Supplementary Information

Fine tuning of intra-lattice electron transfers through site doping in tetraoxolene-bridged iron honeycomb layers

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Experimental section

Preparation of materials

$FeCl_2 \cdot 4H_2O$ (>99 %), NPr_4Br (> 98 %), and CH_3COOLi (> 98 %) were purchased from Wako Pure Chemical Corporation. Chloranilic acid (> 98 %) and bromanilic acid (> 98 %) were purchased from Tokyo Chemical Industry. H_2F_2An was synthesized according to the previous literature.[1]

Synthesis of $(NPr_4)_2[Fe_2(Br_2An)_{0.30}(Cl_2An)_{2.70}] \cdot 2(acetone) \cdot H_2O$ (Br-0.10). The single crystal sample of **Br-0.10** was prepared by a slow diffusion in a narrow-diameter glass tube (ϕ = 8 mm). A water (2 mL) containing $FeCl_2 \cdot 4H_2O$ (7.95 mg, 0.04 mmol), NPr_4Br (42.60 mg, 0.16 mmol) and CH_3COOLi (10.56 mg, 0.16 mmol) was placed in bottom layer of tube (H_2Cl_2An : H_2Br_2An = 9 : 1), then a mixture of acetone (0.5 mL) and water (0.5 mL) was carefully placed on the water layer (buffer layer), finally an acetone (2 mL) of chloranilic acid (11.29mg, 0.054mmol) and bromanilic acid (1.79 mg, 0.006 mmol) was placed on the top (top layer). After standing for 3 weeks, the black hexagonal prismatic crystals were collected from mother liquid at a 35 % yield. Anal. Calcd for $C_{48}H_{70}O_{15}N_2Br_{0.60}Cl_{5.40}Fe_2$: C 45.53, H 5.57, N 2.21, Br 3.79, Cl 15.12. Found: C 45.96, H 5.53, N 2.17, Br 3.78, Cl 15.17.

Synthesis of Br-0.18, Br-0.35, Br-0.65. The Br-doped samples were synthesized in a similar way to **Br-0.10** except mixture of chloranilic acid and bromanilic acid (H_2Cl_2An : H_2Br_2An = 8 : 2, 6 : 4, 3 : 7). Anal. Calcd for $C_{48}H_{70}O_{15}N_2Br_{1.08}Cl_{4.92}Fe_2$(**Br-0.18**): C 44.78, H 5.48, N 2.18, Br 6.70, Cl 13.55. Found: C 44.71, H 5.53, N 2.27, Br 7.19, Cl 13.14. Anal. Calcd for $C_{48}H_{70}O_{15}N_2Br_{2.12}Cl_{3.88}Fe_2$ (**Br-0.35**): C 43.23, H 5.29, N 2.10, Br 12.70, Cl 10.31. Found: C 42.81, H 5.19, N 1.97, Br 12.46, Cl 10.15. Anal. Calcd for $C_{48}H_{70}N_2O_{15}Br_{3.91}Cl_{2.09}Fe_2$ (**Br-0.65**): C 40.79, H 4.99, N 1.98, Br 22.11, Cl 5.24. Found: C 40.53, H 4.74, N 1.84, Br 22.23, Cl 5.21.

Synthesis of F-0.06, F-0.12, F-0.17, F-0.24, F-0.31, F-0.42. The F-doped samples were synthesized in a similar way to **Br-0.10** except mixture of chloranilic acid and fluoranilic acid (H_2Cl_2An : H_2F_2An = 9 : 1; 8 : 2, 7 : 3, 6 : 4, 5 : 5, 4 : 6). Anal. calcd for $C_{48}H_{70}N_2O_{15}Cl_{5.66}F_{0.34}Fe_2$ (**F-0.06**): C 46.72, H 5.72, N 2.27, Cl 16.26, F 0.52. Found: C 47.05, H 5.75, N 2.09, Cl 15.96, F 0.52. Anal. calcd for $C_{48}H_{70}N_2O_{15}Cl_{5.31}F_{0.69}Fe_2$ (**F-0.12**): C 46.94, H 5.75, N 2.28, Cl 15.33, F 1.07. Found: C 47.39, H 5.81, N 2.26, Cl 15.74, F 1.10. Anal. calcd for $C_{48}H_{70}N_2O_{15}Cl_{4.98}F_{1.02}Fe_2$ (**F-0.17**): C 47.15, H 5.77, N 2.29, Cl 14.44, F 1.58. Found: C 47.61, H 5.75, N 2.20, Cl 14.81, 1.62. Anal. calcd for $C_{48}H_{70}N_2O_{15}Cl_{4.55}F_{1.45}Fe_2$ (**F-0.24**): C 47.43, H 5.80, N 2.30, Cl 13.27, F 2.27. Found: C 47.87, H 5.80, N 2.20, Cl 13.51, F 2.30. Anal. calcd for $C_{48}H_{70}N_2O_{15}Cl_{4.16}F_{1.84}Fe_2$ (**F-0.31**): C 47.68, H 5.83, N 2.32, Cl 12.20, F 2.89. Found: C 47.79, H 5.56, N 2.53, Cl 12.56, F 3.09. Anal. calcd for $C_{48}H_{70}N_2O_{15}Cl_{3.49}F_{2.51}Fe_2$ (**F-0.42**): C 48.12, H 5.89, N 2.34, Cl 10.33, F 3.98. Found: C 47.81, H 5.51, N 2.58, Cl 10.42, F 4.01.

Preparation of desolvated samples. The crystallization solvent molecules inside pores and channels

of solvated samples (**X-Y**) could be removed by vacuuming (ultimate pressure ca. 8 mbar) for 12 hours at room temperature to form the desolvated samples (**X-Y-d**). Anal. calcd for $C_{42}H_{56}N_2O_{12}Br_{0.6}Cl_{5.4}Fe_2$ (**Br-0.10-d**): C 44.56, H 4.99, N 2.47, Cl 16.91, Br 4.24. Found: C 44.29, H 5.09, N 2.49, Cl 16.88, Br 4.09. Anal. calcd for $C_{42}H_{56}N_2O_{12}Br_{1.08}Cl_{4.92}Fe_2$ (**Br-0.18-d**): C 43.74, H 4.89, N 2.43, Cl 15.12, Br 7.48. Found: C 43.52, H 4.94, N 2.56, Cl 15.11, Br 7.28. Anal. calcd for $C_{42}H_{56}N_2O_{12}Br_{2.12}Cl_{3.88}Fe_2$ (**Br-0.35-d**): C 42.05, H 4.71, N 2.34, Cl 11.47, Br 14.12. Found: C 41.72, H 4.81, N 2.33, Cl 11.16, Br 13.76. Anal. calcd for $C_{42}H_{56}N_2O_{12}Br_{3.88}Cl_{2.12}Fe_2$ (**Br-0.65-d**): C 39.48, H 4.42, N 2.19, Cl 5.88, Br 24.26. Found: C 39.12, H 4.32, N 2.28, Cl 5.69, Br 23.81. Anal. calcd for $C_{42}H_{56}N_2O_{12}Cl_{5.66}F_{0.34}Fe_2$ (**F-0.06-d**): C 45.87, H 5.13, N 2.55, Cl 18.25, F 0.59. Found: C 45.78, H 5.21, N 2.80, Cl 18.16, F 0.55. Anal. calcd for $C_{48}H_{56}N_2O_{12}Cl_{5.31}F_{0.69}Fe_2$ (**F-0.12-d**): C 46.11, H 5.16, N 2.56, Cl 17.21, F 1.20. Found: C 45.94, H 5.15, N 2.56, Cl 17.52, F 0.98. Anal. calcd for $C_{42}H_{56}N_2O_{12}Cl_{4.98}F_{1.02}Fe_2$ (**F-0.17-d**): C 46.34, H 5.19, N 2.57, Cl 16.22, F 1.78. Found: C 46.24, H 5.26, N 2.51, Cl 16.36, F 1.63. Anal. calcd for $C_{42}H_{56}N_2O_{12}Cl_{4.55}F_{1.45}Fe_2$ (**F-0.24-d**): C 46.65, H 5.22, N 2.59, Cl 14.92, F 2.55. Found: C 46.26, H 5.24, N 2.55, Cl 14.93, F 2.25. Anal. calcd for $C_{42}H_{56}N_2O_{12}Cl_{4.16}F_{1.84}Fe_2$ (**F-0.31-d**): C 46.92, H 5.25, N 2.61, Cl 13.72, F 3.25. Found: C 46.83, H 5.36, N 2.58, Cl 13.27, F 3.28. Anal. calcd for $C_{42}H_{56}Cl_{3.49}F_{2.51}Fe_2N_2O_{12}$ (**F-0.42-d**): C 47.41, H 5.30, N 2.63, Cl 11.63, F 4.48. Found: C 47.49, H 5.54, N 2.56, Cl 11.23, F 4.21.

Physical characteristics measurements. Elemental analyses were measured on J-SCIENCE Lab JM-10 and YANAKO YHS-11 in Research and Analytical Center for Giant Molecules, Tohoku University. Thermally gravimetric analysis (TGA) were recorded on a Shimadzu DTG-60H apparatus under a flowing N_2 atmosphere from 20 to 500 ºC at a heating rate of 5 ºC min^{-1}. Magnetic properties measurements were conducted with a SQUID magnetometer (MPMS-XL, Quantum Design, U.S.A.). Magnetization measurements were performed by applying a certain DC magnetic field in a temperature range from 1.8-400 K. The temperature dependences of χ_m associated with the TDET behavior were measured heating process followed by cooling process at 1.0 K/min in the sweep mode (Fig. 2, Fig.3). In Fig.S5 and Fig.S6, field-cooled χ_m was measured with a dc field (H_{dc}) of 1 kOe for a temperature range of 1.8 K to 300 K at 2.0 K/min in the settle mode. AC measurements were performed at various frequencies ranging from 1 to 1488 Hz with an AC field amplitude of 3 Oe and without application of DC field.

X-ray Crystallographic Analyses. Data collections were made on a charge-coupled device (CCD) diffractometer (Rigaku Saturn 724M) with multilayer mirror monochromated Mo Kα radiation (λ = 0.71075 Å). A single crystal was mounted on a thin Kapton film using Nujol and cooled under N_2. The structures were solved using direct methods (SHELXT Version 2014/5) for which were expanded using Fourier techniques. All calculations except for refinement were performed using the Crystal Structure crystallographic software package, and the refinement was performed using SHELXL

Version 2014/7.[2] The structural diagrams were prepared using VESTA software.[3] The details of the crystal structure analyses with CCDC numbers are summarized in Table S1, S2, S3 and S4.

Powder X-ray diffraction (PXRD) patterns were collected for samples at 0.02º steps, filled into a glass capillary (ϕ = 0.5 mm) and installed on a RIGAKU Ultima IV diffractometer, with Cu Kα radiation (λ = 1.5418 Å) at room temperature.

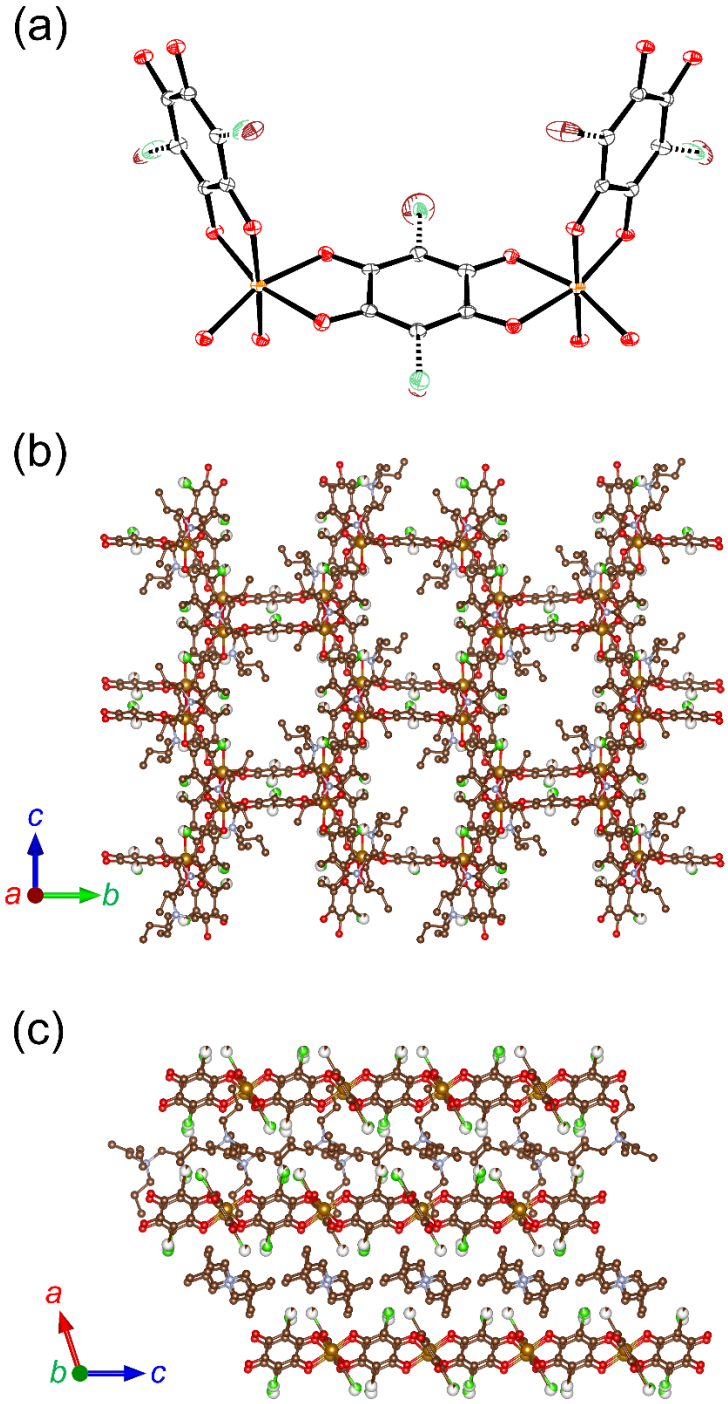

Fig. S1 Crystal Structure of **Br-0.10**. (a) Thermal ellipsoid plot of the formula unit of **Br-0.10** at 103 K, where Fe, O, C, and Cl/Br are represented in orange, red, black, and green/brown, respectively, and crystallization solvent (acetone and water molecules), tetrapropyl ammonium cation, and hydrogen atoms are omitted for clarity. Packing structures of alternating anionic layers of $[Fe_2(Cl_2An/X_2An)_3]^{2-}$ and NPr_4^+ cations in **Br-0.10**. (b) Projecting along the crystallographic *a*-axis; (c) Projecting along the crystallographic *b*-axis. Fe, C, O, Cl/Br, and N atoms are represented in orange, brown, red, green/red brown and light blue spheres, respectively, and crystallization solvent (acetone and water molecules) and hydrogen atoms are omitted for clarity.

Table S1 Crystallographic data for solvated compound **Br-Y**.

Compounds	**Br-0.10**	**Br-0.18**	**Br-0.35**	**Br-0.65**
Formula	$C_{48}H_{70}Cl_{5.40}Br_{0.60}Fe_2N_2O_{15}$	$C_{48}H_{70}Cl_{5.12}Br_{1.08}Fe_2N_2O_{15}$	$C_{48}H_{70}Cl_{3.88}Br_{2.23}Fe_2N_2O_{15}$	$C_{48}H_{70}Cl_{3.00}Br_{3.98}Fe_2N_2O_{15}$
Formula Weight	1266.15	1287.49	1333.72	1413.28
Habit	hexagonal	hexagonal	hexagonal	hexagonal
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	20.2076(7)	20.2837(8)	20.3278(4)	20.4745(6)
b / Å	21.8087(7)	21.7936(7)	21.7798(3)	21.8256(5)
c / Å	14.3967(5)	14.4042(6)	14.4219(3)	14.4440(4)
β / °	108.080(4)	108.042(4)	107.935(2)	107.895(3)
V / Å^3	6031.4(4)	6054.4(4)	6074.8(2)	6142.3(3)
Z	4	4	4	4
Temperature	103 K	103 K	103 K	103 K
Crystal size / mm^3	0.127×0.118×0.027	0.140×0.112×0.033	0.212×0.127×0.052	0.168×0.143×0.049
D_{calc} / g cm^{-3}	1.394	1.412	1.458	1.528
F_{000}	2627.0	2662.0	2737.0	2866.0
λ / Å	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα) / mm^{-1}	1.178	1.469	2.103	3.166
Data measured	49540	49159	41976	42253
Data unique	13837	13874	11085	11244
R_{int}	0.0570	0.1020	0.0273	0.0420
No. of observations	13837	13874	11085	11244
No. of variables	727	715	727	733
$R1$ ($I > 2.00\sigma(I)$)[a]	0.0519	0.0815	0.0383	0.0484
R (all reflections)[a]	0.1009	0.1758	0.0535	0.0731
$wR2$ (All reflections)[b]	0.1399	0.2207	0.1071	0.1273
GOF	1.019	1.014	1.054	1.057
CCDC No.	2014810	2014808	2014806	2014809

[a] $R1 = R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$

Table S2 Crystallographic data for solvated compound **F-Y**.

Compounds	**F-0.06**	**F-0.12**	**F-0.17**	**F-0.24**
Formula	$C_{48}H_{30}Cl_{3.36}F_{0.24}Fe_2N_2O_{15}$	$C_{48}H_{30}Cl_{3.12}F_{0.69}Fe_2N_2O_{15}$	$C_{48}H_{30}Cl_{4.98}F_{1.02}Fe_2N_2O_{15}$	$C_{48}H_{30}Cl_{4.55}F_{1.37}Fe_2N_2O_{15}$
Formula Weight	1233.88	1228.13	1222.70	1215.62
Habit	hexagonal	hexagonal	hexagonal	hexagonal
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	20.1787(5)	20.1163(7)	20.0262(4)	19.8773(6)
b / Å	21.8982(6)	21.8555(5)	21.8928(4)	21.9737(7)
c / Å	14.4000(3)	14.3929(5)	14.3496(3)	14.2912(5)
β / °	108.000(3)	108.051(4)	107.832(2)	107.608(4)
V / Å^3	6051.6(3)	6016.4(4)	5989.0(2)	5949.6(4)
Z	4	4	4	4
Temperature	103 K	103 K	103 K	103 K
Crystal size / mm^3	0.232×0.179×0.067	0.177×0.128×0.052	0.23×0.188×0.062	0.153×0.108×0.052
D_{calc} / g cm^{-3}	1.354	1.356	1.356	1.357
F_{000}	2573.0	2562.0	2551.0	2538.0
λ / Å	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα) / mm^{-1}	0.790	0.780	0.770	0.757
Data measured	42133	42236	41330	40793
Data unique	11040	10859	10938	10874
R_{int}	0.0207	0.0386	0.0256	0.0501
No. of observations	11040	10859	10938	10874
No. of variables	697	697	709	733
$R1$ ($I > 2.00\sigma(I)$)[a]	0.0359	0.0500	0.0427	0.0634
R (all reflections)[a]	0.0410	0.0718	0.0498	0.0877
$wR2$ (All reflections)[b]	0.1066	0.1492	0.1294	0.2026
GOF	1.032	1.023	1.047	1.042
CCDC No.	2014812	2014814	2014813	2014816

[a] $R1 = R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]$

Table S2 (continued) Crystallographic data for solvated compound **F-Y**.

Compounds	**F-0.31**	**F-0.42**
Formula	$C_{48}H_{30}Cl_{4.16}F_{1.84}Fe_2N_5O_{15}$	$C_{48}H_{30}Cl_{3.49}F_{2.51}Fe_2N_5O_{15}$
Formula Weight	1209.20	1198.18
Habit	hexagonal	hexagonal
Crystal System	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / Å	19.8524(7)	19.6602(8)
b / Å	21.9805(8)	22.2123(10)
c / Å	14.2863(5)	14.2016(6)
β / °	107.662(4)	107.210(4)
V / Å^3	5940.2(4)	5924.1(5)
Z	4	4
Temperature	103 K	103 K
Crystal size / mm^3	0.188×0.112×0.036	0.188×0.182×0.061
D_{calc} / g cm^{-3}	1.352	1.343
F_{000}	2525.0	2504.0
λ / Å	0.71073	0.71073
μ(Mo Kα) / mm^{-1}	0.742	0.716
Data measured	41974	41206
Data unique	10791	10838
R_{int}	0.0361	0.0327
No. of observations	10791	10838
No. of variables	721	733
$R1$ ($I > 2.00\sigma(I)$)[a]	0.0591	0.0754
R (all reflections)[a]	0.0881	0.1022
$wR2$ (All reflections)[b]	0.1874	0.2567
GOF	1.032	1.016
CCDC No.	2014821	2014822

[a] $R1 = R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]$

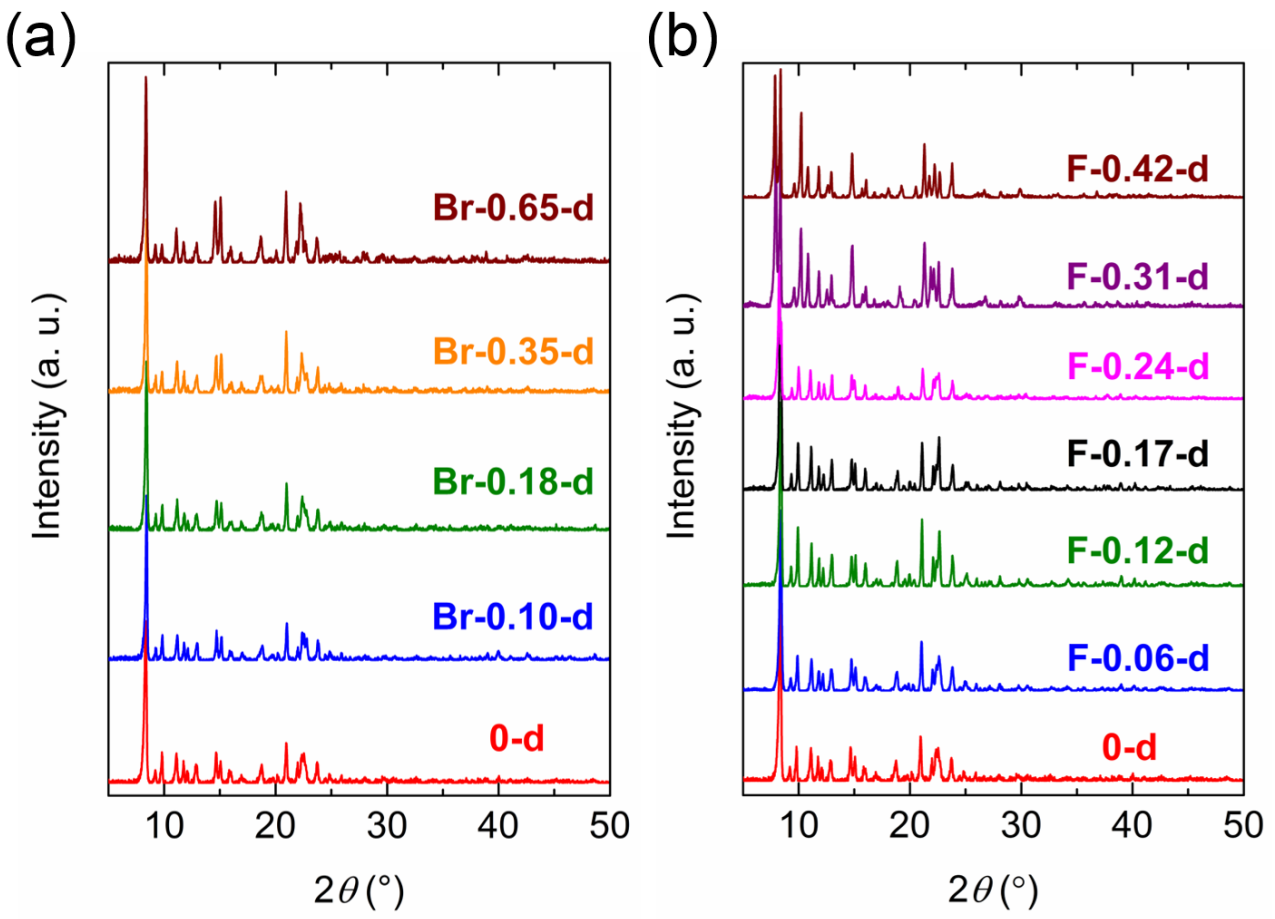

Fig. S2 PXRD patterns for **Br-Y-d** (a) and **F-Y-d** (b) measured at room temperature.[4,5]

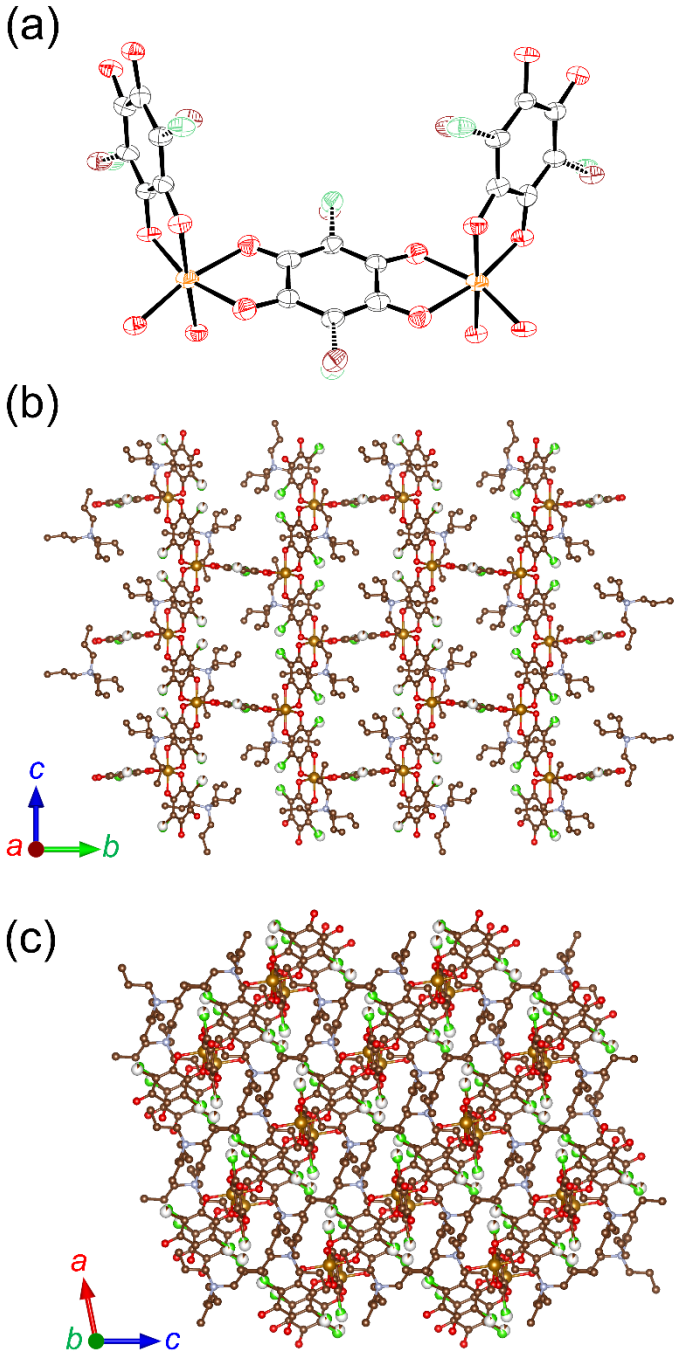

Fig. S3 Crystal Structure of **Br-0.10-d**. (a) Thermal ellipsoid plot of the formula unit of **Br-0.10** with the atomic numbering scheme at 103 K, where Fe, O, C, and Cl/Br are represented in orange, red, black, and green/brown, respectively, and tetrapropyl ammonium cation, and hydrogen atoms are omitted for clarity. Packing structures of alternating anionic layers of $[Fe_2(Br_2An/Cl_2An)_3]^{2-}$ and NPr_4^+ cations in **Br-0.10-d**: (b) Projecting along the crystallographic *a*-axis; (c) Projecting along the crystallographic *b*-axis. Fe, C, O, Cl/Br, and N atoms are represented in orange, brown, red, green and light blue spheres, respectively, and hydrogen atoms are omitted for clarity.

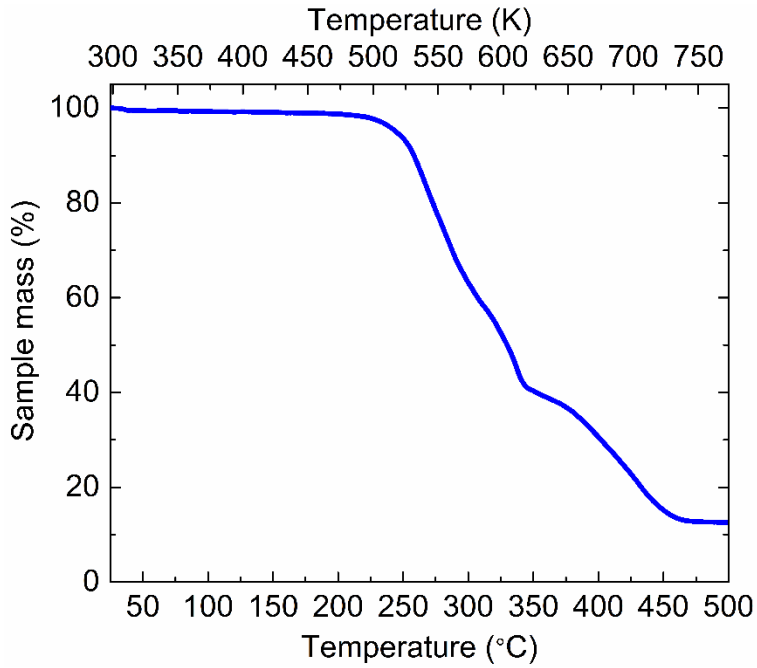

Fig. S4 Thermally gravimetric analysis (TGA) profiles of **Br-0.65-d** with a heating rate of 5 °C min^{-1}.

Table S3 Crystallographic data for solvated compound **Br-Y-d**.

Compounds	**Br-0.10-d**	**Br-0.18-d**	**Br-0.35-d**	**Br-0.65-d**
Formula	$C_{42}H_{56}Cl_{5.52}Br_{0.48}Fe_2N_2O_{12}$	$C_{42}H_{56}Cl_{4.92}Br_{1.08}Fe_2N_2O_{12}$	$C_{42}H_{56}Cl_{3.88}Br_{2.12}Fe_2N_2O_{12}$	$C_{42}H_{56}Cl_{2.12}Br_{3.88}Fe_2N_2O_{12}$
Formula Weight	1126.63	1153.31	1199.54	1277.78
Habit	hexagonal	hexagonal	hexagonal	hexagonal
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	10.7693(7)	10.8043(10)	10.8837(10)	10.9142(5)
b / Å	20.6834(12)	20.7436(17)	20.7386(13)	20.5604(9)
c / Å	12.2409(8)	12.2725(11)	12.3417(11)	12.3173(5)
β / °	101.308(6)	101.419(9)	101.410(9)	101.617(4)
V / Å^3	2673.7(3)	2696.1(4)	2730.6(4)	2707.4(2)
Z	2	2	2	2
Temperature	103 K	103 K	103 K	103 K
Crystal size / mm^3	0.171×0.127×0.04	0.168×0.133×0.046	0.165×0.128×0.043	0.151×0.125×0.03
D_{calc} / g cm^{-3}	1.399	1.421	1.459	1.567
F_{000}	1161.0	1183.0	1220.0	1284.0
λ / Å	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα) / mm^{-1}	1.232	1.637	2.326	3.558
Data measured	22556	20498	20720	21279
Data unique	7609	6142	6116	6175
R_{int}	0.0872	0.0707	0.0714	0.0565
No. of observations	7609	6142	6116	6175
No. of variables	322	320	314	314
$R1$ ($I > 2.00\sigma(I)$)[a]	0.1294	0.0796	0.1010	0.0548
R (all reflections)[a]	0.2150	0.1359	0.1544	0.0964
$wR2$ (All reflections)[b]	0.3004	0.1734	0.2303	0.1056
GOF	1.036	1.117	1.169	1.071
CCDC No.	2014805	2014803	2014804	2014807

[a] $R1 = R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$

Table S4 Crystallographic data for solvated compound **F-Y-d**.

Compounds	**F-0.06-d**	**F-0.12-d**	**F-0.17-d**	**F-0.24-d**
Formula	$C_{42}H_{56}Cl_{5.66}F_{0.34}Fe_2N_2O_{12}$	$C_{42}H_{56}Cl_{5.31}F_{0.69}Fe_2N_2O_{12}$	$C_{42}H_{56}Cl_{4.98}F_{1.02}Fe_2N_2O_{12}$	$C_{42}H_{56}Cl_{4.55}F_{1.45}Fe_2N_2O_{12}$
Formula Weight	1099.71	1093.95	1088.52	1081.45
Habit	hexagonal	hexagonal	hexagonal	hexagonal
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	10.7147(3)	10.6805(6)	10.6203(4)	10.5632(6)
b / Å	20.7638(7)	20.8987(11)	20.9025(5)	21.1362(10)
c / Å	12.2126(4)	12.2445(6)	12.2015(4)	12.2412(8)
β / °	101.108(3)	101.108(5)	101.021(4)	100.998(6)
V / Å^3	2666.13(15)	2681.9(2)	2658.67(15)	2682.8(3)
Z	2	2	2	2
Temperature	103 K	103 K	103 K	103 K
Crystal size / mm^3	0.189×0.152×0.061	0.357×0.219×0.07	0.307×0.273×0.137	0.241×0.148×0.067
D_{calc} / g cm^{-3}	1.370	1.355	1.360	1.339
F_{000}	1139.0	1133.0	1128.0	1121.0
λ / Å	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα) / mm^{-1}	0.884	0.862	0.854	0.826
Data measured	20643	20637	21062	21209
Data unique	6013	6140	5996	6006
R_{int}	0.0269	0.0187	0.0191	0.0303
No. of observations	6013	6140	5996	6006
No. of variables	302	302	320	320
$R1$ ($I > 2.00\sigma(I)$)[a]	0.0484	0.0479	0.0369	0.0588
R (all reflections)[a]	0.0638	0.0567	0.0441	0.0830
$wR2$ (All reflections)[b]	0.1144	0.1246	0.0978	0.1597
GOF	1.103	1.105	1.105	1.088
CCDC No.	2014811	2014818	2014817	2014815

[a] $R1 = R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S4 (continued) Crystallographic data for solvated compound **F-Y-d**.

Compounds	**F-0.31-d**	**F-0.42-d**
Formula	$C_{42}H_{56}Cl_{4.16}F_{1.84}Fe_2N_2O_{12}$	$C_{42}H_{56}Cl_{3.49}F_{2.51}Fe_2N_2O_{12}$
Formula Weight	1075.03	1064.00
Habit	hexagonal	hexagonal
Crystal System	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a / Å	10.4941(6)	10.4272(5)
b / Å	21.1640(13)	21.1795(9)
c / Å	12.1914(8)	12.1426(4)
β / °	101.118(6)	101.168(4)
V / Å^3	2656.9(3)	2630.83(19)
Z	2	2
Temperature	103 K	103 K
Crystal size / mm^3	0.212×0.103×0.027	0.218×0.127×0.037
D_{calc} / g cm^{-3}	1.344	1.343
F_{000}	1115.0	1104.0
λ / Å	0.71073	0.71073
μ(Mo Kα) / mm^{-1}	0.816	0.792
Data measured	21412	21256
Data unique	6103	5916
R_{int}	0.0377	0.0504
No. of observations	6103	5916
No. of variables	314	314
$R1$ ($I > 2.00\sigma(I)$)[a]	0.0534	0.0642
R (all reflections)[a]	0.0873	0.1005
$wR2$ (All reflections)[b]	0.1418	0.1925
GOF	1.023	1.032
CCDC No.	2014819	2014820

[a] $R1 = R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]$

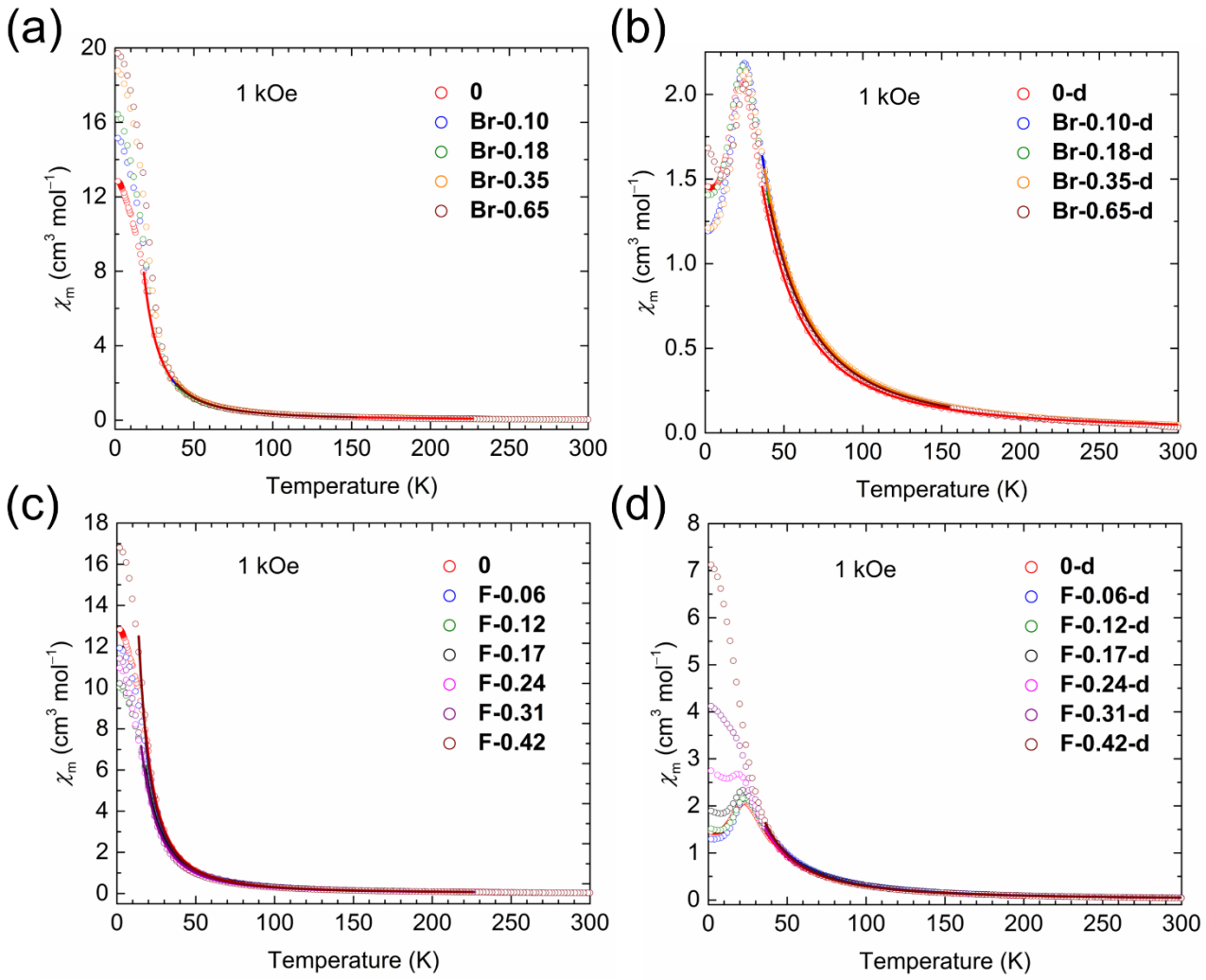

Fig. S5 Temperature dependence of χ_m measured at H_{dc} =1 kOe ($\chi_m = M_m/H_{dc}$) for **B-Y** (a), **B-Y-d** (b), **F-Y** (c) and **F-Y-d** (d), respectively.[4,5] The solid lines represent the best-fit line with a Seiden model using alternating classical $S = 5/2$ and quantum $S = 1/2$ spins (see Table S5).

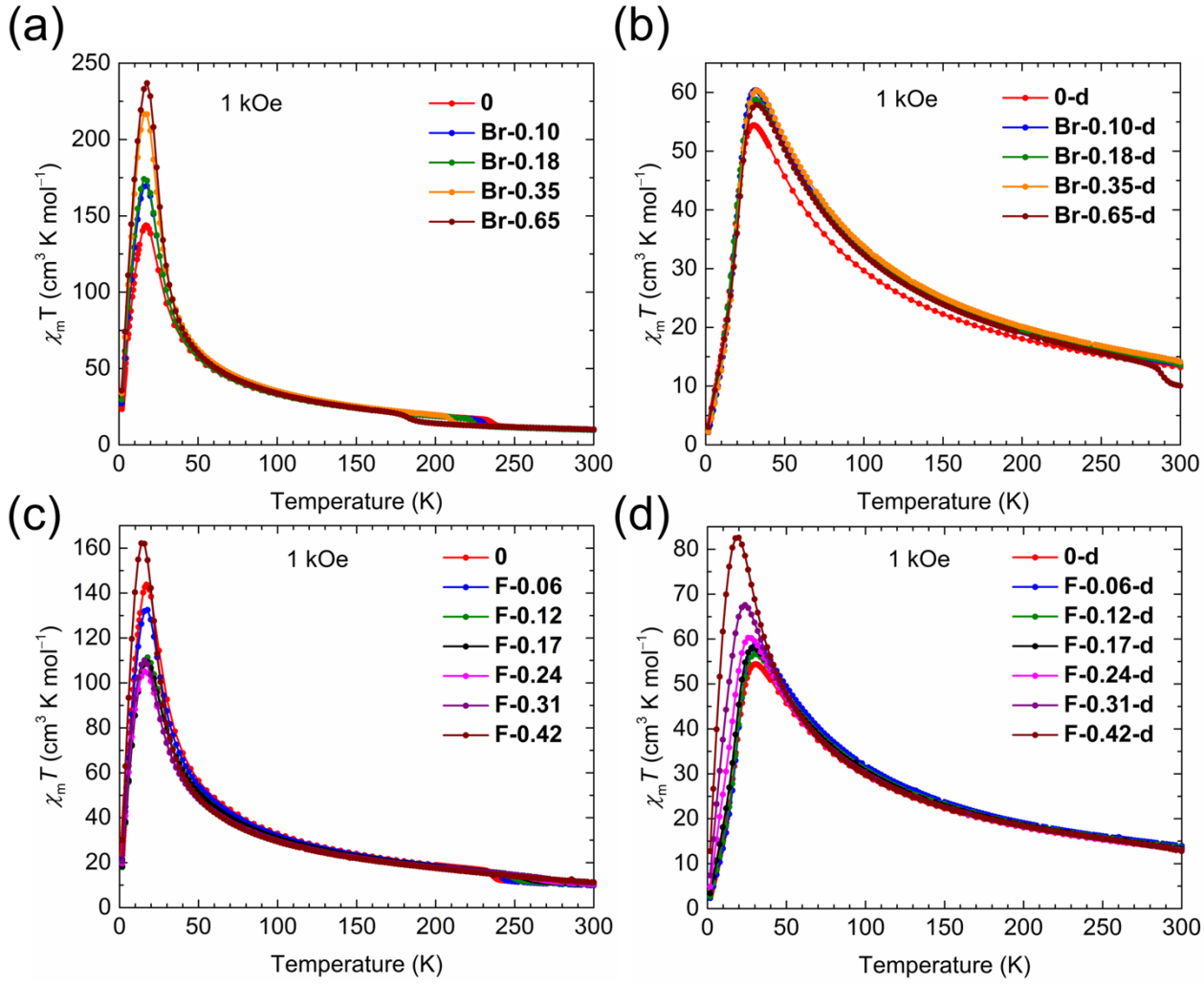

Fig. S6 Temperature dependence of $\chi_m T$ measured at H_{dc} =1 kOe ($\chi_m = M_m/H_{dc}$) for **B-Y** (a), **B-Y-d** (b), **F-Y** (c) and **F-Y-d** (d), respectively.[4,5]

Table S5 Magnetic parameters of J and zJ' obtained from the simulation for magnetic profiles for **X-Y** and **X-Y-d** using a Seiden model $\hat{H} = -2J\Sigma[\hat{S}_{Li}\cdot(\hat{S}_{Fei} + \hat{S}_{Fei+1})]$ with an alternating spin model of classical $S = 5/2$ and quantum $S = 1/2$ spins for the data, including a mean-field approximation (zJ') to consider interchain interactions.[4,5,6,7,8] The simulated fines were depicted in Fig. S4.

Compounds **X-Y**	$\chi_m T$ at 300 K / cm^3 K mol^{-1}	J / cm^{-1}	zJ' / cm^{-1}	Simulation range (K)
0	10.19	–130.6	–0.27	18-227
Br-0.10	9.72	–134.6	–0.36	35-154
Br-0.18	9.84	–136.6	–0.90	39-153
Br-0.35	10.05	–144.0	–0.24	37-153
Br-0.65	10.07	–136.8	–0.05	39-153
F-0.06	9.89	–126.7	–0.42	18-227
F-0.12	10.26	–120.4	–1.03	18-227
F-0.17	10.47	–120.4	–1.13	18-227
F-0.24	10.44	–111.6	–1.12	18-227
F-0.31	10.95	–118.4	–1.46	14-226
F-0.42	11.28	–128.5	–0.33	14-226
Compounds **X-Y-d**				
0-d	13.30	–125.2	–0.27	35-300
Br-0.10-d	13.74	–141.3	–0.24	35-300
Br-0.18-d	13.56	–142.1	–0.27	36-300
Br-0.35-d	14.12	–149.3	–0.26	35-300
Br-0.65-d	10.05	–141.9	–0.27	34-300
F-0.06-d	13.94	–137.5	–0.25	36-300
F-0.12-d	13.53	–133.0	–0.27	35-300
F-0.17-d	13.30	–130.2	–0.25	36-300
F-0.24-d	12.98	–125.7	–0.23	36-300
F-0.31-d	13.03	–124.3	–0.20	36-300
F-0.42-d	12.77	–120.9	–0.15	36-300

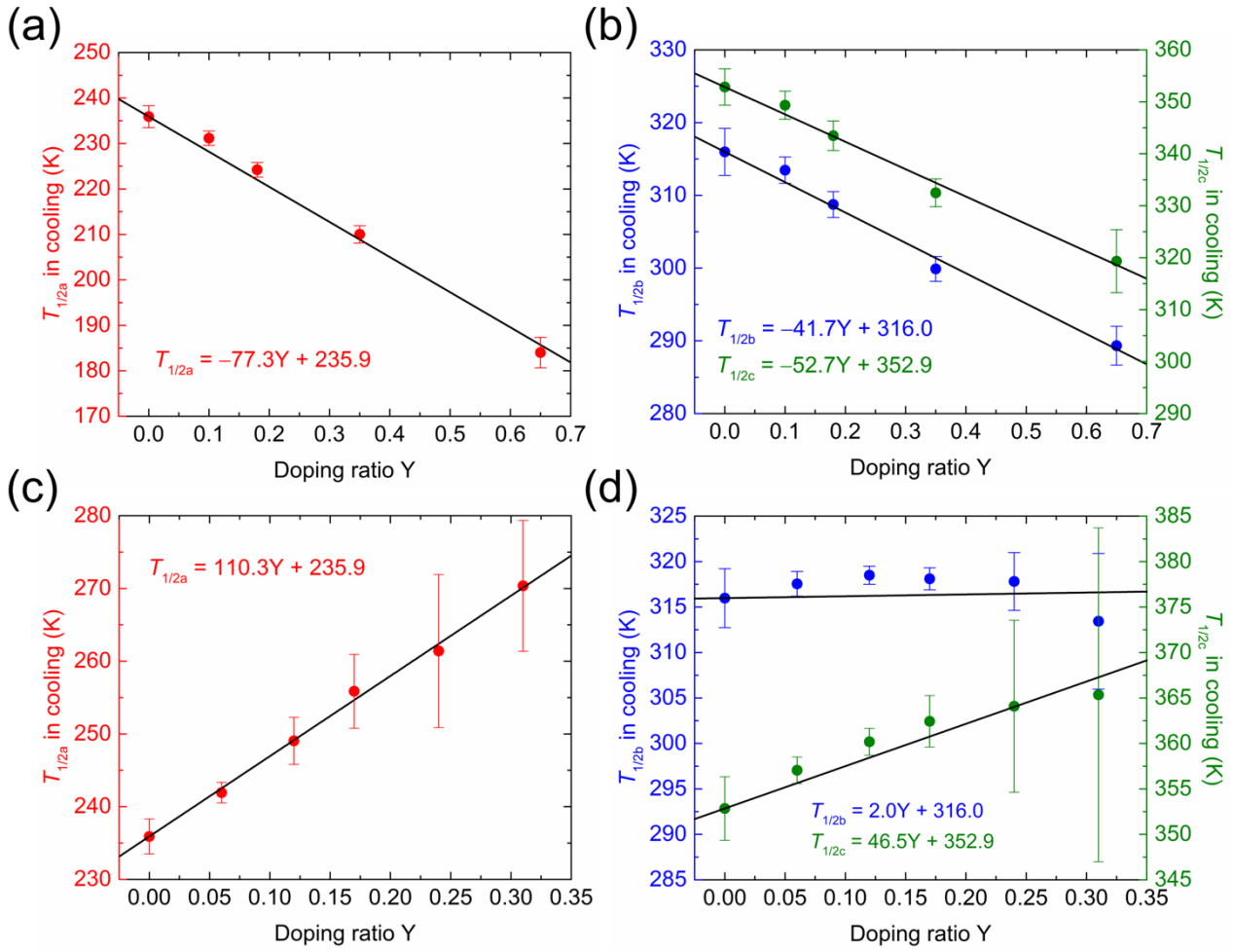

Fig. S7 Doping rate (Y) dependence of $T_{1/2a}$ for **Br-Y** (a), **F-Y** (c), and $T_{1/2b}$, $T_{1/2c}$ for **Br-Y-d** (b), and **Br-Y-d** (d). The black solid lines are least-square linear fitting lines.[4,5]

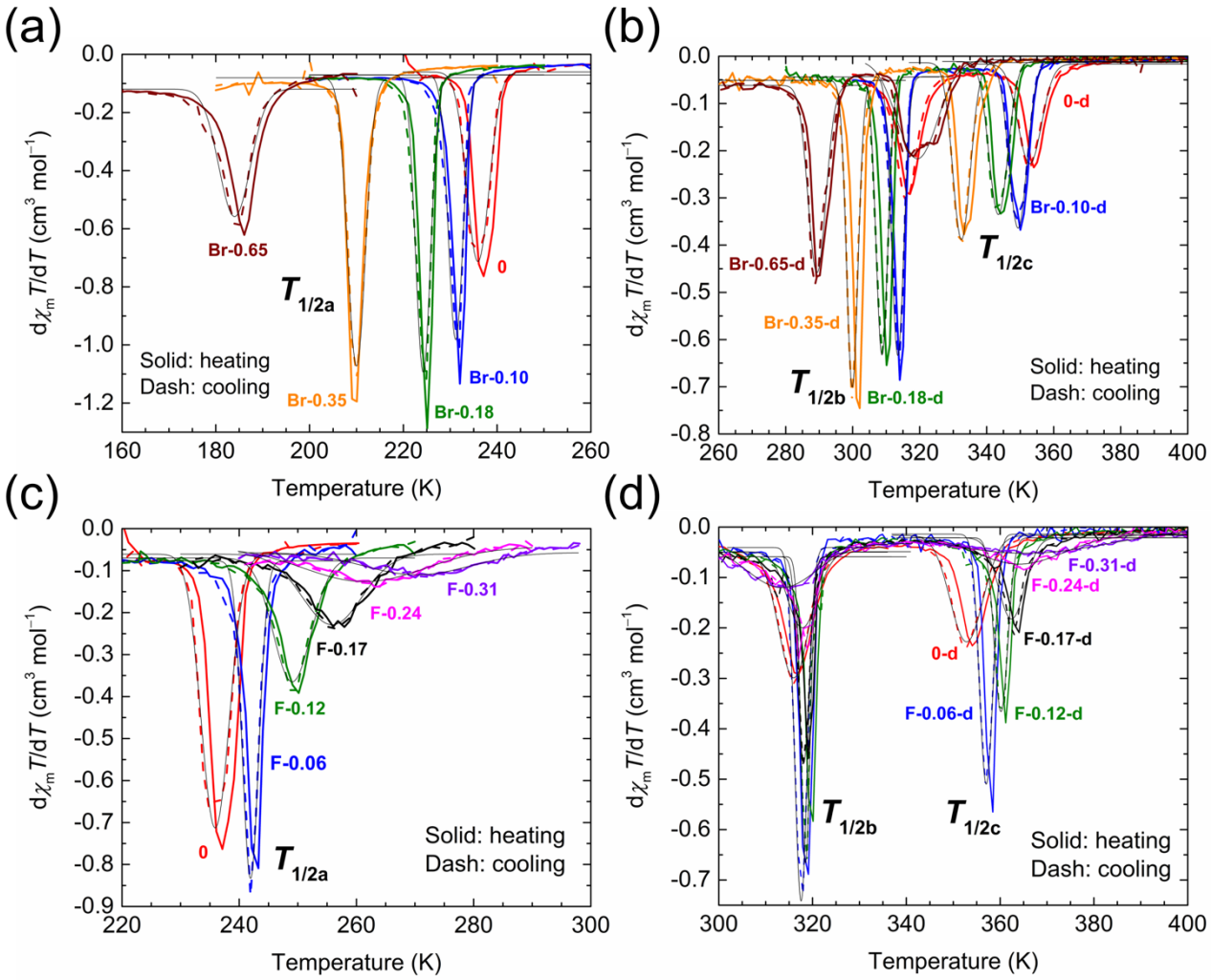

Fig. S8 Temperature dependence of the derivative of $\chi_m T$ with respect to temperature, $d\chi_m T/dT$ for (a) **Br-Y**, (b) **Br-Y-d**, (c) **F-Y**, and (d) **F-Y-d**.[4,5]

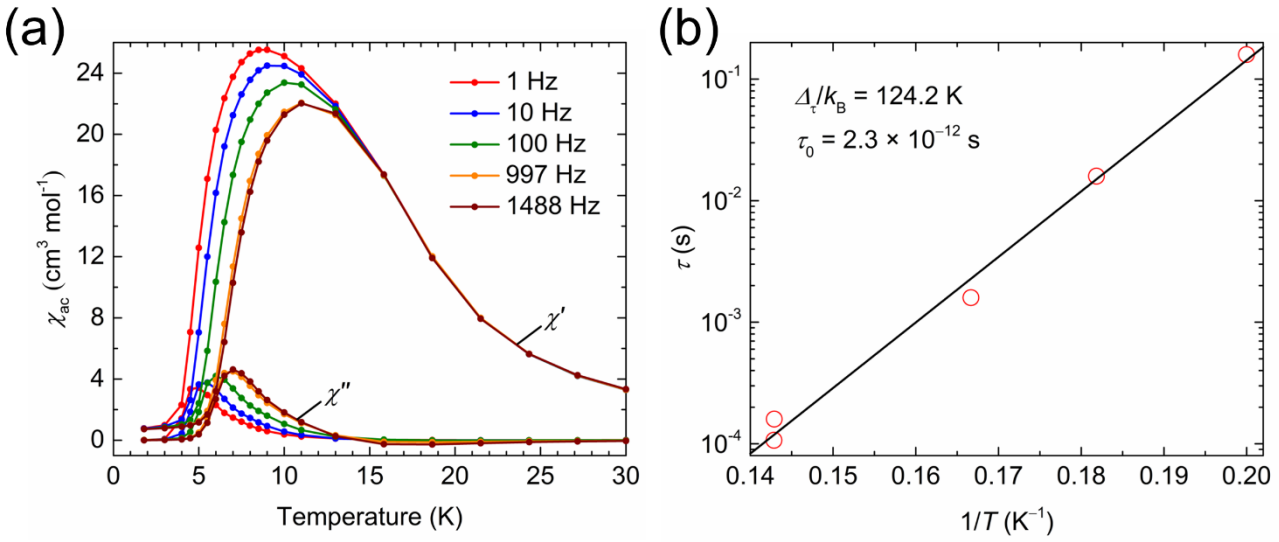

Fig. S9 Temperature dependence of χ' and χ'' under the 0 Oe dc field and a 3 Oe ac oscillating field at several frequencies ranging from 1 Hz to 1488 Hz for **Br-0.10** (a). Arrhenius plots made from peak maxima in χ'' versus ν plots (b).

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