Heteroatom Substitution Effects in Spin Crossover Dinuclear Complexes

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S1. Single crystal X-ray diffraction

The CCDC reference numbers are 1884823-1884827 for **furtrz-S** (250 K), **furtrz-Se** (250 K), **thtrz-S** (100 K), **furtrz-Se** (100 K), **furtrz-S** (100 K), respectively.

S1-1 *Structure solution and refinement details for* **furtrz-S** and **furtrz-Se**

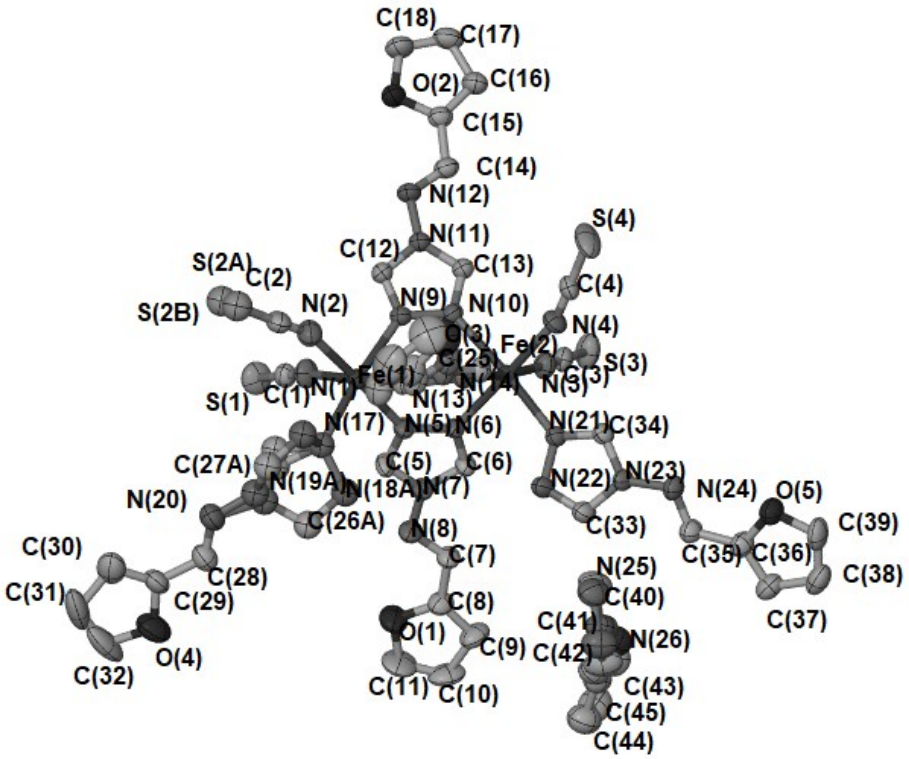

Figure S1: ORTEP representation (50% probability) of the **furtrz-S** (250 K) ASU. Hydrogen atoms omitted for clarity. For clarity, only Part A of the disordered triazole ligand shown.

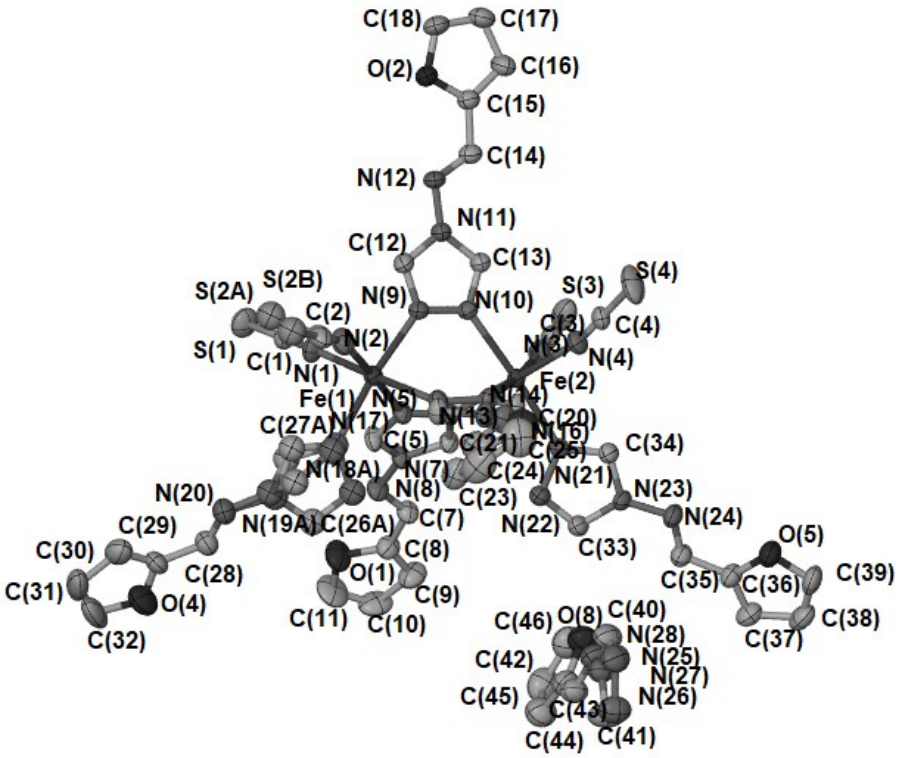

Figure S2: ORTEP representation (50% probability) of the **furtrz-S** (100 K) ASU. Hydrogen atoms omitted for clarity. For clarity, only Part A of the disordered triazole ligand shown.

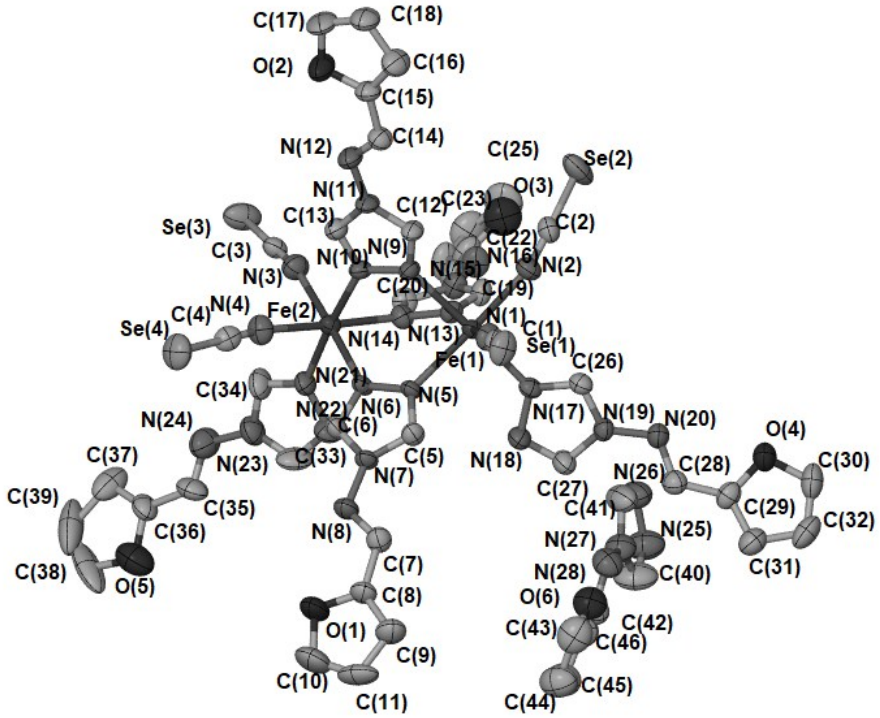

Figure S3: ORTEP representation (50% probability) of the **furtrz-Se** (250 K) ASU. Solvent molecules and hydrogen atoms omitted for clarity.

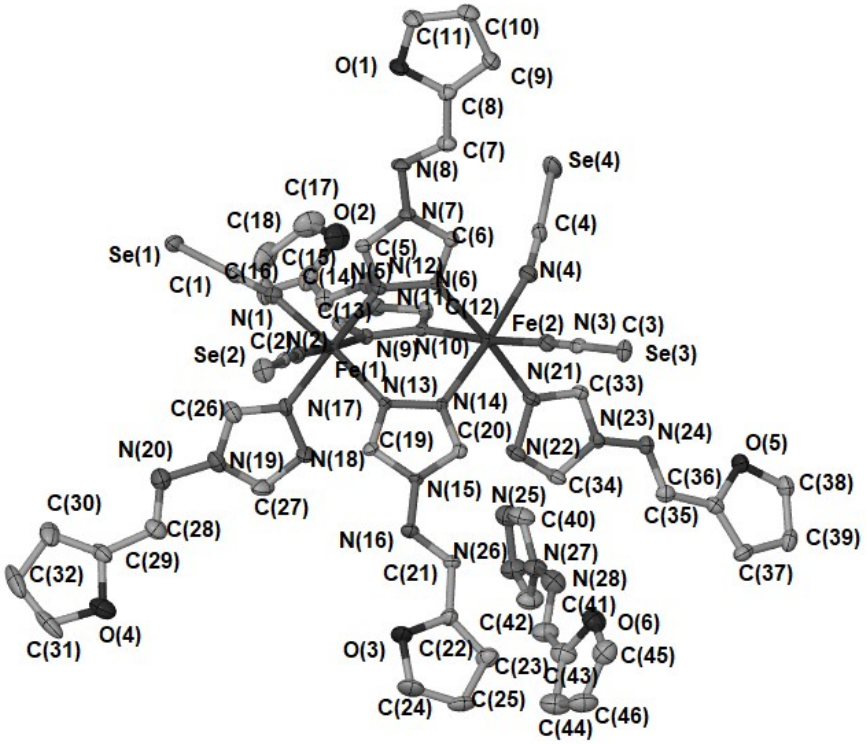

Figure S4: ORTEP representation (50% probability) of the **furtrz-Se** (100 K) ASU. Solvent molecules and hydrogen atoms omitted for clarity.

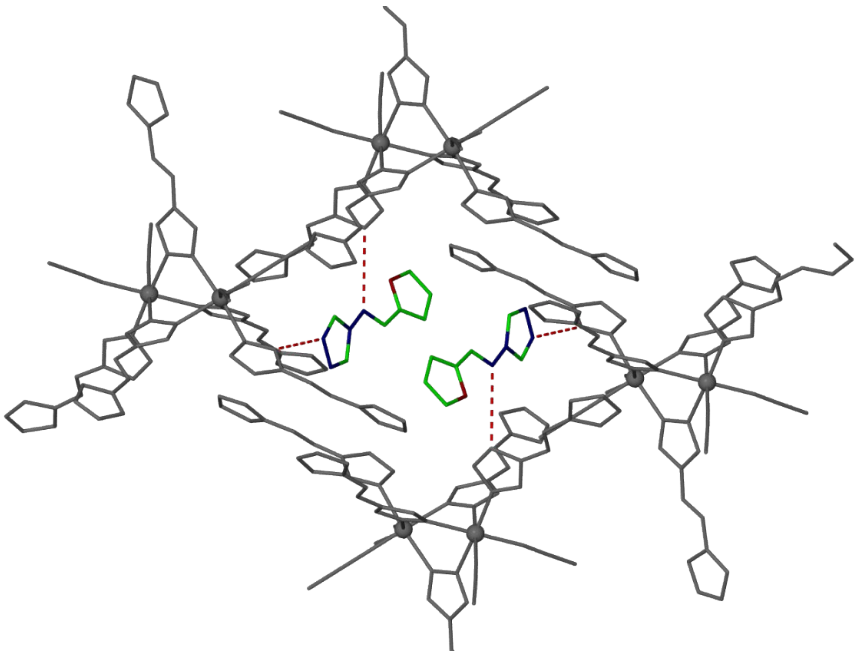

Figure S5: Structural illustration of unbound fur ligand to dinuclear interactions in **furtrz-S**. The free fur ligands engage in two types of dinuclear…ligand hydrogen bonding interactions (**furtrz-S**(250 K): $C(H)^{trz}$…$N^{trz\text{-}free}$: 3.09 Å and C(H)trz…N(imine): 3.55 Å)

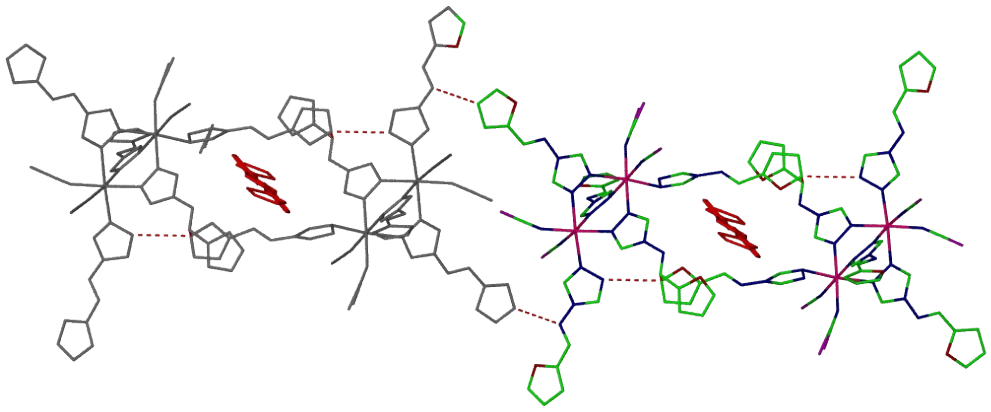

Figure S6: Structural illustration of hydrogen bond connectivity between dimeric units in **furtrz-S** (grey and red) of interacting dinuclear species. Unbound fur ligands shown in red. Dimeric hydrogen bonding interactions shown in red dashes.

Table S1. Crystallographic data for **furtrz-S** and **furtrz-Se**.

	furtrz-S		**furtrz-Se**	
Formula	$[Fe_2(NCS)_4(furtrz)_5]\cdot furtrz\cdot MeOH$		$[Fe_2(NCSe)_4(furtrz)_5]\cdot furtrz\cdot MeOH$	
Formula weight	1349.01		1536.61	
Temperature/K	250	100	250	100
Crystal system	triclinic			
Space group	*P*-1			
***a* / Å**	11.7242(11)	11.5733(4)	11.8072(6)	11.6669(6)
***b* / Å**	13.7606(6)	13.6118(3)	13.7471(7)	13.5850(6)
***c* / Å**	20.3784(10)	20.0702(5)	20.5258(10)	20.2298(10)
α / °	82.165(4)	82.150(2)	82.769(4)	82.736(4)
β / °	75.456(6)	75.238(3)	75.162(4)	75.108(4)
γ / °	76.699(6)	77.043(2)	76.841(4)	77.118(4)
Volume / Å^3	3086.2(4)	2968.92(15)	3127.9(3)	3012.5(3)
Z	2	2	2	2
ρ_{calc}mg / mm^3	1.452	1.509	1.632	1.694
Data / restraints / parameters	14494/9/802	14003/9/818	14907/12/775	14351/0/775
Goodness–of–fit on F^2	1.071	1.046	0.840	1.000
Final R indexes [I>=2σ (I)][a], [b]	R_1 = 0.0591, wR_2 = 0.1423	R_1 = 0.0464, wR_2 = 0.1022	R_1 = 0.0661, wR_2 = 0.1635	R_1 = 0.0522, wR_2 = 0.1086
Final R indexes [all data] [a], [b]	R_1 = 0.0932, wR_2 = 0.1661	R_1 = 0.0632, wR_2 = 0.1102	R_1 = 0.1445, wR_2 = 0.2074	R_1 = 0.0871, wR_2 = 0.1227

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma[w(Fo_2 - Fc_2)_2]/\Sigma[w(Fo_2)_2]]_{1/2}$.

S1-2 *Structure solution and refinement details for* **thtrz-S** and **thtrz-Se**

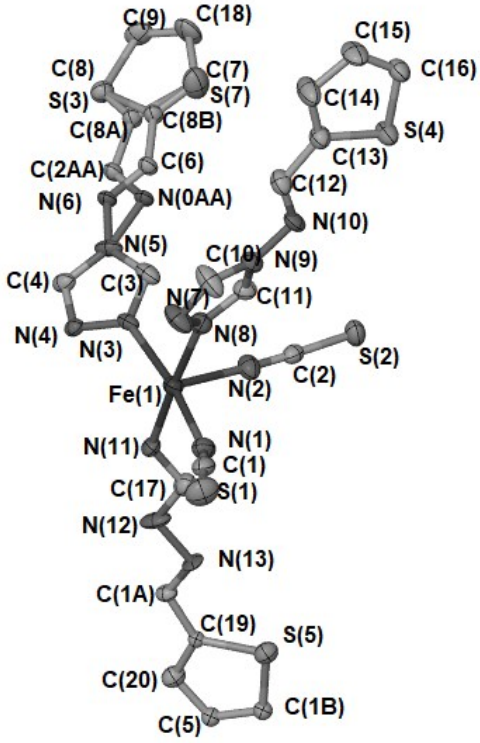

Figure S7: ORTEP representation (50% probability) of the ASU of **thtrz-S** (100 K). Hydrogen atoms omitted for clarity.

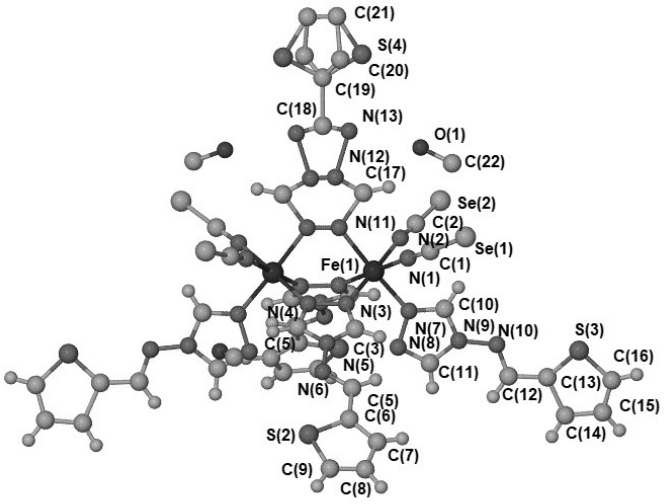

Figure S8: Ball-and-stick representation of a complete dinuclear unit of **thtrz-Se** (185 K) with the ASU labelled. Qualitative representation only.

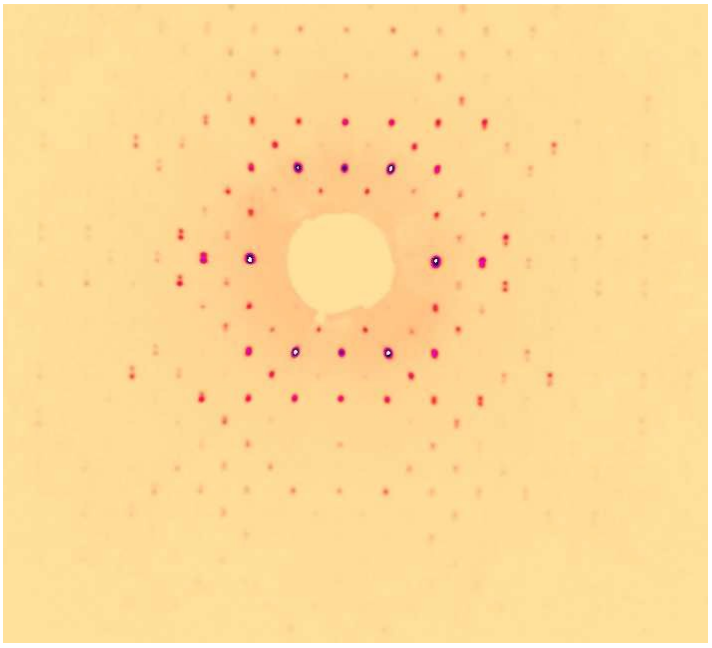

Figure S9: Example procession image (0kl) for **thtrz-Se** showing the partially overlapped twinning that could not be adequately resolved for a quantitative structure solution.

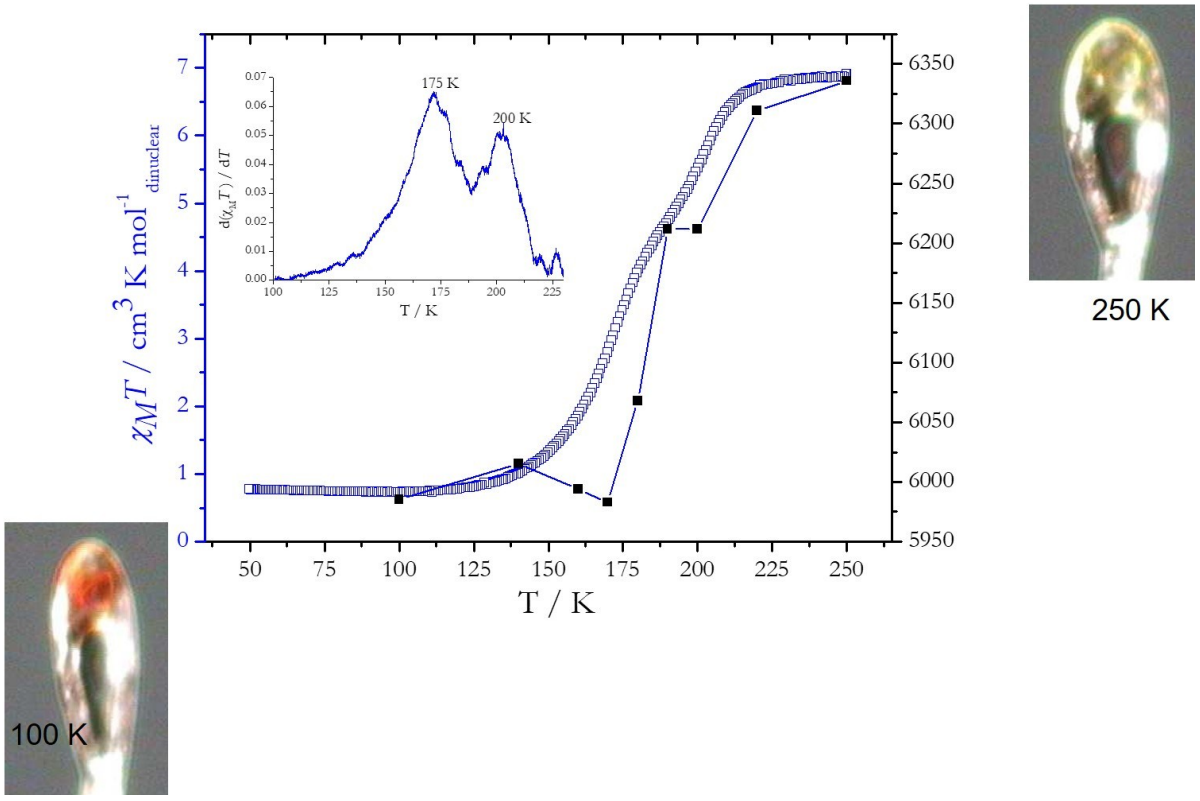

Figure S10: Variable temperature magnetic susceptibility comparison to variable temperature unit cell evolution for **thtrz-Se**. Inset: crystal colour changes over the HS to LS transition.

Table S2. Crystallographic data for **thtrz-S** and **thtrz-Se**.*

	thtrz-S	**thtrz-Se**		
Formula	$[Fe_2(NCS)_4(thtrz)_5]\cdot 4MeOH$	$[Fe_2(NCSe)_4(thtrz)_5]\cdot 4MeOH$		
Formula weight	1363.28	1518.71		
Temperature/K	100	250	185	100
Crystal system	monoclinic			
Space group	*C*2/*c*			
***a* / Å**	20.9095(9)	18.792(4)	18.468(2)	18.331(3)
***b* / Å**	13.9867(4)	18.021(2)	17.813(2)	17.760(2)
***c* / Å**	21.1519(8)	19.522(3)	19.199(3)	19.145(3)
α / °	90	90	90	90
β / °	108.665(4)	106.57(2)	106.520(14)	106.20(2)
γ / °	90	90	90	90
Volume / Å^3	5860.6(4)	6336(2)	6054(2)	5985(2)
Z	4			
ρ_{calc}mg / mm^3	1.545			
Data / restraints / parameters	7475/7/354			
Goodness–of–fit on F^2	0.954			
Final R indexes [I>=2σ (I)][a], [b]	$R_1 = 0.0646$, $wR_2 = 0.1143$			
Final R indexes [all data] [a], [b]	$R_1 = 0.1416$, $wR_2 = 0.1349$			

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma[w(Fo_2 - Fc_2)_2]/\Sigma[w(Fo_2)_2]]_{1/2}$.

*thio-Se single crystal data unit cells provided, full structure analysis was not possible due to partial overalapped twinning. Structure provided for qualitative purposes.

S2. Temperature Dependent Magnetic Measurements

S2-1 Fitting details for **thiotrz-S**

The energy difference between the triplet and lower energy singlet state was calculated using the Heisenberg Hamiltonian $\hat{H}_{ij} = -2\boldsymbol{J}_{ij}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$, where $\boldsymbol{J}$ is the exchange parameter and $\hat{\boldsymbol{S}}$ is the spin operator for a pair of interacting spin centres ($\boldsymbol{S}$) where $\boldsymbol{S}_i = \boldsymbol{S}_j = 2$.[1] The Hamiltonian used is based on the assumption that the ions are isotropic and, as per similar systems,[2-4] first order angular momentum and zero-field splitting have not been included in this model. With the energy levels of the system known, the theoretical magnetic susceptibility was calculated using the Van Vleck equation for a pair of S=2 dimers (1):[1-5]

$$\chi_M T = \frac{2N_A g^2 \beta^2}{k} \frac{e^x + 5e^{3x} + 14e^{6x} + 30e^{10x}}{1 + 3e^x + 5e^{3x} + 7e^{6x} + 9e^{10x}} \qquad (1)$$

$$\text{with } x = \frac{J}{kT}$$

where T is the temperature, N_A is Avogadro's number, β is the Bohr magneton and k is the Boltzmann constant.

S3. References

(1) Kahn, O. *Molecular Magnetism*; VCH, 1993.

(2) Wu, X. X.; Wang, Y. Y.; Yang, P.; Xu, Y. Y.; Huo, J. Z.; Ding, B.; Wang, Y.; Wang, X. *Crystal Growth & Design* **2013**, *14*, 477.

(3) Scott, H. S.; Ross, T. M.; Moubaraki, B.; Murray, K. S.; Neville, S. M. *Eur. J. Inorg. Chem.* **2013**, *2013*, 803.

(4) O. Roubeau, R. Gamez, S. J. Teat*, Eur. J. Inorg. Chem.* **2013**, 934-942.

(5) Carlin, R. L. *Magnetochemistry*; Springer-Verlag, **1986**.