Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The effect of chlorine and fluorine substitutions on tuning the ionization potential of benzoate-bridged paddlewheel diruthenium(II, II) complexes

Wataru Kosaka,[a,b] Masahisa Itoh,[b] and Hitoshi Miyasaka,*[a,b]

[a] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[b] Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan

e-mail: miyasaka@imr.tohoku.ac.jp

Corresponding author*
Prof. Dr. Hitoshi Miyasaka
Institute for Materials Research, Tohoku University, 2–1–1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan
E-mail: miyasaka@imr.tohoku.ac.jp
Tel: +81-22-215-2030
FAX: +81-22-215-2031

Materials.

All the reagents and chemicals used were obtained from commercial sources, unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer operating at 400 MHz. The infrared spectra were measured using KBr disks employing a JASCO FT/IR-4200 spectrometer. 2,4,5-trichloro-1-iodobenzene was prepared according to the literature method.[1] 3’,4’,5’-trichloroacetophenone was prepared from 4’-amino-3’,5’-dichloroacetophenone by modified Sandmayer reaction.[2] 2,3,4-trichlorobenzoic acid and 3,4,5-trichlorobenzoic acid was prepared by the oxidation of the corresponding acetophenone with tert-buthylhydroperoxide.[3] 2,3,5-trichlorobenzoic acid was prepared by the oxidation of the corresponding aldehyde with sodium chlorite.[4] 2,4,5-trichlorobenzoic acid was prepared by an iodine-Grignard exchange reaction followed by the carboxylation of 2,4,5-trichloro-1-iodobenzene.[5]

Preparation of 3’,4’,5’-Trichloroacetophenone.

$CuCl_2$ (19.4 g, 144 mmol) was added to a suspension of 4’-amino-3’,5’-dichloroacetophenone (24.5 g, 120 mmol) in CH_3CN (300 ml). The mixture was stirred for 20 min at room temperature, and then, t-BuONO, 90% (21.6 ml, 180 mmol) was added dropwise over 1 hour. After completion of the addition, the mixture was heated to 65 ºC for 1 hour. Solvent was then evaporated in vacuo. Water and EtOAc were added, and the mixture was agitated in the flask until the black-brown color disappeared. The whole mixture was filtered through Celite and washed with EtOAc. The EtOAc layer was separated, washed with brine, dried (Na_2SO_4), and concentrated. The residue was recrystallized by hexane to give 3’,4’,5’-trichloroacetophenone as brown needle: 21.5 g (80% yield). ^{1}H NMR ($CDCl_3$) δ 2.58 (s, 3 H), 7.92 (s, 2 H). ^{13}C NMR ($CDCl_3$) δ 128.3, 135.0, 136.3, 136.6, 194.7. mp 70–72°C. IR (ν_{max}, cm^{-1}, KBr): 3079, 3066, 1692, 1576, 1550, 1421, 1378, 1356, 1254, 1199, 1101, 1042, 969, 903, 890, 875, 804, 970, 632, 576.

Preparation of 2,3,4-Trichlorobenzoic Acid.

A solution of 4.0 g (100 mmol) NaOH in 10 ml of water was added dropwise to a stirred mixture of 5.6 g (25 mmol) of 2’,3’,4’-trichloroacetophenone, 12.9 g (100 mmol) of tert-buthylhydroperoxide (70% aqueous solution) and 0.6 g (2.5 mmol) of WO_3 with cooling in ice-water bath. After the complete addition, the mixture was heated to 80°C and stirred for 15 hour. After cooling to 0°C, the solution was acidified by 6N HCl, which was extracted with ethyl acetate. The organic layer was washed with brine, and dried over Na_2SO_4. After evaporation of the solvents, the residue was recrystallized from chloroform, which gave 2,3,4-trichlorobenzoic acid as white powder: 3.8 g (68 % yield). ^{1}H NMR ($CDCl_3$) δ 7.49 (d, 1 H), 7.83 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 128.4, 129.0, 130.1, 134.2, 134.8, 138.9, 168.6. mp 190–191°C. IR (ν_{max}, cm^{-1}, KBr): 3000-2500, 1704, 1569, 1415, 1359, 1290, 1252, 1186, 877, 837, 769, 731, 566.

Preparation of 3,4,5-Trichlorobenzoic Acid.

A solution of 4.0 g (100 mmol) NaOH in 10 ml of water was added dropwise to a stirred mixture of 5.6 g (25 mmol) of 3',4',5'-trichloroacetophenone, 12.9 g (100 mmol) of tert-buthylhydroperoxide (70% aqueous solution) and 0.6 g (2.5 mmol) of WO_3 with cooling in ice-water bath. After their complete addition, the mixture was heated to 80°C and stirred for 15 hour. After cooling to 0°C, the solution was acidified by 6N HCl, which was extracted with ethyl acetate. The organic layer was washed with brine, and dried over Na_2SO_4. After evaporation of the solvents, the residue was recrystallized from toluene, which gave 3,4,5-trichlorobenzoic acid as white needle: 5.0 g (89 % yield). ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 2 H). ^{13}C NMR ($CDCl_3$) δ 128.9, 130.1, 135.0, 137.6, 168.6. mp 209–210°C. IR (ν_{max}, cm^{-1}, KBr): 3100-2500, 1701 1583, 1554, 1440, 1401, 1391, 1378, 1280, 1267, 1190, 1131, 1043, 1034, 913, 891, 810, 767, 724, 697, 585, 497.

Preparation of 2,3,5-Trichlorobenzoic Acid.

A solution of 5.7 g (44 mmol) $NaClO_2$ (70 % purity) in 35 ml of water was added dropwise in 2 h to a stirred mixture of 4.9 g (23.5 mmol) of 2,3,5-trichlorobenzealdehyde in 25 ml of acetonitrile, 0.8 g (6.7 mmol) of NaH_2PO_4 in 10 ml of water and 2.5 ml (26 mmol) of 35% H_2O_2 while cooling in an ice-water bath. After their complete addition, the mixture was stirred for a further 4 hour. After Na_2SO_3 was added slowly to destroy the unreacted HOCl and H_2O_2 until the yellow color of solution disappeared, acetonitrile was evaporated under vacuum. The precipitated 2,3,5-trichloro benzoic acid was collected by filtration, washed with water, which did not require further purification: 5.0 g (95 % yield). ^{1}H NMR ($CDCl_3$) δ 7.68 (d, 1 H), 7.86 (d, 1H). ^{13}C NMR ($CDCl_3$) δ 130.4, 131.5, 131.7, 133.0, 134.0, 136.0, 168.7. mp 162–163°C. IR (ν_{max}, cm^{-1}, KBr): 3400-2500, 1721, 1696, 1574, 1554, 1436, 1423, 1410, 1399, 1378, 1284, 1247, 1201, 1172, 1133, 1105, 1057, 901, 874, 829, 781, 710, 635, 552.

Preparation of 2,4,5-Trichlorobenzoic Acid.

7.3 ml (22 mmol) of EtMgBr (3.0 M in Et_2O) was added dropwise in 15 min to a stirred solution of 6.2 g (20 mmol) of 2,4,5-trichloro-1-iodebenzene in 50 ml of THF at 0°C, which was stirred for a further 5 hour. An excess amount of dry ice was added to the reaction mixture at −78°C, and the mixture was allowed to reach room temperature and then stirred for 3 h. The reaction was quenched with 30 ml of H_2O, and THF was evaporated under vacuum. The residue was acidified with 10% aqueous solution of HCl, which was extracted with Et_2O. The organic layer was washed with brine, and dried over Na_2SO_4. After evaporation of the solvents, the residue was recrystallized from toluene, which gave 2,4,5-trichlorobenzoic acid as white needle: 2.8 g (62 % yield). ^1H NMR ($CDCl_3$) δ 7.55 (s, 1 H), 8.05 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 128.9, 129.9, 130.5, 132.0, 132.4, 134.2, 169.2. mp 165–166°C. IR (ν_{max}, cm^{-1}, KBr): 3000–2400, 1722, 1661, 1577, 1534, 1430, 1409, 1339, 1303, 1282, 1259, 1161, 1132, 1075, 906, 871, 813, 640, 508.

Table S1. Crystallographic Data.

	***m*-Cl**	***p*-Cl**	**2,3-Cl_2**	**2,4-Cl_2**	**2,5-Cl_2**	**2,6-Cl_2**
formula	$C_{36}H_{32}Cl_4O_{10}Ru_2$	$C_{44}H_{48}Cl_4O_{12}Ru_2$	$C_{36}H_{28}Cl_8O_{10}Ru_2$	$C_{36}H_{28}Cl_8O_{10}Ru_2$	$C_{36}H_{28}Cl_8O_{10}Ru_2$	$C_{36}H_{28}Cl_8O_{10}Ru_2$
formula weight	968.59	1112.81	1106.38	1106.38	1106.38	1106.38
crystal system	monoclinic	triclinic	triclinic	Triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P-1$	$P-1$	$P-1$	$P-1$	$P2_1/c$
a / Å	8.9314(9)	12.2925(11)	7.9515(8)	7.9931(19)	9.3505(5)	20.670(4)
b / Å	19.650(2)	13.8331(13)	11.1817(12)	11.5843(18)	19.7565(11)	20.241(4)
c / Å	11.0250(12)	15.0599(15)	11.4337(12)	11.800(3)	22.4500(13)	9.547(2)
α / deg	90	71.143(5)	108.035(2)	66.08(2)	90.0602(7)	90
β / deg	102.797(2)	71.494(5)	94.766(2)	84.46(3)	97.1420(10)	94.726(3)
γ / deg	90	71.502(6)	95.4834(8)	78.06(3)	100.4293(9)	90
V / Å^3	1886.9(4)	2231.4(4)	955.4(2)	977.1(4)	4045.9(4)	3981(2)
Z	2	2	1	1	4	4
crystal size / mm^3	0.47×0.13×0.09	0.33×0.18×0.09	0.12×0.04×0.01	0.35×0.14×0.06	0.44×0.21×0.20	0.30×0.30×0.20
T / K	97(1)	93(1)	97(1)	123(1)	93(1)	93(1)
D_{calc} / g·cm^{-3}	1.705	1.656	1.923	1.880	1.816	1.846
F_{000}	968.00	1128.00	548.00	548.00	2192.00	2192.00
λ / Å	0.71075	0.71075	0.71075	0.71070	0.71075	0.71075
μ(Mo Kα) / cm^{-1}	11.393	9.784	14.083	13.769	13.301	13.519
data measured	12253	15096	6605	10394	27455	26584
data unique	3249	7674	3305	4317	13891	6919
R_{int}	0.0817	0.0983	0.0262	0.0410	0.0128	0.0237
no. of observations	3249	7674	3305	4317	13891	6919
no. of variables	235	594	262	262	1018	532
$R1$ ($I > 2.00\sigma(I)$)^a	0.0299	0.0540	0.0307	0.0557	0.0253	0.0427
R (all reflections)^a	0.0306	0.0560	0.0317	0.0667	0.0285	0.0459
$wR2$ (all reflections)^b	0.0819	0.1503	0.0807	0.1648	0.0632	0.1241
GOF	1.055	1.054	1.095	1.099	1.075	1.058
CCDC No.	1041324	1041325	1041313	1041316	1041318	1041320

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

Table S1 (Continued). Crystallographic Data

	3,4-Cl_2	**3,5-Cl_2**	**2,3,4-Cl_3**	**2,3,5-Cl_3**	**2,4,5-Cl_3**	**3,4,5-Cl_3**
formula	$C_{36}H_{28}Cl_8O_{10}Ru_2$	$C_{42}H_{42}Cl_8O_{10}Ru_2$	$C_{36}H_{24}Cl_{12}O_{10}Ru_2$	$C_{42}H_{38}Cl_{12}O_{10}Ru_2$	$C_{36}H_{24}Cl_{12}O_{10}Ru_2$	$C_{36}H_{24}Cl_{12}O_{10}Ru_2$
formula weight	1106.38	1192.55	1244.16	1330.33	1244.16	1244.16
crystal system	triclinic	triclinic	monoclinic	Triclinic	triclinic	triclinic
space group	$P-1$	$P-1$	$P2_1/c$	$P-1$	$P-1$	$P-1$
a / Å	9.7894(9)	8.924(4)	10.5437(11)	9.988(3)	9.3702(17)	7.771(5)
b / Å	11.6023(9)	11.032(3)	12.9354(14)	10.925(4)	10.3639(18)	11.887(7)
c / Å	19.987(2)	13.5070(19)	15.4899(18)	11.720(4)	12.289(2)	12.322(7)
α / deg	75.265(4)	68.76(7)	90	86.02(4)	69.520(11)	80.866(12)
β / deg	84.039(5)	71.86(8)	92.213(4)	76.50(4)	71.324(9)	87.02(2)
γ / deg	69.065(4)	74.94(8)	90	76.40(4)	77.853(11)	89.75(2)
V / Å^3	2050.4(3)	1161.4(9)	2111.0(4)	1208.4(7)	1052.5(4)	1122.2(12)
Z	2	1	2	1	1	1
crystal size / mm^3	0.28×0.06×0.01	0.34×0.20×0.01	0.73×0.44×0.12	0.26×0.10×0.02	0.12×0.09×0.01	0.11×0.07×0.01
T / K	97(1)	123(1)	123(1)	123(1)	97(1)	93(1)
D_{calc} / g·cm^{-3}	1.792	1.705	1.957	1.828	1.963	1.841
F_{000}	1096.00	598.00	1224.00	662.00	612.00	612.00
λ / Å	0.71075	0.71070	0.71070	0.71070	0.71075	0.71075
μ(Mo Kα) / cm^{-1}	13.124	11.651	15.309	13.436	15.353	14.400
data measured	14159	10965	21201	11571	7044	7641
data unique	7077	4050	4353	4225	3615	3871
R_{int}	0.0368	0.0375	0.0897	0.0802	0.0289	0.0297
no. of observations	7077	4050	4353	4225	3615	3871
no. of variables	505	280	271	298	271	271
$R1$ ($I > 2.00\sigma(I)$)^a	0.0871	0.0328	0.0497	0.0975	0.0407	0.0559
R (all reflections)^a	0.0964	0.0373	0.0534	0.1109	0.0447	0.0642
$wR2$ (all reflections)^b	0.2491	0.0938	0.1333	0.2707	0.1278	0.1455
GOF	1.075	1.060	1.041	1.045	1.177	1.121
CCDC No.	1041322	1041323	1041310	1041311	1041315	1041321

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

Table S1 (Continued). Crystallographic Data.

	2,3,4,5-Cl$_4$	**2,3-F$_2$**	**2,4-F$_2$**	**2,5-F$_2$**	**2,3,5-F$_3$**
formula	$C_{40}H_{28}Cl_{16}O_{11}Ru_2$	$C_{36}H_{28}F_8O_{10}Ru_2$	$C_{36}H_{28}F_8O_{10}Ru_2$	$C_{44}H_{40}F_{12}O_{12}Ru_2$	$C_{38}H_{28}F_{12}O_{10.5}Ru_2$
formula weight	1454.04	974.74	974.74	1114.92	1082.75
crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P-1$	$P-1$	$P-1$	$P-1$	Cc
a / Å	9.008(2)	7.7411(19)	7.8183(10)	10.013(4)	14.915(4)
b / Å	11.722(3)	10.973(3)	10.9306(9)	10.618(5)	15.272(3)
c / Å	12.262(3)	11.011(3)	11.4882(11)	10.661(5)	18.323(4)
α / deg	97.328(4)	106.408(3)	67.979(11)	84.303(13)	90
β / deg	97.679(4)	92.403(3)	82.99(2)	72.127(11)	94.955(7)
γ / deg	93.683(4)	101.099(4)	76.43(2)	78.646(12)	90
V / Å^3	1268.3(5)	875.8(4)	884.1(2)	1056.6(8)	4158(2)
Z	1	1	1	1	4
crystal size / mm^3	0.10×0.04×0.01	0.12×0.12×0.01	0.52×0.09×0.08	0.14×0.11×0.01	0.25×0.12×0.01
T / K	97(1)	97(1)	123(1)	123(1)	123(1)
D_{calc} / g·cm^{-3}	1.904	1.848	1.831	1.752	1.729
F_{000}	716.00	484.00	484.00	560.00	2144.00
λ / Å	0.71075	0.71075	0.71070	0.71070	0.71070
μ(Mo Kα) / cm^{-1}	14.940	9.648	9.557	8.152	8.364
data measured	8788	5824	9268	10870	18978
data unique	4382	3001	3621	4313	7260
R_{int}	0.0377	0.0162	0.0411	0.0693	0.0634
no. of observations	4382	3001	3621	4313	7260
no. of variables	371	253	262	316	596
$R1$ ($I > 2.00\sigma(I)$)^a	0.0419	0.0301	0.0304	0.0582	0.0686
R (all reflections)^a	0.0547	0.0312	0.0348	0.0758	0.0746
$wR2$ (all reflections)^b	0.1042	0.0852	0.0817	0.1700	0.1880
GOF	1.067	1.164	1.083	1.128	1.072
CCDC No.	1041309	1041314	1041317	1041319	1041312

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

Table S2. Magnetic parameters of novel [$\mathrm{Ru_2}^{\mathrm{II,II}}(\mathrm{Cl}_x\mathrm{PhCO_2})_4(\mathrm{THF})_2$] and [$\mathrm{Ru_2}^{\mathrm{II,II}}(\mathrm{F}_x\mathrm{PhCO_2})_4(\mathrm{THF})_2$] compounds obtained from the best-fit of χ vs. T data using a Curie equation for S = 1 with g = 2.00 (fix) and zJ' = 0 (fix) (see text).

Compound	D [K]	χ_{TIP} [× 10^{-6} cm^3 mol^{-1}]	ρ [× 10^{-3}]
_o_-Cl	338(2)	359(25)	21.3(1)
_m_-Cl	374.2(4)	42(4)	1.123(6)
_p_-Cl	358(5)	85(18)	2.58(3)
2,3-Cl$_2$	362.8(7)	62(7)	1.21(1)
2,4-Cl$_2$	361(2)	146(2)	3.58(3)
2,5-Cl$_2$	358.9(9)	32(9)	2.37(2)
2,6-Cl$_2$	341(2)	113(15)	9.8(1)
3,4-Cl$_2$	359.2(8)	9(9)	2.11(2)
3,5-Cl$_2$	334(3)	158(40)	22.45(8)
2,3,4-Cl$_3$	347(2)	12(26)	10.03(5)
2,3,5-Cl$_3$	373.9(3)	60(3)	0.374(5)
2,4,5-Cl$_3$	353(2)	132(18)	10.59(3)
3,4,5-Cl$_3$	358.2(7)	42(8)	2.05(1)
2,3,4,5-Cl$_4$	365(1)	55(15)	2.29(3)
2,3-F$_2$	333(1)	102(14)	1.92(3)
2,4-F$_2$	366.6(6)	46(6)	0.26(1)
2,5-F$_2$	349(1)	65(15)	5.90(3)
2,3,5-F$_3$	340.4(9)	192(11)	1.52(2)

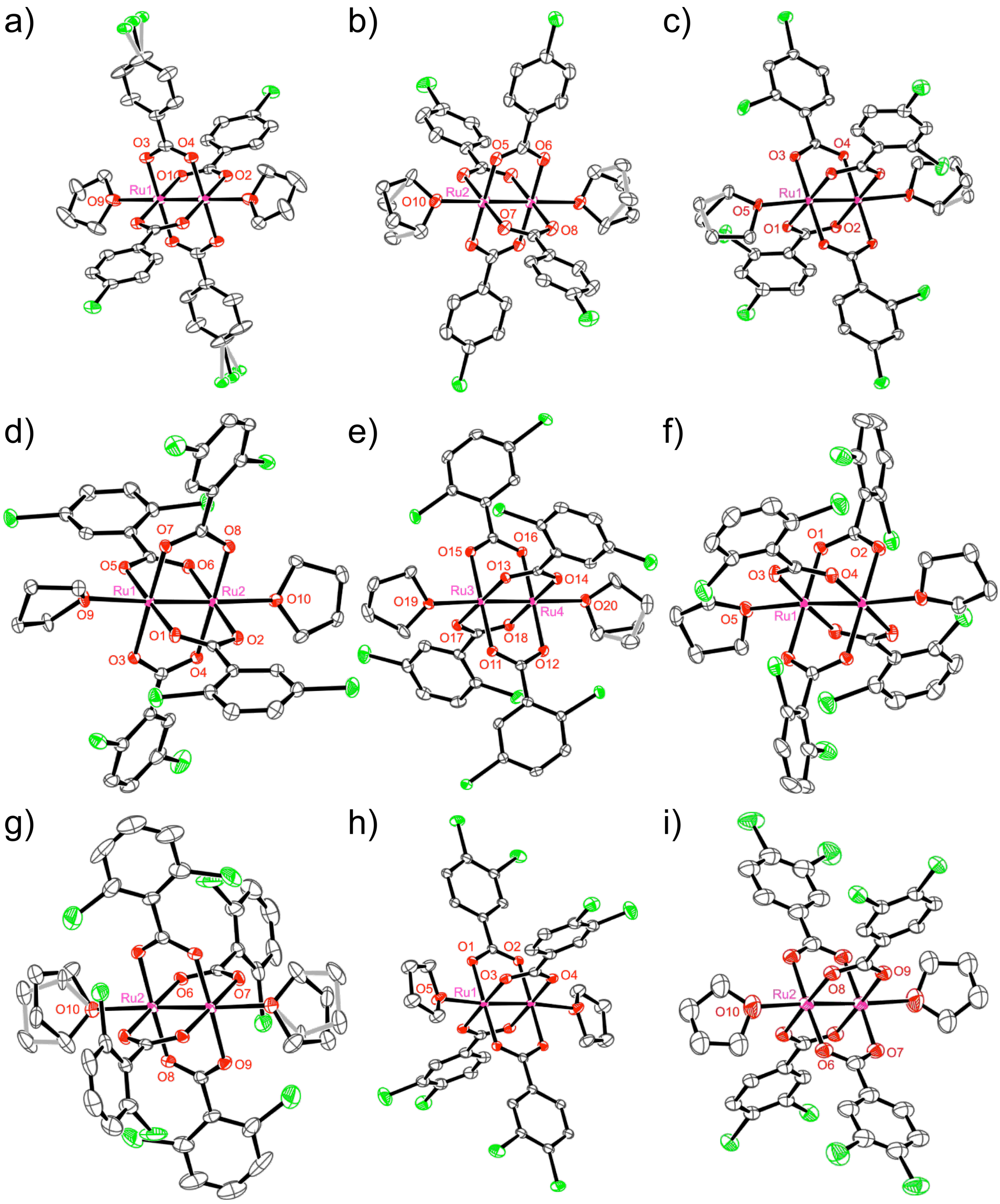

Fig. S1a. ORTEP drawings of structures of ***p*-Cl** (unit 1) (a), ***p*-Cl** (unit 2) (b), **2,4-Cl$_2$** (c), **2,5-Cl$_2$** (unit 1) (d), **2,5-Cl$_2$** (unit 2) (e), **2,6-Cl$_2$** (unit 1) (f), **2,6-Cl$_2$** (unit 2) (g), **3,4-Cl$_2$** (unit 1) (h), **3,4-Cl$_2$** (unit 1) (i) (50% ellipsoids probability level), where red, gray, green, and purple represent O, C, Cl, and Ru, respectively, and the gray bonds represent disordered atomic positions. Hydrogen atoms were omitted for clarity.

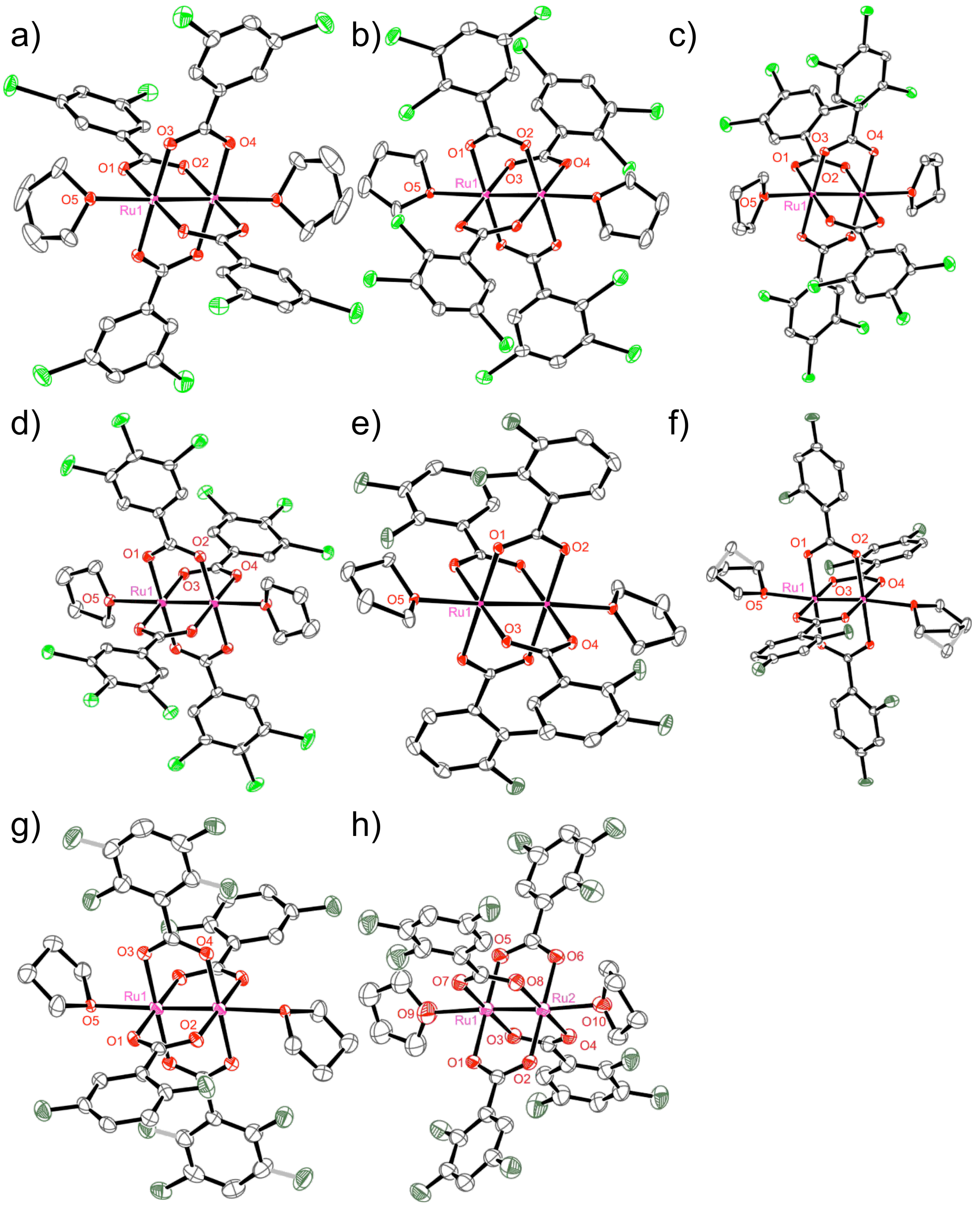

Fig. S1b. ORTEP drawings of structures of **3,5-Cl$_2$** (a), **2,3,5-Cl$_3$** (b), **2,4,5-Cl$_3$** (c), **3,4,5-Cl$_3$** (d), **2,3-F$_2$** (e), **2,4-F$_2$** (f), **2,5-F$_2$** (g), **2,3,5-F$_3$** (h) (50% ellipsoids probability level), where red, gray, green, and purple represent O, C, Cl, and Ru, respectively, and the gray bonds represent disordered atomic positions. Hydrogen atoms were omitted for clarity.

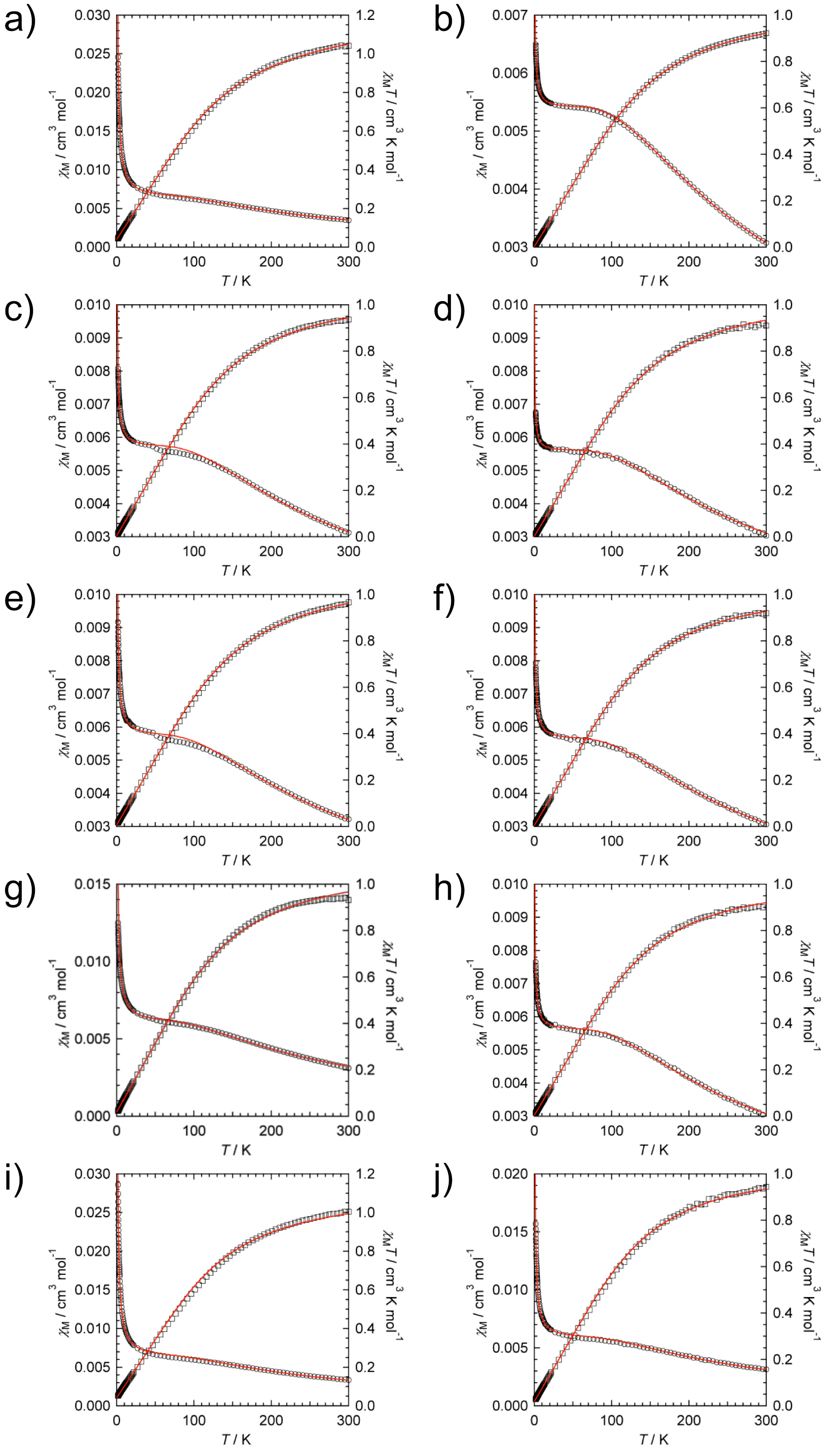

Fig. S2a. Temperature dependence of χ (○) and χT (□) for ***o*-Cl** (a), ***m*-Cl** (b), ***p*-Cl** (c), **2,3-Cl$_2$** (d), **2,4-Cl$_2$** (e), **2,5-Cl$_2$** (f), **2,6-Cl$_2$** (g), **3,4-Cl$_2$** (h), **3,5-Cl$_2$** (i), **2,3,4-Cl$_3$** (j), where the red solid lines represent simulated curves based on a Curie paramagnetic model with S = 1 taking into account zero-field splitting (D), temperature-independent paramagnetism (χ_{TIP}), and impurity with S = 3/2 (ρ).

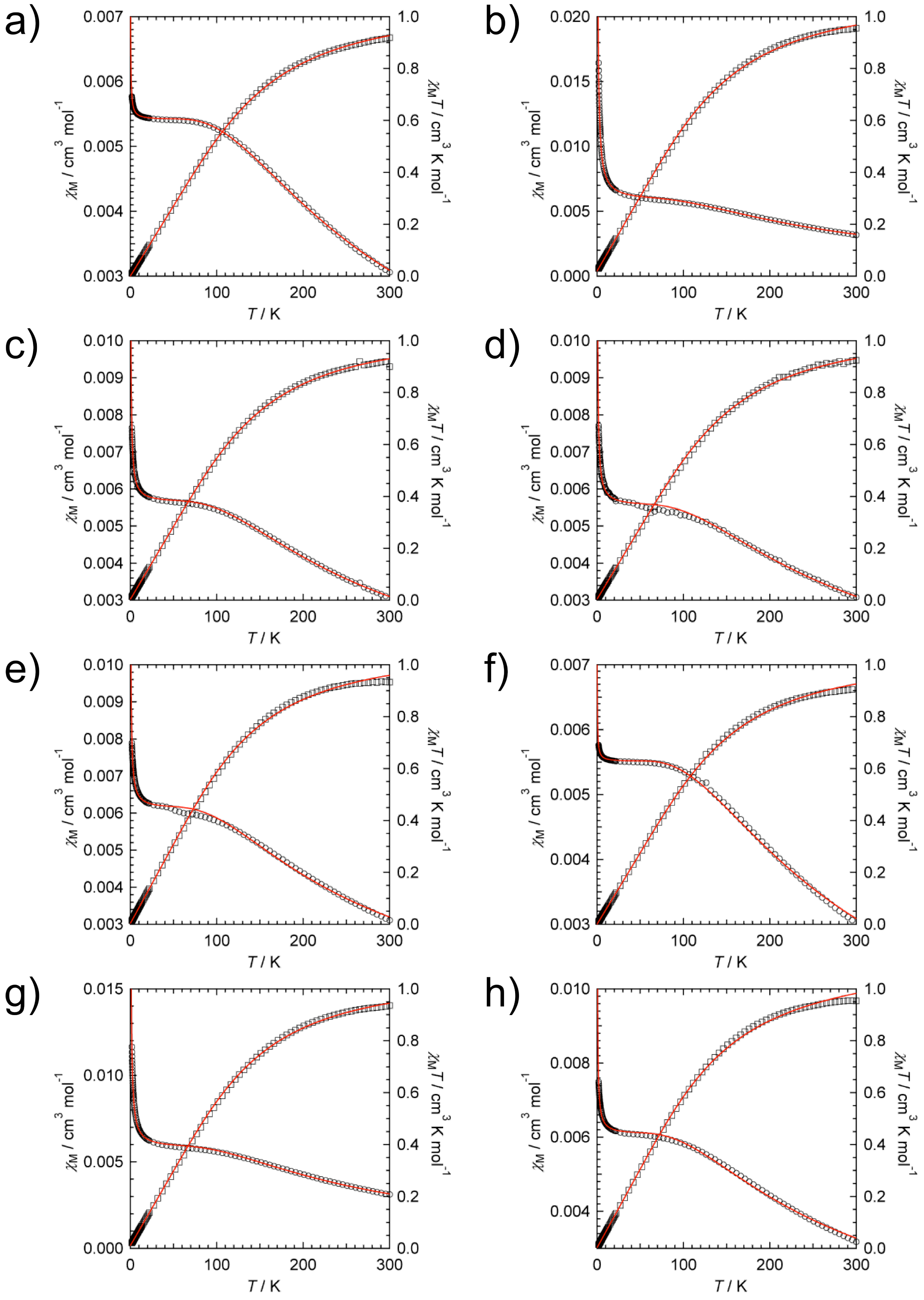

Fig. S2b. Temperature dependence of χ (○) and χT (□) for **2,3,5-Cl$_3$** (a), **2,4,5-Cl$_3$** (b), **3,4,5-Cl$_3$** (c), **2,3,4,5-Cl$_4$** (d), **2,3-F$_2$** (e), **2,4-F$_2$** (f), **2,5-F$_2$** (g), **2,3,5-F$_2$** (h), where the red solid lines represent simulated curves based on a Curie paramagnetic model with $S = 1$ taking into account zero-field splitting (D), temperature-independent paramagnetism (χ_{TIP}), and impurity with $S = 3/2$ (ρ).

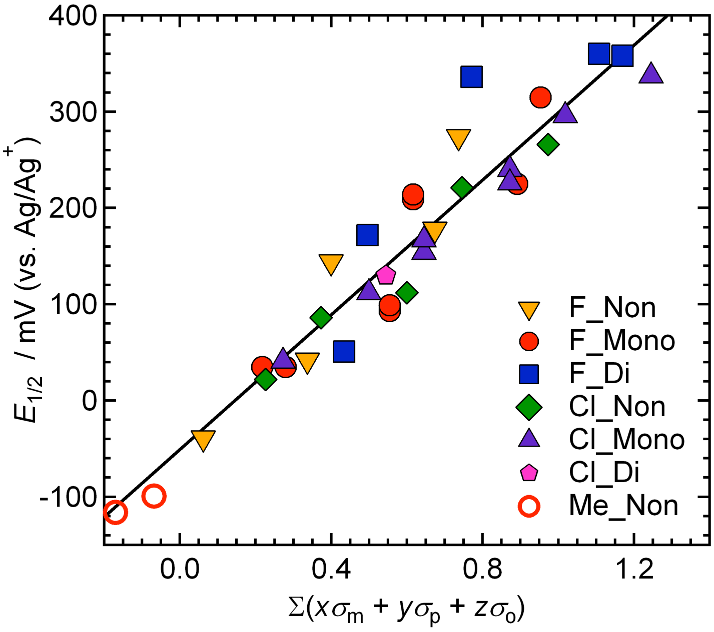

Fig. S3. A total plot of half-wave redox potential ($E_{1/2}$) vs. $\Sigma(x\sigma_m + y\sigma_p + z\sigma_o)$ including the Cl-, F-, and Me-series, where the green (yellow), violet (red), and pink (blue) plots represent non-Cl(F), mono-Cl(F), and di-*o*-Cl(F) substituted groups, respectively, and red circles are for the Me-substituted complexes (see text), and the solid lines represent the least-squares linear fitting line. $E_{1/2}$ and the values of $\Sigma(x\sigma_m + y\sigma_p)$ (a and b) and $\Sigma(x\sigma_m + y\sigma_p + z\sigma_o)$ of all compounds were listed in Table 4.

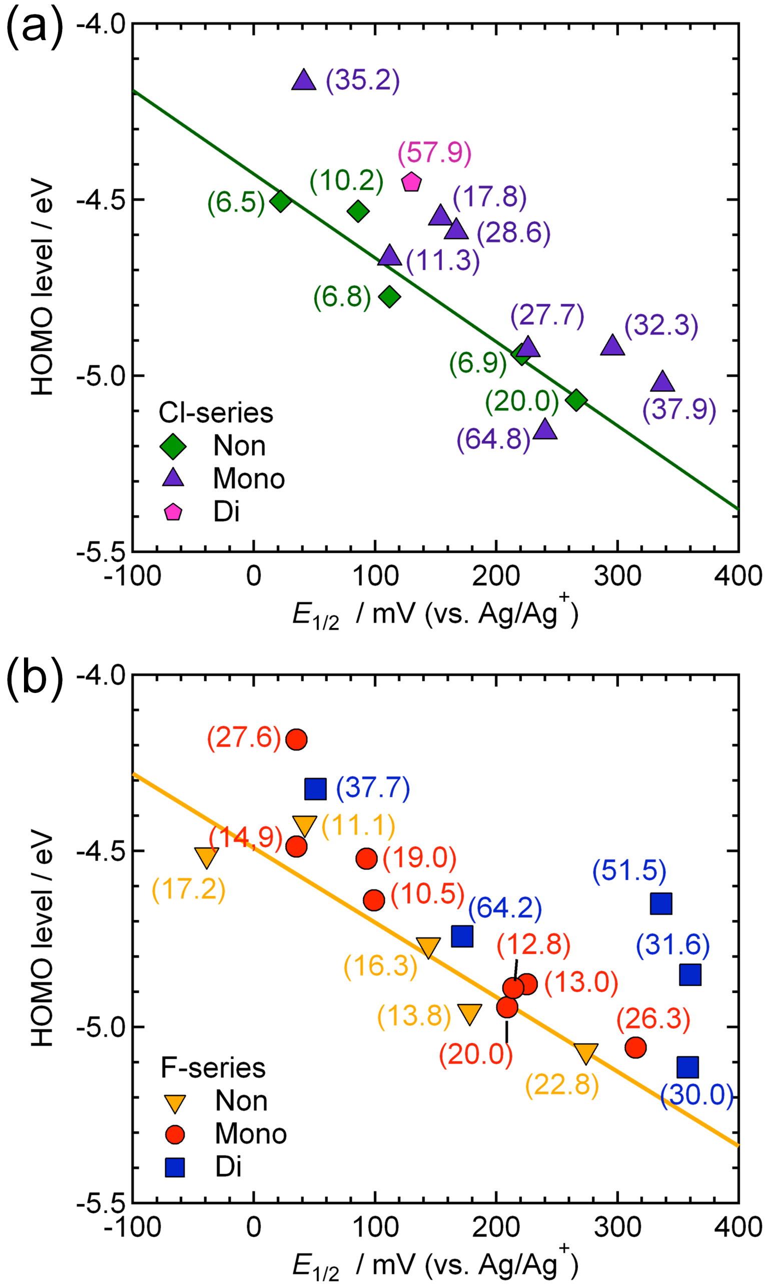

Fig. S4. Plots of HOMO level vs. $E_{1/2}$ for the Cl-series (a) and the F-series, where the green (yellow), violet (red), and pink (blue) plots represent non-Cl(F), mono-Cl(F), and di-*o*-Cl(F) substituted groups, respectively, and the solid lines represent the least-squares linear fitting line for the non-*o*-substituted group in respective series. Values attached to each plot represent the averaged dihedral angle (θ).

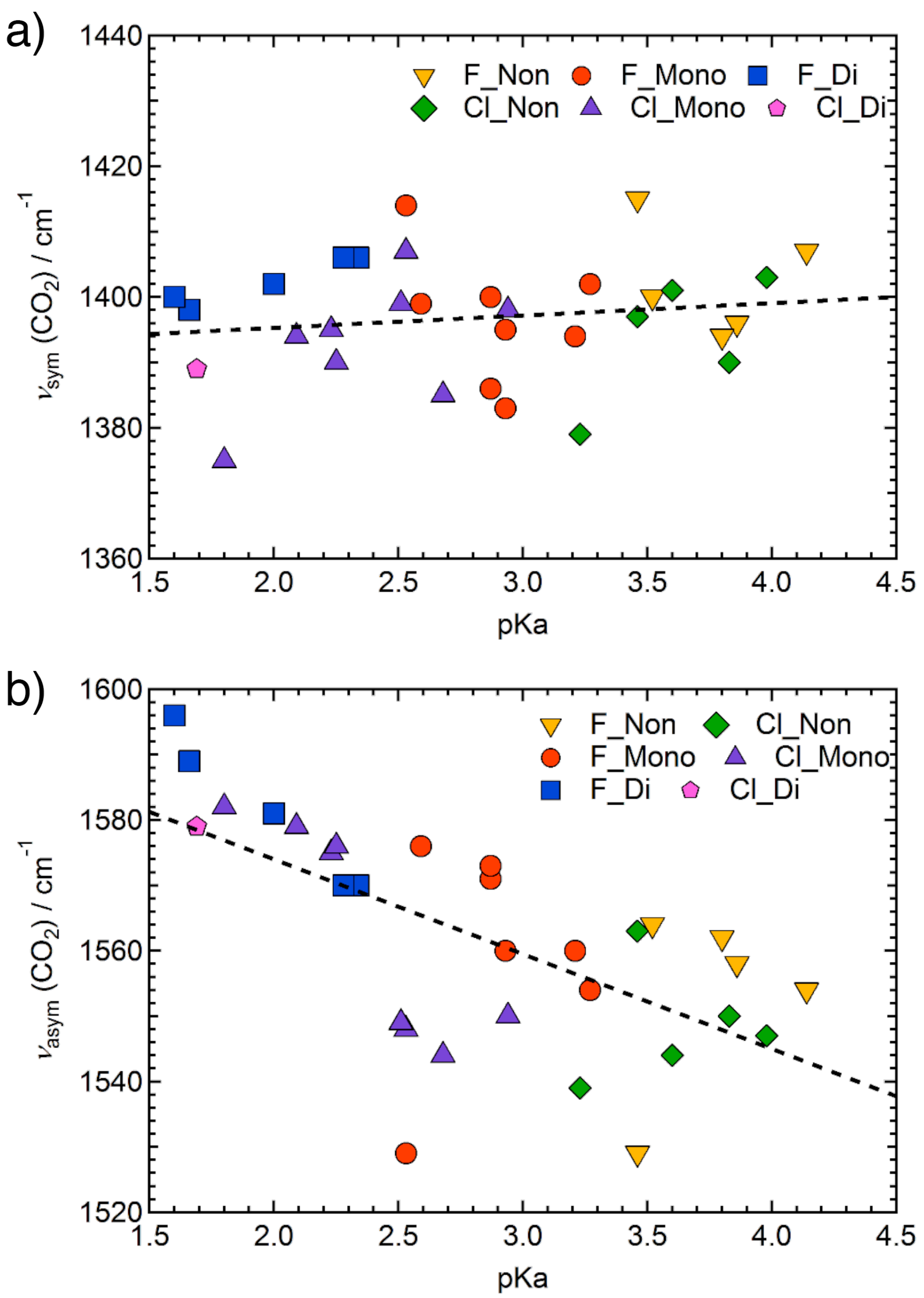

Fig. S5. The variation of frequencies of symmetrical mode (ν_{sym}; a) and asymmetrical mode (ν_{asym}; b) in carboxylate group of benzoate ligands in the Cl- and F-series. The dashed lines represent the least-squares average lines among all compounds.

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