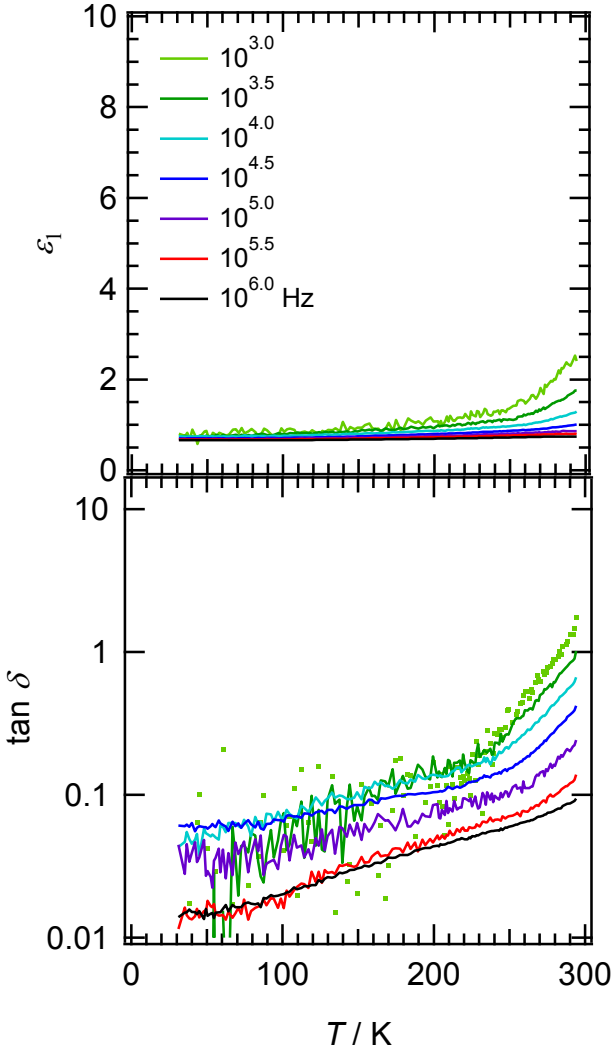

Figure S6. Temperature- and frequency-dependent real part of dielectric constant (ε_1) and tangent delta for crystal **1**.

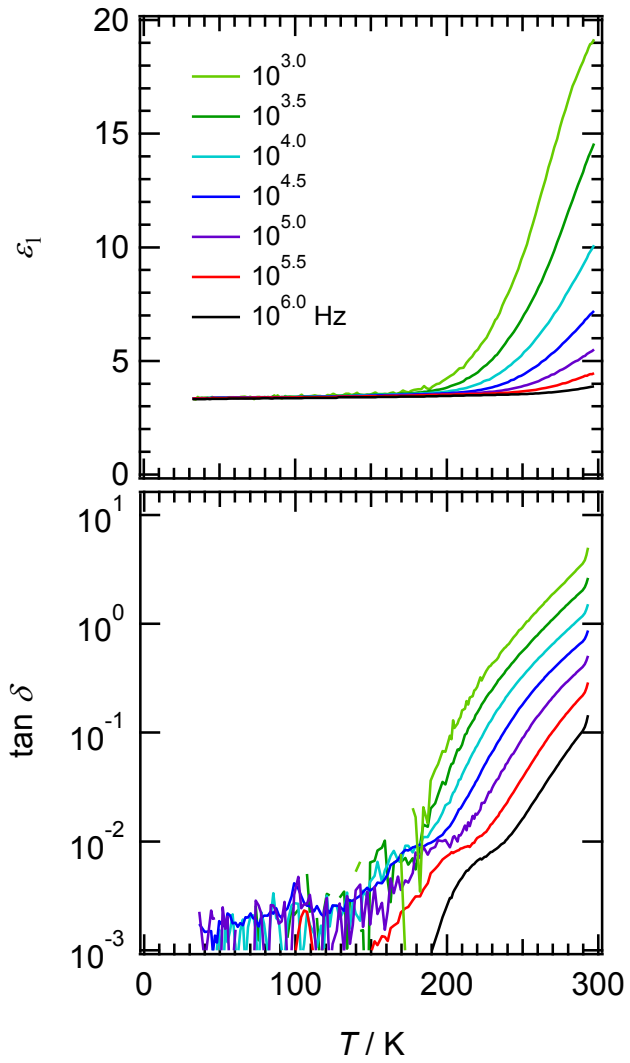

Figure S7. Temperature- and frequency-dependent real part of dielectric constant (ε_1) and tangent delta for crystal **2**.

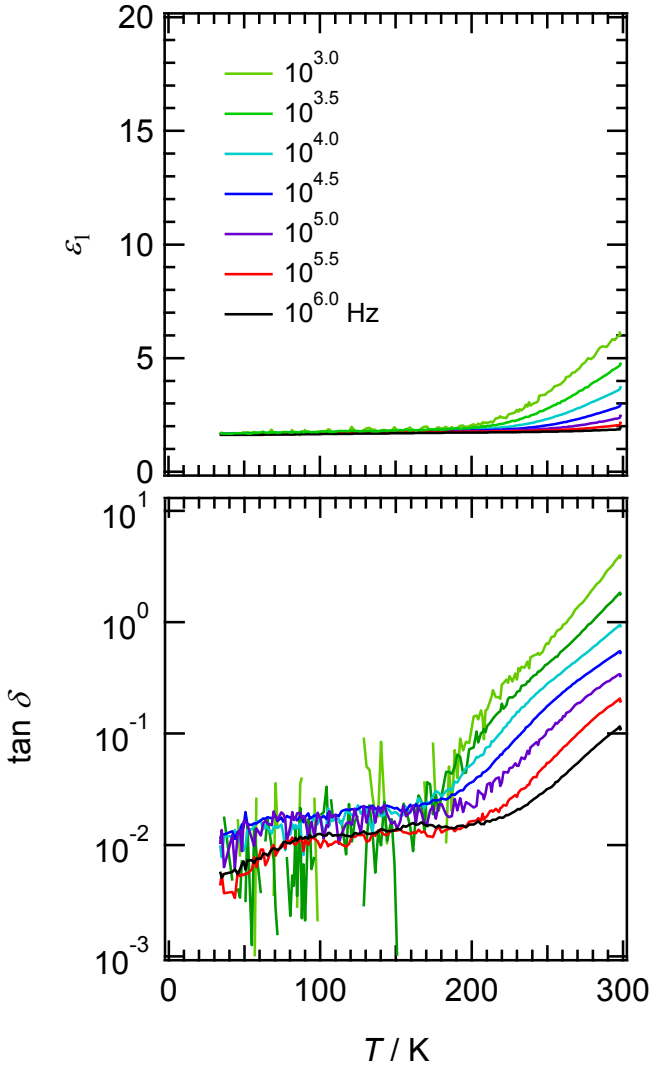

Figure S8. Temperature- and frequency-dependent real part of dielectric constant (ε_1) and tangent delta for crystal **3**.

§6. Transfer integrals between $[Ni(dmit)_2]^-$ molecules in crystals 1-4.

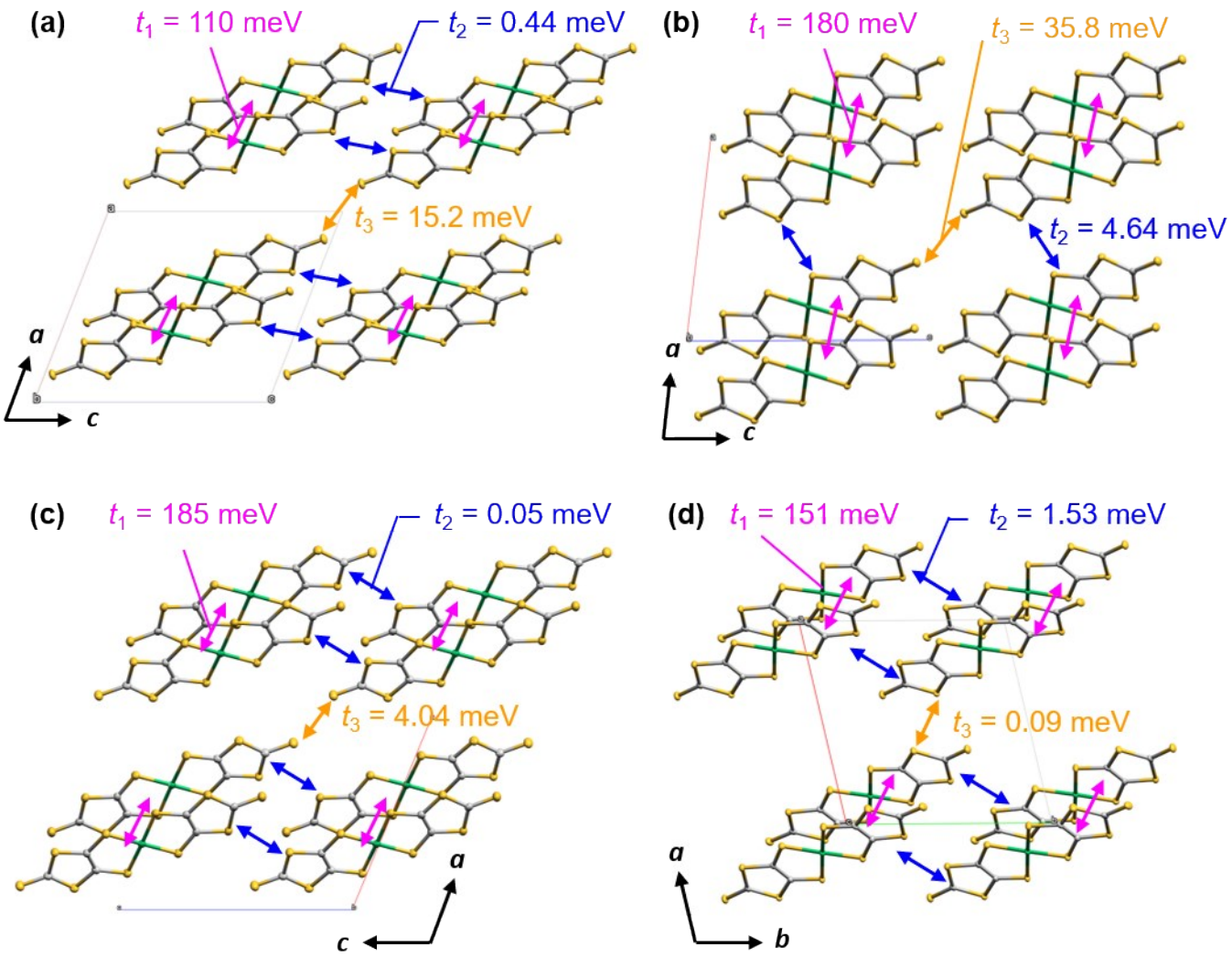

Figure S9. Transfer integral between $[Ni(dmit)_2]^-$ anions in crystals (a) **1**, (b) **2**, (c) **3**, and (d) **4**. t_1 corresponds to the transfer integrals between the intradimer $[Ni(dmit)_2]^-$ anions, whereas t_2 and t_3 are transfer integrals between interdimer $[Ni(dmit)_2]$ anions.