Evidence of new fluorinated coordination compounds in the composition space diagram of FeF_3/ZnF_2-H*amtetraz*-$HF_{aq.}$-DMF system

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SUPPLEMENTARY INFORMATION

1 – [H*dma*]·($Fe^{III}Zn(H_2O)_4F_6$)

Table S1. Atomic coordinates and equivalent isotropic displacement parameters of [H*dma*]·($ZnFe(H_2O)_4F_6$)

Atom	site	x	y	z	B_{eq} (Å^2)
Zn(1)	*4a*	½	½	½	1.34(1)
Fe(1)	*4b*	½	0	½	1.22(1)
F(1)	*8f*	½	0.75807(14)	0.54850(9)	1.74(2)
F(2)	*16h*	0.63263(9)	0.92799(12)	0.41644(6)	2.01(2)
OW(1)	*16h*	0.36375(10)	0.42652(14)	0.59642(7)	1.83(2)
C(1)	*8g*	-0.1190(3)	0.2453(4)	¾	3.52(6)
N(1)	*4c*	0	0.1355(4)	¾	2.63(5)

Table S2. Anisotropic displacement parameters (ADP, Å^2) of [H*dma*]·($ZnFe(H_2O)_4F_6$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	0.01837(17)	0.01237(15)	0.02009(16)	-0.00028(11)	0	0
Fe(1)	0.01376(18)	0.01013(17)	0.0225(2)	-0.00015(13)	0	0
F(1)	0.0314(6)	0.0107(5)	0.0238(6)	0.0006(4)	0	0
F(2)	0.0215(4)	0.0194(4)	0.0353(5)	-0.0018(4)	0.0090(4)	-0.0004(4)
OW(1)	0.0193(5)	0.0181(5)	0.0322(5)	0.0008(4)	0.0044(4)	0.0006(4)
C(1)	0.0466(16)	0.0547(18)	0.0324(13)	0	0	0.0108(14)
N(1)	0.0459(18)	0.0308(14)	0.0230(12)	0	0	0

Table S3. Selected inter-atomic distances (Å) in [H*dma*]·($ZnFe(H_2O)_4F_6$)

Zn(1)-F(1) x2	2.0485(11)
Zn(1)-OW(1) x4	2.0903(10)
Fe(1)-F(2) x2	1.9320(9)
Fe(1)-F(1) x2	1.9370(11)
C(1)-N(1) x2	1.474(3)

Table S4. Selected H-bond distances N-H···Ow and O-H···F, angles in [H*dma*]·($ZnFe(H_2O)_4F_6$)

N-H and O-H	d(H···A) (Å)	<DHA> (°)	d(N···F) (Å)	A
N(1)-H(2)A x2	2.347	143.08	3.114	OW(1)
N(1)-H(2)B x2	2.347	143.08	3.114	OW(1)
OW(1)-HW(1)	1.790	166.83	2.638	F(2)
OW(1)-HW(2)	1.716	170.90	2.625	F(2)

2 – [H*dma*]·[H*gua*]$_2$·($Fe^{III}F_6$).H_2O

Table S5. Atomic coordinates and equivalent isotropic displacement parameters of [H*dma*]·[H*gua*]$_2$·(FeF_6).H_2O

Atom	site	x	y	z	B_{eq} (Å^2)
Fe(1)	*8c*	0.97605(3)	0.11565(3)	0.638485(12)	1.74(1)
F(1)	*8c*	0.99096(14)	0.10268(16)	0.56614(6)	3.28(3)
F(2)	*8c*	0.95155(15)	-0.06716(14)	0.64222(6)	3.07(3)
F(3)	*8c*	0.95587(14)	0.12356(13)	0.71084(5)	2.97(3)
F(4)	*8c*	0.79436(14)	0.14207(13)	0.63242(6)	3.06(3)
F(5)	*8c*	1.15488(13)	0.08957(14)	0.64457(5)	2.73(2)
F(6)	*8c*	1.00313(14)	0.29613(14)	0.63552(6)	3.26(3)
C(1)	*8c*	1.2194(2)	-0.1733(2)	0.55401(9)	2.45(4)
N(1)	*8c*	1.2862(2	-0.2639(2	0.53172(8	3.71(5)
N(2)	*8c*	1.2435(2)	-0.1417(2)	0.60088(9)	3.29(5)
N(3)	*8c*	1.1278(2)	-0.1139(2)	0.52914(9)	3.44(5)
C(2)	*8c*	0.3049(2)	0.0902(2)	0.25859(9)	2.48(4)
N(4)	*8c*	0.2581(2)	-0.0172(2)	0.24086(9)	3.46(5)
N(5)	*8c*	0.4060(2)	0.1439(2)	0.23759(9)	3.58(5)
N(6)	*8c*	0.2499(2)	0.1473(2)	0.29725(9)	3.35(5)
O(1)W	*8c*	0.2337(2)	0.1539(2)	0.42913(8)	4.09(4)
N(7)	*8c*	0.93751(19)	0.53629(19)	0.61664(9)	2.78(4)
C(3)	*8c*	0.9712(3)	0.5581(4)	0.56329(13)	4.94(7)
C(4)	*8c*	1.0130(3)	0.6135(3)	0.65184(14)	4.02(6)

Table S6. Anisotropic displacement parameters (ADP, Å^2) of [H*dma*]·[H*gua*]$_2$·(FeF_6).H_2O

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.02024(19)	0.0202(2)	0.02572(19)	0.00103(13)	0.00095(12)	0.00019(12)
F(1)	0.0436(9)	0.0569(10)	0.0239(7)	-0.0023(7)	-0.0033(6)	0.0032(7)
F(2)	0.0424(9)	0.0220(7)	0.0521(10)	-0.0013(6)	0.0065(7)	-0.0019(6)
F(3)	0.0424(9)	0.0417(9)	0.0286(8)	-0.0010(6)	0.0065(6)	-0.0016(6)
F(4)	0.0214(7)	0.0378(8)	0.0570(10)	-0.0035(7)	-0.0029(6)	0.0003(6)
F(5)	0.0217(7)	0.0439(8)	0.0383(8)	-0.0012(6)	-0.0025(6)	0.0037(6)
F(6)	0.0402(9)	0.0208(8)	0.0628(12)	0.0045(7)	0.0039(7)	-0.0008(6)
C(1)	0.0310(12)	0.0300(12)	0.0321(13)	0.0003(10)	-0.0024(10)	0.0026(10)
N(1)	0.0530(14)	0.0516(14)	0.0363(12)	-0.0100(11)	-0.0096(11)	0.0256(12)
N(2)	0.0404(13)	0.0485(13)	0.0361(13)	-0.0075(10)	-0.0092(9)	0.0216(11)
N(3)	0.0485(14)	0.0473(13)	0.0349(12)	-0.0073(10)	-0.0135(10)	0.0201(11)
C(2)	0.0317(12)	0.0340(13)	0.0285(12)	-0.0029(10)	0.0033(10)	-0.0035(10)
N(4)	0.0433(13)	0.0431(13)	0.0450(13)	-0.0154(10)	0.0171(10)	-0.0165(10)
N(5)	0.0471(14)	0.0411(13)	0.0479(14)	-0.0158(11)	0.0223(11)	-0.0161(11)
N(6)	0.0455(13)	0.0441(13)	0.0376(12)	-0.0165(10)	0.0151(10)	-0.0171(11)
O(1)W	0.0613(14)	0.0550(13)	0.0390(12)	-0.0043(10)	-0.0001(10)	-0.0176(11)
N(7)	0.0301(10)	0.0264(11)	0.0492(14)	0.0062(10)	0.0036(10)	0.0043(9)
C(3)	0.063(2)	0.068(2)	0.056(2)	0.0130(18)	0.0164(16)	0.0068(17)
C(4)	0.0448(17)	0.0401(18)	0.068(2)	-0.0060(15)	-0.0066(15)	-0.0009(13)

Table S7. Selected inter-atomic distances (Å) in [H*dma*]·[H*gua*]$_2$·(FeF_6).H_2O

Fe(1)-F(6)	1.9101(15)	C(1)-N(2)	1.310(3)	N(7)-C(4)	1.468(4)
Fe(1)-F(5)	1.9119(14)	C(1)-N(1)	1.320(3)	N(7)-C(3)	1.476(4)
Fe(1)-F(1)	1.9291(15)	C(1)-N(3)	1.324(3)		
Fe(1)-F(2)	1.9312(15)	C(2)-N(4)	1.314(3)		
Fe(1)-F(3)	1.9316(15)	C(2)-N(6)	1.320(3)		
Fe(1)-F(4)	1.9422(14)	C(2)-N(5)	1.327(3)		

Table S8. Selected H-bond distances N-H···A (A = F, O) and O-H···F, and angles in [H*dma*]·[H*gua*]$_2$·(FeF_6).H_2O

B-H (B=N, O)	**d(H···A) (Å)**	**<DHA> (°)**	**d(B···F) (Å)**	**A**
N(1)-H(1)A	2.046	163.40	2.881	F(1)
N(1)-H(1)B	2.011	169.18	2.860	O(1)W
N(2)-H(2)A	2.117	150.90	2.898	F(6)
N(2)-H(2)A	2.554	135.17	3.222	F(5)
N(2)-H(2)B	2.017	159.76	2.840	F(5)
N(3)-H(3)A	2.010	169.06	2.859	F(1)
N(3)-H(3)B	2.051	148.77	2.822	F(1)
N(4)-H(4)A	1.964	176.74	2.823	F(3)
N(4)-H(4)B	1.995	159.31	2.816	F(5)
N(5)-H(5)A	2.208	165.50	3.048	F(2)
N(5)-H(5)B	2.006	162.61	2.838	F(3)
N(6)-H(6)A	1.955	163.91	2.791	F(2)
N(6)-H(6)B	2.143	150.53	2.923	F(4)
N(6)-H(6)B	2.539	139.32	3.240	F(3)
O(1)W-H(1)WB	2.088	150.20	2.866	F(2)
O(1)W-H(1)WA	1.946	161.65	2.761	F(4)
N(7)-H(7)A	1.844	162.43	2.716	F(4)
N(7)-H(7)B	1.765	168.29	2.652	F(6)

3 – [H*dma*]$_2$·[H*gua*]·[NH_4]·[$ZnFeF_5$(*amtetraz*)$_2$]$_2$

Table S9. Atomic coordinates and equivalent isotropic displacement parameters of [H*dma*]$_2$·[H*gua*]·[NH_4]·[$ZnFeF_5$(*amtetraz*)$_2$]$_2$

Atom	site	τ	x	y	z	B_{eq} (Å^2)
Zn(1)	*8f*	1	0.25186(6)	0.4937(2)	0.75123(9)	3,36(14)
Fe(1)	*8f*	1	0.40355(7)	0.1709(3)	0.56670(11)	3,17(14)
F(1)	*8f*	1	0.2495(3)	0.2444(11)	0.8172(4)	3,47(16)
F(2)	*8f*	1	0.4541(3)	0.1269(13)	0.6636(5)	4,58(24)
F(3)	*8f*	1	0.4161(3)	0.4537(11)	0.5754(4)	3,55(16)
F(4)	*8f*	1	0.4496(3)	0.1300(16)	0.5083(5)	5,29(24)
F(5)	*8f*	1	0.3844(4)	-0.0975(13)	0.5580(5)	4,97(24)
N(1)	*8f*	1	0.1971(4)	0.1421(16)	0.6536(6)	3,32(24)
N(2)	*8f*	1	0.1988(4)	0.3466(15)	0.6566(6)	3,32(24)
N(3)	*8f*	1	0.1699(4)	0.4198(17)	0.5925(6)	3,55(24)
N(4)	*8f*	1	0.3517(4)	0.2329(15)	0.4535(6)	2,92(24)
N(5)	*8f*	1	0.1553(5)	-0.0940(17)	0.5602(7)	4,58(32)
C(1)	*8f*	1	0.1654(4)	0.0957(19)	0.5844(7)	3,00(24)
N(6)	*8f*	1	0.3531(4)	0.2299(15)	0.6390(6)	3,24(24)
N(7)	*8f*	1	0.3312(4)	0.0692(15)	0.6642(6)	3,32(24)
N(8)	*8f*	1	0.3029(4)	0.1405(15)	0.7024(6)	3,08(24)
N(9)	*8f*	1	0.3048(4)	0.3471(15)	0.7054(6)	3,16(24)
N(10)	*8f*	1	0.3501(5)	0.5860(17)	0.6567(9)	5,13(32)
C(2)	*8f*	1	0.3366(4)	0.3926(19)	0.6667(7)	2,84(24)
C(3)	*4e*	1	0	-0.130(3)	¼	4,97(47)
N(11)	*4e*	1	0	0.065(4)	¼	6,40(47)
N(12)	*8f*	1	0.0265(6)	-0.224(2)	0.3135(10)	5,76(39)
N(13)	*8f*	1	0.0432(7)	0.657(4)	0.5959(14)	9,87(71)
C(4)	*8f*	1	0.0436(14)	0.849(4)	0.579(2)	12,95(111)
C(5)	*8f*	1	0.0753(10)	0.586(5)	0.6665(17)	10,03(79)
N(14)	*8f*	0.5	0.2393(12)	0.628(8)	0.486(2)	9,47(150)

Table S10. Anisotropic displacement parameters (ADP, Å^2) of [H*dma*]$_2$·[H*gua*]·[NH_4]·[$ZnFeF_5$(*amtetraz*)$_2$]$_2$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	0.050(2)	0.0321(18)	0.0448(19)	-0.0011(6)	0.0116(8)	-0.0001(6)
Fe(1)	0.046(2)	0.0341(19)	0.040(2)	0.0003(7)	0.0103(9)	0.0040(8)
F(1)	0.060(5)	0.034(4)	0.038(4)	0.003(3)	0.015(3)	-0.001(3)
F(2)	0.062(5)	0.051(5)	0.056(5)	0.003(4)	0.005(4)	0.001(4)
F(3)	0.046(5)	0.041(4)	0.047(5)	-0.003(3)	0.013(3)	-0.001(3)
F(4)	0.074(6)	0.071(6)	0.068(6)	-0.008(5)	0.038(5)	0.006(5)
F(5)	0.093(7)	0.032(4)	0.056(5)	-0.004(4)	0.008(5)	-0.007(4)
N(1)	0.051(6)	0.032(5)	0.038(5)	0.002(4)	0.004(4)	-0.006(5)
N(2)	0.056(7)	0.033(5)	0.036(5)	0.001(4)	0.012(5)	0.003(5)
N(3)	0.047(7)	0.046(6)	0.039(6)	0.003(5)	0.007(5)	0.003(5)
N(4)	0.041(5)	0.034(5)	0.034(5)	-0.008(4)	0.008(4)	-0.006(4)
N(5)	0.072(9)	0.027(6)	0.057(7)	-0.001(5)	-0.011(6)	-0.003(5)
C(1)	0.037(6)	0.037(6)	0.037(6)	0.005(5)	0.006(5)	0.001(5)

N(6)	0.051(6)	0.033(5)	0.042(6)	0.002(4)	0.015(5)	0.002(4)
N(7)	0.052(7)	0.029(5)	0.048(6)	0.005(4)	0.017(5)	0.002(4)
N(8)	0.051(6)	0.030(5)	0.037(5)	-0.004(4)	0.010(4)	0.004(4)
N(9)	0.049(6)	0.031(5)	0.044(6)	-0.002(4)	0.023(5)	-0.011(4)
N(10)	0.084(10)	0.025(6)	0.103(11)	-0.004(6)	0.055(8)	-0.008(6)
C(2)	0.036(6)	0.032(6)	0.040(6)	-0.003(5)	0.011(5)	-0.004(5)
C(3)	0.076(15)	0.035(10)	0.071(15)	0	0.008(12)	0
N(11)	0.094(17)	0.058(13)	0.083(15)	0	0.009(13)	0
N(12)	0.079(10)	0.046(7)	0.082(10)	0.016(7)	-0.002(8)	-0.002(7)
N(13)	0.090(14)	0.14(2)	0.129(18)	-0.061(16)	0.000(13)	0.032(14)
C(5)	0.12(2)	0.14(3)	0.12(2)	-0.01(2)	0.010(18)	0.02(2)
N(14)	0.08(2)	0.21(4)	0.09(2)	-0.12(3)	0.077(19)	-0.09(3)

Table S11. Selected inter-atomic distances (Å) in $[H\textit{dma}]_2\cdot[H\textit{gua}]\cdot[NH_4]\cdot[ZnFeF_5(\textit{amtetraz})_2]_2$

Zn(1)-F(1)	2.025(7)	N(1)-C(1)	1.344(15)	N(9)-C(2)	1.325(14)
Zn(1)-F(1)	2.040(7)	N(1)-N(2)	1.360(14)	N(10)-C(2)	1.369(18)
Zn(1)-N(1)	2.148(11)	N(2)-N(3)	1.299(14)	C(3)-N(11)	1.30(3)
Zn(1)-N(9)	2.160(10)	N(3)-N(4)	1.341(14)	C(3)-N(12)	1.324(17)
Zn(1)-N(2)	2.170(11)	N(4)-N(3)	1.341(14)	C(3)-N(12)	1.324(17)
Zn(1)-N(8)	2.209(10)	N(4)-C(1)	1.343(16)	N(13)-C(5)	1.41(3)
Fe(1)-F(5)	1.864(8)	N(5)-C(1)	1.337(18)	N(13)-C(4)	1.313(10)
Fe(1)-F(3)	1.913(8)	C(1)-N(4)	1.343(16)		
Fe(1)-F(4)	1.917(8)	N(6)-C(2)	1.327(16)		
Fe(1)-F(2)	1.944(9)	N(6)-N(7)	1.377(14)		
Fe(1)-N(4)	2.178(10)	N(7)-N(8)	1.288(14)		
Fe(1)-N(6)	2.221(10)	N(8)-N(9)	1.375(14)		

Table S12. Selected H-bond distances N-H···A (A = F, N) and angles in $[H\textit{dma}]_2\cdot[H\textit{gua}]\cdot[NH_4]\cdot[ZnFeF_5(\textit{amtetraz})_2]_2$

N-H	d(H···A) (Å)	<DHA> (°)	d(N···A) (Å)	A
N(5)-H(5)A	2.153	138.05	2.851	F(3)
N(5)-H(5)A	2.269	132.32	2.918	F(5)
N(5)-H(5)B	2.547	134.87	3.212	F(1)
N(5)-H(5)B	2.577	140.65	3.287	N(3)
N(10)-H(10)A	2.550	140.22	3.258	N(7)
N(10)-H(10)A	2.628	130.92	3.256	F(1)
N(10)-H(10)B	2.106	141.02	2.827	F(3)
N(10)-H(10)B	2.418	130.16	3.045	F(5)
N(11)-H(11)A	1.897	149.93	2.676	F(2)
N(11)-H(11)B	1.897	149.93	2.676	F(2)
N(12)-H(12)A	2.006	165.77	2.847	F(3)
N(12)-H(12)B	1.902	163.52	2.737	F(2)
N(13)-H(13)A	1.823	157.72	2.678	F(4)
N(13)-H(13)B	2.127	128.72	2.780	F(4)
N(13)-H(13)B	2.319	152.21	3.144	F(2)
N(14)-H	-	-	3.144	F(1)
N(14)-H	-	-	3.147	N(7)

4 – [H*dma*]$_2$·[Zn$_{1.6}$Fe$^{II}_{0.4}$Fe^{III}F$_6$(*amtetraz*)$_3$]

Table S13. Atomic coordinates and equivalent isotropic displacement parameters of [H*dma*]$_2$·[Zn$_{1.6}$Fe$_{1.4}$F$_6$(*amtetraz*)$_3$]

Atom	site	τ	x	y	z	B_{eq} (Å^2)
Fe(2)	*2a*	1	1.24739(9)	0.24548(14)	0.49570(6)	0,96(1)
Zn(1)/Fe(1)	*2a*	0.6/0.4	0.49483(7)	0.59155(6)	-0.00549(6)	0,72(1)
Zn(2)	*2a*	1	0.95027(5)	0.40171(8)	-0.00328(7)	0,89(1)
F(1)	*2a*	1	1.1076(4)	0.1489(6)	0.4862(3)	2,01(8)
F(2)	*2a*	1	1.1868(4)	0.5178(6)	0.4646(3)	1,67(6)
F(3)	*2a*	1	1.3077(4)	-0.0230(6)	0.5233(3)	1,69(6)
F(4)	*2a*	1	1.3867(3)	0.3447(6)	0.5033(3)	1,85(6)
F(5)	*2a*	1	0.9701(5)	0.1560(6)	-0.0771(3)	2,20(8)
F(6)	*2a*	1	0.4758(3)	0.3436(5)	0.0714(3)	1,11(5)
N(1)	*2a*	1	1.1755(5)	0.1872(9)	0.3188(4)	1,09(8)
N(2)	*2a*	1	1.1246(5)	0.3420(8)	0.2431(4)	1,26(7)
N(3)	*2a*	1	1.0771(5)	0.2639(8)	0.1439(4)	1,13(6)
N(4)	*2a*	1	1.0919(4)	0.0554(8)	0.1493(4)	1,02(9)
N(5)	*2a*	1	1.1892(5)	-0.1731(9)	0.3013(4)	1,56(9)
C(1)	*2a*	1	1.1525(5)	0.0138(9)	0.2586(5)	0,93(9)
N(6)	*2a*	1	0.8031(4)	0.3564(6)	0.0013(5)	1,03(6)
N(7)	*2a*	1	0.7378(4)	0.5155(7)	-0.0004(6)	1,11(6)
N(8)	*2a*	1	0.6490(4)	0.4449(6)	0.0050(5)	1,09(6)
N(9)	*2a*	1	0.6519(4)	0.2397(7)	0.0091(4)	0,92(6)
N(10)	*2a*	1	0.7843(6)	-0.0088(9)	0.0124(7)	1,97(9)
C(2)	*2a*	1	0.7470(5)	0.1893(9)	0.0061(7)	1,09(8)
N(11)	*2a*	1	1.3152(4)	0.3043(7)	0.6682(4)	1,14(9)
N(12)	*2a*	1	1.3547(5)	0.1525(8)	0.7447(4)	1,18(10)
N(13)	*2a*	1	1.4033(4)	0.2330(8)	0.8441(4)	0,92(8)
N(14)	*2a*	1	1.3991(4)	0.4374(8)	0.8388(4)	1,01(8)
N(15)	*2a*	1	1.3183(5)	0.6698(9)	0.6835(5)	1,75(12)
C(3)	*2a*	1	1.3435(5)	0.4802(9)	0.7283(5)	1,03(9)
N(1)A	*2a*	1	0.9594(5)	0.5920(11)	0.3599(4)	1,96(9)
C(1)A	*2a*	1	0.9318(6)	0.7793(13)	0.2899(7)	2,66(13)
C(1)B	*2a*	1	0.9000(6)	0.4072(16)	0.2941(6)	2,60(13)
N(2)A	*2a*	1	1.4641(5)	0.3798(10)	0.3588(4)	1,91(9)
C(2)A	*2a*	1	1.4095(7)	0.5642(13)	0.2880(7)	2,57(13)
C(2)B	*2a*	1	1.4295(7)	0.1874(13)	0.2945(8)	2,72(14)

Table S14. Anisotropic displacement parameters (ADP, Å^2) of [H*dma*]$_2$·[Zn$_{1.6}$Fe$_{1.4}$F$_6$(*amtetraz*)$_3$]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(2)	0.0148(4)	0.0095(2)	0.0105(3)	0.0000(2)	0.0048(4)	0.0011(3)
Zn(1)/Fe(1)	0.0131(4)	0.00363(19)	0.0095(3)	-0.0003(3)	0.0046(4)	-0.0001(2)
Zn(2)	0.0147(4)	0.0068(2)	0.0108(2)	0.0003(3)	0.0051(4)	-0.0002(2)
F(1)	0.026(2)	0.032(3)	0.020(2)	-0.0006(15)	0.0120(18)	-0.0084(15)
F(2)	0.029(2)	0.0122(17)	0.0129(17)	0.0019(13)	0.0032(16)	0.0054(16)
F(3)	0.034(2)	0.0111(16)	0.0157(18)	-0.0008(13)	0.0097(18)	0.0008(16)

F(4)	0.0200(18)	0.032(2)	0.0183(17)	-0.0004(17)	0.0094(15)	-0.0050(16)
F(5)	0.049(3)	0.0129(16)	0.0112(14)	0.0009(13)	0.006(2)	0.0111(16)
F(6)	0.0227(17)	0.0045(13)	0.0182(15)	-0.0001(12)	0.0127(14)	0.0005(13)
N(1)	0.019(3)	0.013(2)	0.010(2)	-0.0028(17)	0.0075(18)	-0.0012(18)
N(2)	0.022(3)	0.011(2)	0.0113(19)	0.0031(19)	0.005(2)	0.004(2)
N(3)	0.018(2)	0.009(2)	0.0132(19)	-0.0005(16)	0.005(2)	0.004(2)
N(4)	0.016(2)	0.012(3)	0.011(2)	-0.0023(16)	0.0062(17)	-0.0007(17)
N(5)	0.033(3)	0.011(2)	0.010(2)	0.002(2)	0.007(2)	0.005(2)
C(1)	0.012(3)	0.010(3)	0.013(3)	0.000(2)	0.005(2)	0.0011(19)
N(6)	0.017(2)	0.0045(18)	0.0177(18)	0.004(2)	0.008(2)	0.0026(16)
N(7)	0.015(3)	0.0063(18)	0.021(2)	0.001(3)	0.008(3)	0.0000(19)
N(8)	0.018(2)	0.0055(19)	0.020(2)	0.000(2)	0.011(2)	-0.0015(16)
N(9)	0.013(2)	0.0082(17)	0.014(2)	0.000(2)	0.0062(18)	-0.0010(16)
N(10)	0.028(3)	0.008(2)	0.046(4)	0.001(3)	0.023(3)	0.004(2)
C(2)	0.017(3)	0.0061(19)	0.017(3)	0.000(3)	0.007(2)	0.000(2)
N(11)	0.027(3)	0.003(2)	0.011(2)	0.0006(16)	0.0076(18)	0.0010(17)
N(12)	0.024(3)	0.010(2)	0.007(2)	-0.0002(15)	0.004(2)	-0.0022(18)
N(13)	0.015(2)	0.007(2)	0.0124(19)	0.0000(16)	0.0059(16)	-0.0033(18)
N(14)	0.015(2)	0.005(2)	0.017(2)	-0.0031(17)	0.0065(18)	-0.0018(15)
N(15)	0.037(4)	0.006(2)	0.016(2)	-0.001(2)	0.007(2)	0.001(2)
C(3)	0.013(3)	0.011(3)	0.017(3)	0.002(2)	0.008(2)	0.0015(18)
N(1)A	0.018(2)	0.037(3)	0.020(2)	-0.003(3)	0.010(2)	0.008(3)
C(1)A	0.029(4)	0.032(5)	0.047(4)	0.008(3)	0.024(3)	0.004(3)
C(1)B	0.025(3)	0.037(4)	0.039(4)	0.003(4)	0.017(3)	0.005(3)
N(2)A	0.021(2)	0.031(3)	0.020(2)	0.000(2)	0.009(2)	-0.001(2)
C(2)A	0.032(4)	0.028(4)	0.038(4)	0.004(3)	0.017(3)	-0.003(3)
C(2)B	0.034(4)	0.027(4)	0.051(5)	-0.016(3)	0.028(4)	-0.010(3)

Table S15. Selected inter-atomic distances (Å) in [H*dma*]$_2$·[$Zn_{1.6}Fe_{1.4}F_6$(*amtetraz*)$_3$]

Fe(2)-F(3)	1.898(4)	N(1)-C(1)	1.349(8)	N(15)-C(3)	1.356(8)
Fe(2)-F(1)	1.908(4)	N(1)-N(2)	1.371(7)	N(1)A-C(1)B	1.488(12)
Fe(2)-F(4)	1.918(4)	N(2)-N(3)	1.290(6)	N(1)A-C(1)A	1.491(10)
Fe(2)-F(2)	1.923(4)	N(3)-N(4)	1.381(7)	N(2)A-C(2)B	1.479(9)
Fe(2)-N(11)	2.107(5)	N(4)-C(1)	1.335(7)	N(2)A-C(2)A	1.499(10)
Fe(2)-N(1)	2.156(5)	N(5)-C(1)	1.346(8)		
Zn(1)/Fe(1)-F(6)	2.011(3)	N(6)-C(2)	1.347(6)		
Zn(1)/Fe(1)-F(6)	2.019(3)	N(6)-N(7)	1.352(6)		
Zn(1)/Fe(1)-N(14)	2.129(5)	N(7)-N(8)	1.303(6)		
Zn(1)/Fe(1)-N(13)	2.156(5)	N(8)-N(9)	1.349(6)		
Zn(1)/Fe(1)-N(9)	2.159(4)	N(9)-C(2)	1.326(7)		
Zn(1)/Fe(1)-N(8)	2.206(4)	N(10)-C(2)	1.381(8)		
Zn(2)-F(5)	1.987(4)	N(11)-N(12)	1.352(7)		
Zn(2)-F(5)	1.996(4)	N(11)-C(3)	1.360(8)		
Zn(2)-N(6)	2.009(4)	N(12)-N(13)	1.298(7)		
Zn(2)-N(4)	2.054(5)	N(13)-N(14)	1.345(6)		
Zn(2)-N(3)	2.099(5)	N(14)-C(3)	1.348(8)		

Table S16. Selected H-bond distances N-H···A (A = F, N) and angles in [H*dma*]$_2$·[$Zn_{1.6}Fe_{1.4}F_6$(*amtetraz*)$_3$]

N-H	d(H···A) (Å)	<DHA> (°)	d(N···F) (Å)	A
N(5)-H(5)A	2.310	133.55	2.969	F(5)
N(5)-H(5)A	2.579	141.32	3.294	N(2)
N(5)-H(5)B	2.105	141.16	2.827	F(3)
N(5)-H(5)B	2.494	120.77	3.026	F(2)
N(10)-H(10)A	2.488	137.24	3.174	N(7)
N(10)-H(10)A	2.595	130.23	3.218	F(6)
N(15)-H(15)A	2.495	147.89	3.256	N(12)
N(15)-H(15)B	2.094	140.45	2.811	F(2)
N(15)-H(15)B	2.376	122.48	2.929	F(3)
N(1)A-H(1)A1	1.788	177.32	2.687	F(2)
N(1)A-H(1)A2	1.776	177.41	2.676	F(1)
N(2)A-H(2)A1	1.852	164.85	2.730	F(3)
N(2)A-H(2)A2	1.747	170.74	2.639	F(4)

5 – [H*dma*]·[Zn_4F_5(*amtetraz*)$_4$]

Table S17. Atomic coordinates and equivalent isotropic displacement parameters of **[H*dma*]·[Zn_4F_5(*amtetraz*)$_4$]**

Atom	site	τ	x	y	z	B_{eq} (Å^2)
Zn(1)	*2n*	1	0.29709(13)	½	0.59708(10)	0.67(2)
Zn(2)	*1a*	1	0	0	0	0.74(2)
Zn(3)	*1d*	1	½	0	0	1.22(2)
F(1)	*2m*	1	0.2579(7)	0	0.1383(5)	0.88(7)
F(2)	*2n*	1	0.3852(7)	½	0.3822(6)	0.96(7)
F(3)	*1f*	1	0	½	½	1.03(9)
N(1)	*4o*	1	0.1415(7)	0.1557(5)	0.8626(5)	0.74(6)
N(2)	*4o*	1	0.4157(7)	0.2550(5)	0.7767(6)	1.02(7)
N(3)	*4o*	1	0.3480(7)	0.1557(5)	0.8610(5)	0.84(7)
N(4)	*4o*	1	0.2530(7)	0.3241(4)	0.7171(5)	0.84(6)
C(1)	*4o*	1	0.0856(8)	0.2612(6)	0.7728(7)	0.92(8)
N(5)	*4o*	1	-0.1095(8)	0.2952(6)	0.7376(7)	2.36(12)
C(2)	*1g*	1	½	0	½	5.61(63)
C(3)	*2m*	0.5	0.1570(8)	0	0.5067(7)	2.53(32)
N(6)	*4o*	0.25	0.3518(8)	0.0506(6)	0.4373(7)	1.89(39)

Table S18. Anisotropic displacement parameters (ADP, $Å^2$) of [H*dma*]·[Zn_4F_5(*amtetraz*)$_4$]

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Zn(1)	0.0122(4)	0.0049(4)	0.0083(4)	0	0.0011(3)	0
Zn(2)	0.0111(5)	0.0065(5)	0.0106(6)	0	0.0007(5)	0
Zn(3)	0.0189(6)	0.0109(6)	0.0162(6)	0	-0.0019(6)	0
F(1)	0.012(2)	0.012(2)	0.010(2)	0	-0.0016(16)	0
F(2)	0.013(2)	0.013(2)	0.010(2)	0	0.0030(17)	0
F(3)	0.014(3)	0.011(3)	0.014(3)	0	0.001(3)	0
N(1)	0.0095(18)	0.0060(18)	0.013(2)	0.0032(16)	0.0019(15)	-0.0002(15)
N(2)	0.014(2)	0.007(2)	0.018(2)	0.0051(17)	0.0006(17)	0.0009(16)
N(3)	0.013(2)	0.0054(18)	0.014(2)	0.0028(16)	0.0025(16)	-0.0005(15)
N(4)	0.012(2)	0.0064(18)	0.013(2)	0.0044(15)	-0.0003(16)	-0.0001(16)
C(1)	0.014(2)	0.008(2)	0.013(2)	0.0024(18)	-0.0004(18)	0.0014(19)
N(5)	0.013(2)	0.026(3)	0.051(4)	0.028(3)	0.001(2)	0.003(2)
C(2)	0.15(3)	0.052(12)	0.009(7)	0	0.005(12)	0
C(3)	0.039(12)	0.034(11)	0.023(9)	0	0.002(9)	0
N(6)	0.039(13)	0.019(9)	0.014(10)	0.002(8)	0.001(9)	-0.002(9)

Table S19. Selected inter-atomic distances (Å) in [H*dma*]·[Zn_4F_5(*amtetraz*)$_4$]

Zn(1)-F(2)	1.949(5)	Zn(3)-F(1) x2	1.997(5)	N(4)-C(1)	1.349(7)
Zn(1)-N(4) x2	2.021(4)	Zn(3)-N(3) x4	2.168(5)	C(1)-N(5)	1.353(7)
Zn(1)-F(2)	2.089(5)	N(1)-C(1)	1.334(7)	C(2)-N(6)	1.212(5)
Zn(1)-F(3)	2.1131(9)	N(1)-N(3)	1.354(6)	C(3)-N(6)	1.499(4)
Zn(2)-F(1) x2	2.060(5)	N(2)-N(3)	1.290(6)		
Zn(2)-N(1) x4	2.141(4)	N(2)-N(4)	1.357(6)		

Table S20. Selected H-bond distances N-H···A (A = F, N) and angles in [H*dma*]·[Zn_4F_5(*amtetraz*)$_4$]

N-H	**d(H···A) (Å)**	**<DHA> (°)**	**d(N···F) (Å)**	**A**
N(5)-H(5)A	2.468	138.02	3.160	N(2)
N(5)-H(5)A	2.540	136.07	3.215	F(1)
N(5)-H(5)B	2.165	139.59	2.874	F(2)
N(5)-H(5)B	2.218	143.21	2.952	F(3)

Table S21. Selected inter-atomic distances (Å) and valence bond calculations

	i-j	d_{ij}	s_{ij}		i-j	d_{ij}	s_{ij}
1	Fe(1)-F(2) x 4 Fe(1)-F(1) x 2 Zn(1)-F(1) x 2 Zn(1)-Ow(1) x 4	1.9320(9) 1.9370(11) 2.0485(11) 2.0903(10)	0.49 0.49 0.31 0.35	**2**	Fe(1)-F(1) Fe(1)-F(2) Fe(1)-F(3) Fe(1)-F(4) Fe(1)-F(5) Fe(1)-F(6)	1.9291(15) 1.9312(15) 1.9316(15) 1.9422(14) 1.9119(14) 1.9101(15)	0.50 0.49 0.49 0.48 0.52 0.52
	Σs_{ij}				Σs_{ij}		
	ΣFe(1) = 2.94 ΣZn(1) = 2.04 ΣF(1) = 0.80	ΣF(2) = 0.49 ΣOw(1) = 1.90			ΣFe(1) = 3.01 ΣF(1) = 0.50 ΣF(2) = 0.49 ΣF(3) = 0.49	ΣF(4) = 0.48 ΣF(5) = 0.52 ΣF(6) = 0.52	
3	Fe(1)-F(2) Fe(1)-F(3) Fe(1)-F(4) Fe(1)-F(5) Fe(1)-N(4) Fe(1)-N(6) Zn(1)-F(1) Zn(1)-F(1) Zn(1)-N(1) Zn(1)-N(2) Zn(1)-N(8) Zn(1)-N(9)	1.944(9) 1.913(8) 1.917(8) 1.864(8) 2.178(10) 2.221(10) 2.025(7) 2.040(7) 2.148(11) 2.170(11) 2.209 (10) 2.160(10)	0.48 0.52 0.51 0.59 0.37 0.33 0.33 0.32 0.36 0.34 0.30 0.35		N(1)-C(1) N(1)-N(2) N(2)-N(3) N(3)-N(4) N(4)-C(1) N(5)-C(1) N(6)-C(2) N(6)-N(7) N(7)-N(8) N(8)-N(9) N(9)-C(2) N(10)-C(2)	1.344(15) 1.360(14) 1.299(14) 1.341(14) 1.343(16) 1.337(18) 1.327(16) 1.377(14) 1.288(14) 1.375(13) 1.322(14) 1.369(18)	1.30 1.24 1.46 1.28 1.31 1.33 1.36 1.19 1.51 1.19 1.37 1.22
	Σs_{ij}						
	ΣFe(1) = 2.81 ΣZn(1) = 2.01 ΣF(1) = 0.66 ΣF(2) = 0.48	ΣF(3) = 0.52 ΣF(4) = 0.51 ΣF(5) = 0.59			ΣN(1) = 2.90 ΣN(2) = 3.04 ΣN(4) = 2.96	ΣN(6) = 2.88 ΣN(8) = 3.00 ΣN(9) = 2.91	
4	Fe(2)-F(1) Fe(2)-F(2) Fe(2)-F(3) Fe(2)-F(4) Fe(2)-N(1) Fe(2)-N(11) Zn(1)/Fe(1)-F(6) Zn(1)/Fe(1)-F(6) Zn(1)/Fe(1)-N(8) Zn(1)/Fe(1)-N(9) Zn(1)/Fe(1)-N(13) Zn(1)/Fe(1)-N(14) Zn(2)-F(5) Zn(2)-F(5) Zn(2)-N(3) Zn(2)-N(4) Zn(2)-N(6)	1.908(4) 1.923(4) 1.898(4) 1.918(4) 2.156(5) 2.107(5) 2.011(3) 2.019(3) 2.206(4) 2.159(4) 2.156(5) 2.129(5) 1.987(4) 1.996(4) 2.099(5) 2.054(5) 2.009(4)	0.53 0.50 0.54 0.51 0.40 0.45 0.35 0.34 0.31 0.35 0.35 0.38 0.37 0.36 0.41 0.46 0.52		N(1)-C(1) N(1)-N(2) N(2)-N(3) N(3)-N(4) N(4)-C(1) N(5)-C(1) N(6)-C(2) N(6)-N(7) N(7)-N(8) N(8)-N(9) N(9)-C(2) N(10)-C(2) N(11)-N(12) N(11)-C(3) N(12)-N(13) N(13)-N(14) N(14)-C(3) N(15)-C(3)	1.349(8) 1.371(7) 1.290(6) 1.381(7) 1.335(7) 1.346(8) 1.347(6) 1.352(6) 1.303(6) 1.349(6) 1.326(7) 1.381(8) 1.352(7) 1.360(8) 1.298(7) 1.345(6) 1.348(8) 1.356(8)	1.28 1.21 1.51 1.17 1.33 1.30 1.29 1.28 1.46 1.28 1.36 1.18 1.28 1.24 1.48 1.29 1.28 1.26

	Σs_{ij}						
	ΣZn(1)/Fe(1)= 2.08 ΣFe(2) = 2.93 ΣZn(2) = 2.13 ΣF(1) = 0.53 ΣF(2) = 0.50	ΣF(3) = 0.54 ΣF(4) = 0.51 ΣF(5) = 0.73 ΣF(6) = 0.69		ΣN(1) = 2.89 ΣN(3) = 3.09 ΣN(4) = 2.97 ΣN(6) = 3.09 ΣN(8) = 3.04	ΣN(9) = 2.99 ΣN(11) = 2.97 ΣN(13) = 3.12 ΣN(14) = 2.95		
5	Zn(1)-F(2) Zn(1)-F(2) Zn(1)-F(3) Zn(1)-N(4) x 2 Zn(2)-F(1) x 2 Zn(2)-N(1) x 4 Zn(3)-F(1) x 2 Zn(3)-N(3) x 4	1.949(5) 2.089(5) 2.1131(9) 2.021(4) 2.060(5) 2.141(4) 1.997(5) 2.168(5)	0.41 0.28 0.26 0.51 0.30 0.37 0.36 0.34		N(1)-C(1) N(1)-N(3) N(2)-N(3) N(2)-N(4) N(4)-C(1) N(5)-C(1)	1.334(7) 1.354(6) 1.290(6) 1.357(6) 1.349(7) 1.353(7)	1.33 1.27 1.50 1.25 1.29 1.27
	Σs_{ij}						
	ΣZn(1) = 1.97 ΣZn(2) = 2.08 ΣZn(3) = 2.09	ΣF(1) = 0.67 ΣF(2) = 0.69 ΣF(3) = 0.53		ΣN(1) = 2.97 ΣN(3) = 3.11 ΣN(4) = 3.04			

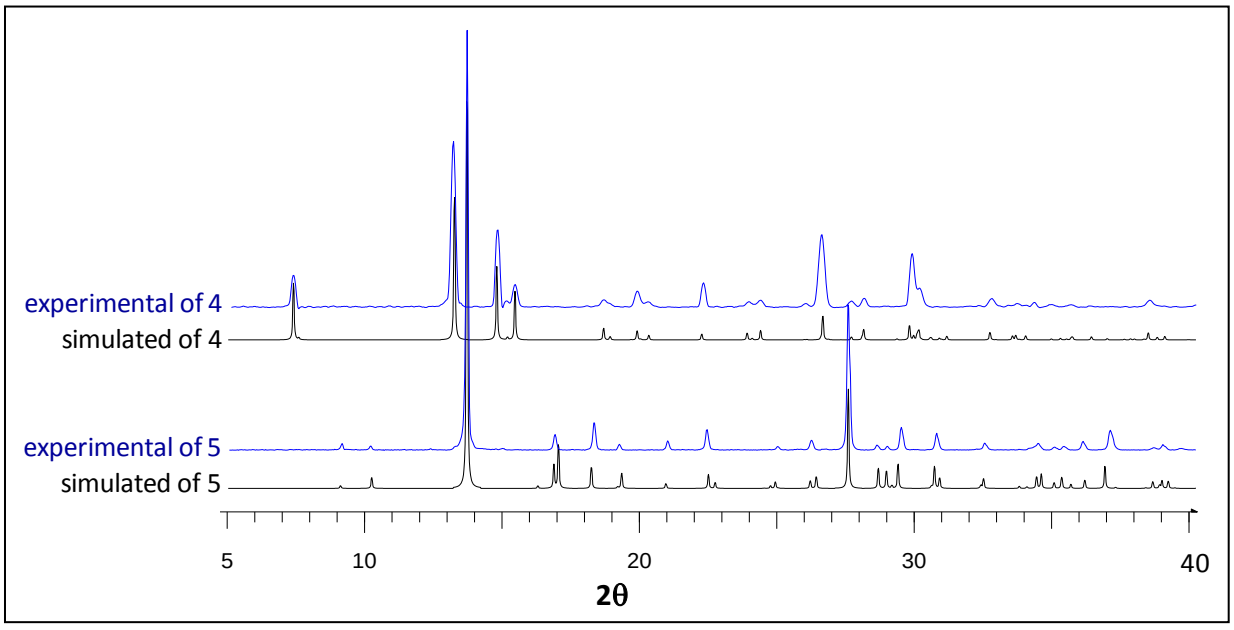

Figure S1. Experimental and simulated XRD patterns of $[H\textit{dma}]_2{\cdot}(Zn_{1.6}Fe_{1.4}F_6(\textit{amtetraz})_3)$ (**4**) and $[H\textit{dma}]{\cdot}(Zn_4F_5(\textit{amtetraz})_4)$ (**5**)

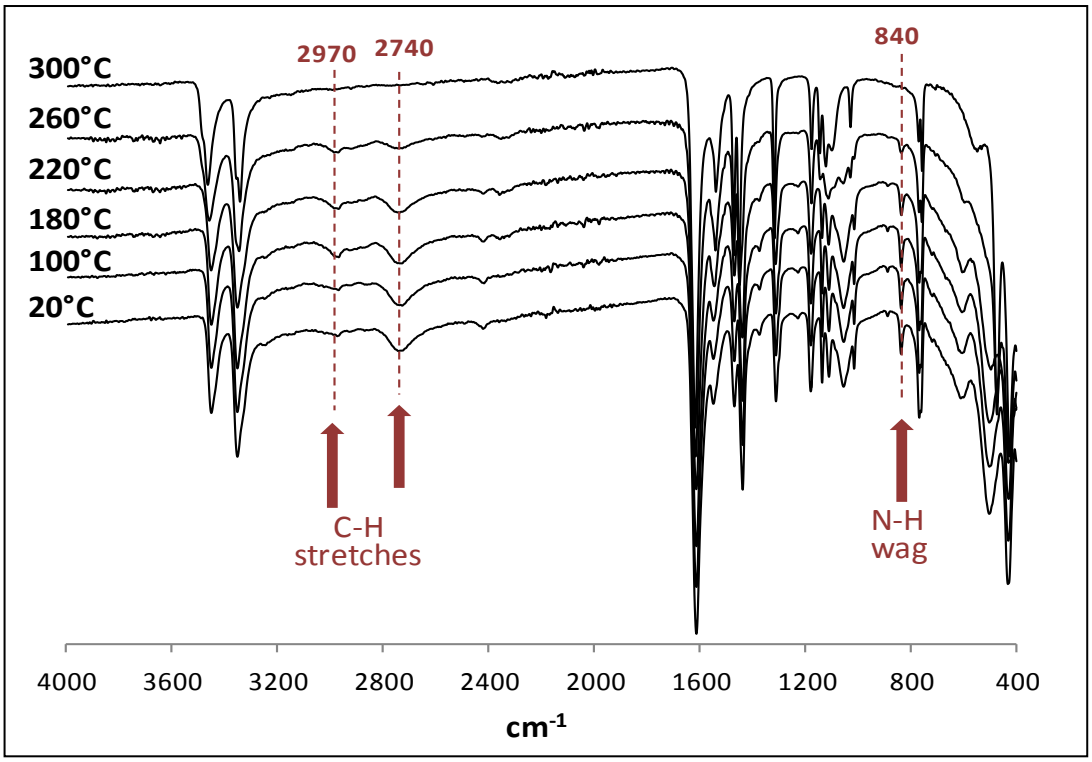

Figure S2. Evolution of infrared spectra of [H*dma*]·(Zn_4F_5(*amtetraz*)$_4$) (**5**) with the temperature

Experimental section S1: Microwave Plasma analyses

The elemental analyses have been performed by Microwave Plasma (MP) analysis using an Agilent 4100 MP-AES. From an initial solution containing iron and zinc cations (100 ppm), standard solutions have been prepared to obtain the concentrations: 0, 0.5, 1, 2, 5, 10 and 20 ppm. The intensity of the signal as a function of the element concentration, obtained for each element (Zn, Fe) is reported in Figure S3; good correlation coefficients are obtained (Figure S3). The solids were dissolved in a mixture of deionized water and nitric acid (5mL HNO_3 in 1L of H_2O).

► 8.3 mg of [H*dma*]$_2$·($Zn_{1.6}Fe_{1.4}F_6$(*amtetraz*)$_3$) are digested in 100 mL HNO_3/H_2O.

- $[Zn^{2+}]_{exp}/[Zn^{2+}]_{théo}$ (ppm): 9.15/8.59 or $[Zn^{2+}]_{exp}/[Zn^{2+}]_{théo}$ (mmol.L^{-1}): 0.164/0.154

- $[Fe^{n+}]_{exp}/[Fe^{n+}]_{théo}$ (ppm): 10.70/11.50 or $[Fe^{n+}]_{exp}/[Fe^{n+}]_{théo}$ (mmol.L^{-1}): 0.163/0.176

►4.4 mg of [H*dma*]·(Zn_4F_5(*amtetraz*)$_4$) are digested in 100 mL HNO_3/H_2O.

- $[Zn^{2+}]_{exp}/[Zn^{2+}]_{théo}$ (ppm): 15.58/15.75 or $[Zn^{2+}]_{exp}/[Zn^{2+}]_{théo}$ (mmol.L^{-1}): 0.238/0.241

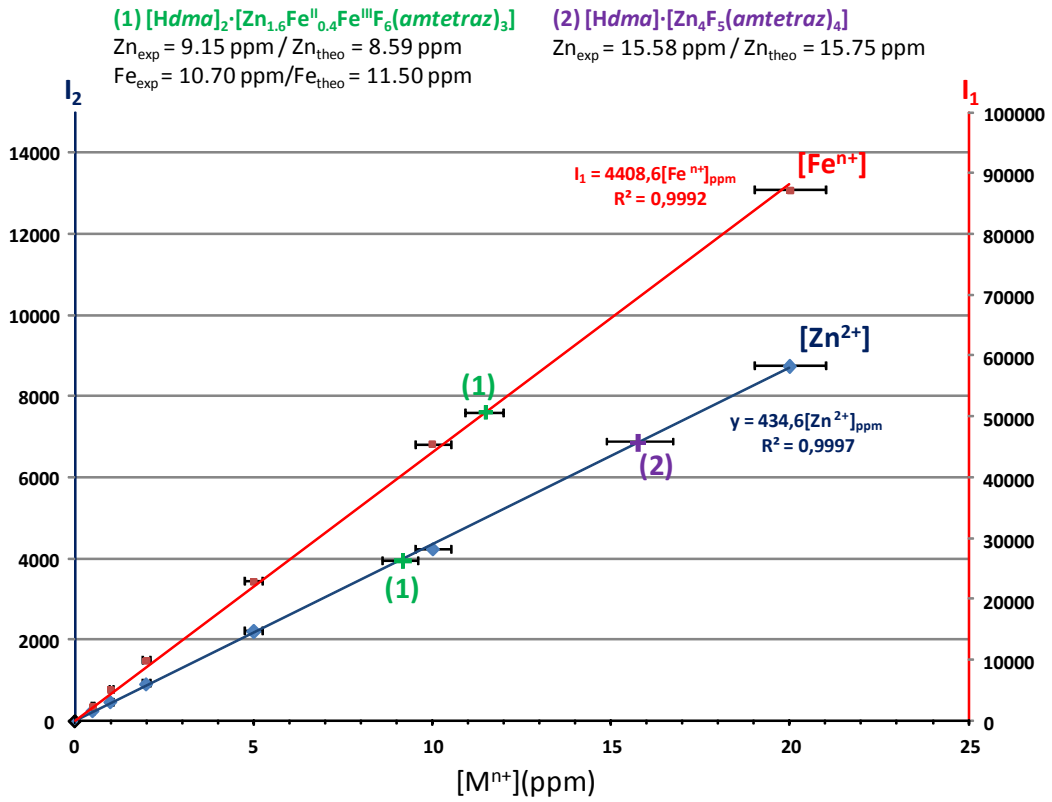

Figure S3. Microwave Plasma analyses of [H*dma*]$_2$·($Zn_{1.6}Fe_{1.4}F_6$(*amtetraz*)$_3$) (**4**) and [H*dma*]·(Zn_4F_5(*amtetraz*)$_4$) (**5**)