Electronic Supporting Information

Valency engineering of ionic molecular crystals: Monovalent–divalent phase diagram for biferrocene–tetracyanoquinodimethane salts

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Table S1. Composition, valence state, intramolecular and intermolecular distances, overlap integral in the dimer, and acceptor charges in **1b**–**4c**.

Compound		Valence state	Fe–$Cp_{centroid}$/ Å	Intradimer A···A distances[a] / Å (S^b)	Interdimer A···A distances[a] / Å (S^b)	Acceptor charge[c]
1b[d]	$(I_2\text{-bifc})(Cl_1\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.686, 1.679	3.451	7.049	–0.61[e]
1c[d]	$(I_2\text{-bifc})(F_2\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.683, 1.673	3.406 (19.3×10^{-3})	7.010 (5.19×10^{-3})	–0.51
1d[d]	$(I_2\text{-bifc})(Cl_2\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.685, 1.677	3.506 (16.4×10^{-3})	7.114 (4.61×10^{-3})	–0.45
2a	$(MeSe_2\text{-bifc})(F_1\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.678, 1.674	3.404	7.090	–0.56
2b	$(MeSe_2\text{-bifc})(Cl_1\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.680, 1.671	3.414	7.207	–0.57[e]
3a	$(MeS_2\text{-bifc})(F_1\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.680, 1.674	3.394	6.973	–0.54
3b	$(MeS_2\text{-bifc})(Cl_1\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.681, 1.671	3.408	7.083	–0.40[e]
3c	$(MeS_2\text{-bifc})(F_2\text{-TCNQ})_2$	$[D]^{2+}[A_2]^{2-}$	1.709, 1.701	3.232 (27.6×10^{-3})	7.069 (4.34×10^{-3})	–0.88
3d	$(MeS_2\text{-bifc})(Cl_2\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.684, 1.678	3.500 (17.5×10^{-3})	7.253 (7.60×10^{-3})	–0.53
4b	$(Et_2\text{-bifc})(Cl_1\text{-TCNQ})_2$	$[D]^+[A_2]^-$	1.689, 1.673	3.421	6.962	–0.58[e]
4c	$(Et_2\text{-bifc})(F_2\text{-TCNQ})_2$	$[D]^{2+}[A_2]^{2-}$	1.712, 1.707	3.283 (25.2×10^{-2})	7.074 (3.38×10^{-3})	–0.98

[a]Centroid–centroid distances. [b]Overlap integrals calculated by the extended Hückel molecular orbital method for salts with non-disordered acceptors (Ref. 13). [c]Estimated from the bond lengths (Ref. 12). [d]Ref. 9. [e]The four bonds opposite to the dominant Cl site were used for the estimation.

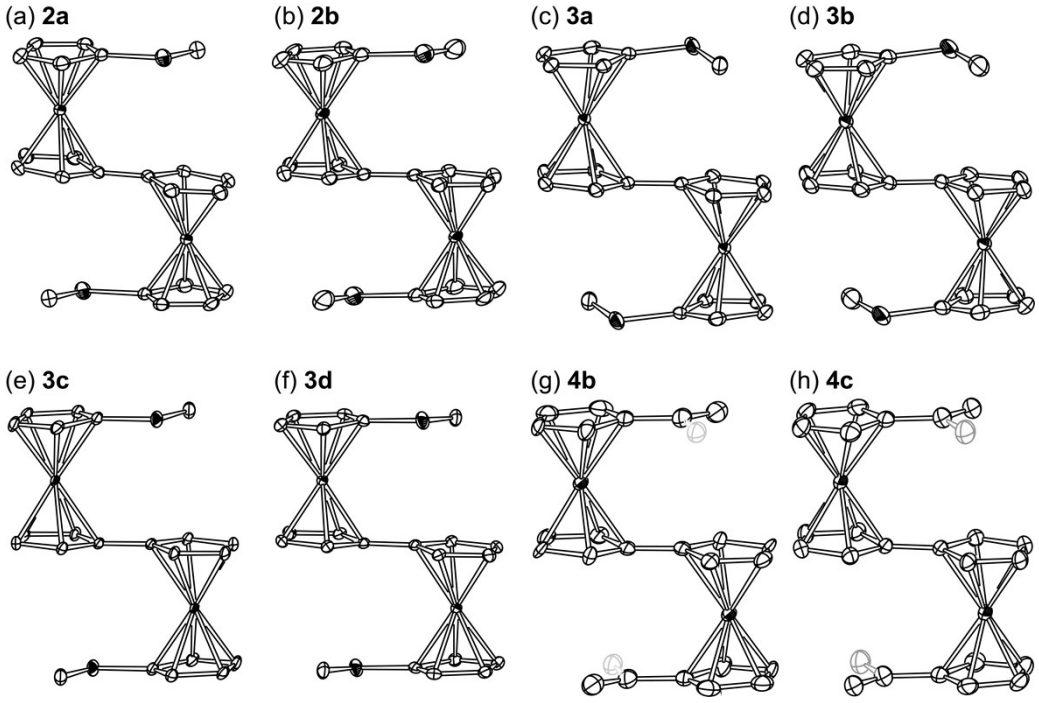

Fig. S1. Ortep drawings of the molecular structures of the cation in each salt. One of the disordered moieties in **4b** and **4c** are displayed in gray. Hydrogen atoms have been omitted for clarity.

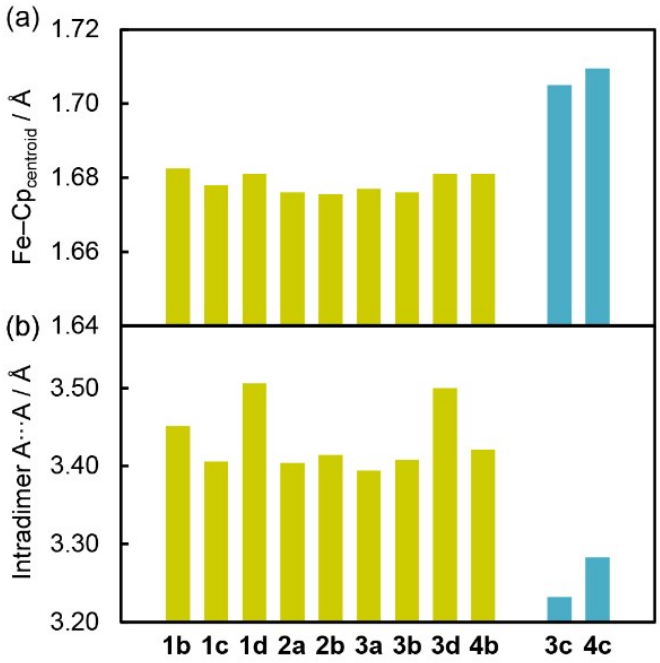

Fig. S2. (a) Average Fe–Cp$_{centroid}$ distances in the cation and (b) intermolecular distances (centroid–centroid) in the acceptor dimers in monovalent salts (yellow) and divalent salts (blue).

Table S2. Crystallographic Parameters.

	2a	**2b**	**3a**	**3b**
Empirical formula	C46H28F2Fe2N8Se2	C46H28Cl2Fe2N8Se2	C46H28F2Fe2N8S2	C46H28Cl2Fe2N8S2
Formula weight	1000.38	1033.28	906.58	939.48
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
a / Å	8.7623(9)	8.7700(12)	8.7638(7)	8.8205(8)
b / Å	9.1250(10)	9.2110(12)	9.0088(7)	9.0902(8)
c / Å	13.4315(14)	13.5822(19)	13.4894(11)	13.6352(13)
α / deg	90.012(2)	89.993(3)	90.103(2)	90.168(2)
β / deg	106.064(2)	75.599(3)	106.079(2)	104.444(2)
γ / deg	107.409(2)	71.823(3)	107.018(2)	107.949(2)
V / Å	980.68(18)	1006.1(2)	974.55(13)	1003.40(16)
Space group	*P*–1	*P*–1	*P*–1	*P*–1
Z value	1	1	1	1
D_{calc} / g cm^{-3}	1.694	1.705	1.545	1.555
F (000)	498	514	462	478
No. of reflections	7290	7433	7228	7478
No. of observations	4807	4946	4769	4941
Parameters	282	282	282	282
Temperature / K	173	173	173	173
R_1[a],R_w[b] ($I > 2\sigma$)	0.0410, 0.1039	0.0599, 0.1526	0.0438, 0.1068	0.0664, 0.1705
R_1[a],R_w[b] (all data)	0.0603, 0.1132	0.1001, 0.1787	0.0585, 0.1143	0.0805, 0.1809
Goodness of fit	1.052	1.059	1.048	1.046

[a]$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; [b]$R_w = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$

Table S3. Crystallographic Parameters.

	3c	**3d**	**4b**	**4c**
Empirical formula	C46H26F4Fe2N8S2	C46H26Cl4Fe2N8S2	C48H32Cl2Fe2N8	C48H30F4Fe2N8
Formula weight	942.57	1008.37	903.42	906.51
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
a / Å	8.7754(10)	8.8175(12)	8.654(3)	8.7951(13)
b / Å	9.0556(11)	9.1617(12)	9.111(3)	9.1673(13)
c / Å	13.2444(16)	13.8108(18)	13.738(4)	13.4002(18)
α / deg	91.068(2)	90.540(2)	89.225(5)	92.358(12)
β / deg	105.733(2)	103.988(2)	75.034(5)	104.633(12)
γ / deg	108.766(2)	109.5500(10)	73.200(5)	109.317(11)
V / Å	952.7(2)	1015.2(2)	999.6(5)	977.3(2)
Space group	*P*–1	*P*–1	*P*–1	*P*–1
Z value	1	1	1	1
D_{calc} / g cm^{-3}	1.643	1.649	1.501	1.540
F (000)	478	510	462	462
No. of reflections	6775	4872	4231	4780
No. of observations	4605	3535	3346	4487
Parameters	281	281	290	284
Temperature / K	173	150	173	296
R_1[a],R_w[b] ($I > 2\sigma$)	0.0465, 0.1149	0.0373, 0.0839	0.0783, 0.1838	0.0314, 0.0768
R_1[a],R_w[b] (all data)	0.0600, 0.1227	0.0500, 0.0911	0.1437, 0.2199	0.0433, 0.0811
Goodness of fit	1.036	1.027	0.969	1.020

[a]$R_1 = \Sigma|| F_o | - |F_c|| / \Sigma| F_o |$; [b]$R_w = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$

Table S5. Redox potentials of acceptors (in V vs. $[FeCp_2]^{0/+}$) measured in CH_2Cl_2 solutions containing Bu_4NClO_4 (0.1 mol dm^{-3}) as the supporting electrolyte (scan rate 0.1 Vs^{-1}).

Table S4. Redox potentials of donors (in V vs. $[FeCp_2]^{0/+}$) measured in CH_2Cl_2 solutions containing Bu_4NClO_4 (0.1 mol dm^{-3}) as the supporting electrolyte (scan rate 0.1 Vs^{-1}).

	Bifc$^{+/0}$			Bifc$^{2+/+}$			
Compound	E_p^a	E_p^c	$E_{1/2}^1$	E_p^a	E_p^c	$E_{1/2}^2$	$\Delta E_{1/2}$
I_2-bifc (**1**)	0.09	0.02	0.06	0.40	0.31	0.35	0.30
$SeMe_2$-Bifc (**2**)	–0.04	–0.11	–0.08	0.23	0.17	0.20	0.28
SMe_2-Bifc (**3**)	–0.06	–0.15	–0.11	0.23	0.13	0.18	0.29
Et_2-bifc (**4**)	–0.13	–0.20	–0.16	0.22	0.14	0.18	0.34

	[A]$^{-/0}$			[A]$^{2-/-}$			
Compound	E_p^a	E_p^c	$E_{1/2}^1$	E_p^a	E_p^c	$E_{1/2}^2$	$\Delta E_{1/2}$
F_1-TCNQ (**a**)	–0.06	–0.14	–0.10	–0.60	–0.74	–0.67	0.57
Cl_1-TCNQ (**b**)	–0.04	–0.11	–0.07	–0.55	–0.66	–0.61	0.53
F_2-TCNQ (**c**)	0.03	–0.05	–0.01	–0.51	–0.63	–0.57	0.56
Cl_2-TCNQ (**d**)	0.07	0.00	0.03	–0.43	–0.55	–0.49	0.52

Table S6. Unit cell volumes of **3a**–**c** at different temperatures.

compound	V (293 K) / Å^3	V (173 K) / Å^3	ΔV/ Å^3
3a	992.3	974.6	–17.8 (–1.8%)
3b	1026.2	1003.4	–22.8 (–2.2%)
3c	969.3	952.7	–16.6 (–1.7%)