Supporting Information

for

The Halogen Effect on the Magnetic Behaviour of Dimethylformamide Solvates in $[Fe(halide\text{-}salEen)_2]BPh_4$

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Table S1. Crystallographic data and refinement details for complexes **1** and **3** at 150(2) K.

	1 (150 K)	**3** (150 K)
Formula	$C_{49}H_{55}BBr_2FeN_5O_3$	$C_{52}H_{62}BF_2FeN_6O_4$
Molar mass / g·mol^{-1}	988.46	939.73
λ / Å	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group[25]	$P2_12_12_1$	$P2_1/n$
a / Å	15.6150(12)	14.401(6)
b / Å	15.0250(12)	18.570(7)
c / Å	19.8280(16)	19.138(8)
β / °	90	107.239(9)
V (Å^3)	4652.0(6)	4888(3)
Z	4	4
ρ_{calc} / g·cm^{-3}	1.411	1.277
μ / mm^{-1}	2.089	0.367
Crystal size / mm	0.30 x 0.25 x 0.20	0.30 x 0.20 x 0.16
Crystal colour	Brown	Red
Crystal description	Block	Prism
θ_{max} / °	25.240	25.350
No. of reflections	55132	65384
No. of unique reflections	8264	8932
R_{int}	0.0934	0.4023
R_1 [I>2σ(I)]	0.0375	0.1203
wR_2 (all data)	0.0712	0.3018
GooF (all data)	1.005	1.011
ρ_{min}	-0.501	-0.962
ρ_{max}	0.404	0.897

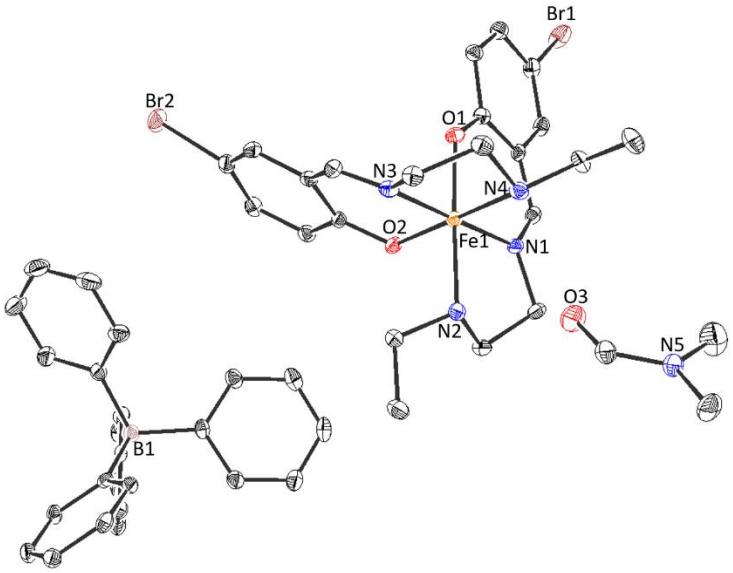

Figure S1. ORTEP-3 diagram of **1** (150 K), using 30% probability level ellipsoids. Hydrogen atoms are omitted for clarity.

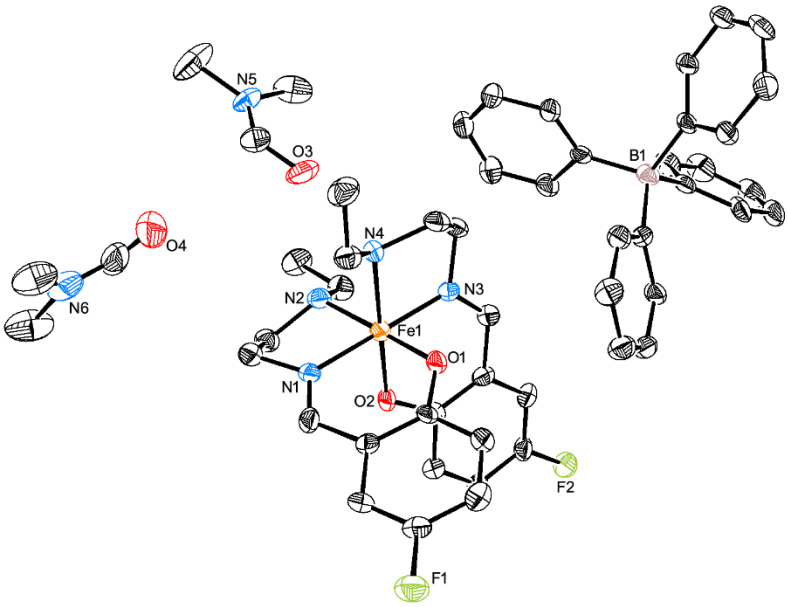

Figure S2. ORTEP-3 diagram of complex **3** (150 K), using 30% probability level ellipsoids. Hydrogen atoms are omitted for clarity.

Table S2. Hydrogen bonds for complexes **1**, **2**, and **3** at room temperature in Å and °.

	D-H...A	d(H...A)	d(D...A)	<(DHA)
1	N2–H1···O3	2.21(5)	2.947(8)	177(5)
	N4–H3···O3	2.08(6)	2.943(7)	165(5)
1 (150 K)	N2–H2···O3	1.92(5)	2.882(8)	160(5)
	N4–H4···O3	2.03(6)	2.870(10)	164(7)
2	N2–H1···O3	2.01(4)	2.913(5)	156(4)
	N4–H3···O3	1.91(4)	2.874(5)	168(5)
3	N2–H1···O3	2.14(4)	2.952(6)	169(3)
	N4–H4···O3	2.21(4)	2.977(5)	166(3)
3 (150 K)	N2–H2···O3	2.08(4)	2.914(5)	163(4)
	N4–H4···O3	2.62(5)	2.901(6)	160(4)
	C4–H4A···O4	2.54	3.406(14)	146
	C47–H47A···O4	2.39	3.108(15)	132

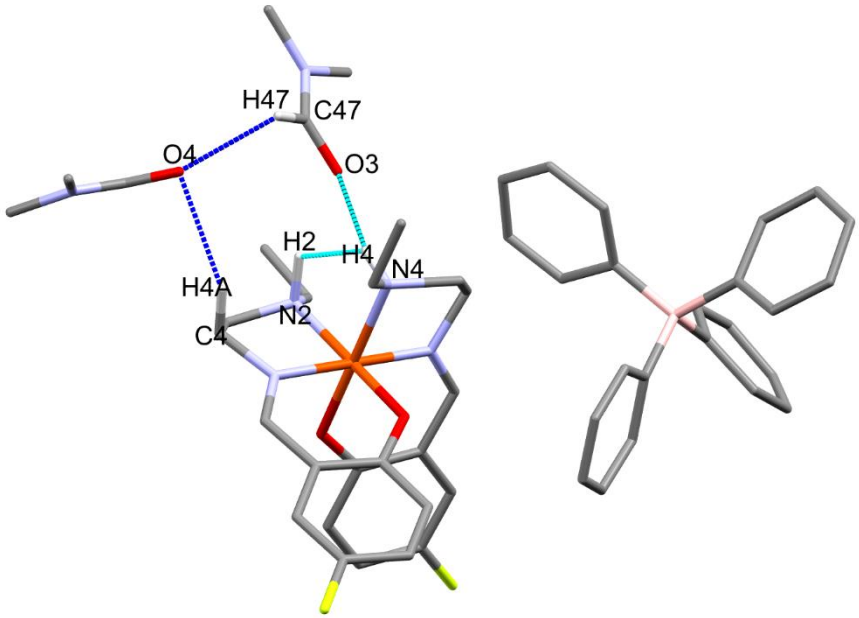

Figure S3. Crystal packing of complex **3** displaying the hydrogen bonds between the DMF solvent molecule and the NH groups of the cation, observed at 150 K. Light-blue dashed lines and dark blue dashed lines represent N–H···O and C–H···O hydrogen bonds, respectively.

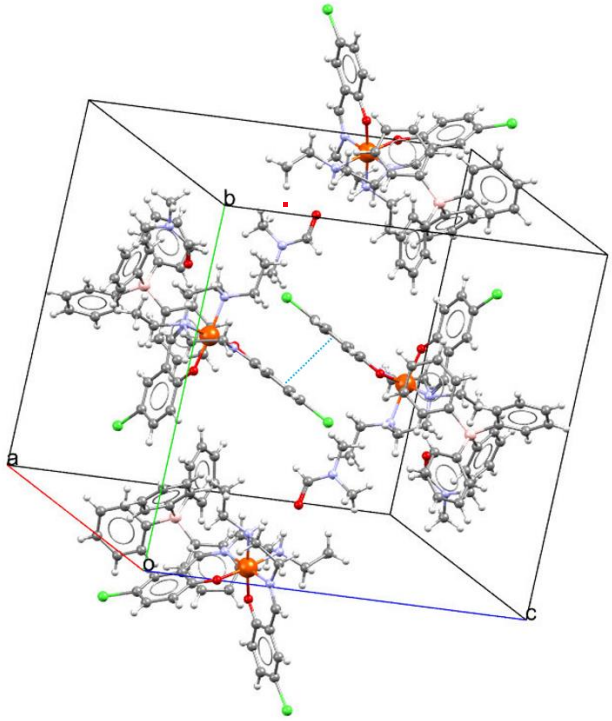

Figure S4. Unit cell of complex **2** showing π–π stacking in a dashed blue line.

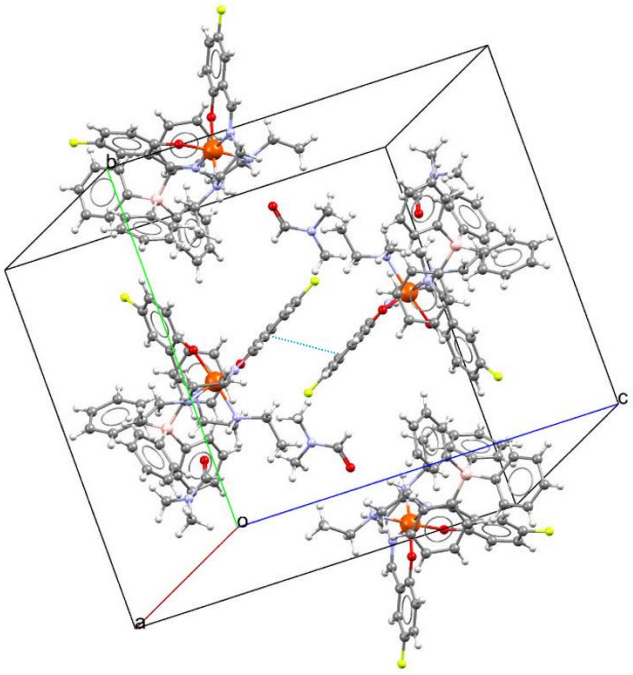

Figure S5. Unit cell of complex **3** showing π–π stacking in a dashed blue line.

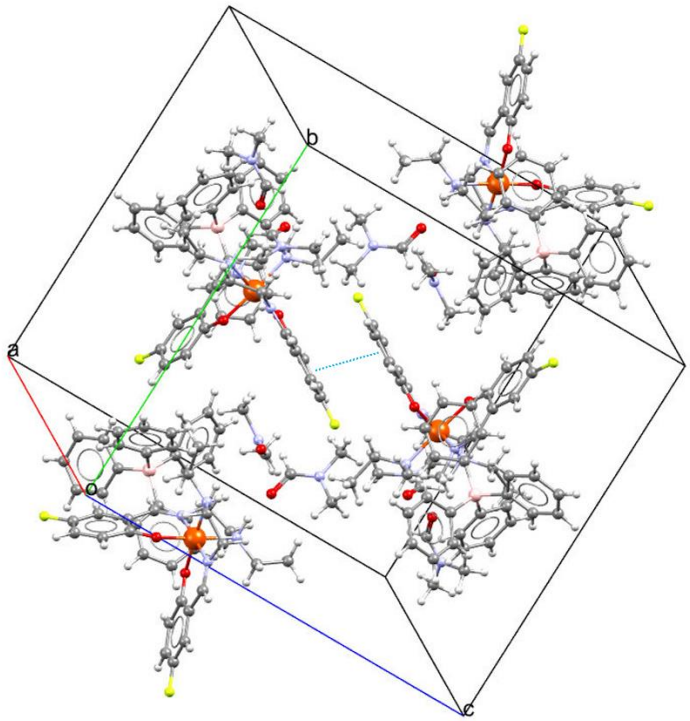

Figure S6. Unit cell of complex **3** (150 K) showing π–π stacking in a dashed blue line.

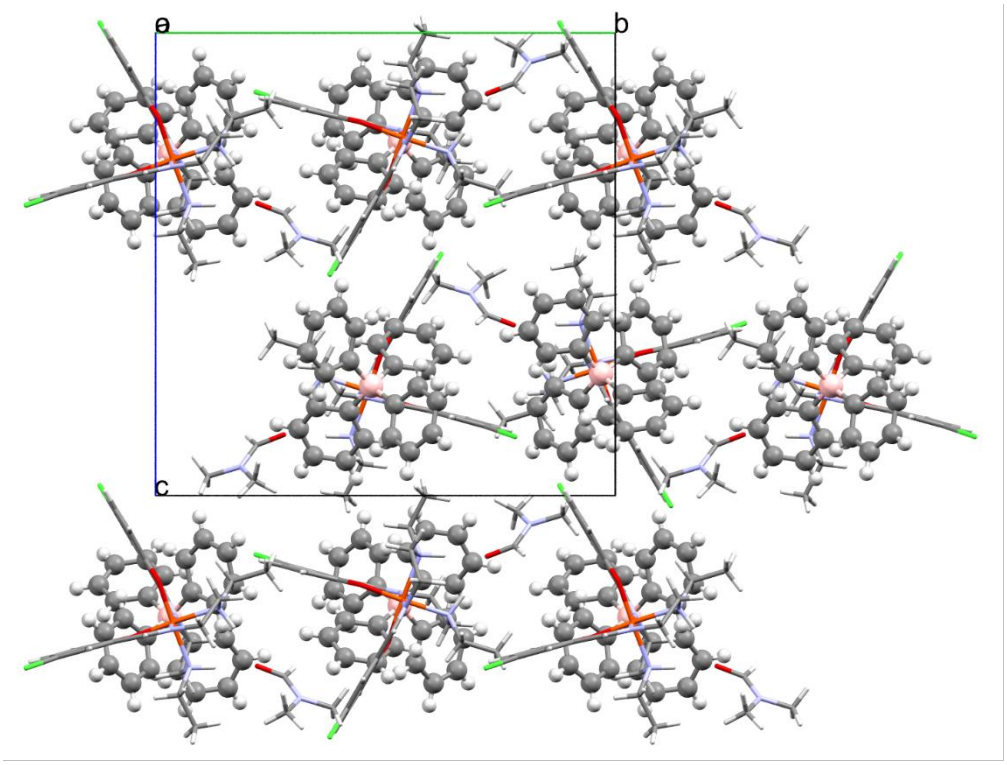

Figure S7. Crystal packing of complex **2** viewed along the crystallographic direction *a* with atoms of BPh_4^- anions drawn as spheres showing the formation of consecutive rows.

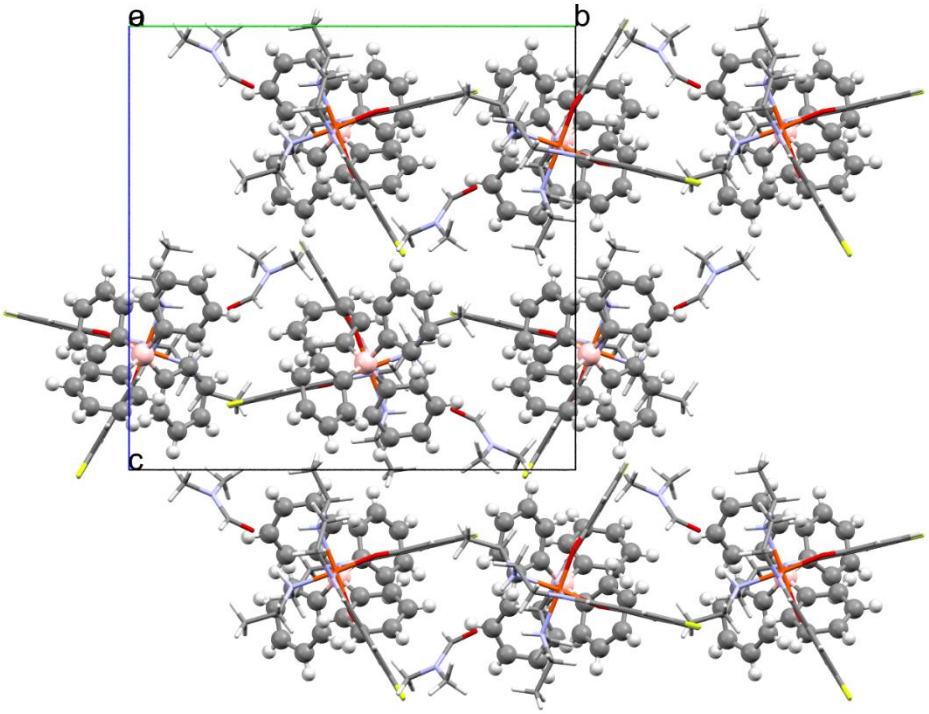

Figure S8. Crystal packing of complex **3** at room temperature viewed along the crystallographic direction *a* with atoms of BPh_4^- anions drawn as spheres showing the formation of consecutive rows.

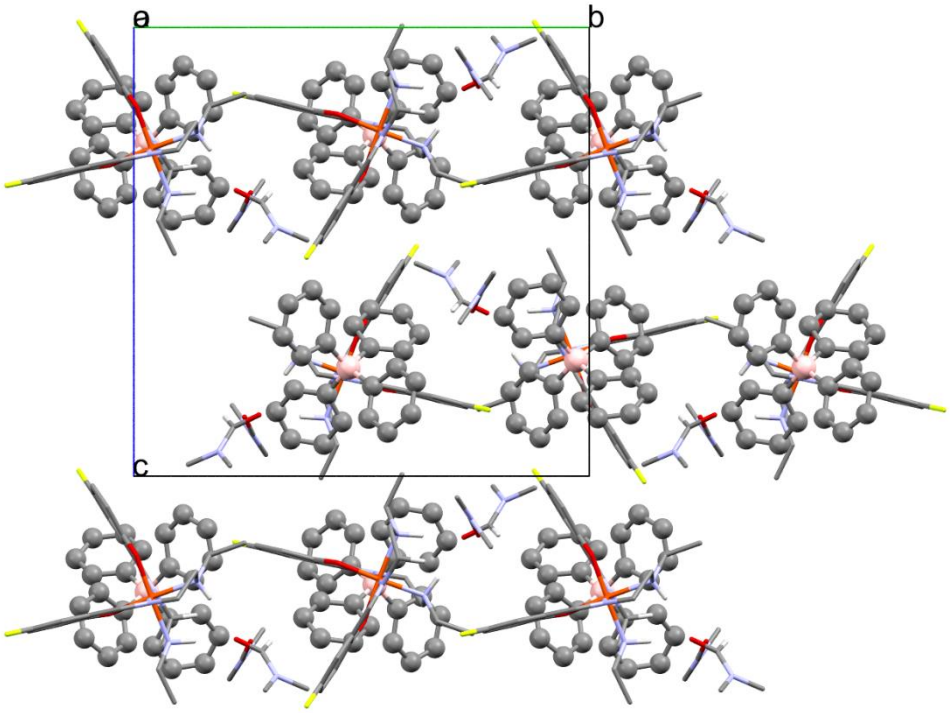

Figure S9. Crystal packing of complex **3** at 150 K viewed along the crystallographic direction *a* with atoms of BPh_4^- anions drawn as spheres showing the formation of consecutive rows.

Table S3. Relevant distances (Å) calculated (ADF, B3LYP*/TZP) for the three molecular models (CA, CS, CAS) of complexes **1** (Br), **2** (Cl), **3** (F) and their iodine (**4**) analogue (Å) and experimental ones (bold).

Bond	CAS model		**Exp**		CA model		CS model	
	LS	HS	**150 K**	**RT**	LS	HS	LS	HS
1 (Br)								
Fe-O	1.918	1.953	**1.867**	**1.880**	1.919	1.944	1.911	1.934
	1.922	1.956	**1.878**	**1.870**	1.922	1.948	1.912	1.937
Fe-N_{im}	1.979	2.148	**1.919**	**1.923**	1.982	2.149	1.982	2.152
	1.980	2.151	**1.917**	**1.930**	1.986	2.163	1.983	2.154
Fe-N_{am}	2.119	2.306	**2.021**	**2.050**	2.128	2.296	2.135	2.310
	2.131	2.309	**2.049**	**2.020**	2.128	2.296	2.138	2.319
2 (Cl)								
Fe-O	1.918	1.974	-	**1.866**	1.919	1.971	1.911	1.962
	1.922	1.979		**1.866**	1.922	1.976	1.912	1.965
Fe-N_{im}	1.979	2.174	-	**1.926**	1.982	2.170	1.982	2.173
	1.980	2.176		**1.925**	1.987	2.185	1.983	2.174
Fe-N_{am}	2.120	2.305	-	**2.052**	2.126	2.307	2.136	2.322
	2.131	2.313		**2.031**	2.129	2.313	2.137	2.326
3 (F)								
Fe-O	1.914	1.963,	**1.856**	**1.883**	1.913	1.962	1.901	1.959
	1.917	1.975	**1.873**	**1.891**	1.914	1.977	908	1.961
Fe-N_{im}	1.977	2.159	**1.897**	**1.950**	1.976	2.164	1.980	2.165
	1.978	2.185	**1.897**	**1.949**	1.980	2.173	1.981	2.166
Fe-N_{am}	2.121	2.274	**2.028**	**2.061**	2.132	2.333	2.134	2.316
	2.129	2.316	**2.019**	**2.083**	2.121	2.294	2.137	2.319
4 (I)								
Fe-O	1.919	1.977	-	-	1.921	1.972	1.911	1.962
	1.923	1.981			1.922	1.976	1.915	1.964
Fe-N_{im}	1.980	2.174	-	-	1.982	2.174	1.983	2.176
	1.981	2.178			1.985	2.185	1.985	2.178
Fe-N_{am}	2.122	2.306	-	-	2.131	2.307	2.132	2.319
	2.133	,2.311			2.132	2.315	2.141	2.329

Table S4. Relevant distances (Å) for the calculated for the two periodic models (CAS, CA) and supercell (CA) of complexes **1** (Br), **2** (Cl), **3** (F) and their iodine (**4**) analogue (Å) and experimental ones (bold).

Bond	Crystal		**Exp**		Cation-anion		Super cell	
	LS	HS	**150 K**	**RT**	LS	HS	LS	HS
1 (Br)								
Fe-O	1.884	1.937	**1.867**	**1.880**	1.875	1.957	1.876	1.974
	1.899	1.974	**1.878**	**1.870**	1.891	1.926	1.876	1.942
Fe-N_{im}	1.906	2.101	**1.919**	**1.923**	1.908	2.093	1.921	2.105
	1.905	2.129	**1.917**	**1.930**	1.908	2.125	1.925	2.107
Fe-N_{am}	2.031	2.189	**2.021**	**2.050**	2.036	2.286	2.309	2.302
	2.054	2.259	**2.049**	**2.020**	2.062	2.210	2.367	2.338
2 (Cl)								
Fe-O	1.880	1.942	-	**1.866**	1.874	1.931	1.883	1.944
	1890	1.951		**1.866**	1.877	1.944	1.884	1.959
Fe-N_{im}	1.902	2.103	-	**1.926**	1.910	2.101	1.904	2.067
	1.902	2.088		**1.925**	1.906	2.080	1.909	2.112
Fe-N_{am}	2.046	2.217	-	**2.052**	2.055	2.343	2.070	2.303
	2.045	2.265		**2.031**	2.048	2.249	2.074	2.325
3 (F)								
Fe-O	1.875	1.938	**1.856**	**1.883**	1.875	1.926	1.898	1.964
	1.887	1.944	**1.873**	**1.891**	1.875	1.936	1.898	1.967
Fe-N_{im}	1.902	2.091	**1.897**	**1.950**	1.913	2.097	1.903	2.084
	1.902	2.096	**1.897**	**1.949**	1.910	2.095	1.899	2.088
Fe-N_{am}	2.051	2.238	**2.028**	**2.061**	2.056	2.268	2.058	2.359
	2.043	2.246	**2.019**	**2.083**	2.056	2.273	2.071	2.372
4 (I)								
Fe-O	1.899	1.976	-	-	1.890	1.930	1.809	1.930
	1.882	1.940			1.877	1.963	1.878	1.994
Fe-N_{im}	1.903	2.091	-	-	1.906	2.085	1.904	2.094
	1.903	2.119			1.907	2.117	1.909	2.103
Fe-N_{am}	2.057	2.186	-	-	2.065	2.221	2.067	2.313
	2.033	2.262			2.038	2.289	2.073	2.335

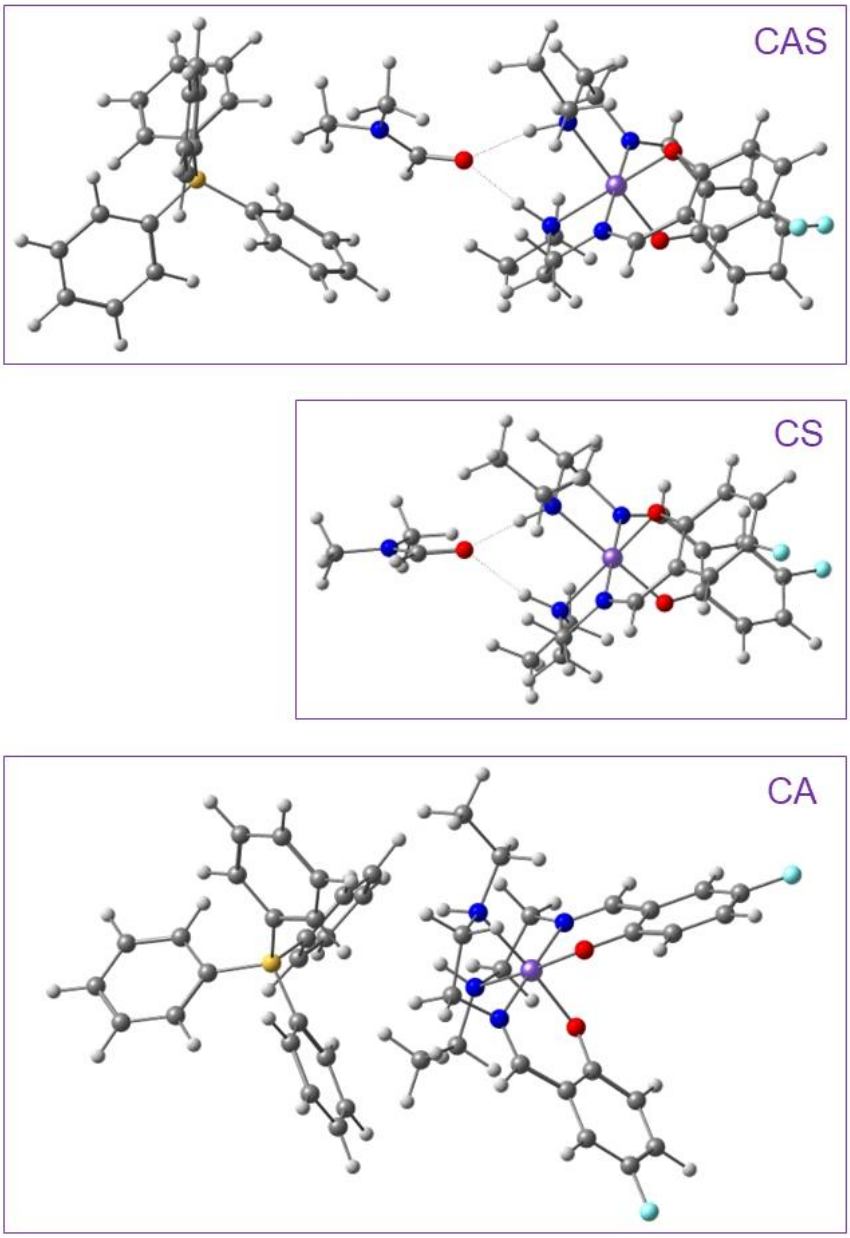

Figure S10. Optimized molecular structures of the three models of complex **3**: CAS (top), CS (middle), CA (bottom).

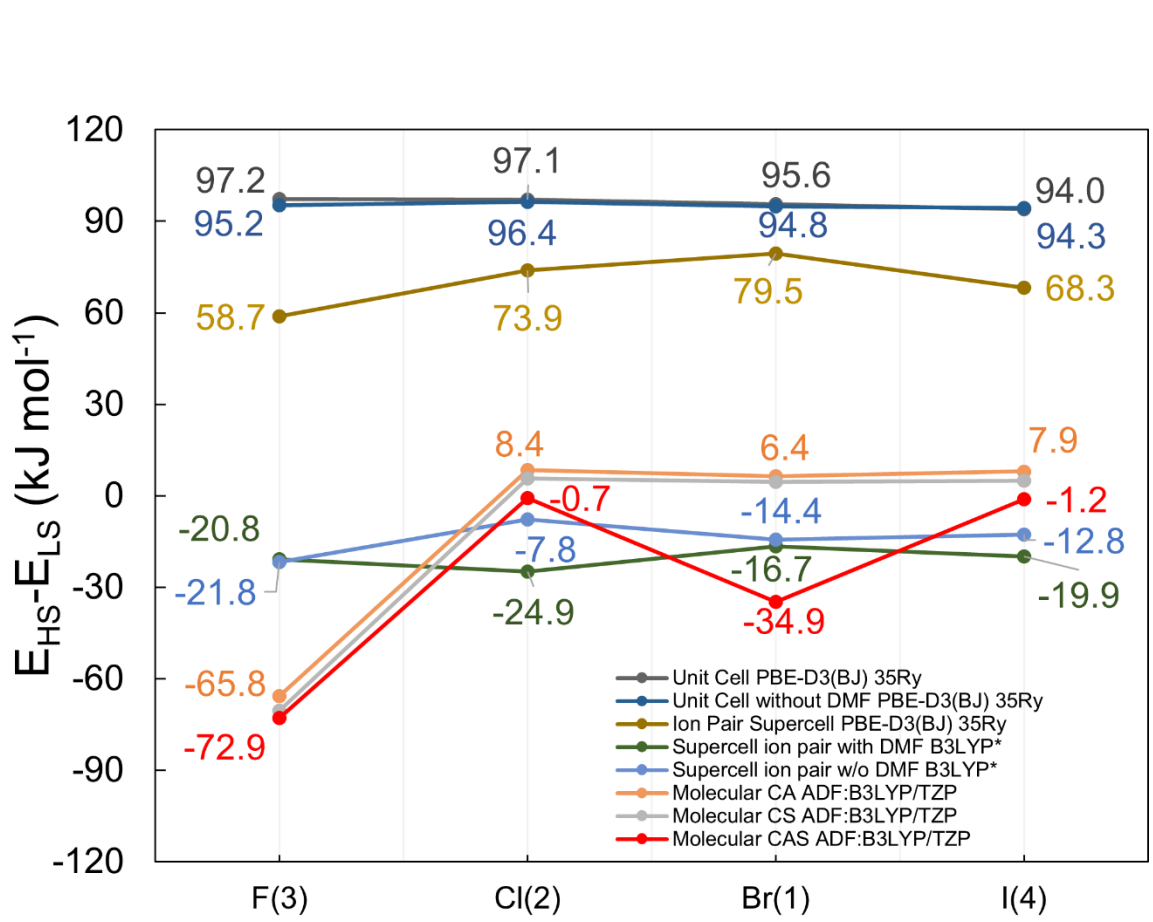

Figure S11. Energy difference between spin states (ΔE_{HS-LS} / kJ mol^{-1}) for all the periodic and molecular DFT calculations of complexes **1** (Br), **2** (Cl), **3** (F), and **4** (I).