Supplementary Information

Synthesis of zinc complex (8): N,N'-Bis-(2,2'-bipyridine-6-ylmethyl)-2,2'-biphenylenediamine[1] (L^1) (260 mg, 0.5 mmol) and $[Zn(H_2O)_6][ClO_4]_2$ (222 mg, 0.6 mmol) were stirred under an argon atmosphere in dry CH_3CN (5 mL) for 3 h. Then water (15 mL), dichloromethane (15 mL) and $[NH_4][PF_6]$ (326 mg, 2.0 mmol) were added, the organic phase was seperated, dried over $MgSO_4$ and reduced to dryness, to afford the zinc complex **8** (350 mg, 80%). Further purification was achieved by diffusion of diethyl ether vapors to a solution of complex **8** in CH_3CN to afford the complex as colourless cystals.
^{1}H-NMR (δ, CD_3CN): 3.89 (dd, J = 19.0, 5.2 Hz, 2H, CH_2), 4.41 (dd, J = 19.0, 9.7 Hz, 2H, CH_2), 5.15 (dd, J = 9.4, 4.8 Hz, 2H, NH), 6.29 (d, J = 8.0 Hz, 2H), 6.86 (t, J = 7.7 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 7.13 (t, J = 7.5 Hz, 2H), 7.30 (d, J = 7.3 Hz, 2H), 7.59 (dd, J = 7.4, 4.9 Hz, 2H), 8.11 (t, J = 7.9 Hz, 2H), 8.12 (d, J = 5.0 Hz, 2H), 8.31 (t, J = 8.2 Hz, 2H), 8.43 (d, J = 7.9 Hz, 2H)), 8.58 (d, J = 8.1 Hz, 2H). elemental analysis calcd (%) for C_{34} $H_{28}F_{12}N_6P_2Zn \cdot 1.5H_2O$ (901.12 g mol^{-1}): C 45.22, H 3.46, N 9.31; found C 45.12, H 3.52, N 9.10.

NMR

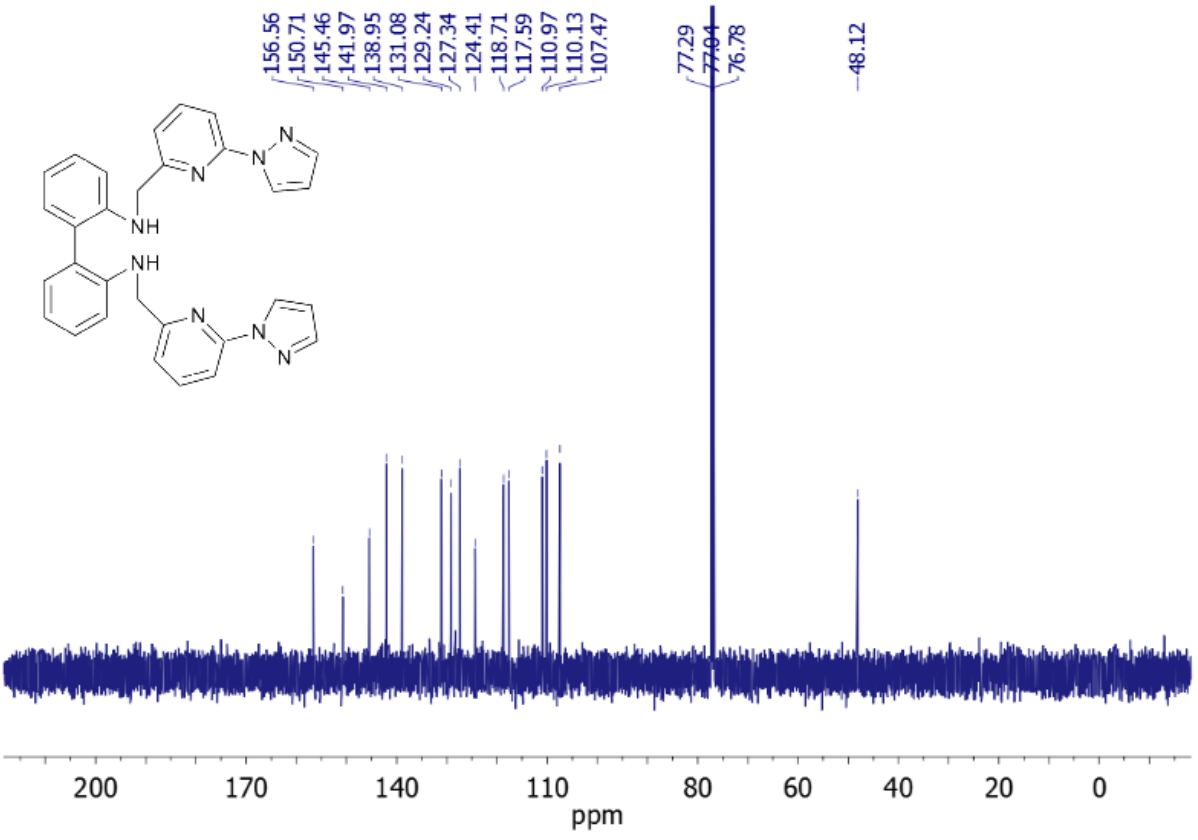

Figure S1: ^{13}C NMR of hexadentate ligand 3 in $CDCl_3$ at 298K.

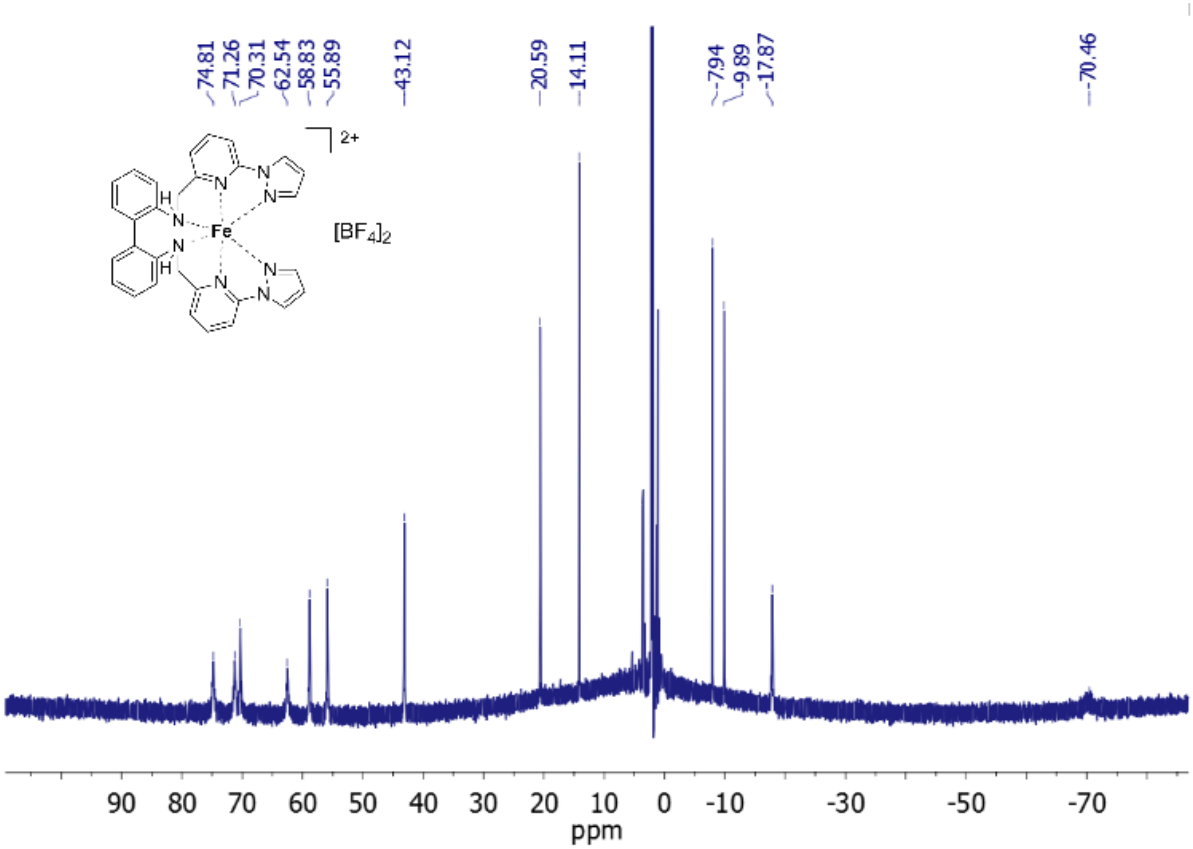

Figure S2: ^{1}H NMR of the tetrafluoroborate salt 4 in CD_3CN at 298K.

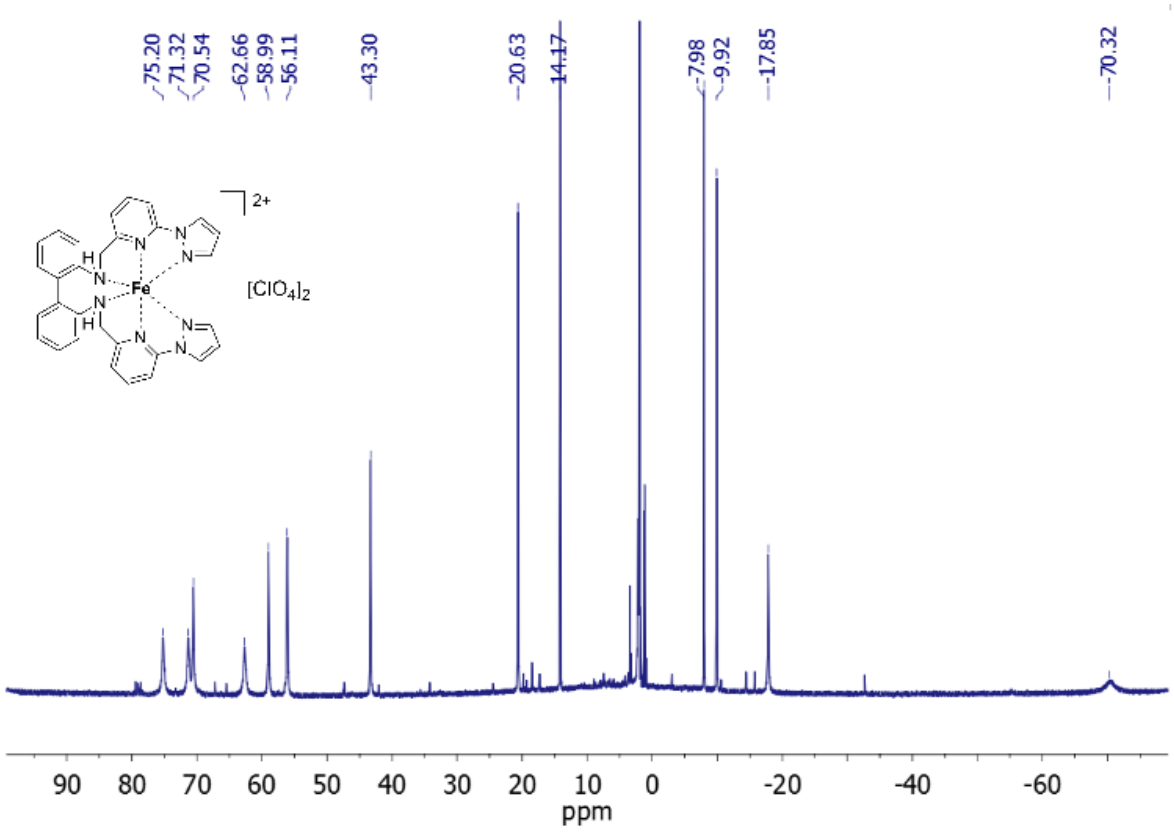

Figure S3: ^{1}H NMR of the perchlorate salt 5 in CD_3CN at 298K.

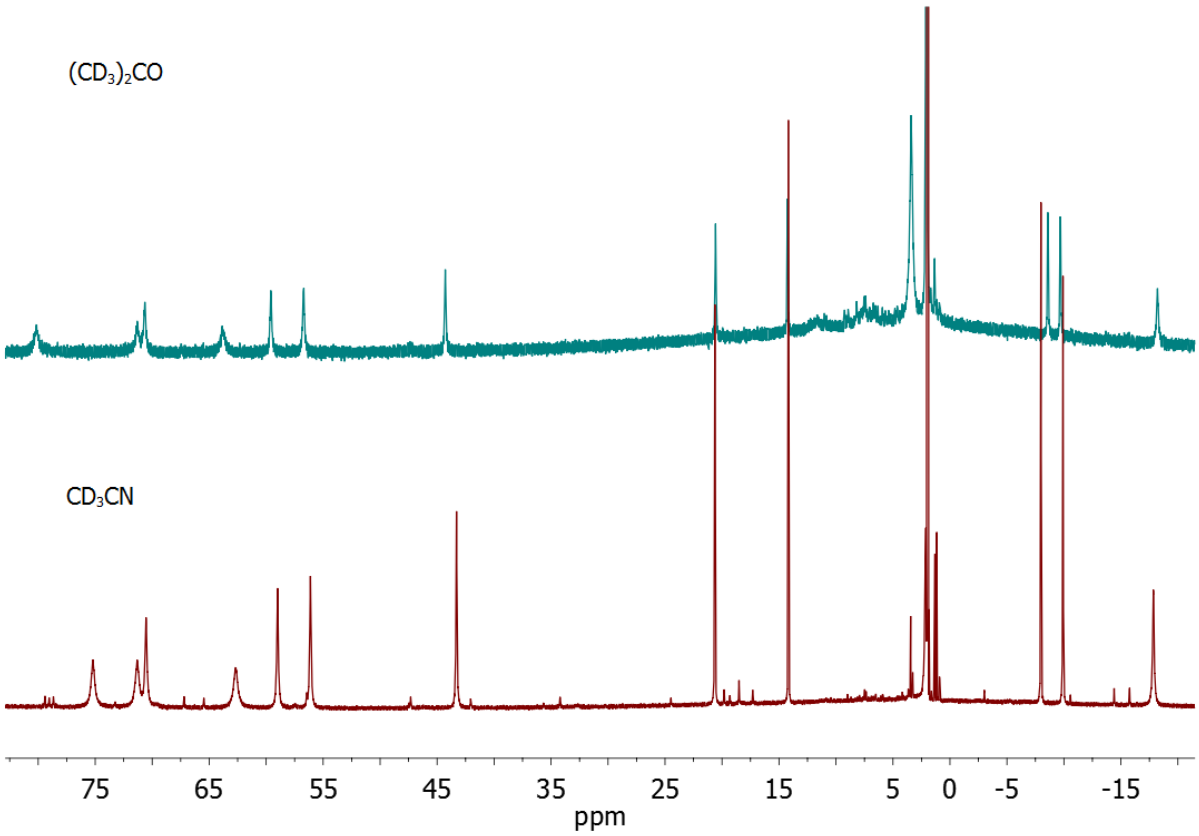

Figure S4: ^{1}H NMR of the perchlorate salt 5 in CD_3CN (bottom) and in $(CD_3)_2CO$ (top) at 298K.

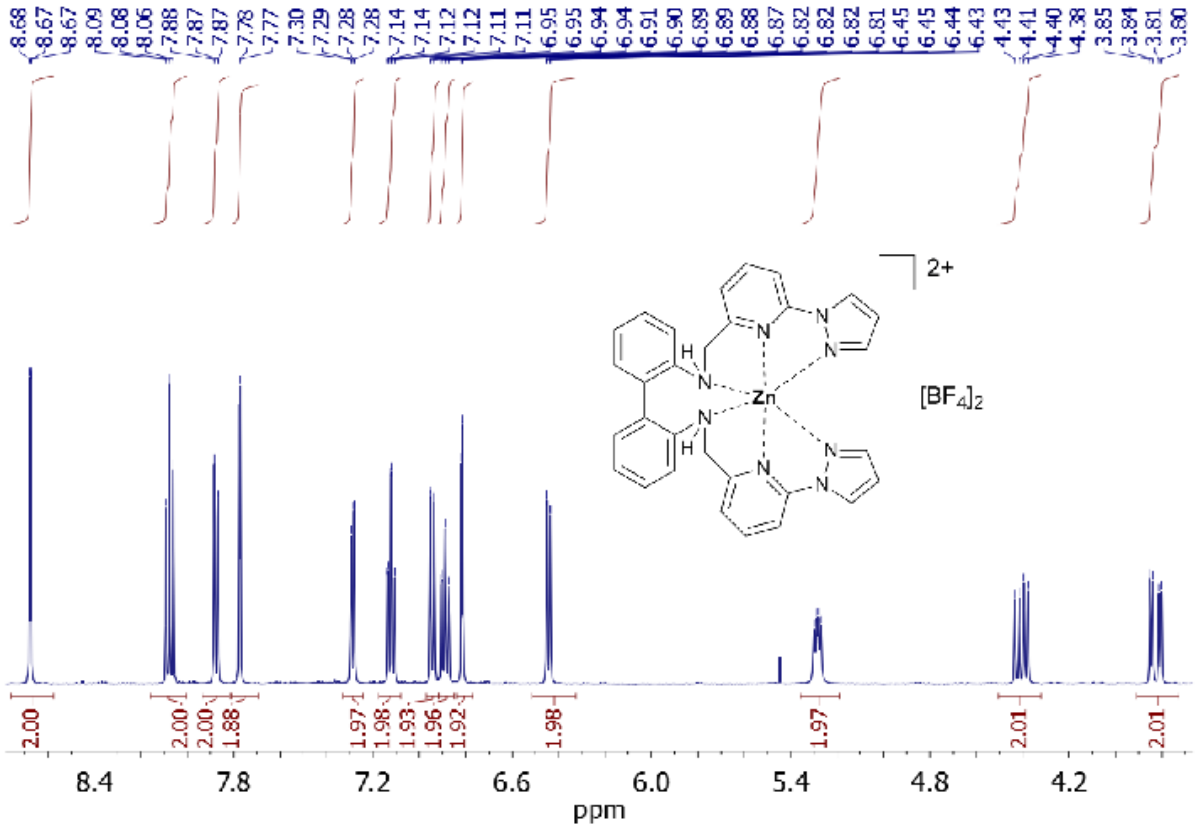

Figure S5: ^{1}H NMR of 6 in CD_3CN at 298K.

TIESST Relaxation kinetics

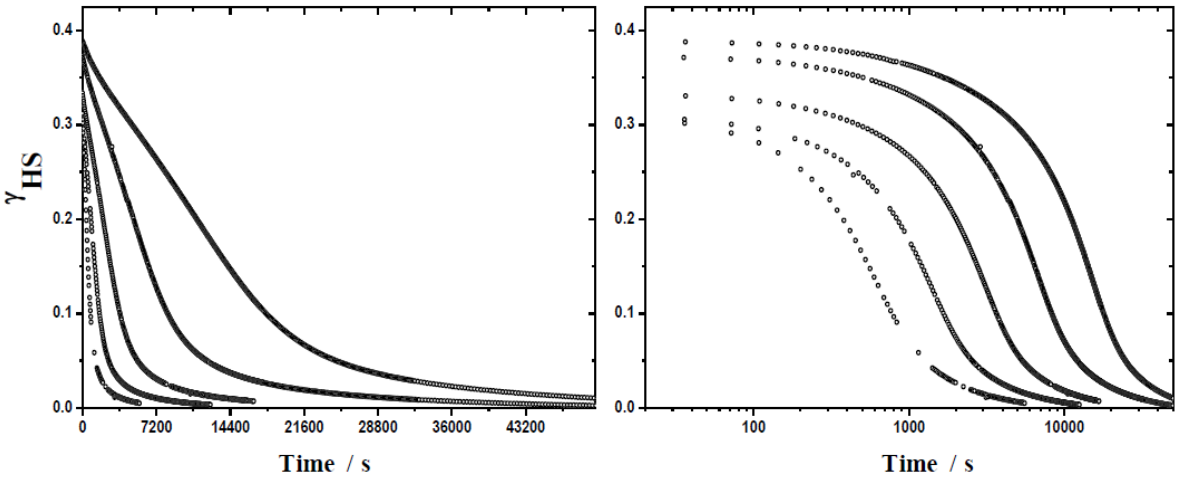

Figure S6: Plot of relaxation kinetics of the quickly cooled phase (TIESST) in the range from 70 to 80K.

X-Ray

Reflection data have been collected on an Oxford Gemini S diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The structures have been solved by direct methods and refined against $|F_0|^2$ with the SHELXS 97[2] and SHELXL 97,[3] respectively. All non-hydrogen and non-solvent atoms were refined anisotropically. All hydrogens bound to those atoms were found in difference Fourier syntheses but were placed at calculated position using a riding model if bound to carbon atoms, protons bound to N1 and N4 were refined freely. Mercury for Windows[4] was employed for structure representation.

Table S1. Data for single crystal X-ray structure analysis.

	[Fe(**3**)][BF_4]$_2$ (**4**) low-spin	[Fe(**3**)][BF_4]$_2$ (**4**) high-spin	[Fe(**3**)][ClO_4]$_2$ (**5**) low-spin	[Fe(**3**)][ClO_4]$_2$ (**5**) high-spin	[Zn(**3**)][BF_4]$_2$ (**6**)	[Zn(L^1)][PF_6]$_2$ (**8**)
empirical formula	$C_{30}H_{26}B_2F_8FeN_8$	$C_{30}H_{26}B_2F_8FeN_8$	$C_{30}H_{26}Cl_2FeN_8O_8$	$C_{30}H_{26}Cl_2FeN_8O_8$	$C_{30}H_{26}B_2F_8FeN_8$	$C_{35}H_{31}F_{12}N_7P_2Zn$
formula weight ($g\cdot mol^{-1}$)	728.06	728.06	753.34	753.34	737.58	916.99
T/K	90	298	110	298	110	110
crystal system	monoclinic	Monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group(No.)	P2(1)/n	P2(1)/c	P2(1)/n	P2(1)/c	P2(1)/n	P2(1)/n
a/ Å	20.4210(9)	10.5414(3)	20.6794(5)	10.6583(5)	20.6854(5)	15.4044(4)
b/ Å	13.0531(4)	13.0245(4)	13.0498(2)	13.0183(6)	12.8812(2)	15.0872(2)
c/ Å	23.2971(9)	23.2290(7)	23.5787(5)	23.5210(14)	23.2003(5)	17.6485(5)
α/°	90	90	90	90	90	90
β/°	105.612(4)	101.677(3)	105.980(2)	102.085(5)	100.953(2)	115.232(3)
γ/°	90	90	90	90	90	90
V/$Å^3$	5980.9(4)	3123.25(16)	6117.1(2)	3191.3(3)	6069.2(2)	3710.33(15)

Z	8	4	8	4	8	4
ρ ($g \cdot cm^{-3}$)	1.617	1.548	1.636	1.568	1.614	1.642
μ (cm^{-1})	5.93	5.68	6.148	5.892	8.97	8.48
reflections collected	25047	13036	19707	9664	25179	20450
Reflections with I > 2σ(I)	5945	3981	6365	3295	8172	5065
independent Reflections / R_{int}	10501/0.0549	5517/0.0336	9577/0.0398	5030/0.0502	10655/0.0354	6506/0.0283
Parameters/restrains	929/336	542/298	877/0	450/0	899/2	532/0
$\Theta_{min/max}$	3.10/25	2.92/25.05	3.34/ 62.09	3.84/ 62.71	2.93/25	2.95/25
Completeness to Θ	0.996	0.997	0.993	0.984	0.997	0.997
wR_2 (all reflections F^2)[a]	0.1724	0.1068	0.1106	0.1793	0.0947	0.0730
R_1 (I > 2σ(I))[a]	0.0671	0.0400	0.0456	0.0634	0.0412	0.0288
GooF[b]	0.890	0.943	0.912	0.983	1.020	0.983
extrema ΔF ($e \cdot Å^{-3}$)	1.714/-0.683	0.306/-0.207	0.816/ -0.421	0.814/-0.508	0.539/-0.320	0.439/ -0.349
absorption correction	'semi-empirical'	'semi-empirical'	'semi-empirical'	'semi-empirical'	'semi-empirical'	'semi-empirical'
$T_{min/max}$	0.443/1	0.84846/1	0.65644/1	0.74156/1	0.88638/1	0.84795/1
CCDC No.	895361	895362	895359	895360	895363	895358

[a] Definition of *R* indices: $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma|F_o|$ $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.. [b] = $\{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (°) of molecular structure of **4**,**5**,**6** and **8** in the solid state.

	$[Fe(3)][BF_4]_2$ (**4**) low-spin	$[Fe(3)][BF_4]_2$ (**4**) high-spin	$[Fe(3)][ClO_4]_2$ (**5**) low-spin	$[Fe(3)][ClO_4]_2$ (**5**) high-spin	$[Zn(3)][BF_4]_2$ (**6**)	$[Zn(L^1)][PF_6]_2$ (**8**)
Fe – N1	2.035(3)	2.2368(19)	2.054(3)	2.247(4)	2.233(2)	2.2795(18)
Fe – N2	1.895(3)	2.1207(17)	1.911(3)	2.137(4)	2.112(2)	2.0621(16)
Fe – N3/N4	1.955(4)	2.171(2)	1.968(3)	2.176(4)	2.138(2)	2.1217(18)
Fe – N4/N5	2.053(3)	2.237(2)	2.063(3)	2.252(4)	2.239(2)	2.3123(17)
Fe – N5/N6	1.916(3)	2.1066(17)	1.911(3)	2.118(4)	2.099(2)	2.0684(16)
Fe – N6/N8	1.979(3)	2.1538(19)	1.980(3)	2.170(4)	2.162(2)	2.1193(16)
N1 – Fe – N2	81.67(14)	75.38(7)	81.83(12)	75.12(15)	75.94(8)	76.60(6)

N2 – Fe – N3/N4	80.92(15)	73.65(7)	81.01(13)	74.19(15)	75.16(8)	77.81(7)
N4/N5 – Fe – N5/N6	100.63(13)	75.96(7)	81.73(12)	75.51(16)	76.76(8)	76.31(6)
N5/N6 – Fe – N6/N8	79.93(14)	74.44(7)	80.66(12)	74.58(15)	75.16(8)	77.82(6)
N3/N4 – Fe – N5/N6	96.78(14)	117.28(7)	97.04(12)	117.34(15)	111.21(8)	111.72(7)
N2 – Fe – N6/N8	99.96(14)	109.91(7)	99.47(13)	109.94(15)	108.79(8)	115.65(6)
N1 – Fe – N4/N5	94.62(13)	93.91(7)	94.68(12)	93.64(17)	94.36(9)	92.80(7)
N2 – Fe – N5/N6	177,69(15)	168.39(7)	178.04(13)	167.78(15)	172.62(8)	163.81(7)
N3/N4 – Fe – N6/N8	88.79(14)	94.29(8)	88.75(12)	94.22(16)	93.22(8)	93.12(6)
C6 – C1 – C7 – C12	55.9(5)	63.1(3)	56.3(5)	68.5(7)	66.5(4)	70.7(3)
C2 – C1 – C7 – C8	56.7(5)	66.2(3)	56.0(5)	62.7(7)	63.0(3)	72.0(3)
N1 ... N4/N5	3.0055(57)	3.2730(32)	3.0275(44)	3.2804(61)	3.2617(28)	3.3255(26)

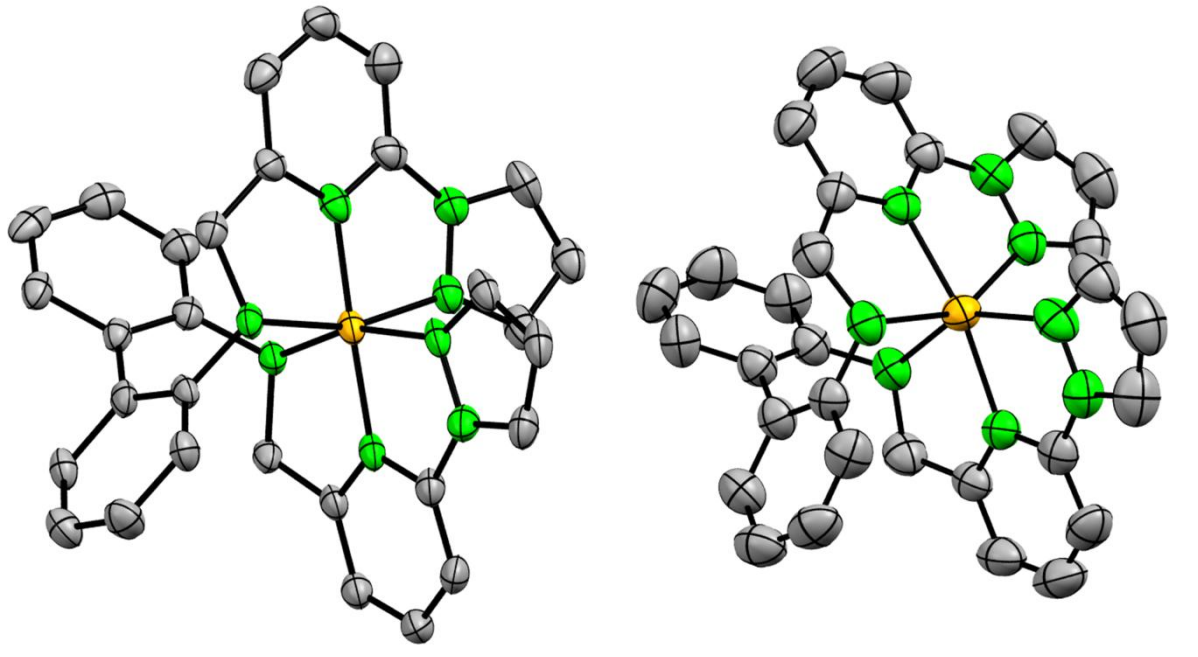

Figure S7: Comparison of low-spin (left) and high-spin (right) structures of 4. Thermal ellipsoids are drawn at 50 %. Counter ions are omitted for clarity.

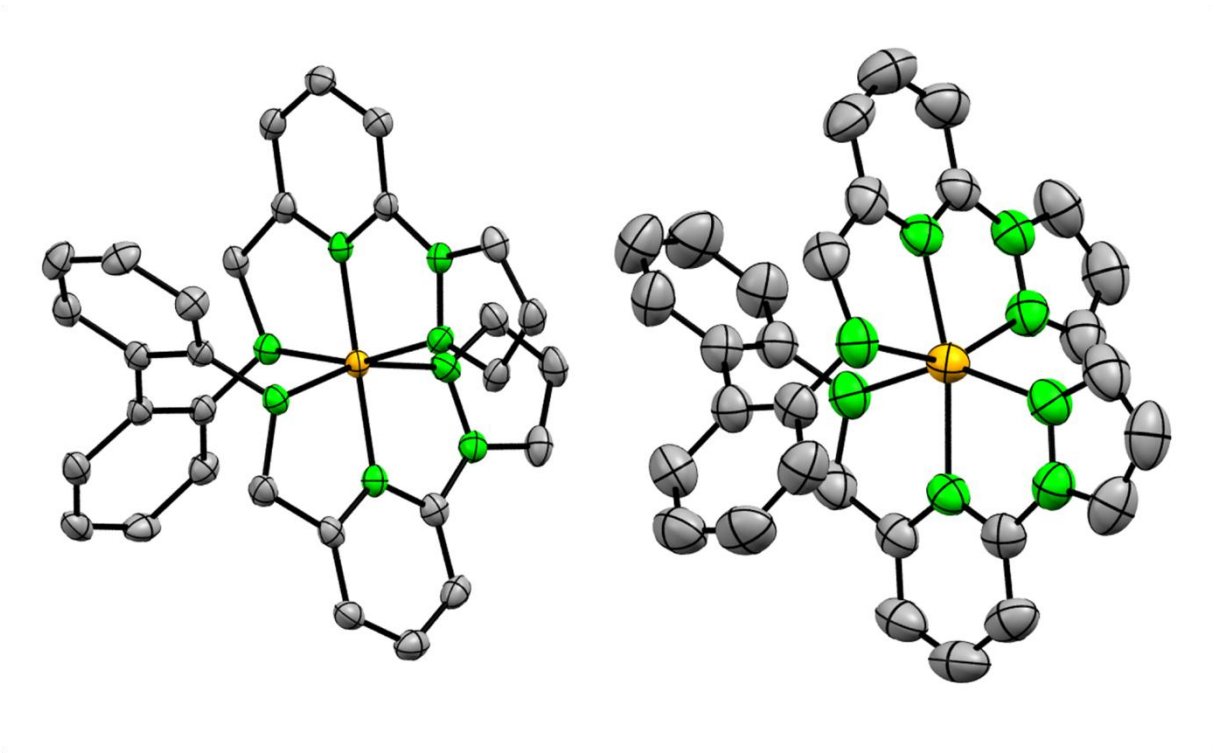

Figure S8: Comparison of low-spin (left) and high-spin (right) structures of 5. Thermal ellipsoids are drawn at 50 %. Counter ions are omitted for clarity.

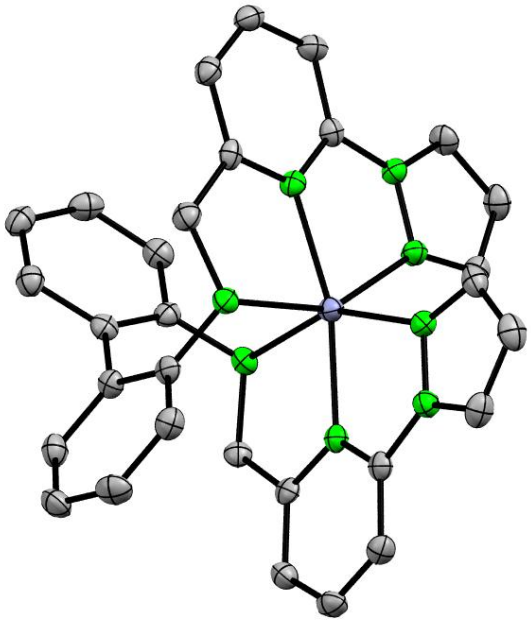

Figure S9: Structure of 6 in the solid state. Thermal ellipsoids are drawn at 50 %. Counter ions are omitted for clarity.

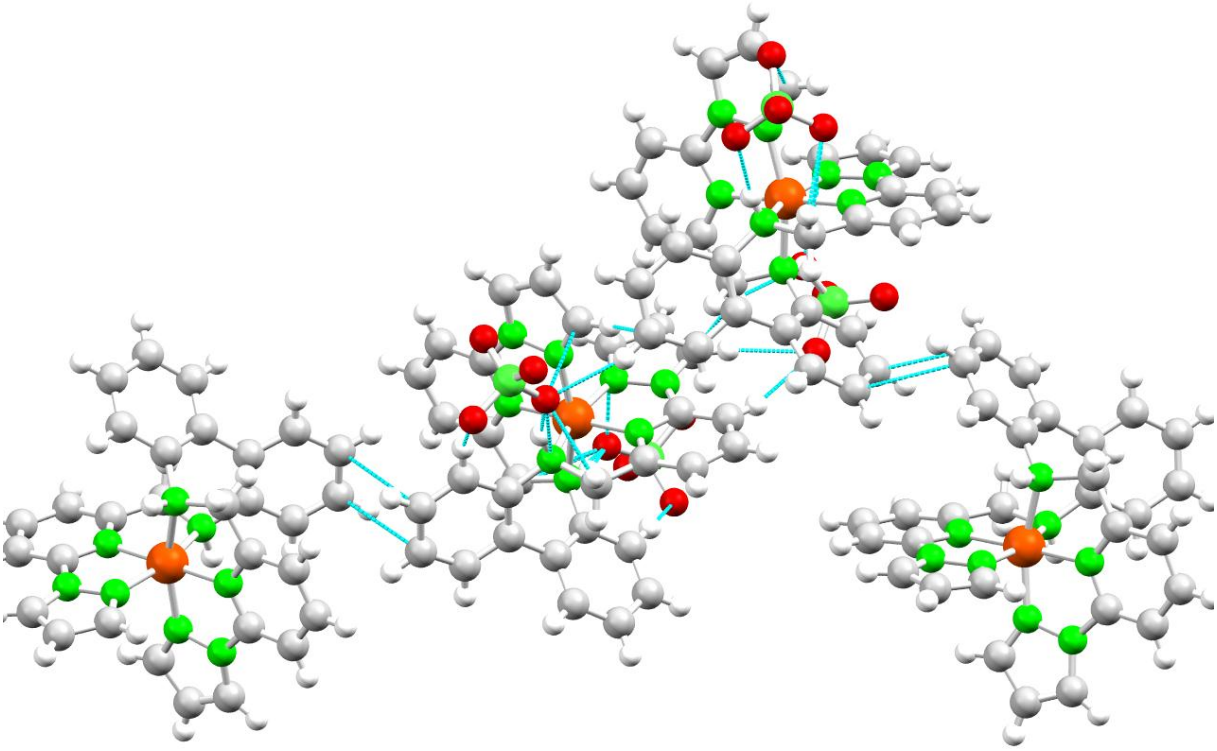

Figure S10: Asymmetric unit of 5 at 110K (center) with hydrogen bonds to perchlorate anions. To the left and right two more complex molecules are shown, which are connected to the complex molecules in the asymmetric unit by π-π-contacts.

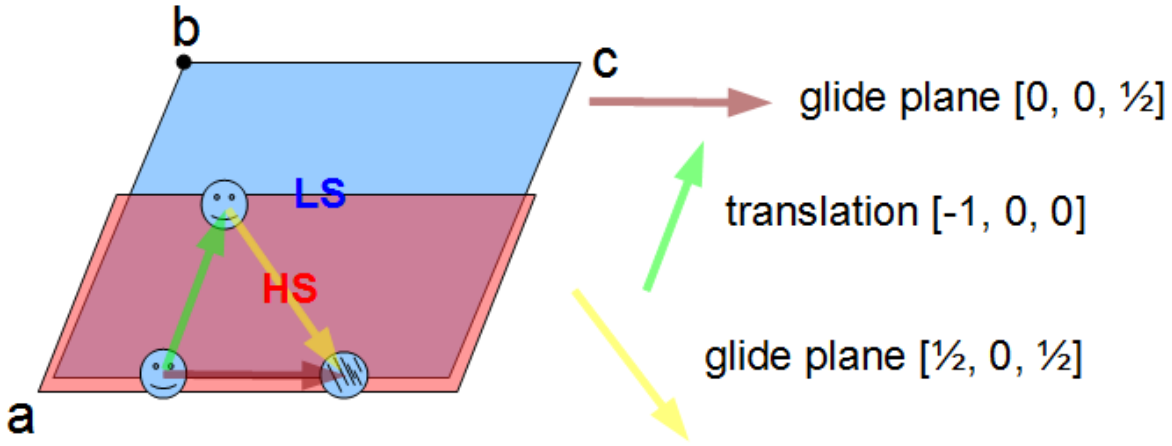

Figure S11: The cell of the LS structure of 4 & 5 can be derived from the HS structure by doubling the a axis. Due to the lower symmetry of this part of the LS cell the space group changes from P21/c to P21/n. The glide plane (yellow) is also included in the cell of the HS fraction but is not explicitly the same as it is a combination of the translation (green) and the glide plane (brown). The last two symmetry elements are not included in the LS cell, however the glide plane (yellow) is still an appropriate symmetry element.

XRD

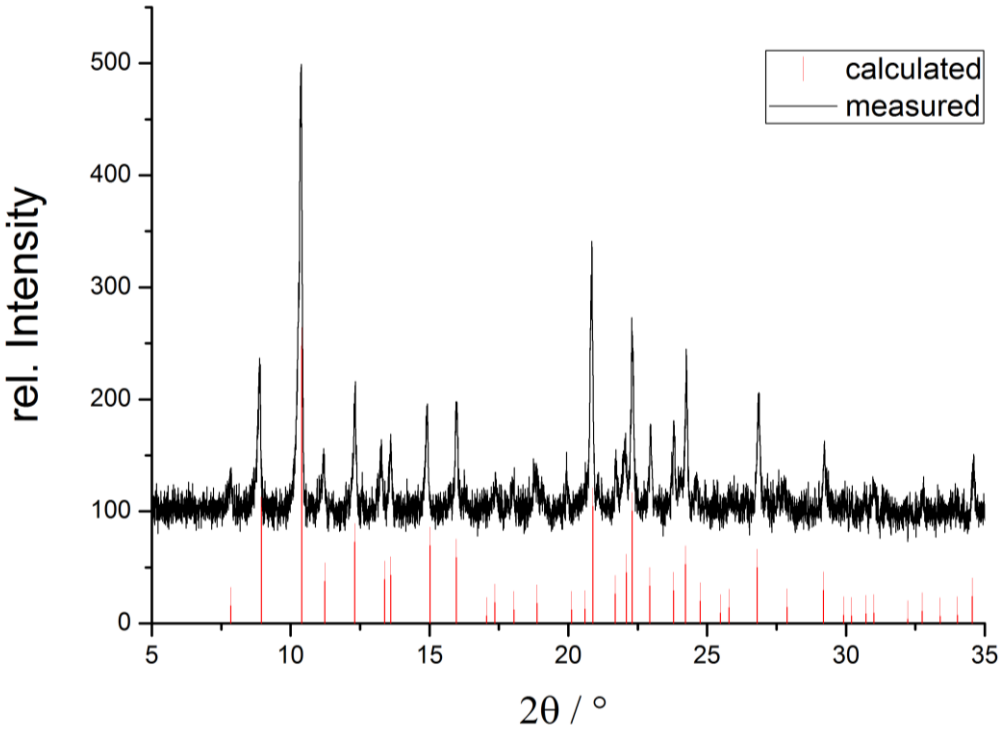

Figure S12: Experimental XRD pattern of 4 at 120K compared with calculated reflexes (from X-Ray).

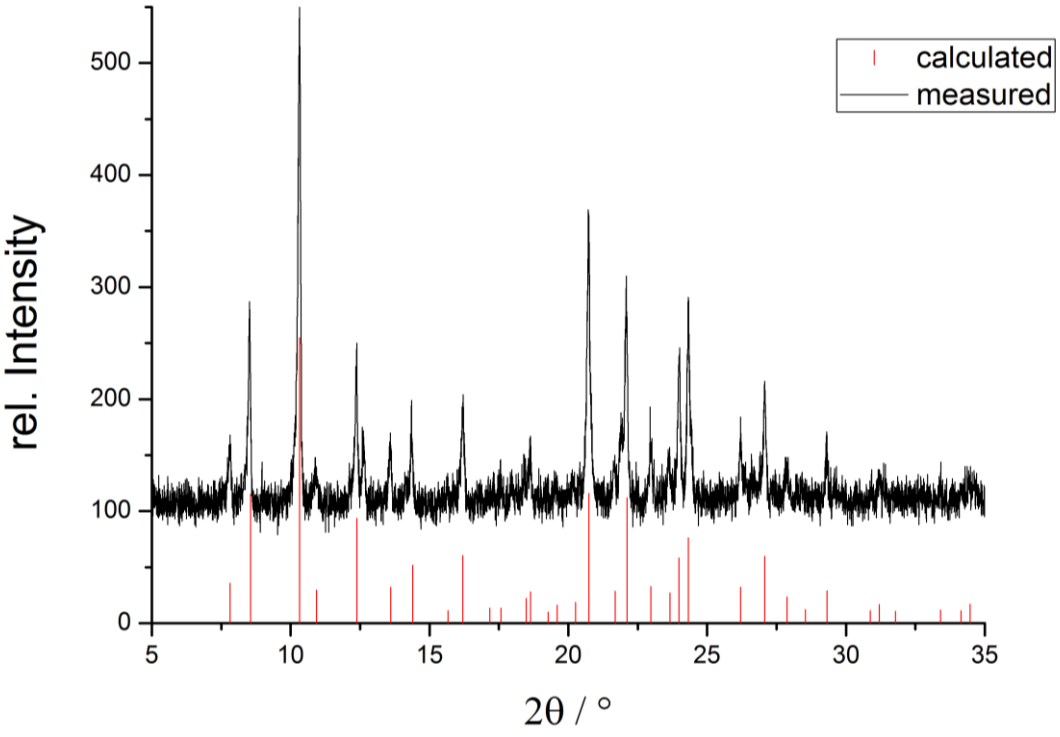

Figure S13: Experimental XRD pattern of 4 at 295K compared with calculated reflexes (from X-Ray).

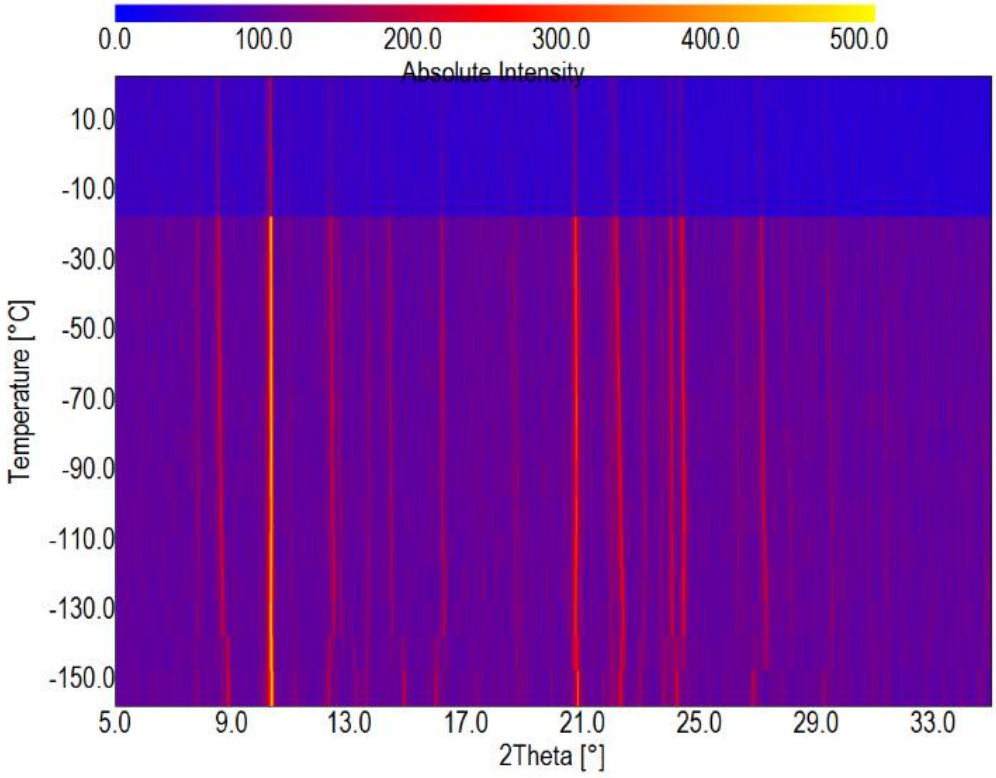

Figure S14*: Temperature dependent change of signals in the XRD of 4.*

Literature

[1] H. Petzold, S. Heider, *Eur. J. Inorg. Chem.* 2011, 1249–1254.

[2] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1990, **46**, 467–473.

[3] G.M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, **1997**.

[4] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453–457.