Electronic Supplementary Information for Dalton Transactions

Supplementary Information

Tuning of the ionization potential of paddlewheel diruthenium(II, II) complexes with fluorine atoms on the benzoate ligands

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Table S1 Crystallographic data of **2,4,5-F_3-NDMA** and **3,4,5-F_3-NDMA**

	2,4,5-F_3-NDMA	**3,4,5-F_3-NDMA**
formula	$C_{62}H_{52}N_4O_8F_{12}Ru_2$	$C_{70}H_{68}N_4O_{10}F_{12}Ru_2$
formula weight	1411.24	1555.45
crystal system	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$
a / Å	9.172(4)	12.153(5)
b / Å	28.238(12)	20.238(8)
c / Å	11.634(6)	13.955(6)
α / deg	90	90
β / deg	104.482(9)	109.579(5)
γ / deg	90	90
V / Å^3	2918(2)	3234(2)
Z	2	2
crystal size	0.10 × 0.10 × 0.05	0.25 × 0.15 × 0.15
T / K	93(1)	93(1)
D_{calc} / g·cm^{-3}	1.606	1.597
F_{000}	1424.00	1584.00
λ / Å	0.71070	0.71070
μ(Mo Kα) / cm^{-1}	6.158	5.659
data measured	22297	24649
data unique	6552	7144
R_{int}	0.081	0.060
no. of observations	6552	7144
no. of variables	423	443
$R1$ ($I > 2.00s(I)$)[a]	0.0615	0.0434
R (all reflections)[a]	0.01169	0.0670
$wR2$ (all reflections)[b]	0.1184	0.1117
GOF	0.956	1.027
Flack Parameter	–	–
CCDC No.	766139	766143

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

Table S2 Estimated energy levels (eV) of π*- and δ*-characteristic orbitals for $[Ru_2^{II,II}(F_xPhCO_2)_4(THF)_2]$

Electron character	Orbital character	***o*-F**	***m*-F**	***p*-F**	**2,6-F_2**	**3,4-F_2**	**3,5-F_2**	**2,3,4-F_3**
β	π*	-1.485	-1.775	-1.826	-1.765	-2.038	-2.345	-2.442
	π*	-1.606	-1.882	-1.921	-1.803	-2.155	-2.430	-2.542
	δ*	-4.101	-4.346	-4.397	-4.310	-4.632	-4.916	-4.994
α	δ*	-4.538	-4.785	-4.833	-4.740	-5.068	-5.348	-5.416
	π*	-4.688	-4.992	-5.046	-4.961	-5.253	-5.538	-5.584
	π*	-4.838	-5.123	-5.161	-5.000	-5.404	-5.661	-5.718

Electron character	Orbital character	**2,3,6-F_3**	**2,4,5-F_3**	**2,4,6-F_3**	**3,4,5-F_3**	**2,3,4,5-F_4**	**2,3,5,6-F_4**	**F_5**
β	π*	-1.901	-2.340	-2.095	-2.691	-3.122	-2.120	-2.531
	π*	-2.005	-2.459	-2.226	-2.840	-3.267	-2.259	-2.676
	δ*	-4.543	-4.929	-4.714	-5.242	-5.640	-4.766	-5.135
α	δ*	-4.980	-5.354	-5.139	-5.662	-6.056	-5.206	-5.563
	π*	-5.139	-5.489	-5.286	-5.817	-6.209	-5.340	-5.654
	π*	-5.261	-5.644	-5.438	-5.999	-6.415	-5.499	-5.862

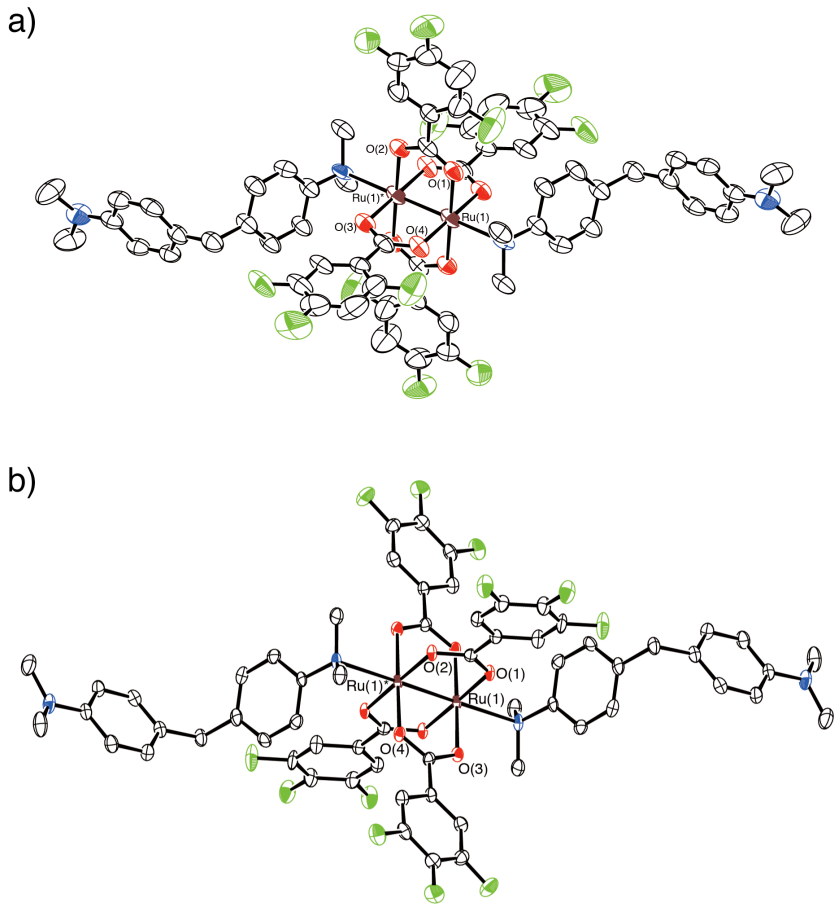

Fig. S1 ORTEP drawings of complexes bearing NDMA-me-NDMA in axial positions: $[Ru_2^{II,II}(2,4,5\text{-}F_3PhCO_2)_4(NDMA\text{-}me\text{-}NDMA)_2]$ (**2,4,5-F_3-NDMA**) (a) and $[Ru_2^{II,II}(3,4,5\text{-}F_3PhCO_2)_4(NDMA\text{-}me\text{-}NDMA)_2]$ (**3,4,5-F_3-NDMA**) (b), where NDMA-me-NDMA stands for 4,4'-methylenebis(*N*,*N*-dimethylaniline) (50 % probability thermal ellipsoids; symmetry operations (*) $-x, -y+1, -z+1$ for **2,4,5-F_3-NDMA**; $-x+1, -y+1, -z+1$ for **3,4,5-F_3-NDMA**).

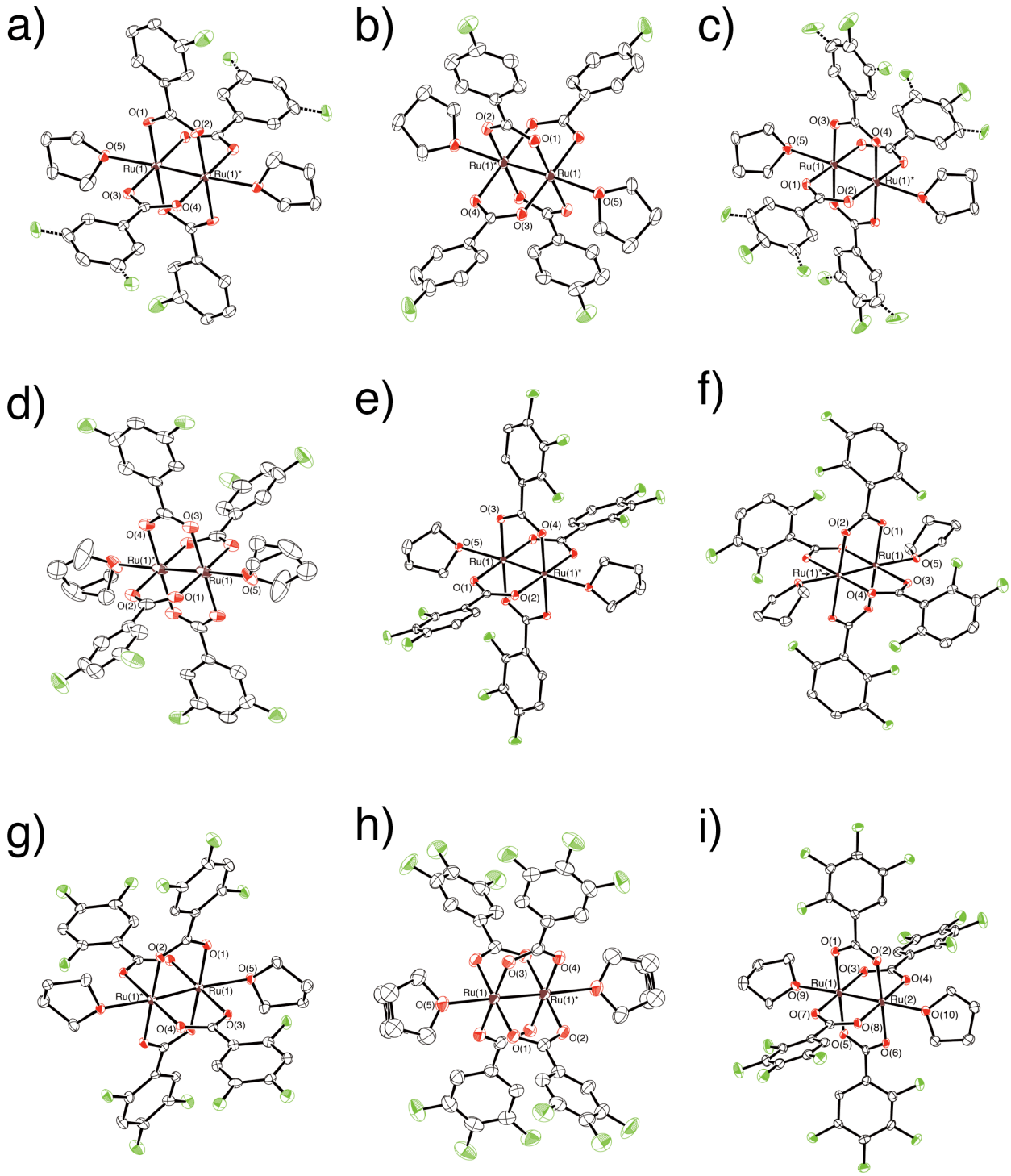

Fig. S2 ORTEP drawings of (a) ***m*-F**, (b) ***p*-F**, (c) **3,4-F$_2$**, (d) **3,5-F$_2$**, (e) **2,3,4-F$_3$**, (f) **2,3,6-F$_3$**, (g) **2,4,5-F$_3$**, (h) **3,4,5-F$_3$**, and (i) **2,3,4,5-F$_4$**, where the dotted bonds for F atoms represent disordered atomic positions (50 % probability thermal ellipsoids; symmetry operations (*) $-x+2, -y, -z$ for ***m*-F**; $-x+1, -y+1, -z+2$ for ***p*-F**; $-x+1, -y+2, -z+1$ for **3,4-F$_2$** and **3,5-F$_2$**; $-x+1, -y+1, -z+1$ for **2,3,4-F$_3$**, **2,4,5-F$_3$**, and **3,4,5-F$_3$**; $-x+1, -y, -z+1$ for **2,3,6-F$_3$**).

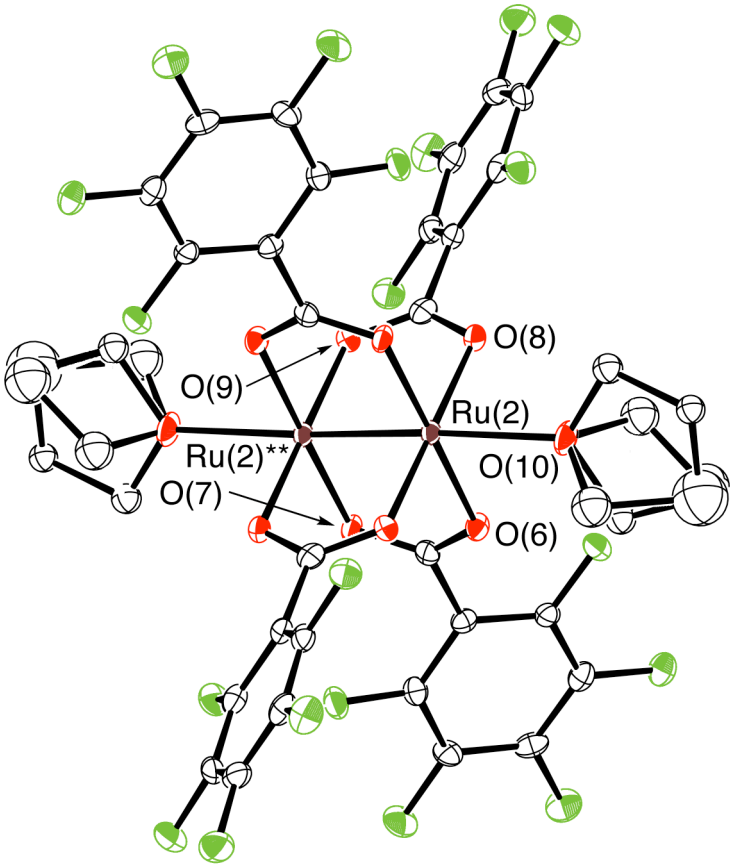

Fig. S3 ORTEP drawing of the other unit of $\mathbf{F_5}$ (one is depicted in Fig. 1e; 50 % probability thermal ellipsoids; symmetry operation (**) $-x+1, -y, -z+2$).

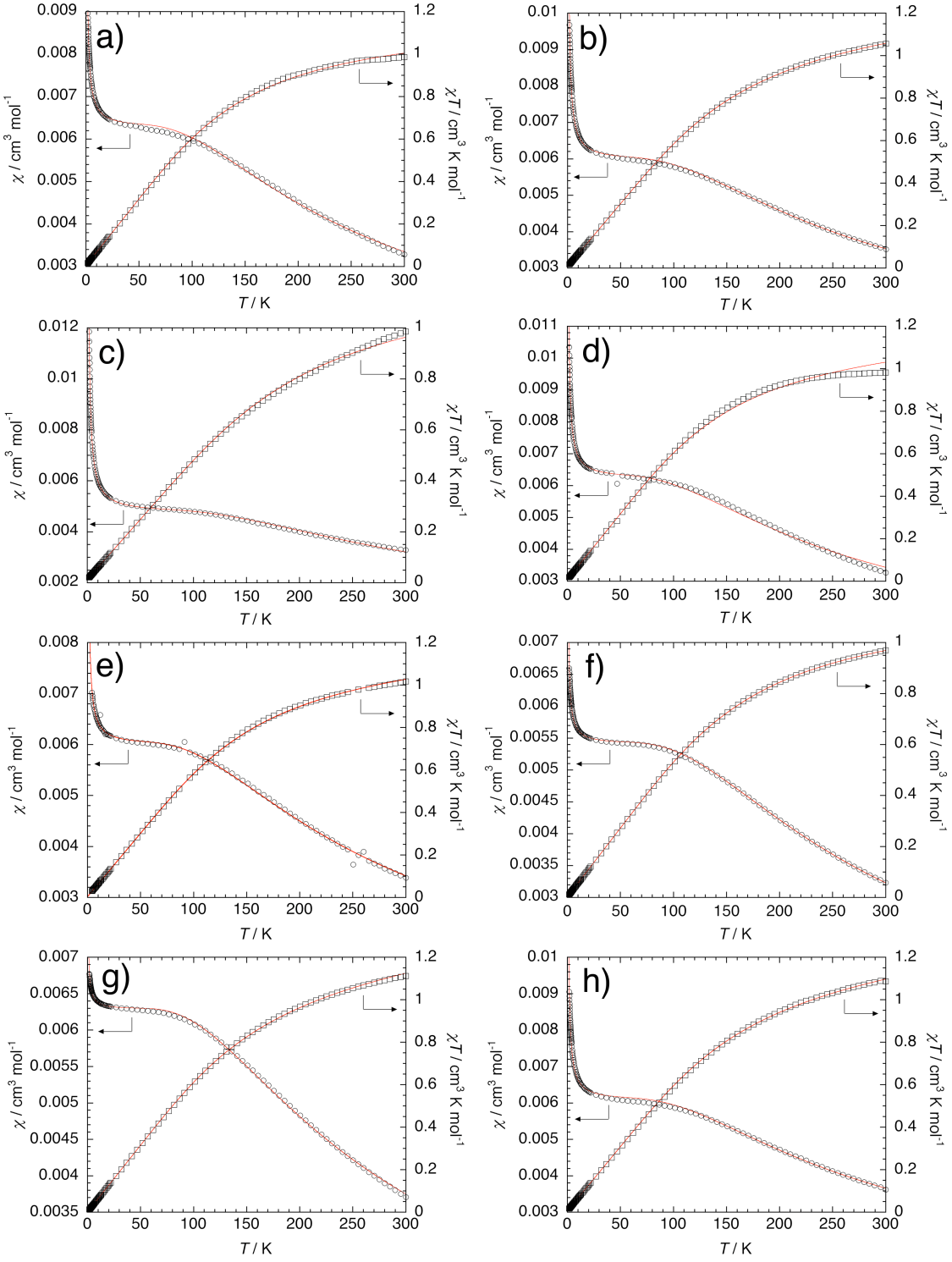

Fig. S4a χ and χT vs. T plots of ***o*-F** (a), ***m*-F** (b), ***p*-F** (c), **2,6-F$_2$** (d), **3,4-F$_2$** (e), **3,5-F$_2$** (f), **2,3,4-F$_3$** (g), and **2,3,6-F$_3$** (h).

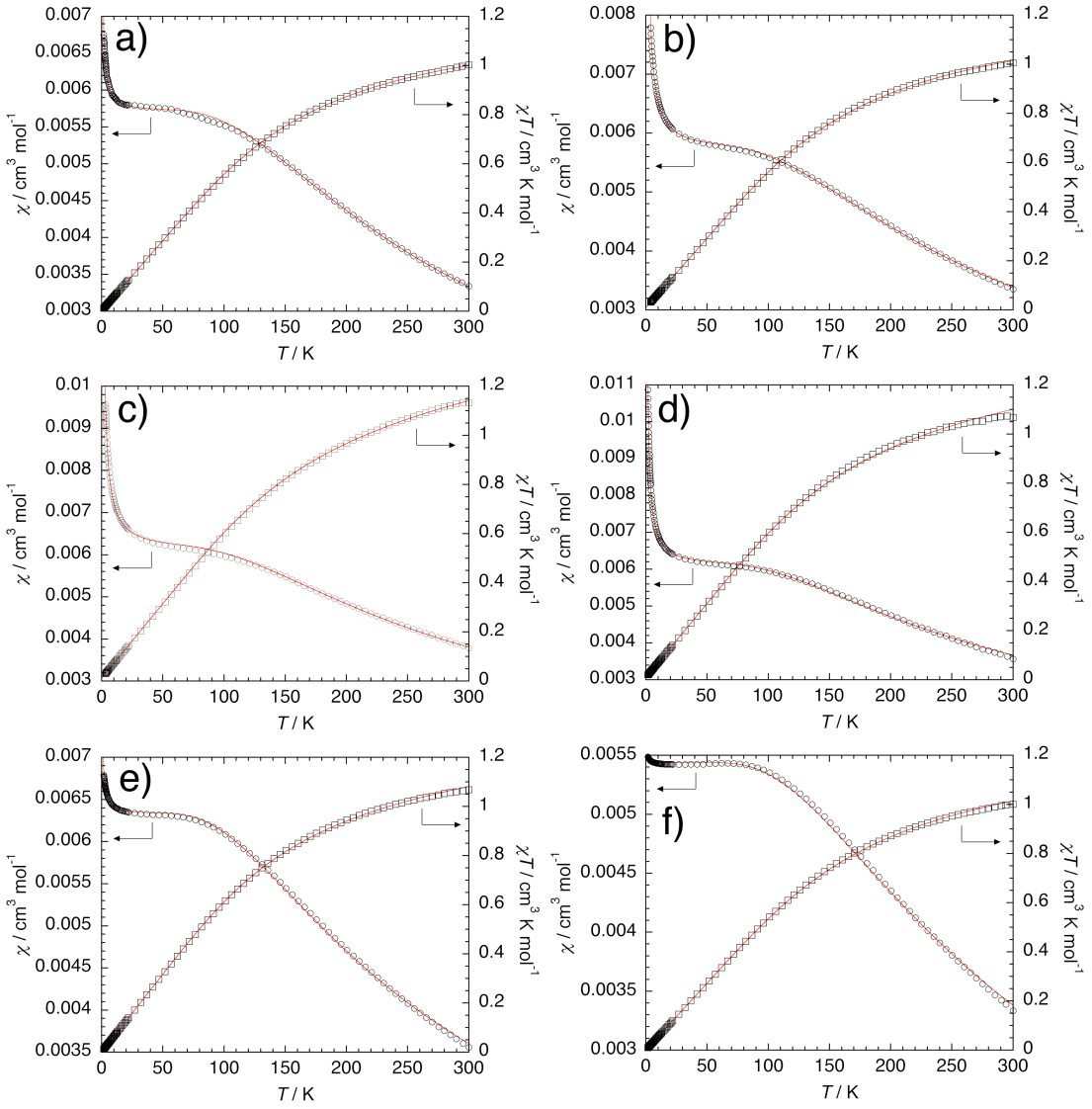

Fig. S4b χ and χT vs. T plots of **2,4,5-F$_3$** (a), **2,4,6-F$_3$** (b), **3,4,5-F$_3$** (c), **2,3,4,5-F$_4$** (d), **2,3,5,6-F$_4$** (e), and **F$_5$** (f).

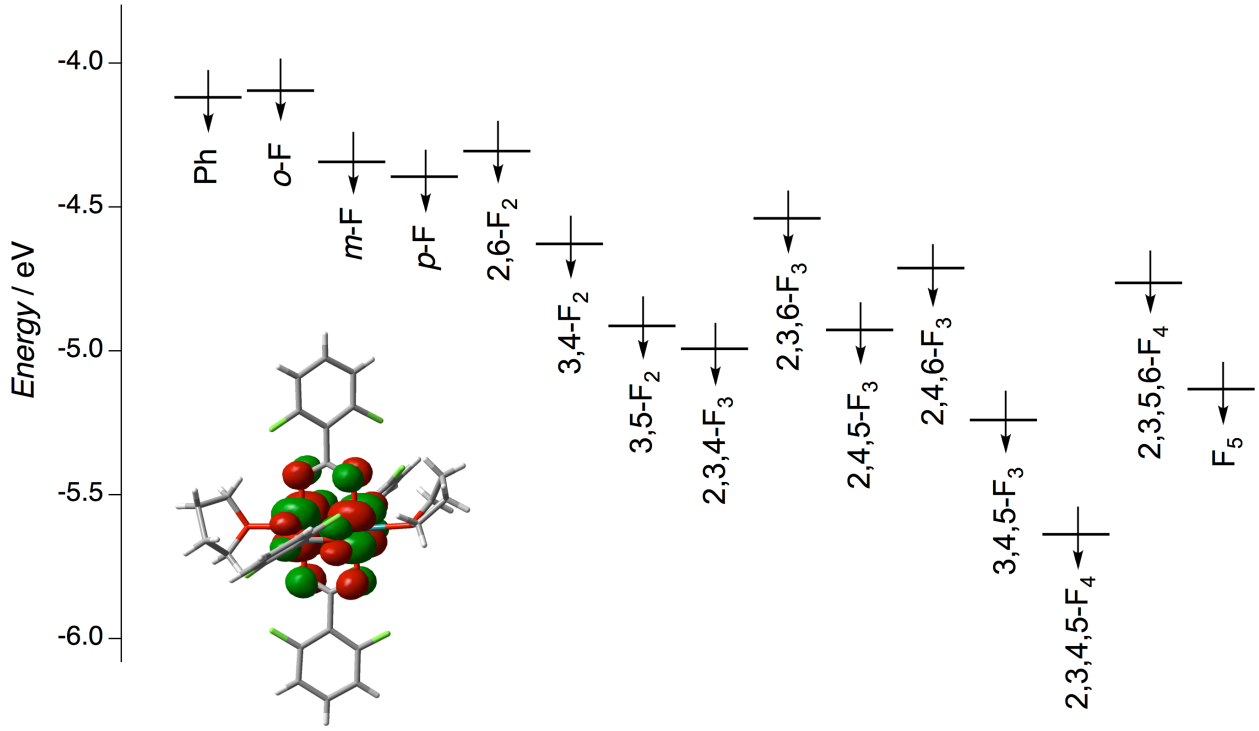

Fig. S5 The energy level (eV) of a frontier orbital (β spin) associated with δ^* orbital of the diruthenium units, for which the actual value is given in Table S1. The illustration (**2,6-F_2**) displays a represent example of the frontier orbital with the β spin.