magnetochemistry

Supplementary: Abrupt spin crossover behavior in a linear *N1, N2*-Triazole Bridged trinuclear Fe(II) complex

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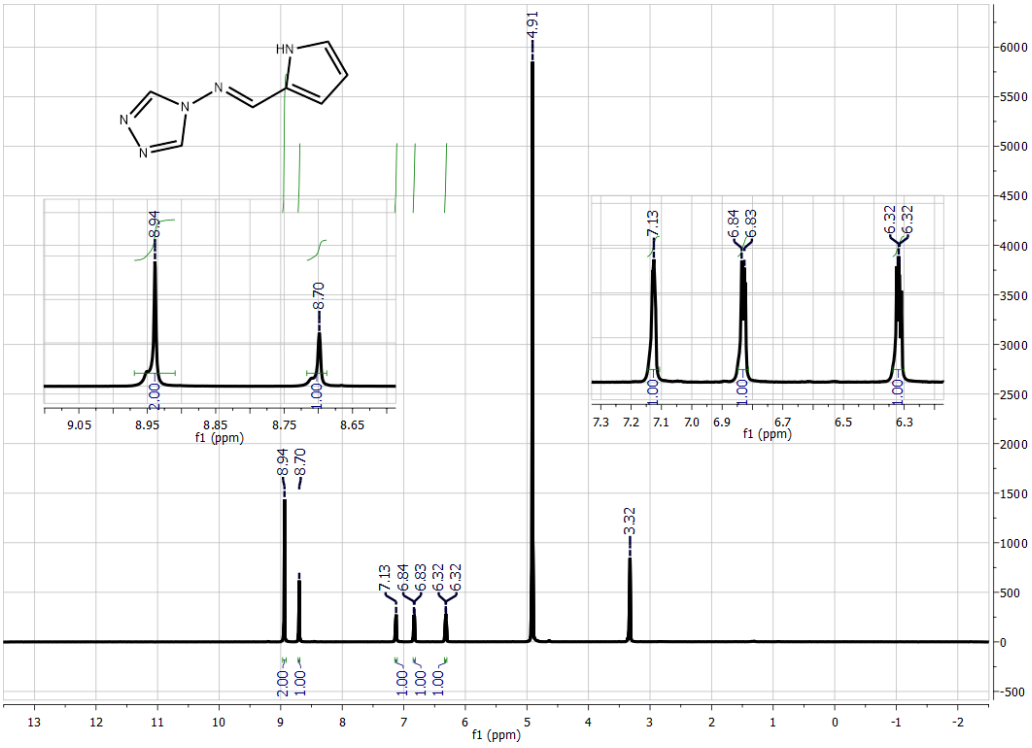


Figure S1. ^{1}H-NMR spectrum of pyrtrz ligand.

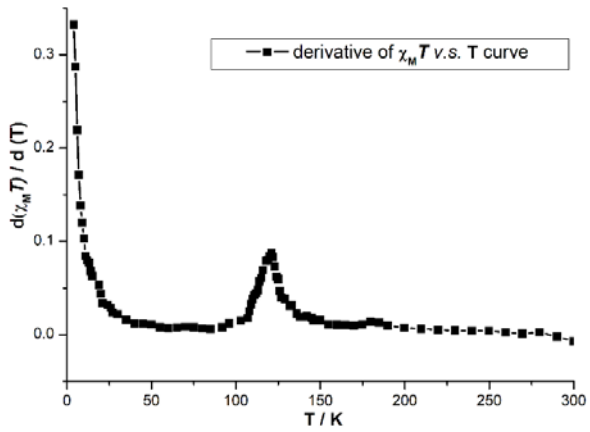


Figure S2. A derivative plot of the χ_MT v.s. T curve for compound **2**.

Table S1. Dinuclear Fe(II) Complexes Based on Functionalized 4-R-1,2,4-Triazole Ligands.

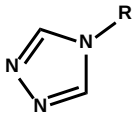
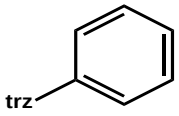
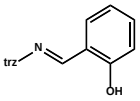
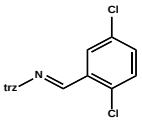
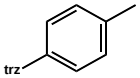
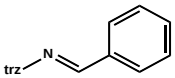
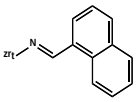
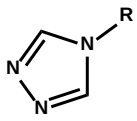
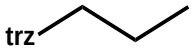
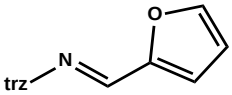
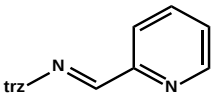
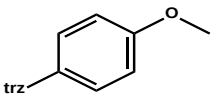
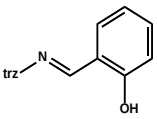
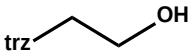
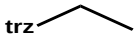
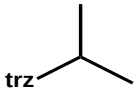
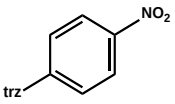
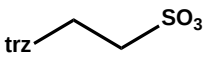
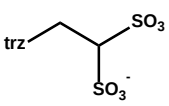
	dinuclear complex	SCO behavior / $T_{1/2}$	Ref
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot CH_3OH\cdot CH_3CH_2OH$	incomplete / $T_{1/2}$ = 116 K	1
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot 2CH_3CH_2OH$	incomplete / $T_{1/2}$ = 122 K	1
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot 2CH_3CH_2OH.1.5H_2O$	HS	1
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot 4MeOH$	abrupt / $T_{1/2}$ = 157 K	2
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot 4H_2O$	HS	3
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot H_2O$	gradual / $T_{1/2}$ = 150 K	4
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot[Fe(L)_2(NCS)_2(H_2O)_2]$	abrupt / $T_{1/2}$ = 111 K	5
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot 3.5MeOH$	gradual / $T_{1/2}$ = 115 K	6
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot 2H_2O$	HS	7
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\cdot CH_3OH\ CH_3CH_2OH$	incomplete / $T_{1/2}$ = 116 K	7
	$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCSe)_4]\cdot 2DMF\cdot 2H_2O$	HS with LIESST effect	8

Table S2. Trinuclear Fe(II) Complexes Based on Functionalized 4-R-1,2,4-Triazole Ligands.

	Trinuclear complex	SCO behavior / T1/2	Ref
	$[Fe_3(\mu_2\text{-}L)_6(ReO_4)_4(H_2O)_2](ReO_4)_2{\cdot}H_2O$	gradual / T1/2=185 K	9
	$[Fe_3(\mu_2\text{-}L)_6(Tos)_2](Tos)_4{\cdot}4MeOH$	gradual / T1/2~170 K	10
	$[Fe_3(\mu_2\text{-}L)_6(L)_2H_2O)_4](NO_3)_6$	gradual / T1/2=208 K	11
	$[[Fe_3(\mu_2\text{-}L)_6(L)_2H_2O)_4](ClO_4)_6$	HS	11
	$[Fe_3(\mu_2\text{-}L)_6(L)_2H_2O)_4](Br)_6$	HS	11
	$[Fe_3(\mu_2\text{-}L)_6(L)_2(H_2O)_4](BF_4)_6{\cdot}2H_2O$	HS	12
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_6](Tos)_6{\cdot}4H_2O$	gradual / T1/2 =245 K	12
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_6](Tos)_6$	gradual / T1/2=330 K	12
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_2(EtOH)_4](ClO_4)_6{\cdot}2EtOH$	HS	3
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_6](CF_3SO_3)_6$	gradual / T1/2=290 K	13
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_6](CF_3SO_3)_6$	abrupt / T1/2=205 K	14, 15
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_6](Tos)_6{\cdot}2H_2O$	gradual / T1/2=242 K	16
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_6](CF_3SO_3)_6$	gradual / T1/2=185 K	16
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_2(EtOH)_4](Tos)_6{\cdot}4EtOH$	gradual / T1/2=148 K	17
	$[Fe_3(\mu_2\text{-}L)_6(H_2O)_6]\ 5H_2O$	Hysteresis with T1/2(↑)=357 K, T1/2(↓)=343K	18
	$(Me_2NH_2)_6[Fe_3(\mu_2\text{-}L)_6(H_2O)_6]$	Hysteresis with T1/2(↑)=400 K, T1/2(↓)=310K	19

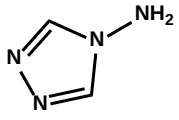
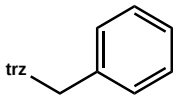
	$[Fe_3(\mu_2\text{-}L)_6(SCN)_5(H_2O)](SCN)\cdot 4H_2O$	Hysteresis with T1/2(↑)=222 K, T1/2(↓)=218K	20, 21
	$[Fe_3(\mu_2\text{-}L)_6(tcnset)_6]$ (tcnset = 1,1,3,3-tetracyano-2-thioethylpropenide)	abrupt / T1/2 = 318 K	22

Table S3 Selected bond lengths [Å] and angles [°] for Compounds **1** and **2**.

Compound **1**					
Fe(1)-N(1)	2.142(5)	Fe(1)-N(28)	2.095(11)	Fe(2)-N(12)	2.201(9)
Fe(1)-N(7)	2.142(5)	Fe(1)-N(29)	2.128(11)	Fe(2)-N(16)	2.108(6)
Fe(1)-N(11)	2.172(9)	Fe(2)-N(2)	2.161(5)	Fe(2)-N(26)	2.090(10)
Fe(1)-N(22)	2.163(6)	Fe(2)-N(6)	2.134(5)	Fe(2)-N(27)	2.094(11)
N(1)-Fe(1)-N(7)	87.2(3)	N(28)-Fe(1)-N(29)	92.6(4)	N(16)-Fe(2)-N(12)	88.5(3)
N(1)-Fe(1)-N(11)	86.7(3)	N(29)-Fe(1)-N(1)	90.0(3)	N(26)-Fe(2)-N(2)	176.9(4)
N(1)-Fe(1)-N(22)	86.9(3)	N(29)-Fe(1)-N(7)	90.3(3)	N(26)-Fe(2)-N(6)	89.9(4)
N(7)-Fe(1)-N(11)	90.9(3)	N(29)-Fe(1)-N(11)	176.4(4)	N(26)-Fe(2)-N(12)	90.8(4)
N(7)-Fe(1)-N(22)	173.8(3)	N(29)-Fe(1)-N(22)	87.8(4)	N(26)-Fe(2)-N(16)	86.7(4)
N(22)-Fe(1)-N(11)	90.6(3)	N(2)-Fe(2)-N(12)	86.4(3)	N(26)-Fe(2)-N(27)	92.5(4)
N(28)-Fe(1)-N(1)	177.0(3)	N(6)-Fe(2)-N(2)	88.6(3)	N(27)-Fe(2)-N(2)	90.3(4)
N(28)-Fe(1)-N(7)	91.2(3)	N(6)-Fe(2)-N(12)	87.9(3)	N(27)-Fe(2)-N(6)	92.4(3)
N(28)-Fe(1)-N(11)	90.8(4)	N(16)-Fe(2)-N(2)	94.6(3)	N(27)-Fe(2)-N(12)	176.7(4)
N(28)-Fe(1)-N(22)	94.8(3)	N(16)-Fe(2)-N(6)	175.0(3)	N(27)-Fe(2)-N(16)	91.4(4)
C(36)-N(26)-Fe(2)	161.0(14)	C(38)-N(28)-Fe(1)	174.1(10)	N(27)-C(37)-S(2)	178.7(13)
C(37)-N(27)-Fe(2)	172.9(11)	N(26)-C(36)-S(1)	174.7(17)	N(28)-C(38)-S(3)	179.0(12)
Compound **2**					
Fe(1)-O(1)	2.149(3)	Fe(2)-N(2)	2.093(4)	Fe(3)-O(4)	2.118(5)
Fe(1)-O(2)	2.069(4)	Fe(2)-N(14)	2.075(5)	Fe(3)-O(5)	2.124(5)
Fe(1)-O(3)	2.133(4)	Fe(2)-N(26)	2.094(5)	Fe(3)-O(6)	2.159(5)
Fe(1)-N(1)	2.173(5)	Fe(2)-N(37)	2.081(5)	Fe(3)-N(38)	2.134(5)
Fe(1)-N(13)	2.157(5)	Fe(2)-N(49)	2.130(5)	Fe(3)-N(50)	2.156(5)
Fe(1)-N(25)	2.160(4)	Fe(2)-N(61)	2.108(6)	Fe(3)-N(62)	2.173(6)
O(4)-Fe(3)-O(5)	91.3(2)	O(5)-Fe(3)-O(6)	88.0(2)	N(38)-Fe(3)-O(6)	88.4(2)
O(4)-Fe(3)-O(6)	87.7(3)	O(5)-Fe(3)-N(38)	175.7(2)	N(38)-Fe(3)-N(50)	92.3(2)
O(4)-Fe(3)-N(38)	91.0(2)	O(5)-Fe(3)-N(50)	91.23(19)	N(38)-Fe(3)-N(62)	87.1(2)
O(4)-Fe(3)-N(50)	91.9(2)	O(5)-Fe(3)-N(62)	90.6(2)	N(50)-Fe(3)-O(6)	179.2(2)
O(4)-Fe(3)-N(62)	178.1(2)	O(6)-Fe(3)-N(62)	92.5(2)	N(50)-Fe(3)-N(62)	87.87(19)

Table S4. Geometry of intra-molecular C–H/O ··· π (pyrrole/triazole) in compound **2**.

Atom (X)	centroid	X···centroid distance/Å	φ/deg[a]

C70b–H70b	C94 ring	2.9070(2)	70.509(5)
O13	N61 ring	3.462(5)	79.035(3)
O12 ring	N1 ring	2.992(6)	78.413(3)
C75–H75	C80 ring	2.748(2)	85.609(4)
C60–H60	C80 ring	2.630(2)	86.995(3)
C93–H93a	C60 ring	2.813(2)	89.298(5)

[a] Angle of the X...π axis to the plane of the centroid cycle contacted.

Table S5. Intra- and inter-molecular Hydrogen-bonding interactions in compound **2**.

D–H	A	H···A (Å)	D···A (Å)	<D–H···A (º)	Symmetry codes of A
C27–H27	O19b	2.412	3.231(6)	144(2)	x, y, z
N36–H36	O21b	1.913	2.726(7)	153(1)	x, y, z
C19–H19	O11	2.442	3.169(9)	133(3)	x, y, z
C15–H15	O13	2.267	3.199(7)	166(2)	x, y, z
C63–H63	O23	2.523	3.342(5)	144(3)	x, y, z
N48–H48	O29	1.938	2.799(8)	167(2)	x, y, z
N72–H72	O32	1.914	2.769(6)	166(2)	x, y, z
C27–H27	O20	2.101	3.051(2)	173(2)	x, y, z
C33b–H33a	O21	1.983	2.847(3)	150(3)	x, y, z
C53–H53	O12	2.292	3.161(5)	151(5)	x, y, z
N21–H21	O26	1.932	2.807(9)	173(2)	$-x+1, y+0.5, -z+0.5$
N57–H57	O29b	2.233	2.962(7)	140(5)	$-x, y+0.5, -z+0.5$
N72b–H72b	O7	1.755	2.591(3)	157(2)	$-x+1, y+0.5, -z+0.5$
C3–H3	O22	2.193	3.083(2)	156(5)	$-x, y-0.5, -z+0.5$
C9–H9	O28a	1.975	2.905(6)	166(2)	$-x+1, y-0.5, -z+0.5$
C17–H17	O17	2.156	2.994(7)	147(3)	$-x+1, y-0.5, -z+0.5$
C39–H39	O14	2.241	3.082(9)	147(5)	$-x, y-0.5, -z+0.5$
C41–H41	O18b	2.071	2.991(8)	162(2)	$x, y-1, z$

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