Electronic Supplementary Information

Magnetic and structural correlations in [Fe(nsal$_2$trien)] salts: The role of cation-anion interactions in the spin crossover phenomenon.

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Table S1: LS phases of **6**, including the distances between the average planes of the aromatic systems planes (d_{LL}^{i}) or between a C and the average plane in the closest neighbour in case of **6** (d_{CL}^{i}), , the shortest distances between the centroids of the C6 rings of the ligands (d_{cent}^{i}), shift in the overlap in **1**-**4** (d_{shift}^{i}), rotation angle in **6** (γ_{rot}^{i}), tilt in **6** (ϕ_{tilt}^{i}).

Compound	**1**	**2**	**3**	**4**	**6**	**6**	**6**
Phase	LS	HS	HS	LS	LS	Int	HS
d_{LL}^{I}/d_{CL}^{Ia} (Å)	3.345	3.284	3.234	3.034	3.314[a]	3.388[a]	3.408[a]
d_{LL}^{II}/d_{CL}^{IIa} (Å)	3.235	3.262	3.296	3.268	3.314[a]	3.292[a]	3.408[a]
d_{cent}^{I} (Å)	3.788	4.820	4.904	5.515	4.167	4.260	4.277
d_{cent}^{II} (Å)	4.637	4.332	4.303	3.790	4.167	4.139	4.277
$d_{shift}^{I}/\gamma_{rot}^{Ib}$ (Å/º)	1.774	3.529	3.686	5.025	66.27[b]	66.24[b]	66.50[b]
$d_{shift}^{II}/\gamma_{rot}^{IIb}$ (Å/º)	4.505	3.805	3.805	2.494	66.27[b]	66.13[b]	66.50[b]
ϕ_{tilt}^{I} (º)[b]	0	0	0	0	32.24[b]	35.79[b]	35.91[b]
ϕ_{tilt}^{II} (º)[b]	0	0	0	0	32.24[b]	32.56[b]	35.91[b]

[a] the d_{CL}^{Ia} values correspond to the shortest distance between one C atom and the average plane from a phenoxy ring in the neighboring cation in **6**; [b] it only applies to compound **6**.

Table S2. Key parameters (interatomic separations, *d*, and DH…A angles in the case of hydrogen bonds) of selected intermolecular contacts of compound **1** at 150K. The type of contact and main contribution to the overall connectivity are specified (Ch - intrachain [overlap I or II]; L - intralayer, iL - interlayer).

	d (Å)	DH…A (º)	type	connectivity
DD				
C2…C6	3.401		ππ	Ch [I]
C2…C5	3.412		ππ	Ch [I]
C4…C4	3.437		ππ	Ch [I]
C3…C4	3.447		ππ	Ch [I]
C6H6…C20	2.798	169.67	CH…π	Ch [I]
C6H6…C19	2.882	158.79	CH…π	Ch [I]
C21…C21	3.316		ππ	Ch [II]
C17H17B…C13	2.890	151.64	CH…C	L
C15H15A…C5	2.841	156.41	CH…π	iL
DA				
N3H3A…Cl1	2.193	170.28	NH…Cl	iL
N2H2A…Cl1	2.310	154.11	NH…Cl	iL
C26H26…Cl1	2.727	167.77	CH…Cl	L
cation-ethanol				
O4H4…O1	2.159	130.35	OH…O	L
C91H91B…O2	2.171	134.91	CH…O	L
O4H4…N4	2.403	151.27	OH…N	L
O4H4…C18	2.527	143.94	OH…π	L

C91H91B…N1	2.360	147.33	CH…N	L
C13H13A…C91	2.562	129.32	CH…C	L
C91H91C…C11	2.612	135.71	CH…π	L
C91H91A…C18	2.659	122.28	CH…π	L
C91H91C…C12	2.627	1116.38	CH…C	L
C21H21…C91	2.697	148.49	CH…C	L
cation-water				
C8H8…O3W	2.353	167.13	CH…O	iL
C11H11…O3W	2.674	173.14	CH…O	iL
ethanol-water				
O3WH3C…O4	1.699	163.64	OH…O	L
water-anion				
O3WH3B…Cl	2.059	175.43	OH…Cl	iL

Table S3. Key parameters (interatomic separations, *d*, and DH…A angles in the case of hydrogen bonds) of selected intermolecular contacts of compound **2** at 150K. The type of contact and main contribution to the overall connectivity are specified (Ch - intrachain [overlap I or II]; L - intralayer, iL -interlayer).

	***d* (Å)**	**DH…A (º)**	**type**	**connectivity**
DD				
C11…C7	3.302		ππ	Ch [I]
C6…C11	3.495		ππ	Ch [I]
C8…C10	3.497		ππ	Ch [I]
C26…C26	3.300		ππ	Ch [II]
C12-H12B…C18	2.787	135.66	CH…π	L
C17-H17B…C4	2.862	116.35	CH…π	iL
C16-H16A…C6	2.854	146.94	CH…π	iL
CA				
N2H2A…O5	2.118	163.97	NH…O	iL
N3H3A…O3	2.169	159.71	NH…O	iL
N3H3A…O6	2.440	136.68	NH…O	iL
C14H14B…O6	2.436	136.82	CH…O	iL
C15H15B…O4	2.420	139.71	CH…O	iL
C26H26…O5	2.595	159.30	CH…O	iL
N2H2A…O4	2.637	133.81	NH…O	iL
C2H2…O5	2.617	128.09	CH…O	L
C3H3…O6	2.628	125.37	CH…O	L

Table S4. Key parameters (interatomic separations, *d*, and DH…A angles in the case of hydrogen bonds) of selected intermolecular contacts of compound **3** at 150K. The type of contact and main contribution to the overall connectivity are specified (Ch - intrachain [overlap I or II]; L - intralayer, iL - interlayer).

	***d* (Å)**	**DH…A (º)**	**type**	**connectivity**
DD				
C7…C11	3.278		ππ	Ch [I]
C26…C26	3.322		ππ	Ch [II]
C12-H12A…C18	2.783	134.45	CH…π	L
C13-H13B…O1	2.795	163.53	CH…O	L
C17-H17A…C4	2.838	113.95	CH…π	iL
C17-H17A…C9	2.898	142.07	CH…π	iL
C16-H16B…C6	2.871	150.59	CH…π	iL
DA				
N2H2A…F1	2.134	168.82	NH…F	iL
N3H3A…F4	2.275	162.16	NH…F	iL
C15H15A…F2	2.371	138.69	CH…F	iL
C14H14A…F3	2.383	136.21	CH…F	iL
C3H3…F3	2.547	127.40	CH…F	iL
N2H2A…F2	2.618	133.15	NH…F	iL
C26H26…F1	2.598	160.14	CH…F	iL
N3H3A…F3	2.495	138.42	NH…F	L
C2H2…F1	2.604	125.6	CH…F	L

Table S5. Key parameters (interatomic separations, *d*, and DH…A angles in the case of hydrogen bonds) of selected intermolecular contacts of compound **4** at 150K. The type of contact and main contribution to the overall connectivity are specified (Ch - intrachain [overlap I or II]; L - intralayer, iL - interlayer).

	***d* (Å)**	**DH…A (º)**	**type**	**connectivity**
DD				
C18…C22	3.382		ππ	Ch [I]
C17-H17B…C23	2.865	148.23	CH…π	Ch [I]
C6…C11	3.397		ππ	Ch [II]
C7…C10	3.425		ππ	Ch [II]
C7…C9	3.325		ππ	Ch [II]
C8…C9	3.412		ππ	Ch [II]
C8…C8	3.413		ππ	Ch [II]
C24-H24…C4	2.682	159.66	CH…π	L
C24-H24…C3	2.896	159.37	CH…π	L
DA				
N2H2A…C64	2.455	162.48	NH…π	L
N3H3A…C33	2.491	154.50	NH…π	L
C14H14A…C43	2.552	167.08	CH…π	L
N2H2A…C63	2.710	132.81	NH…π	L
N3H3A…C32	2.755	152.55	NH…π	L
C14H14A…C42	2.781	154.06	CH…π	L
C33H33…C26	2.724	170.25	CH…π	L
C3H3...C44	2.759	146.22	CH…π	iL
C12H12B…C52	2.776	150.21	CH…π	iL
C13H13A…C63	2.777	143.9	CH…π	iL
AA				
C41H41…C54	2.897	148.79	CH…π	iL

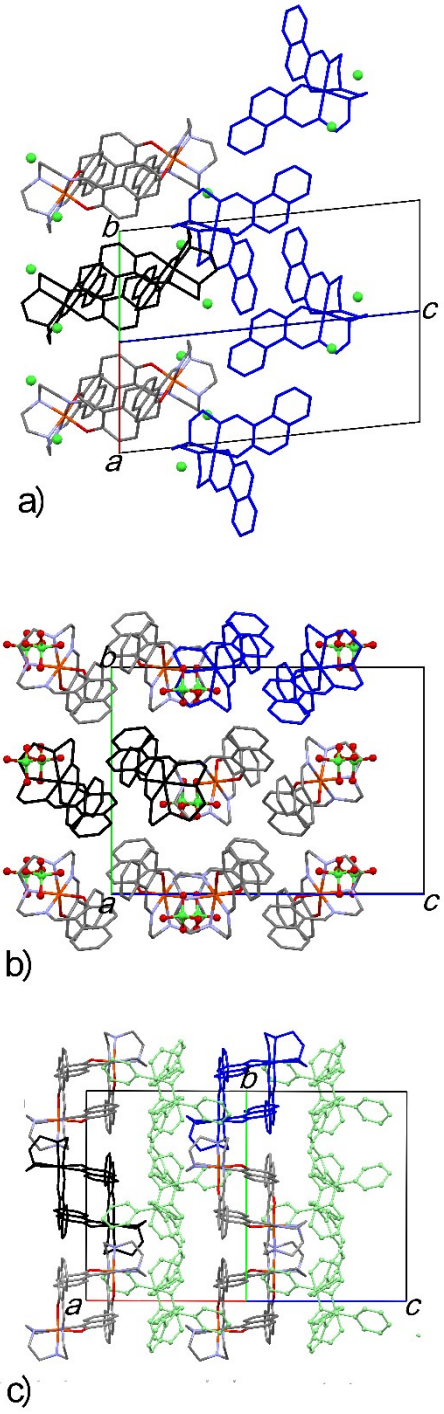


Figure S1 Projections of the crystal structures of **1** (a), **2** (b) and **4** (c), along the directions of the chains [100] in **2** and [101] in **4**. In **1** in the left and right-hand layers the chains are parallel to [110], while in the alternating layers, namely the middle layer they are parallel to $[1\bar{1}0]$. In all compounds one of the chains in each layer of the cationic chains is represented in black for a better identification.

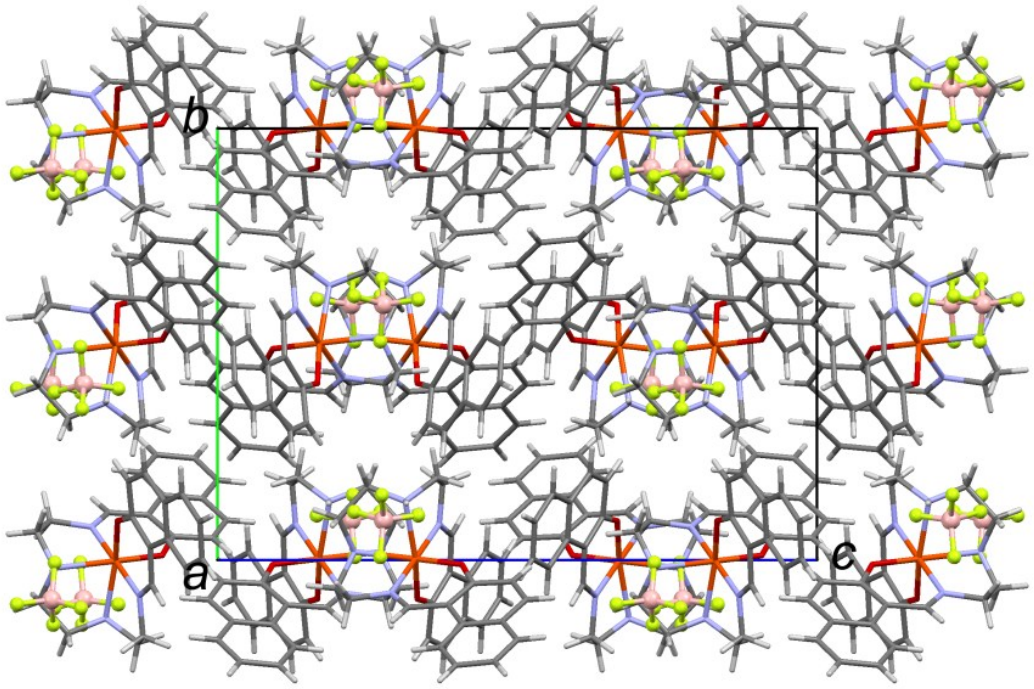


Figure S2 – Projection of the crystal structure of compound **3** along the cationic chain direction [100].

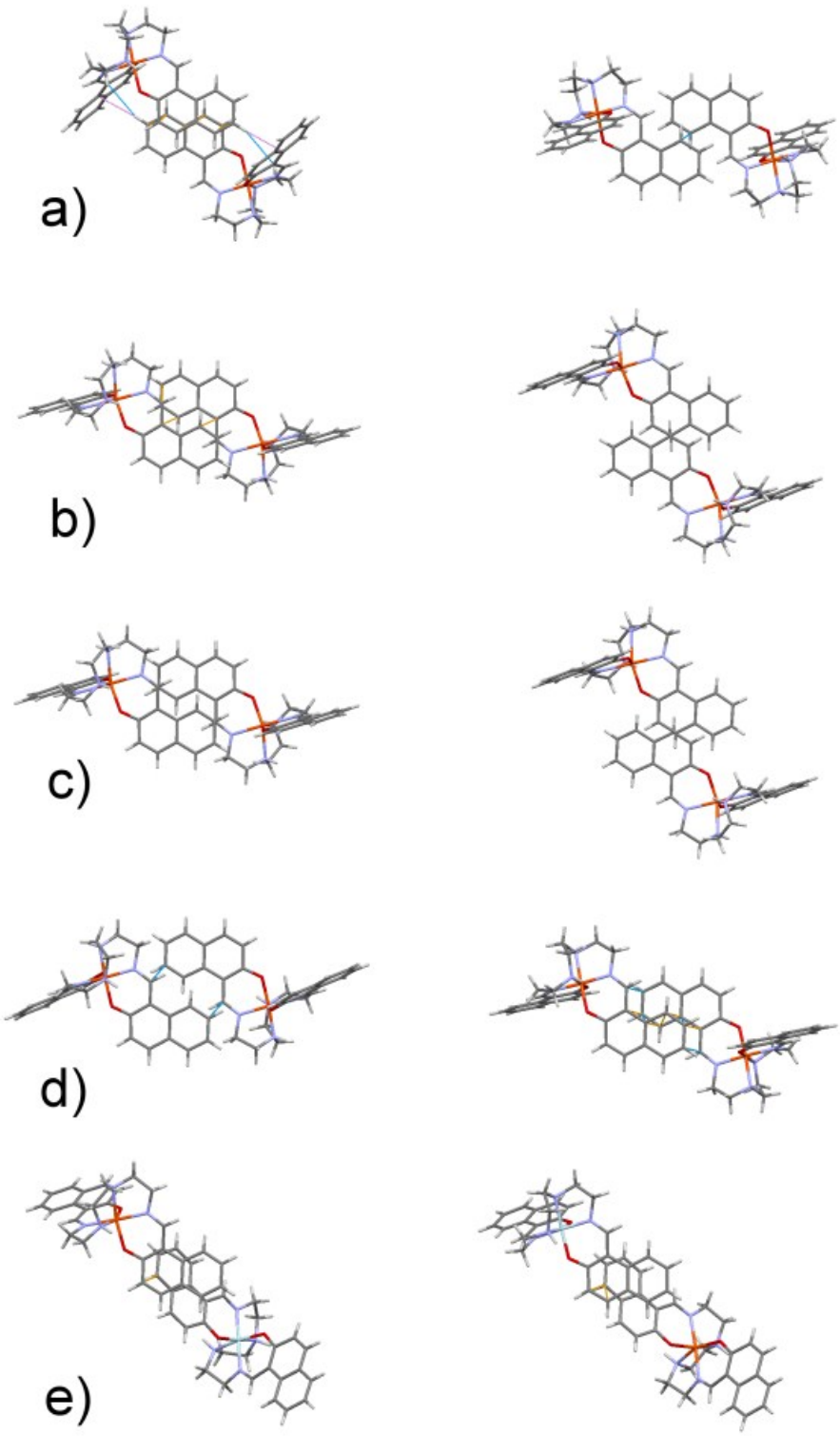


Figure S3 – Projections of overlapping modes I and II (left and right) of the phenoxy rings in the cationic chains of compounds **1**-**4** (a-d) and **6** (e).

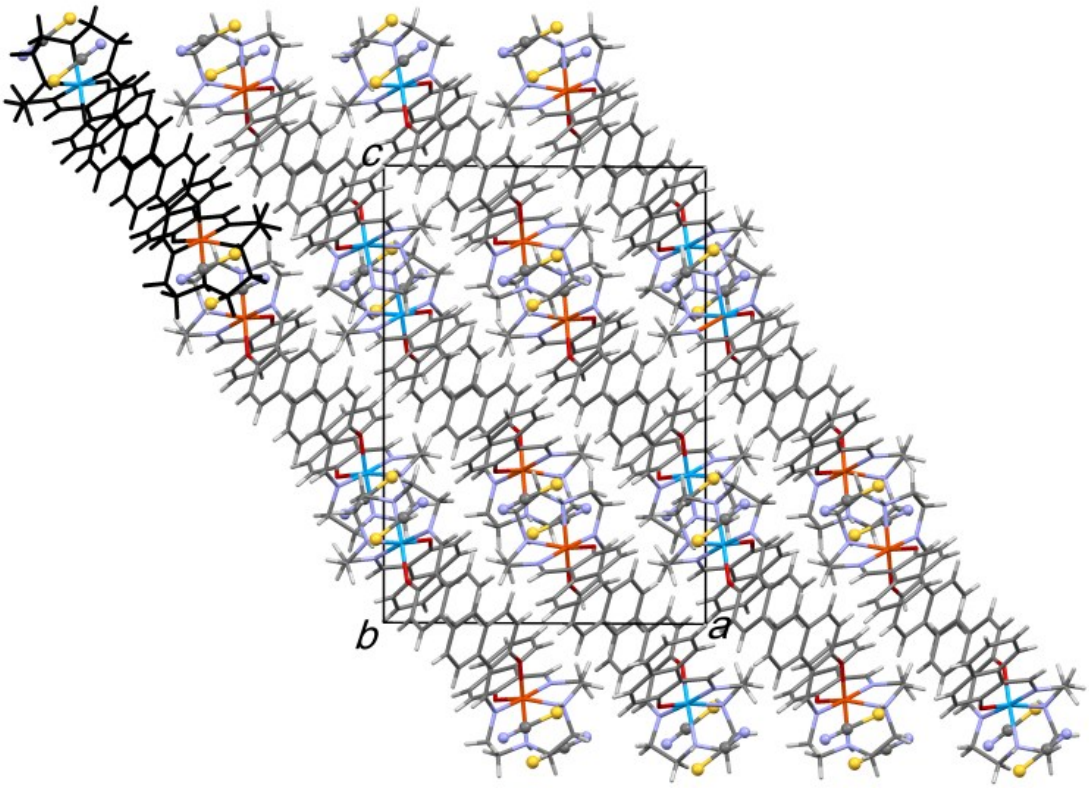


Figure S4 – View of the projection of the crystal structure of **6** (Int phase) along the cationic chain direction [010]. The HS and LS Fe^{III} atoms are depicted in orange and light blue respectively. For a better identification of the chains, the atoms of the cations of the left chain in the top layer are depicted in black (except the HS and LS Fe atoms).

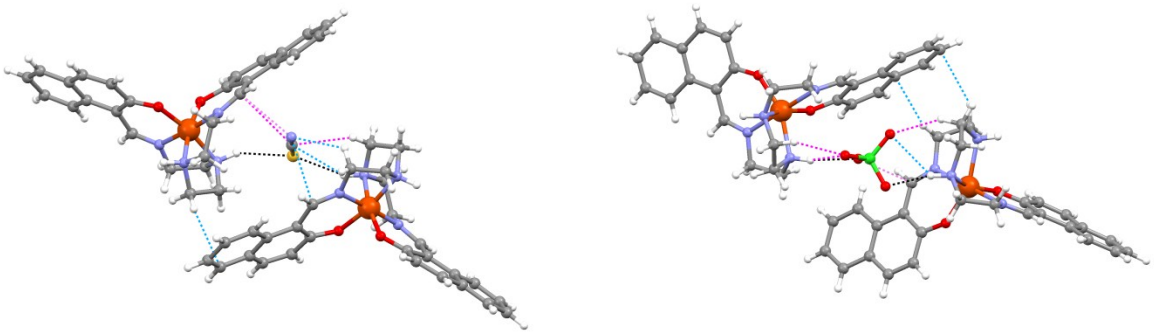


Figure S5 – Comparison of the interlayer DAD arrangements and contacts in the LS phase of **6** (left) and **2** (right). Colour code of the contacts ($\Delta = d - S_{vdW}$): black for $\Delta < -0.5$ Å; dark blue for $\Delta < -0.3$ Å; magenta for $\Delta < -0.2$ Å; violet for $\Delta < -0.1$ Å, light blue for $\Delta < 0$.

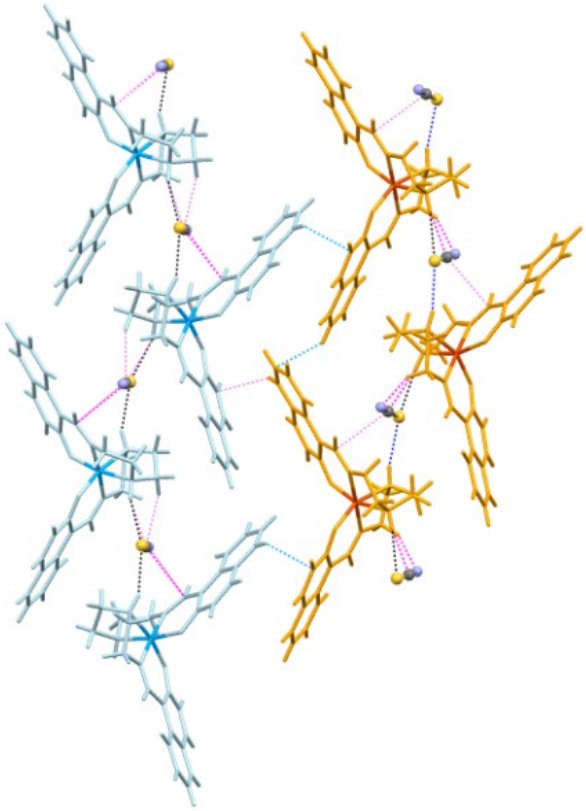


Figure S6 – Detail of the intrachain and interlayer arrangements and respective DD and DA contacts in the Int phase. HS and LS cations are depicted in orange and light blue respectively. Colour code of the contacts ($\Delta = d - S_{vdW}$) in Å: black for $\Delta < -0.5$; dark blue for $\Delta < -0.3$; magenta for $\Delta < -0.2$; violet for $\Delta < -0.1$, light blue for $\Delta < 0$ (DA contacts longer than those corresponding to $\Delta < -0.1$ are omitted).

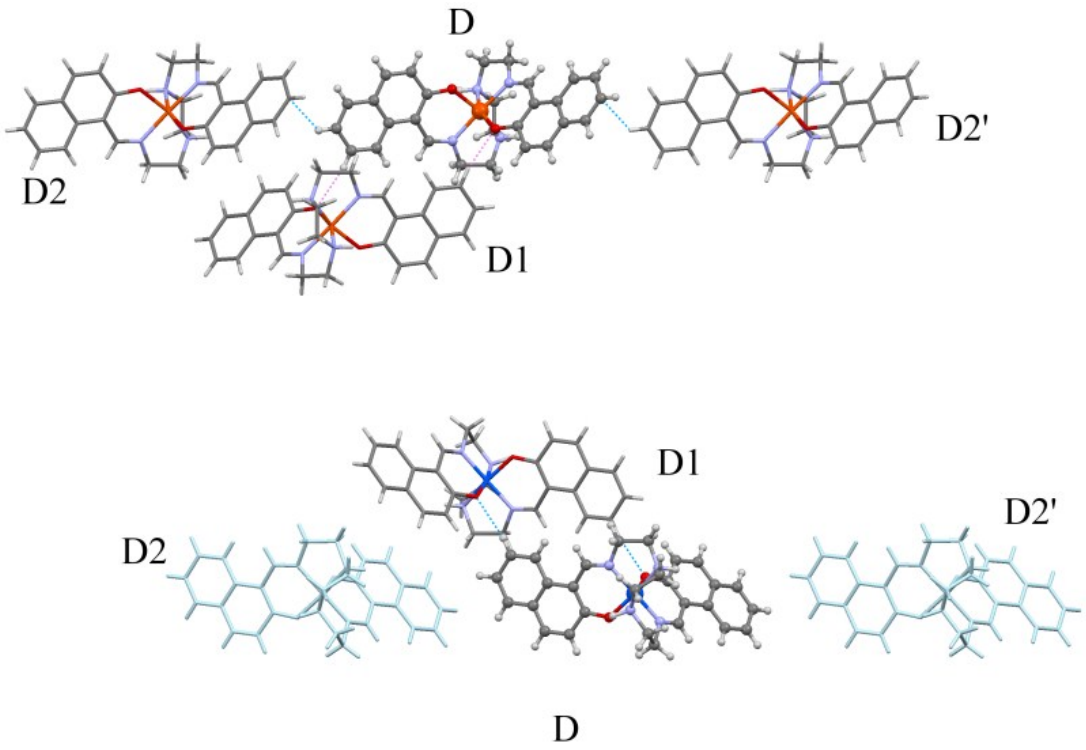
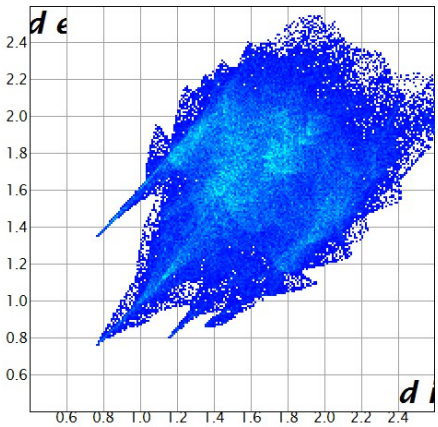
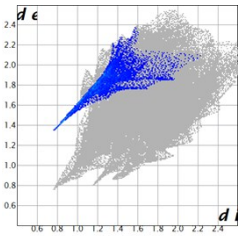


Figure S7 – Comparison of the arrangement of the DD contacts within the HS (top) and LS (bottom) cationic networks in the Int phase. The HS and LS Fe^{III} atoms are depicted in orange and light blue respectively. The arrangements are similar, but the HS cations present CH…π contacts to two cations in the same chain (D2 and D2') and CH…O to a third cation (D1) in a neighbouring chain, while in the LS network those separations are larger and the central cation D only shows short contacts to D1 from a neighbouring chain. Colour code of the contacts ($\Delta = d - S_{vdW}$ in Å): violet for $\Delta < -0.1$, light blue for $\Delta < 0$.

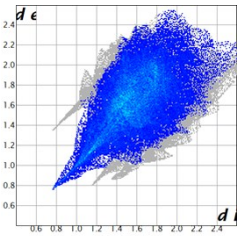
1



HCl (DA)



HH (DD and DSolv)



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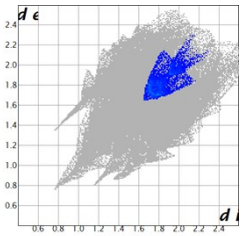
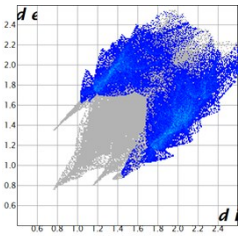


HC (DD and DSolv)



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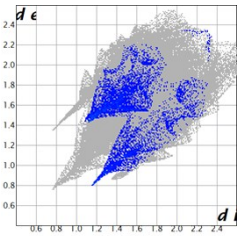

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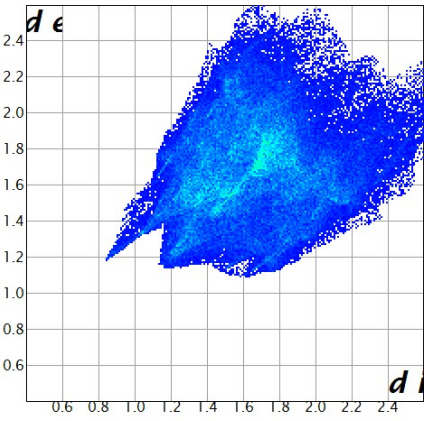

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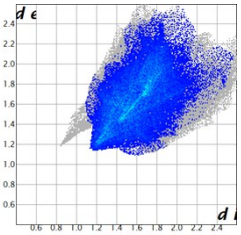
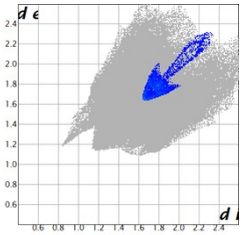
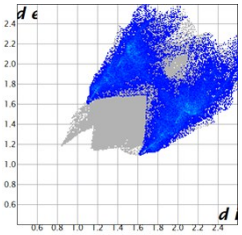


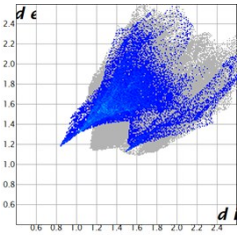
CC (DD)



HC (DD)



HO (DD and DA)



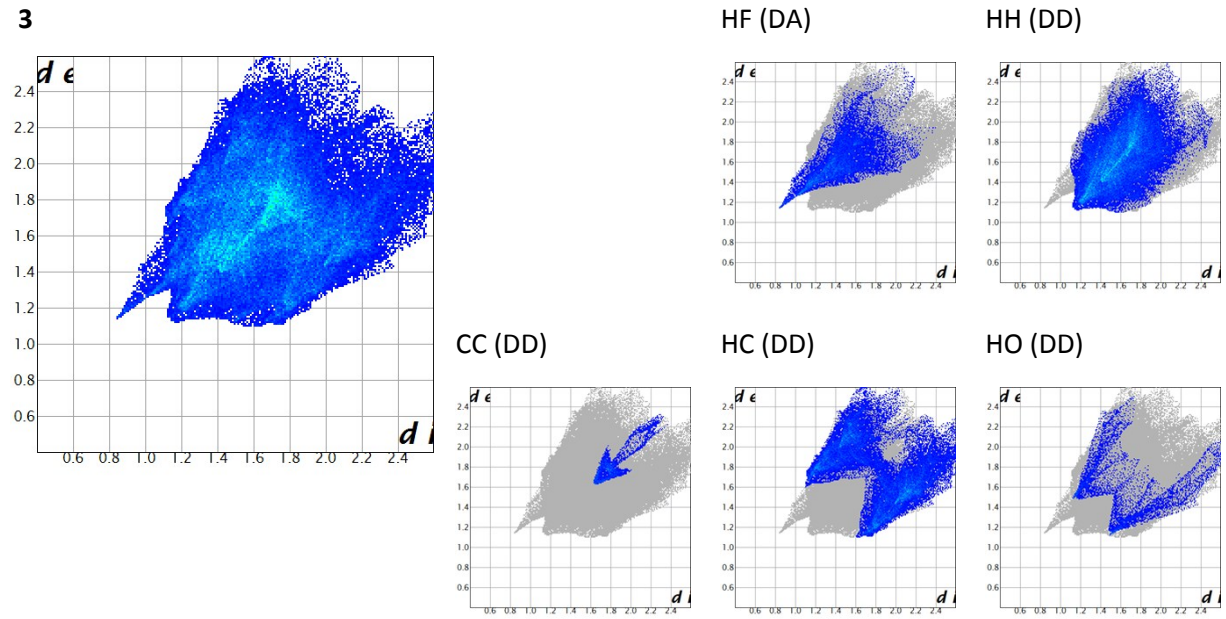
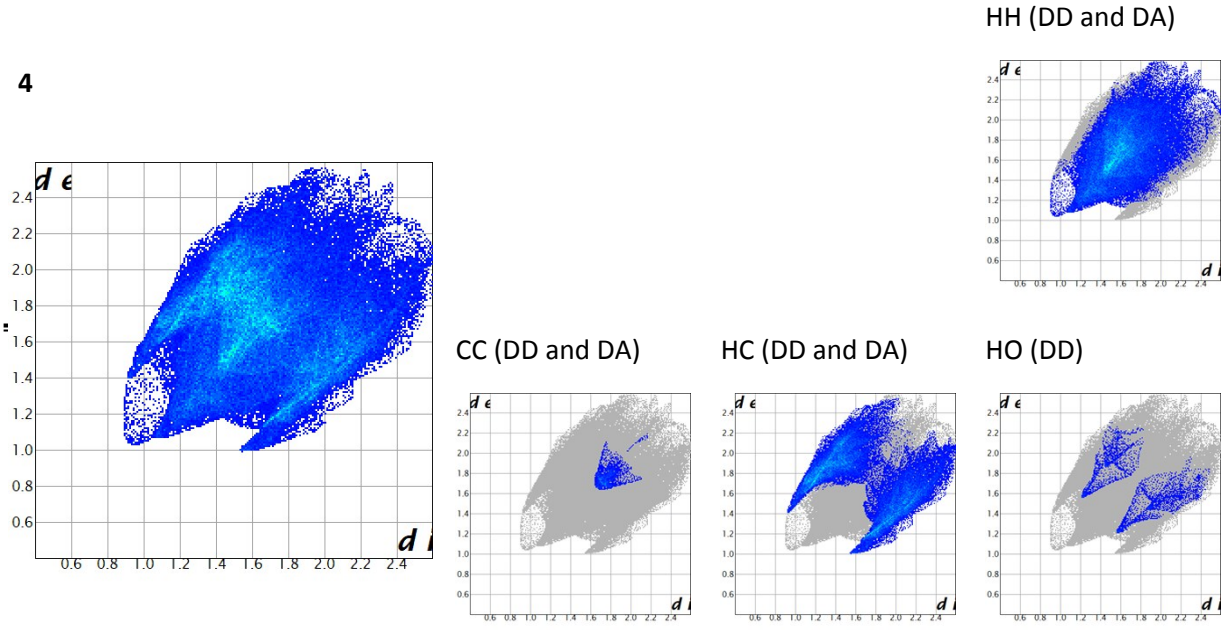


Figure S8 – Fingerprint plot for the $[Fe(nsal_2trien)]^+$ cations in **1-3**. The resolved fingerprint plots into the main intermolecular contacts, H···Cl or H···F; H···H; C···C; H···C (and reciprocal); H···O (and reciprocal), are also shown.



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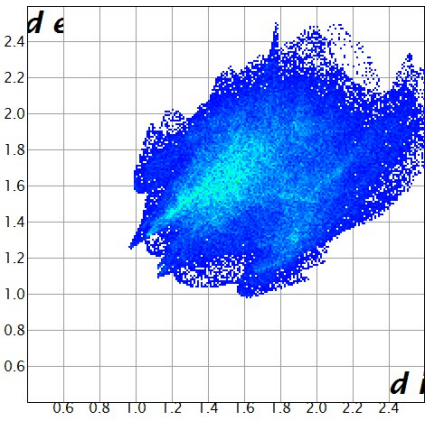
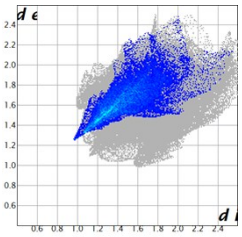
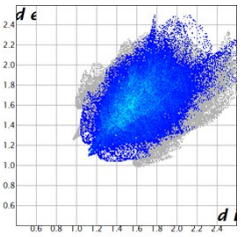


HF (DA)



HH (DD and DSolv)



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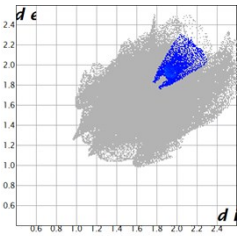
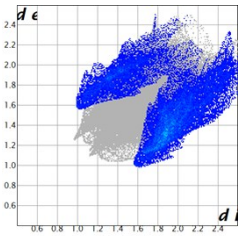


HC (DD and DSolv)



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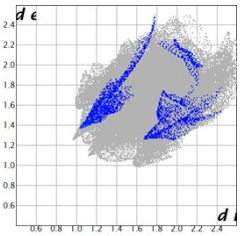
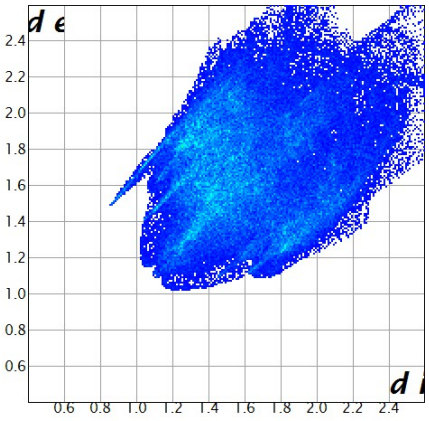


6 (LS)



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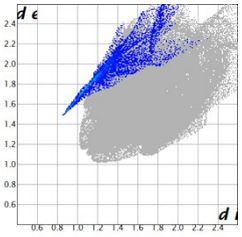

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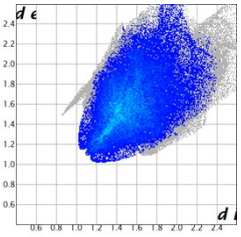

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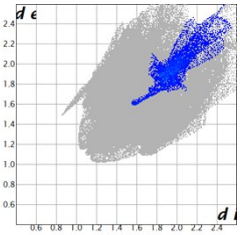
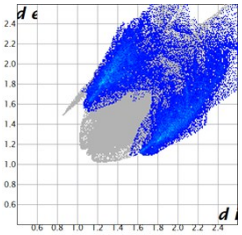
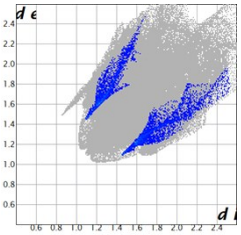


HC (DD and DA)



HO (DD)



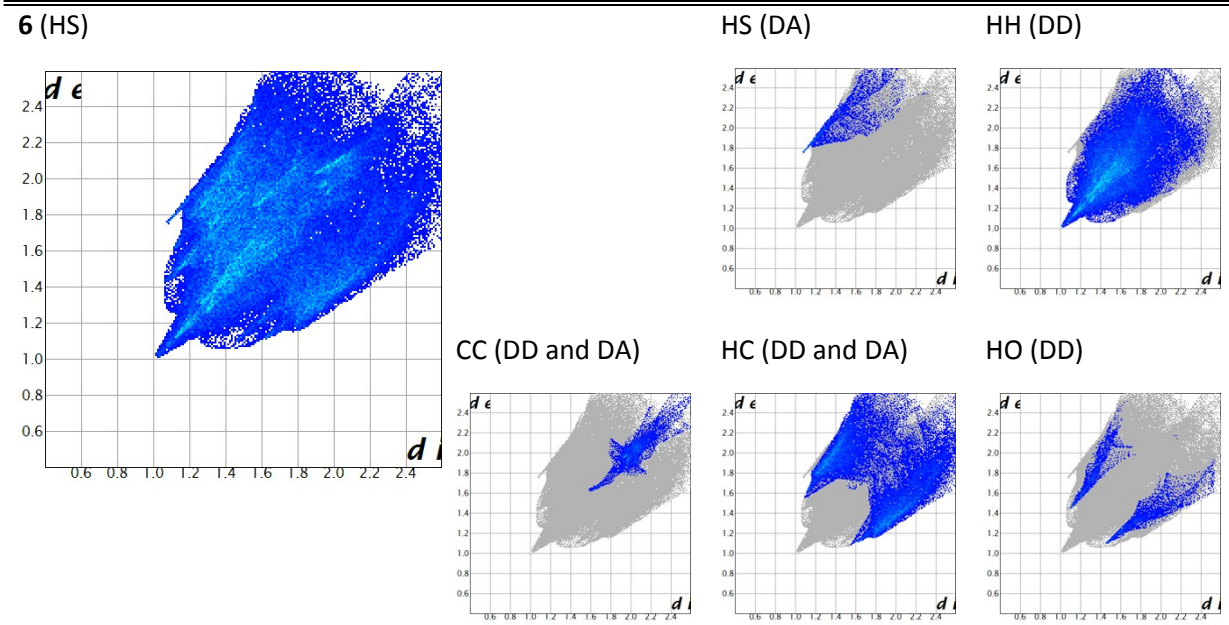
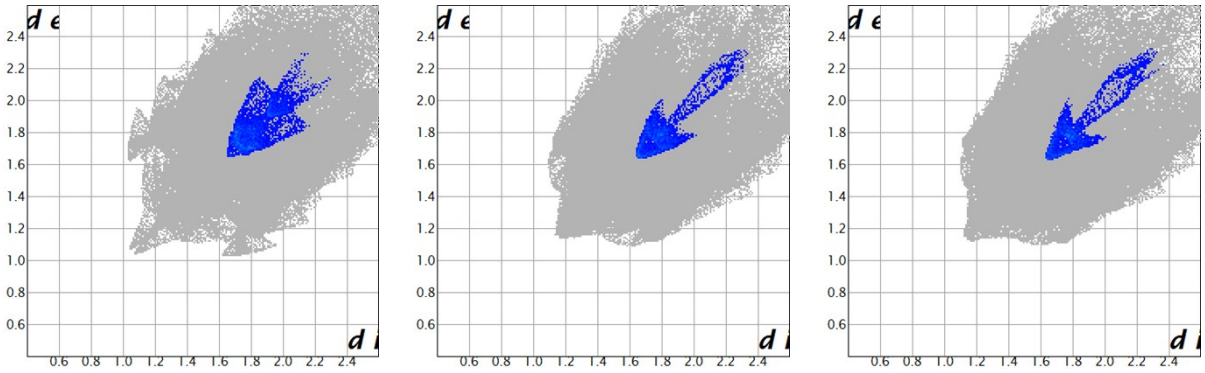
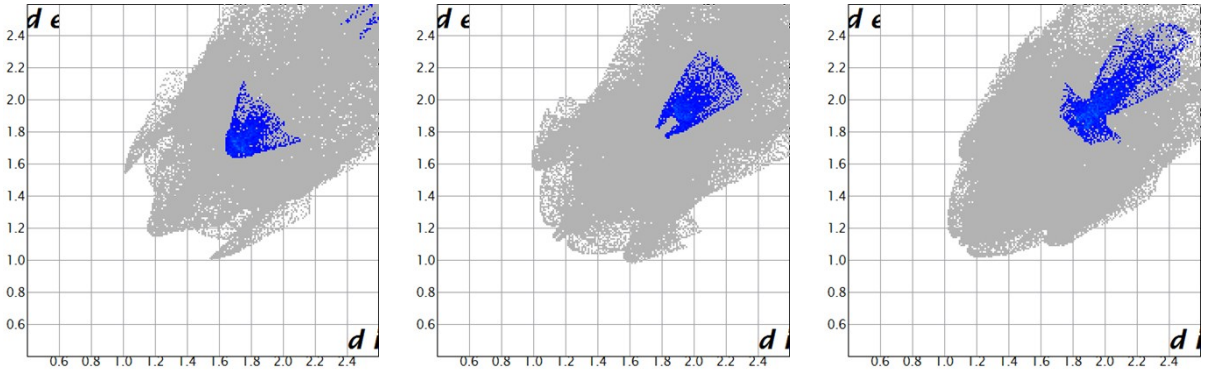


Figure S9 – Fingerprint plot for the $[Fe(nsal_2trien)]^+$ cations in **4-6**. The resolved fingerprint plots into the main intermolecular contacts, H···Cl or H···S; H···H; C···C; H···C (and reciprocal); H···O (and reciprocal), are also shown.

1 CC (DD only) **2** CC (DD only) **3** CC (DD only)



4 CC (DD only) **5** CC (DD only) **6**(LS) CC (DD only)



6 (HS) CC (DD only)

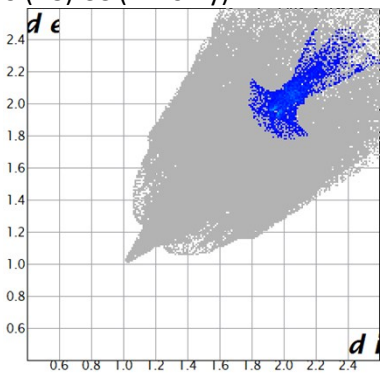


Figure S10 – Fingerprint plot for the $[Fe(nsal_2trien)]^+$ cations in **1-6** resolved into the DD C···C contacts.