Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

## The strong correlations between thermal conductivities and electronic spin states in crystals of Fe(III) spin crossover complexes

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**Contents**

**Sample preparation methods for crystals 1-4.**

All synthetic procedures were performed in an aerobic environment. The reagents were received from commercial suppliers and used without further purification.

**[Fe(salEen)$_2$]NO$_3$ (1).** Salicylaldehyde (105 µl, 1.0 mmol) and *N*-ethyl-ethylenediamine (105 µl, 1.0 mmol) were dissolved in MeOH (2.5 ml) and stirred for 30 min. The solution was put to reaction with triethylamine (139 µl, 1.0 mmol) and MeOH solution (5 ml) of $FeNO_3 \cdot 9H_2O$ (139 mg, 0.5 mmol). The mixture was allowed to stand for several days to obtain black crystals of **1**. Anal: calcd. for $C_{22}H_{32}Fe_1N_5O_5$: C 52.60, H 6.42, N 13.94. Found: C 51.95, H 6.17, N 13.89 %.

**[Fe(salEen)$_2$]OTf (2).** Salicylaldehyde (105 µl (1.0 mmol) and *N*-ethylethylenediamine (105 µl, 1.0 mmol) were dissolved in MeOH (2.5 ml) and stirred for 30 min. Triethylamine (139 µl, 1.0 mmol) was then added to the reaction solution. $FeCl_3 \cdot 6H_2O$ (135 mg, 0.5 mmol) and AgOTf (257 mg, 1.0 mmol) were dissolved in MeOH (5.0 ml) and the mixture was stirred for 30 min. The filtrate was then added to the reaction solution and allowed to stand for several days to obtain black crystals of **2**. Anal: calcd. for $C_{23}H_{32}F_3Fe_1N_4O_5S_1$: C 46.87, H 5.47, N 9.51. Found: C 47.01, H 5.18, N 9.49 %.

**[Fe(5-Br-salEen)$_2$]OTf (3).** 5-bromosalicylaldehyde 201 mg (1.0 mmol) and *N*-ethylethylenediamine (105 µl, 1.0 mmol) were dissolved in MeOH (2.5 ml) and stirred for 30 min. Triethylamine (139 µl, 1.0 mmol) was then added to the reaction solution. $FeCl_3 \cdot 6H_2O$ (135 mg, 0.5 mmol) and AgOTf (257 mg, 1.0 mmol) were dissolved in MeOH (5.0 ml) and the mixture was stirred for 30 min. The filtrate was then added to the reaction solution and allowed to stand for several days to obtain black crystals of **3**. Anal: calcd. for $C_{22}H_{32}Fe_1N_5O_5$: C 36.87, H 4.30, N 7.48. Found: C 37.01, H 3.76, N 7.46 %.

**[Fe(3,5-Cl$_2$-salEen)$_2$]OTf (4).** 3,5-dichlorosalicylaldehyde 191 mg (1.0 mmol) and *N*-ethylethylenediamine (105 µl, 1.0 mmol) were dissolved in MeOH (2.5 ml) and stirred for 30 min. Triethylamine (139 µl, 1.0 mmol) was then added to the reaction solution. $FeCl_3 \cdot 6H_2O$ (135 mg, 0.5 mmol) and AgOTf (257 mg, 1.0 mmol) were dissolved in MeOH (5.0 ml) and the mixture was stirred for 30 min. The filtrate was then added to the reaction solution and allowed to stand for several days to obtain black crystals of **4**. Anal: calcd. for $C_{23}H_{30}Cl_4F_3Fe_1N_4O_5S_1$: C 37.88, H 4.15, N 7.68. Found: C 37.99, H 3.75, N 7.79 %.

**Table S1.** Crystallographic parameters for **1**–**4** at 100 K, $T_{\kappa n}$, $T_{vln}$, and 300 K.

| | $[Fe(salEen)_2]NO_3$ (**1**) | | | |
|---|---|---|---|---|
| Formula | C22 H30 Fe N5 O5 | | | |
| Fw | 500.36 | | | |
| $T$ / K | 100(2) | 128(2) | 246(2) | 300(2) |
| SPGR | $P2_1/c$ (#14) | $P2_1/c$(#14) | $P\bar{1}$(#2) | $P2_1/c$ (#14) |
| $a$ / Å | 10.3752(3) | 10.3846(3) | 10.4125(9) | 10.4344(3) |
| $b$ / Å | 26.2191(7) | 26.2141(8) | 26.399(3) | 26.4890(7) |
| $c$ / Å | 16.9929(5) | 16.9891(5) | 17.1521(15) | 17.3304(4) |
| $\beta$ / ° | 93.921(7) | 93.932(7) | 93.788(7) | 93.497(7) |
| $V$ / Å$^3$ | 4611.7(2) | 4613.9(2) | 4704.5(7) | 4781.1(2) |
| $Z$ | 8 | 8 | 8 | 8 |
| Data | 8400 | 8641 | 8490 | 8641 |
| Parameters | 599 | 599 | 595 | 599 |
| $R1$, $wR2$[†1] [$I > 2\sigma(I)$] | 0.0699, 0.1365 | 0.0666, 0.0991 | 0.0806, 0.2003 | 0.0738, 0.1473 |
| $R1$, $wR2$[†1] (all data) | 0.1403, 0.1772 | 0.1308, 0.1869 | 0.1762, 0.2924 | 0.1621, 0.1985 |
| GoF (all) | 1.078 | 0.881 | 1.078 | 1.029 |

| | $[Fe(salEen)_2]OTf$ (**2**) | | |
|---|---|---|---|
| Formula | C23 H30 F3 Fe N4 O5 S | | |
| Fw | 587.42 | | |
| $T$ / K | 100(2) | 248(2) | 300(2) |
| SPGR | $P\bar{1}$ (#2) | $P\bar{1}$(#2) | $P\bar{1}$ (#2) |
| $a$ / Å | 9.5803(2) | 9.6320(4) | 9.6648(3) |
| $b$ / Å | 17.0105(4) | 17.2317(7) | 17.3665(6) |
| $c$ / Å | 17.8749(4) | 17.9551(7) | 18.0637(6) |
| $\alpha$ / ° | 117.516(8) | 117.790(8) | 117.891(8) |
| $\beta$ / ° | 92.441(7) | 92.580(7) | 92.564(6) |
| $\gamma$ / ° | 99.470(7) | 98.954(7) | 98.773(7) |
| $V$ / Å$^3$ | 2524.7(2) | 2580.6(3) | 2624.8(2) |
| $Z$ | 4 | 4 | 4 |
| Data | 9001 | 9214 | 9349 |
| Parameters | 671 | 667 | 671 |
| $R1$, $wR2$[†1] [$I > 2\sigma(I)$] | 0.0505, 0.0710 | 0.0532, 0.0912 | 0.0575, 0.0972 |
| $R1$, $wR2$[†1] (all data) | 0.1072, 0.1161 | 0.1222, 0.1594 | 0.1233, 0.1398 |
| GoF (all) | 1.078 | 0.823 | 1.021 |

| | [Fe(5-Br-salEen)$_2$](OTf) (**3**) | | | |
|---|---|---|---|---|
| Formula | C23 H28 Br2 F3 Fe N4 O5 S | | | |
| Fw | 745.22 | | | |
| $T$ / K | 100(2) | 232(2) | 254(2) | 300(2) |
| SPGR | $P2_1/c$ (#14) | $P2_1/c$(#14) | $P2_1/c$(#14) | $P2_1/c$ (#14) |
| $a$ / Å | 9.4630(2) | 9.4977(16) | 9.5228(4) | 9.5742(3) |
| $b$ / Å | 24.1569(4) | 24.352(4) | 24.5067(11) | 24.9656(8) |
| $c$ / Å | 12.6631(2) | 12.701(2) | 12.6996(6) | 12.6100(4) |
| $\beta$ / ° | 107.221(8) | 107.220(8) | 106.982(8) | 106.182(8) |
| $V$ / Å$^3$ | 2764.98(14) | 2805.8(8) | 2834.5(2) | 2894.70(19) |
| $Z$ | 4 | 4 | 4 | 4 |
| Data | 5061 | 5086 | 5121 | 5283 |
| Parameters | 354 | 352 | 352 | 354 |
| $R1$, $wR2$[†1] [$I > 2\sigma(I)$] | 0.0295, 0.0724 | 0.0838, 0.2144 | 0.0616, 0.1242 | 0.0590, 0.0981 |
| $R1$, $wR2$[†1] (all data) | 0.0317, 0.0735 | 0.1407, 0.3006 | 0.1232, 0.1498 | 0.1254, 0.1429 |
| GoF (all) | 1.036 | 1.031 | 0.982 | 1.031 |

| | [Fe(3,5-Cl$_2$-salEen)$_2$](OTf) (**4**) | | | |
|---|---|---|---|---|
| Formula | C23 H26 Cl4 F3 Fe N4 O5 S | | | |
| Fw | 725.19 | | | |
| $T$ / K | 100(2) | 166(2) | 206(2) | 300(2) |
| SPGR | $P2_1/n$ (#14) | $P2_1/n$(#14) | $P2_1/n$(#14) | $P2_1/n$ (#14) |
| $a$ / Å | 12.9046(2) | 12.9434(4) | 12.9687(6) | 13.1344(7) |
| $b$ / Å | 16.5620(3) | 16.5560(5) | 16.5697(8) | 16.6871(9) |
| $c$ / Å | 14.1674(3) | 14.1963(4) | 14.2061(7) | 14.2579(7) |
| $\beta$ / ° | 91.087(6) | 91.038(6) | 90.864(6) | 90.518(6) |
| $V$ / Å$^3$ | 3027.40(10) | 3041.64(16) | 3052.4(3) | 3124.8(3) |
| $Z$ | 4 | 4 | 4 | 4 |
| Data | 5536 | 5513 | 5509 | 5647 |
| Parameters | 370 | 370 | 370 | 372 |
| $R1$, $wR2$[†1] [$I > 2\sigma(I)$] | 0.0680, 0.1309 | 0.0625, 0.1253 | 0.0630, 0.1517 | 0.0791, 0.1846 |
| $R1$, $wR2$[†1] (all data) | 0.1212, 0.1527 | 0.1283, 0.1506 | 0.1024, 0.1730 | 0.1841, 0.2361 |
| GoF (all) | 1.031 | 0.936 | 0.976 | 0.993 |

[†1] $R1 = \Sigma\ (|F_o|-|F_c|) / \Sigma\ |F_o|$, $wR2 = \{\Sigma\ [w(F_o^2 - F_c^2)^2] / \Sigma\ [w(F_o^2)^2]\}^{1/2}$.

**Table S2.** Coordination bond lengths for **1**–**4** at 100 K, $T_{kn}$, $T_{vln}$, and 300 K.

| | [Fe(salEen)$_2$]NO$_3$ (**1**) | | | | [Fe(salEen)$_2$]OTf (**2**) | | |
|---|---|---|---|---|---|---|---|
| *T* / K | 100 | 128 | 246 | 300 | 100 | 248 | 300 |
| Fe1-O1 | 1.904(3) | 1.911(3) | 1.920(4) | 1.931(3) | 1.880(2) | 1.874(3) | 1.883(3) |
| Fe1-O2 | 1.906(3) | 1.899(3) | 1.921(5) | 1.923(3) | 1.878(2) | 1.871(3) | 1.882(3) |
| Fe1-N1 | 2.025(4) | 2.028(4) | 2.088(6) | 2.092(4) | 1.925(3) | 1.929(4) | 1.949(3) |
| Fe1-N3 | 2.040(4) | 2.051(4) | 2.113(6) | 2.116(4) | 1.931(3) | 1.926(4) | 1.957(3) |
| Fe1-N2 | 2.146(4) | 2.156(4) | 2.213(6) | 2.220(4) | 2.042(3) | 2.049(3) | 2.072(3) |
| Fe1-N4 | 2.112(4) | 2.134(4) | 2.174(5) | 2.175(4) | 2.030(3) | 2.036(3) | 2.064(3) |
| Fe2-O3 | 1.881(3) | 1.880(3) | 1.882(5) | 1.903(3) | 1.878(2) | 1.881(3) | 1.881(3) |
| Fe2-O4 | 1.869(3) | 1.867(3) | 1.880(4) | 1.895(3) | 1.858(2) | 1.856(3) | 1.861(3) |
| Fe2-N5 | 1.925(4) | 1.922(4) | 1.967(6) | 2.018(4) | 1.928(3) | 1.920(4) | 1.947(3) |
| Fe2-N7 | 1.935(4) | 1.916(4) | 1.964(6) | 2.031(4) | 1.930(3) | 1.923(4) | 1.948(3) |
| Fe2-N6 | 2.057(4) | 2.044(4) | 2.091(6) | 2.154(4) | 2.050(3) | 2.050(3) | 2.062(3) |
| Fe2-N8 | 2.044(4) | 2.055(4) | 2.066(5) | 2.136(4) | 2.036(3) | 2.046(4) | 2.060(3) |

| | [Fe(5-Br-salEen)$_2$]OTf (**3**) | | | | [Fe(3,5-Cl$_2$-salEen)$_2$]OTf (**4**) | | | |
|---|---|---|---|---|---|---|---|---|
| *T* / K | 100 | 232 | 254 | 300 | 100 | 166 | 206 | 300 |
| Fe1-O1 | 1.8698(6) | 1.872(7) | 1.865(4) | 1.890(4) | 1.864(3) | 1.857(3) | 1.858(3) | 1.867(5) |
| Fe1-O2 | 1.8820(16) | 1.875(7) | 1.889(4) | 1.920(4) | 1.873(3) | 1.872(3) | 1.872(3) | 1.870(5) |
| Fe1-N1 | 1.9211(19) | 1.923(7) | 1.957(4) | 2.052(4) | 1.917(4) | 1.912(4) | 1.915(4) | 1.939(6) |
| Fe1-N3 | 1.9216(19) | 1.927(7) | 1.942(4) | 2.037(4) | 1.928(4) | 1.909(4) | 1.919(4) | 1.931(6) |
| Fe1-N2 | 2.061(2) | 2.076(8) | 2.080(5) | 2.188(4) | 2.039(4) | 2.031(4) | 2.029(4) | 2.038(6) |
| Fe1-N4 | 2.053(2) | 2.060(9) | 2.079(5) | 2.185(4) | 2.030(4) | 2.032(4) | 2.033(4) | 2.053(6) |

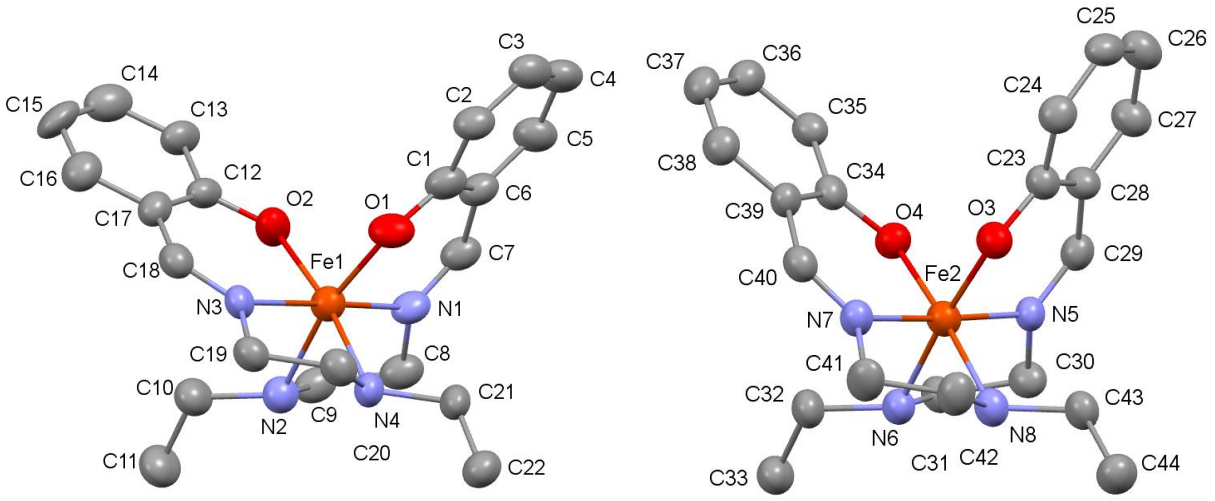



**Fig. S1** Numbering schemes for the crystal structure analyses. Note that numbers for Fe, C, N, and O atoms are unified in the CIF.

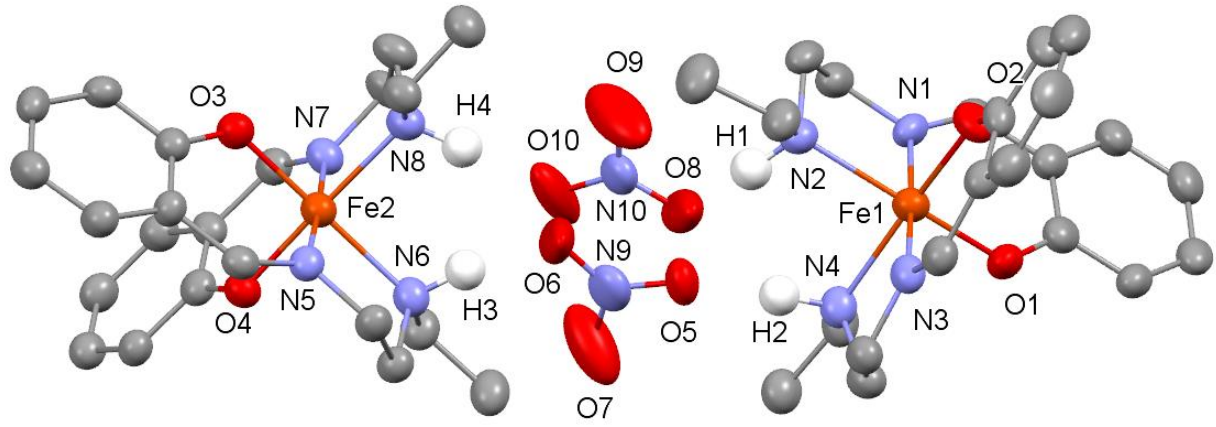



**Fig. S2** A view of the cations dimerized with two $NO_3^-$ anions via hydrogen bonding in crystal **1** at 100 K. The close N(amino)-O(nitric) contacts are at distances of; N2-O8 = 3.388 (7) Å, N2-O9 = 3.441 (7) Å, N4-O5 = 2.990(5) Å, N4-O8 = 3.346(7) Å, N6-O6* = 3.559(7) Å, N6-O7* = 3.300(7) Å, N8-O10* = 3.195(6) Å. A symmetry for the key *; $2 - x$, $1 - y$, $1 - z$.

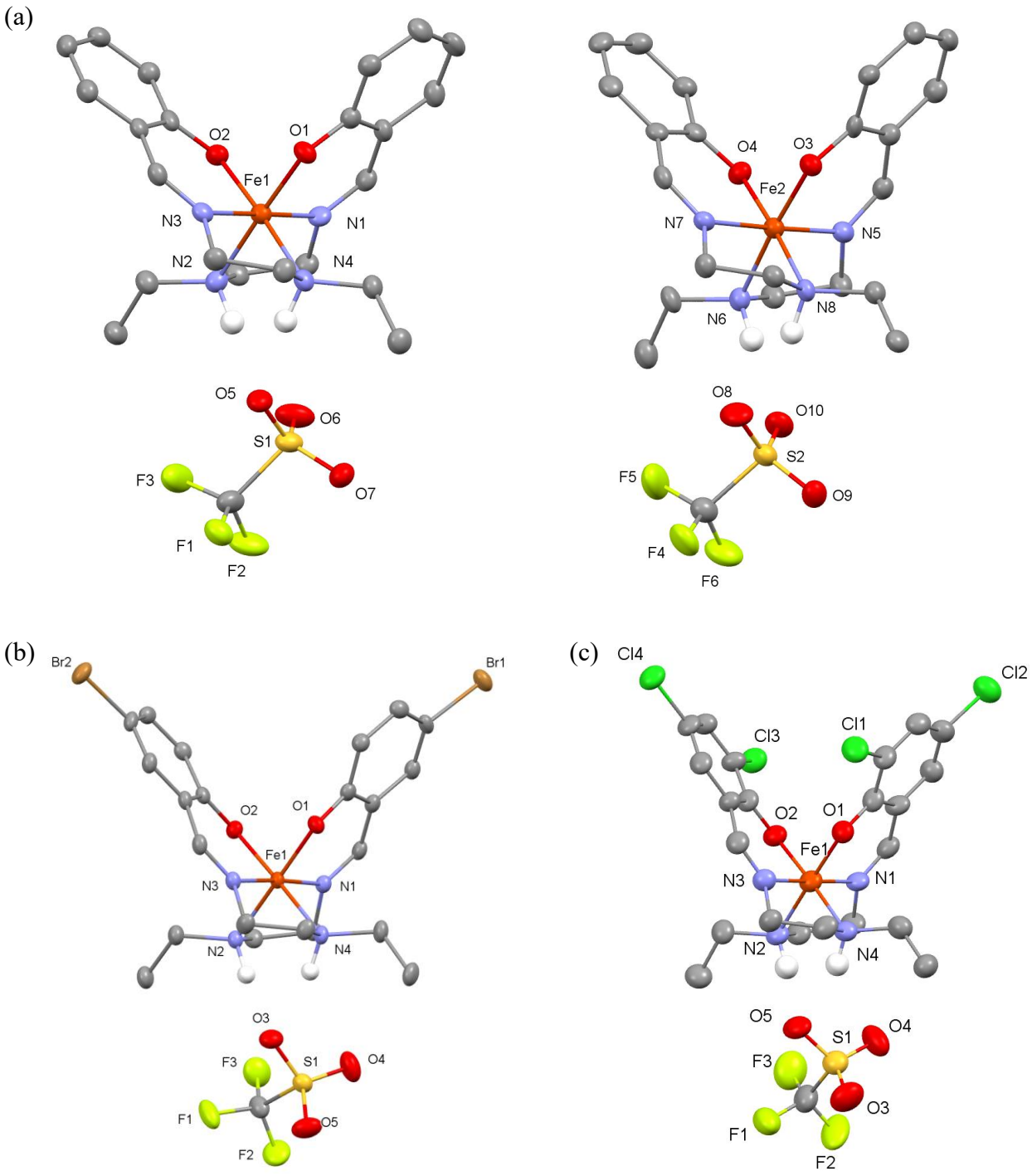
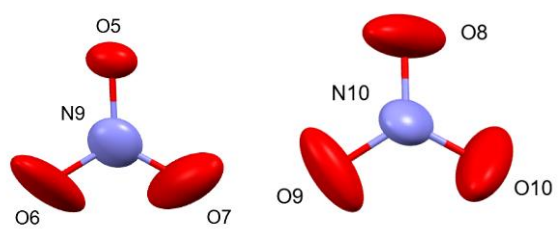
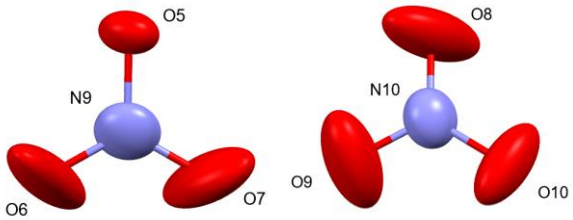



**Fig. S3** Thermal ellipsoid views of the cation-anion interactions at 100 K (a) in crystal **2**, (b) **3** and (d) **4**. The close N(amino)-O(sulfoxy) contacts are at the distances of; (a) N2-O5 = 2.974(4) Å, N4-O5 = 2.945(4) Å, N6-O10 = 3.035(4) Å, N8-O8 = 3.165(4) Å, N8-O10 = 3.260(4) Å, (b) N2-O3 = 3.004(3) Å, N4-O3 = 2.995(3) Å, (c) N2-O5 = 3.085(5) Å, N4-O5 = 3.003(5) Å.

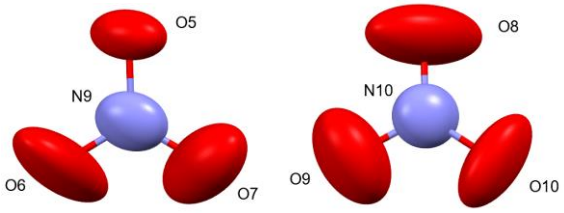
(a)



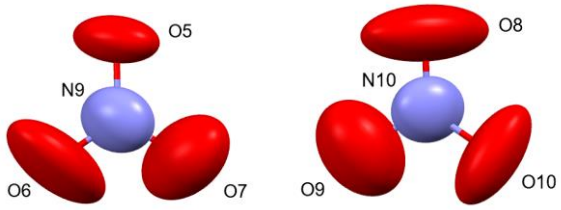

100 K




128 K ($T_{\kappa 1}$)

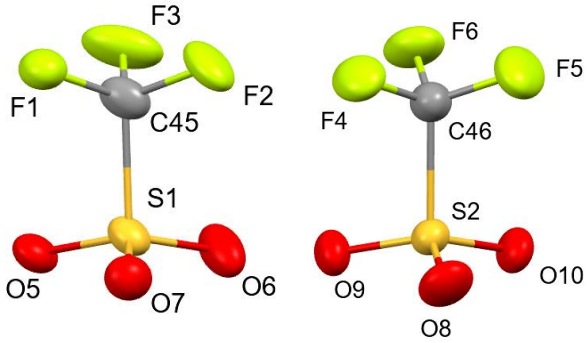



246 K ($T_{vl1}$)

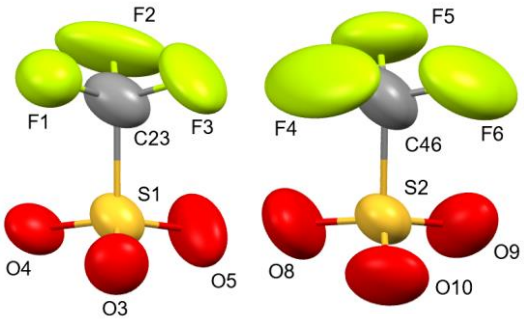



300 K

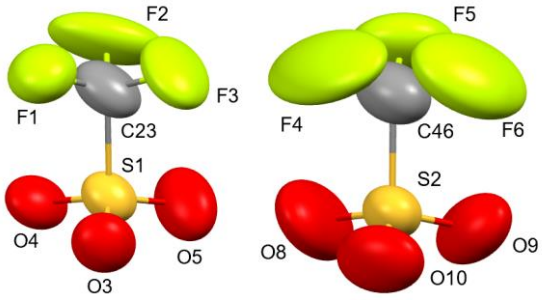
(b)




100 K




248 K ($T_{\kappa 2}$)




300 K

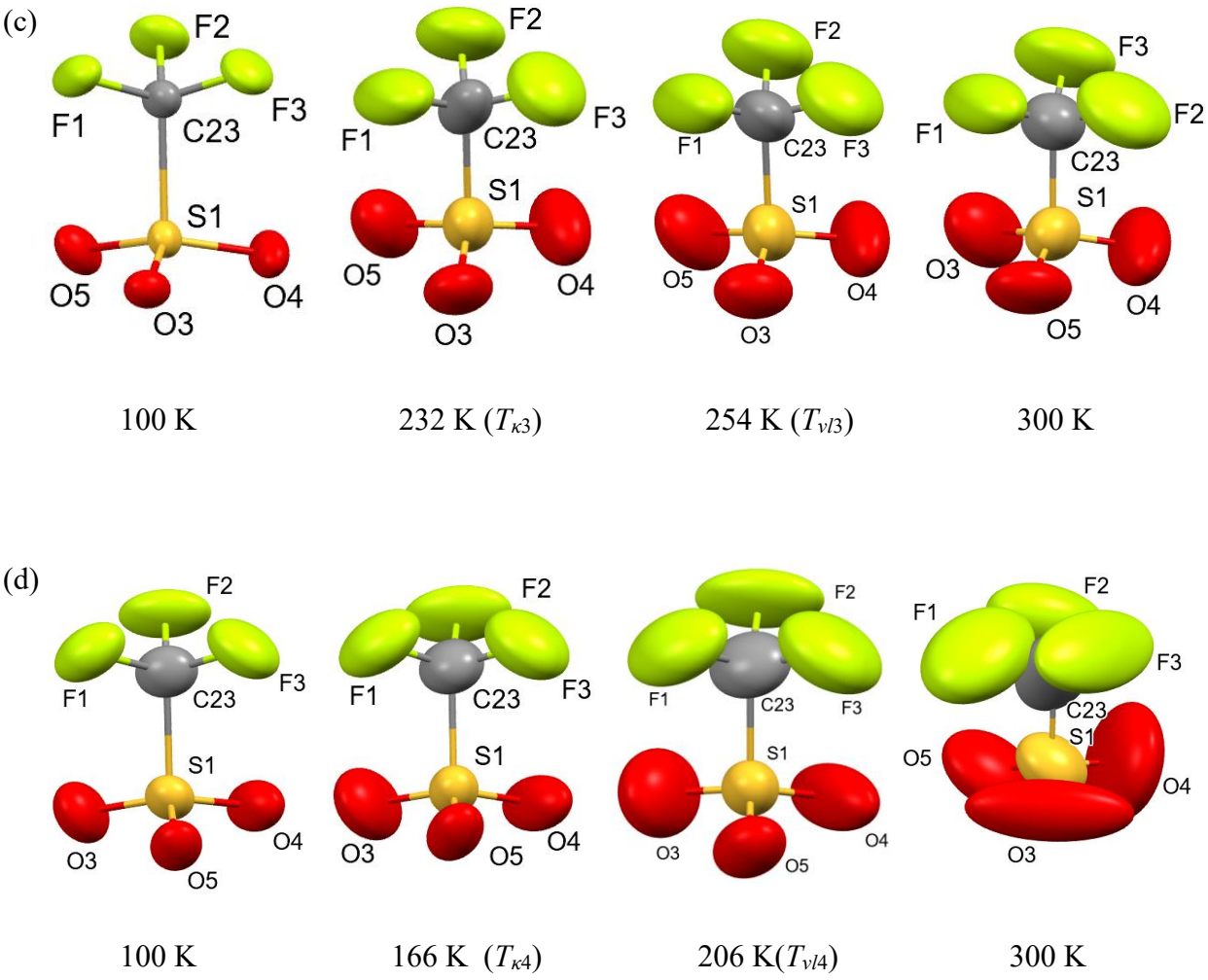
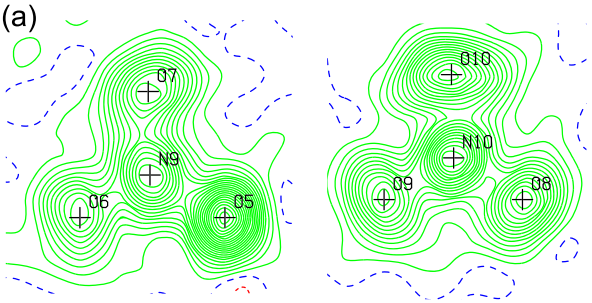
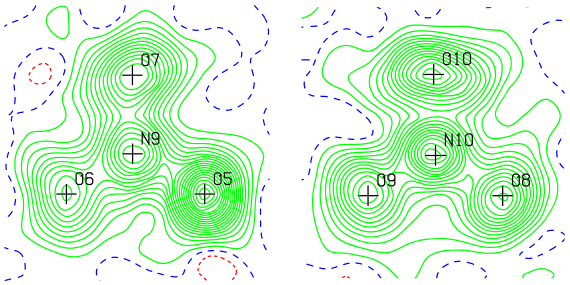



**Fig. S4** Thermal ellipsoid views of the anions in crystals **1**−**4** at 100 K, $T_{кn}$, $T_{vln}$, and 300 K at a probability level of 50 %.

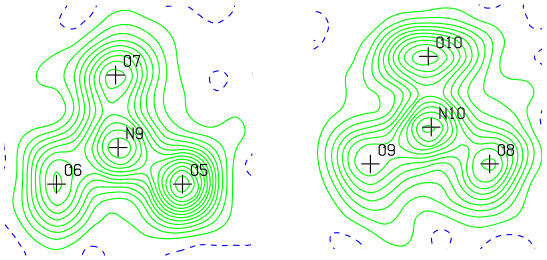
(a)



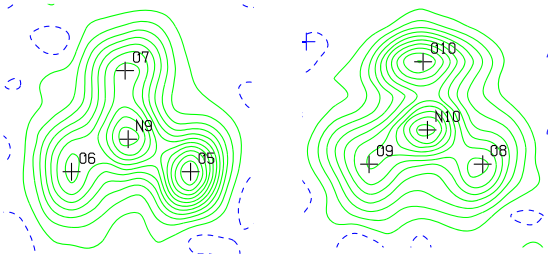

100 K




128 K ($T_{\kappa 1}$)

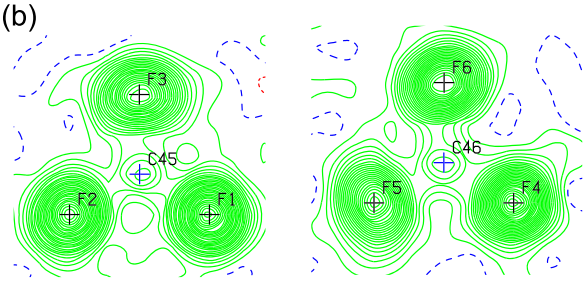



246 K ($T_{vl1}$)

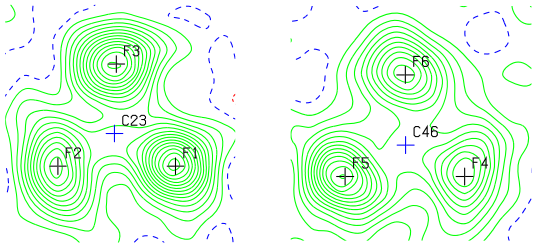



300 K

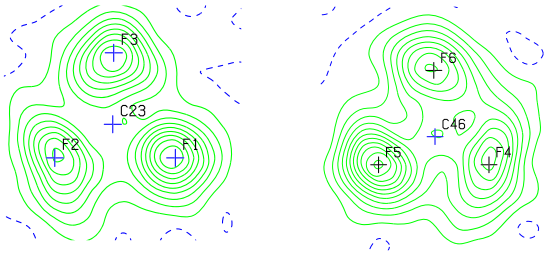
(b)




100 K




248 K ($T_{\kappa 1}$)




300 K

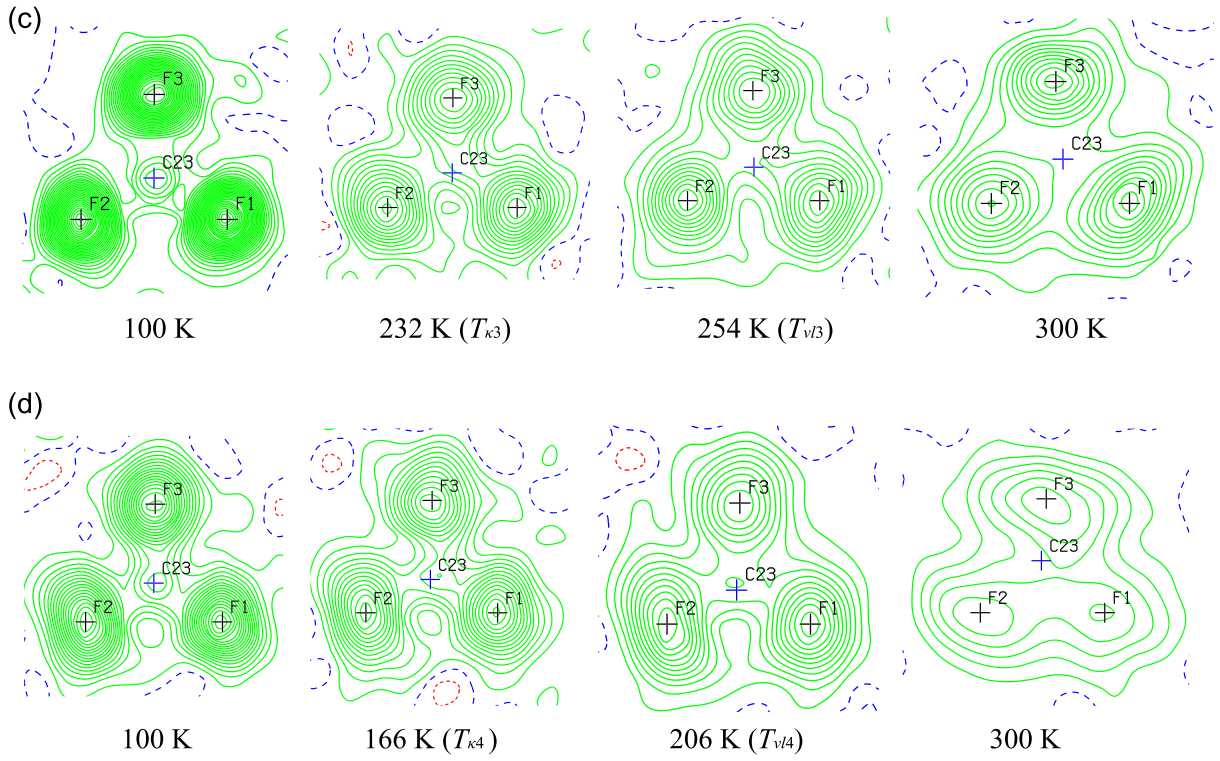



**Fig. S5** Electron-density maps around (a) the $NO_3^-$ anions in **1** and (b–d) -$CF_3$ groups in **2**, **3**, and **4** at 100 K, $T_к$, $T_{vl}$, and 300 K, respectively. The contour interval is 0.5 Å$^3$.

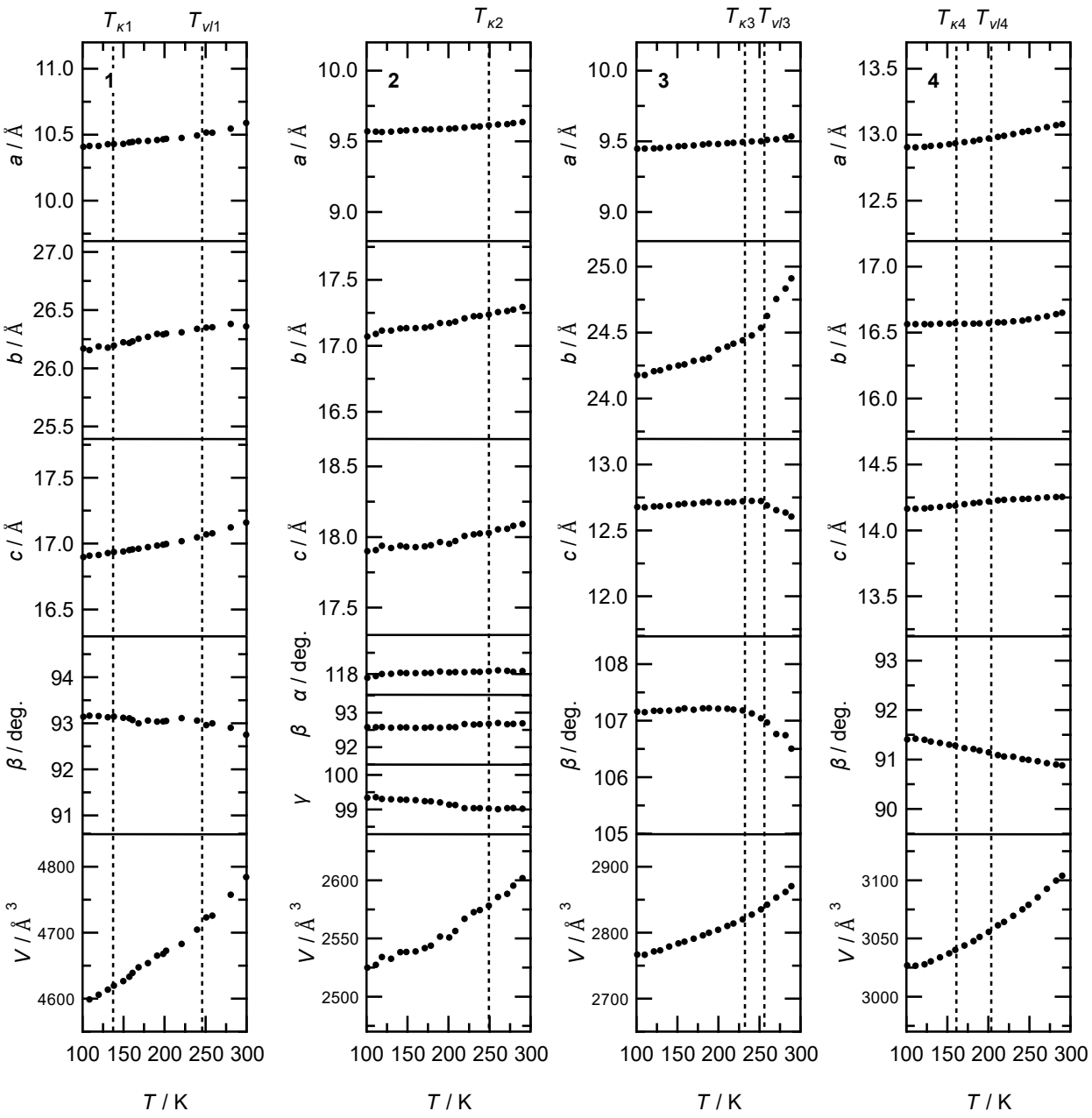



**Fig. S6** Temperature-dependent unit-cell constants of crystals **1**−**4** calculated using powder X-ray diffraction data using the LeBail method in the temperature range of 100–300 K. $T_{\kappa}$ and $T_{vl}$ are indicated by broken lines.

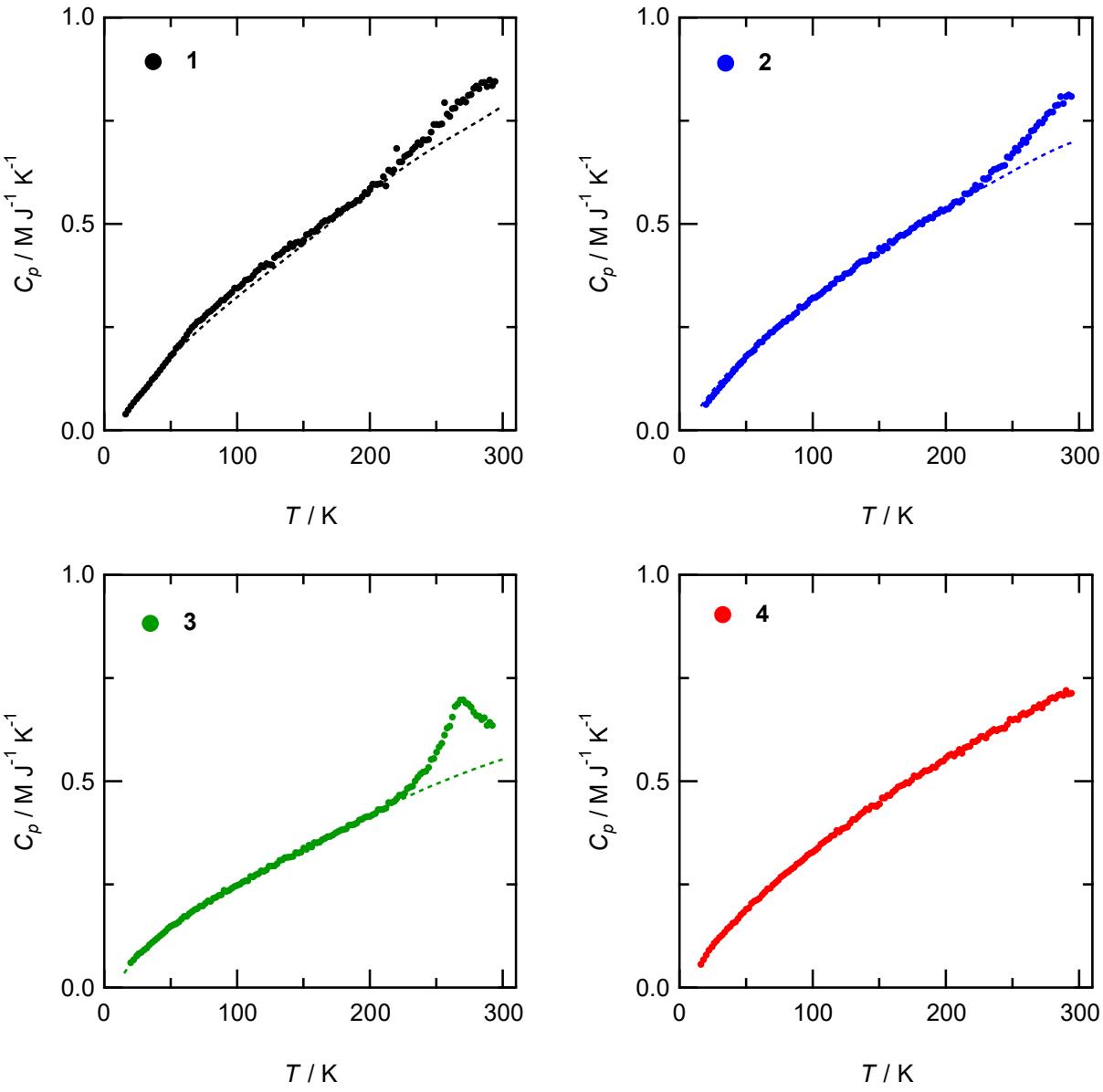
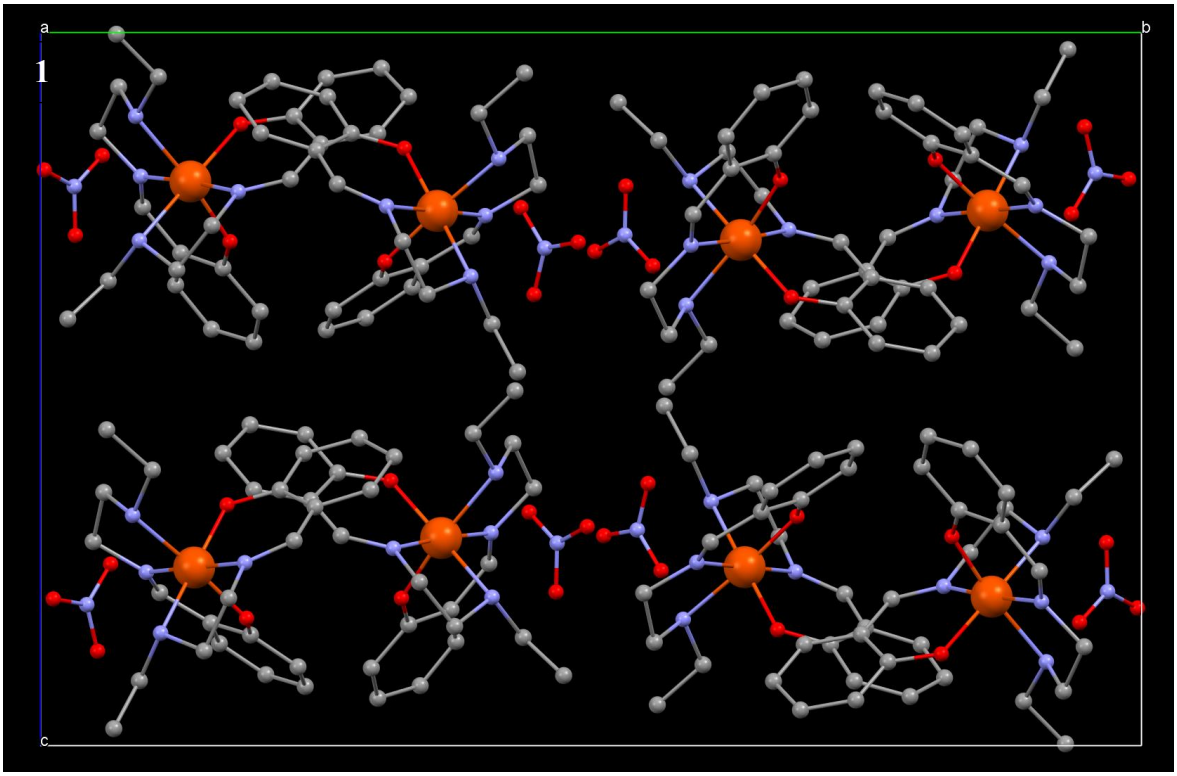
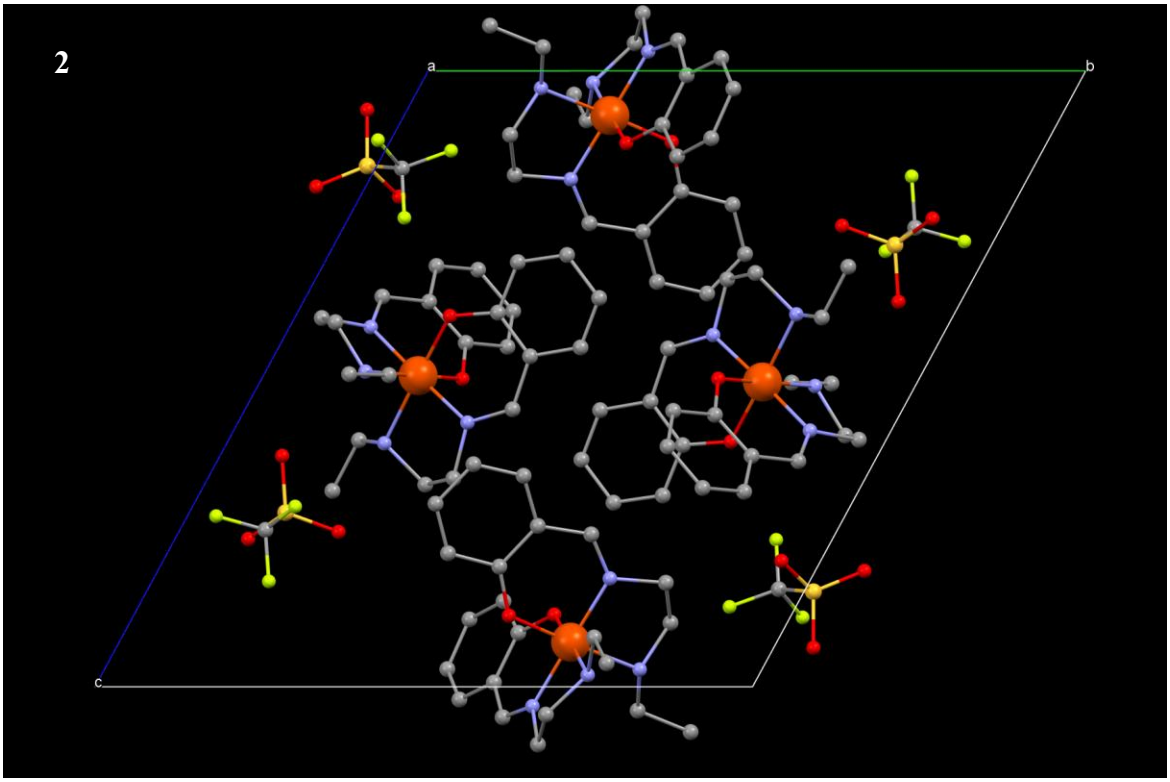



**Fig. S7** Measured heat capacities (markers) and estimated specific heats (broken lines) for **1**–**4**.


1
a
b
c


2
a
b
c

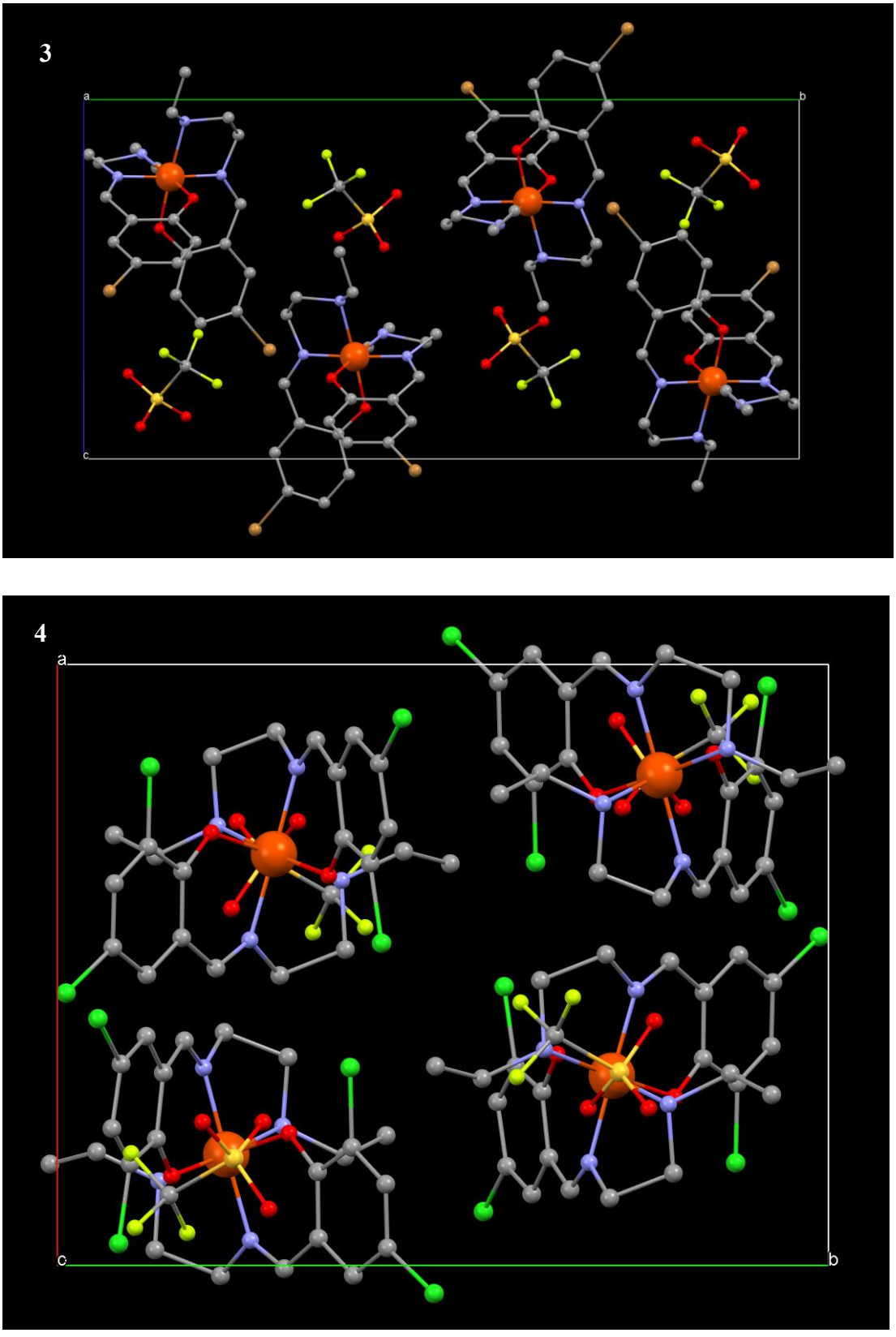



**Fig. S8** Crystal packing structures of **1**–**4**.