Supporting Information

Solvent effect in an axially symmetric Fe^{III}₄ single-molecule

magnet

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List of Supporting Information

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SI1 Physical measurement

Magnetic measurements were performed on a Quantum Design MPMS XL-5 SQUID magnetometer on polycrystalline samples. Data were corrected for the diamagnetism of the samples using Pascal constants and of the sample holder by measurement. The experiments below 1.8 K were measured on the *i*Helium Measurement Console in coordination with MPMS MultiVu.

The X-ray measurements of **1***R* were measured at 100 K on a Bruke Kappa ApexII Duo diffractometer with graphite monochromated Mo_{Ka} radiation ($\lambda = 0.71073$ Å). The X-ray measurements of **1S** were carried on a Saturn724+ CCD diffractometer with Confocal-monochromator Mo-Ka radiation ($\lambda = 0.71073$ Å) at 173 K. Intensities were collected using CrystalClear (Rigaku Inc., 2008) technique and absorption effects were collected using the multi-scan technique. The structures were solved by the direct methods and refined on *F*² by full-matrix least squares using SHELXTL97.¹ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

CD spectral measurements in solution and solid state were performed on a JASCO J-815 CD spectropolarimeter.

High-frequency EPR spectra of powder sample (260 - 380 GHz) were recorded in Stuttgart on a home-built spectrometer. Its radiation source is a 0 - 20 GHz signal generator (Anritsu) in combination with an amplifier-multiplier chain (VDI) to obtain the required frequencies. It features a quasi-optical bridge (Thomas Keating) and induction mode detection. The detector is a QMC magnetically tuned InSb hot electron bolometer. The sample is located in an Oxford Instruments 15/17T cryomagnet equipped with a variable temperature insert (1.5 – 300K).

The single crystal HFEPR data were recorded at the Grenoble High Magnetic Field Laboratory on a homemade spectrometer using Gunn diodes as source excitation and higher harmonic multipliers. Crystals were embedded in N-grease to have them well fixed. Due to the visual procedural of alignment, the orientation error up to 3° can occur.



Scheme S1.1 The structure of the ligands H_2L_R and H_2L_S .

SI2 Synthesis details

All starting materials were purchased as reagent grade and were used without further purification.

Synthesis of the Schiff base ligands



Compound H₂**L**_{*R*}. A solution of 2-hydroxy-5-nitrobenzaldehyde (1.67 g, 10.0 mmol) and (*R*)-2-amino-2-phenylethanol (1.37 g, 10.0 mmol) in ethanol was stirred under reflux for 3 h and the color of the solution was turned to yellow. After removal of the solvents under reduced pressure, the crude product was purified by recrystallization in the mixture solvent of ethanol and petroleum ether to give compound H₂L_{*R*} as needlelike crystals (2.72 g, 95 %). ¹H NMR (400 MHz, CDCl₃): δ 14.63 (br, 1 H), 8.50 (s, 1 H), 8.23 (d, *J* = 2.4 Hz, 1 H), 8.18 (d d, *J*₁ = 9.2 Hz, *J*₂ = 2.8 Hz, 1 H), 7.43–7.33 (m, 5 H), 6.98 (d, *J* = 8.8 Hz, 1 H), 4.59 (t, *J* = 6.4 Hz, 1 H), 3.98 (d, *J* = 5.6 Hz, 2 H). Anal. Calcd for C₁₅H₁₄N₂O₄: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.38; H, 5.01; N, 9.68.MS (ESI): *m/z* 287.10 [M + 1]⁺. IR (pure sample): *v* = 3255(w), 3088(w), 3064(w), 3033(w), 2928(w), 2874(w), 1955(w), 1810(w), 1642(s), 1613(s), 1584(m), 1547(m), 1524(m), 1492(m), 1452(m), 1402(w), 1336(s), 1299(m), 1228(m), 1175(w), 1131(w), 1096(m), 1067(m), 1029(m), 1003(w), 943(w), 902(w), 837(m), 757(m), 729(w), 700(m), 637(w).

The enantiomer compound H_2L_S was synthesized by using 2-hydroxy-5nitrobenzaldehyde and (*S*)-2-amino-2-phenylethanol as start materials in the same way.

Synthesis of the compounds 1R and 1S

Compound 1*R*. ([Fe₄(L_R)₆]·9DMA): A mixture of H₂ L_R (429 mg, 1.5 mmol) and Et₃N (4.3 mL, 3 mmol) in methanol (20 mL) was stirred at room temperature. A dark red precipitate was generated as soon as the solution of FeCl₂·4H₂O (198 mg, 1 mmol) in methanol (10 mL) was added dropwise (the Fe ions were oxidated from +2 valence to +3 valence in the air immediately), and the mixture was stirred at room temperature for 12 h. After then, the resulting solution was filtered and the solvent was removed under vacuum. The brown precipitate obtained was dried under vacuum then redissoved in hot DMA (40 mL). Dark red chunks were obtained within two weeks in 70-80 % yield by slow evaporation of the resulting solution. The crystals are stable at room temperature and no loss of solvent is observed. Anal. Calcd for C₁₂₆H₁₅₃Fe₄N₂₁O₃₃: C, 55.78; H, 5.68; N, 10.84. Found: C, 55.41; H, 5.92; N, 10.99. IR (pure sample): v =3649(w), 3062(w), 3030(w), 2928(w), 2865(w), 2706(w), 1752(w), 1631(m), 1605(m), 1556(m), 1503(m), 1469(m), 1435(w), 1412(w), 1383(m), 1316(s), 1265(w), 1246(w), 1190(w), 1130(w), 1102(m), 1067(w), 1038(m), 1030(m), 950(w), 935(w), 907(w), 846(w), 805(w), 757(w), 730(w), 698(m), 655(m), 643(w). HRMS (ESI): Calcd. For C₉₀H₇₃Fe₄N₁₂O₂₄⁺: 1929.2267. Found: 1929.2311.

The enantiomer complexes of **1***S* ([Fe₄(L_{*S*})₆]·7DMA) was synthesized by using H₂L_{*S*} as ligand in the same way. Anal. Calcd for C₁₁₈H₁₃₅Fe₄N₁₉O₃₁: C, 55.82; H, 5.36; N, 10.38. Found: C, 55.34; H, 5.91; N, 10.87. IR (pure sample): v = 3649(w), 3062(w), 3030(w), 2929(w), 2864(w), 2708(w), 1753(w), 1631(m), 1605(m), 1556(m), 1503(m), 1469(m), 1435(w), 1412(w), 1384(m), 1355(m), 1316(s), 1265(w), 1248(w), 1190(w), 1130(w), 1102(m), 1068(w), 1038(m), 1030(m), 950(w), 935(w), 911(w), 846(w), 805(w), 757(w), 730(w), 698(m), 655(m), 643(w).

 $(H_2L_R = (R)-2-((2-hydroxy-1-phenylethylimino)methyl)-4-nitrophenol, H_2L_S = (S)-2-((2-hydroxy-1-phenylethylimino)methyl)-4-nitrophenol)$

References

1. Sheldrick, G. M. SHELXS-97; University of Gottingen: Gottingen, Germany, 1997.



Figure S2.1. ¹H NMR spectrum of H_2L_R (400 MHz) in CDCl₃ (10 mM).



Figure S2.2. Positive-mode high resolution ESI-MS spectrum of 1*R*.



Figure S2.3. CD spectra of 1R and 1S at 298 K (5 × 10⁻⁵ M, DMF).



Figure S2.4. The solid-state CD spectra of 1R (black) and 2S (red) in KBr pellet at 298

K.

SI 3 Structure details

Table 3.1. Crystal data, data collection, solution, and refinement information ofcompounds 1R and 1S.

	1 <i>R</i>	1 <i>S</i>
Formula	C ₉₀ H ₇₂ Fe ₄ N ₁₂ O ₂₄	C ₉₀ H ₇₂ Fe ₄ N ₁₂ O ₂₄
Formula weight	1929.00	1929.00
Crystal system	Trigonal	Trigonal
Space group	R32	R32
<i>a</i> , Å	29.7005(17)	29.778(4)
b, Å	29.7005(17)	29.778(5)
<i>c</i> , Å	13.7937(8)	13.885(3)
α , deg	90	90
β , deg	90	90
γ, deg	120	120
V, Å ³	10537.5(10)	10663(3)
Ζ	3	3
<i>T</i> , K	100(2)	173(2)
F(000)	2976	2976
$D_{\rm C}$, g cm ⁻³	0.912	0.901
μ , mm ⁻¹	0.457	0.452
λ, Å	0.71073	0.71073
Crystal size, mm ³	$0.60 \times 0.42 \times 0.34$	$0.32 \times 0.28 \times 0.25$
T_{\min} and T_{\max}	0.6788, 0.7457	0.6930, 1.0000
$\theta_{\min}, \theta_{\max}, \deg$	1.68, 28.33	2.37, 27.49
no. total reflns.	41624	29068
no. uniq. reflns, $R_{\rm int}$	5850, 0.0656	5348, 0.0997
no. obs. $[I \ge 2\sigma(I)]$	5421	5288
no. params	197	197
$R1 [I \ge 2\sigma(I)]$	0.0448	0.0607
wR2 (all data)	0.1185	0.1741
S	1.056	1.092
$\Delta \rho^{a}$, e/ Å ³	0.397, -0.732	0.365, -0.684
max and mean Δ/σ^b	0.001, 0.000	0.000, 0.000
Flack parameter	0.084(17)	0.00(3)
CCDC Number	941225	941226

Fe(1)-O(2)	2.0207(18)	Fe(2)-O(1)	1.9408(17)
Fe(1)-O(2)#1	2.0207(18)	Fe(2)-O(1)#5	1.9408(17)
Fe(1)-O(2)#2	2.0207(18)	Fe(2)-O(2)#5	2.0031(18)
Fe(1)-O(2)#3	2.0207(18)	Fe(2)-O(2)	2.0031(18)
Fe(1)-O(2)#4	2.0207(18)	Fe(2)-N(1)	2.142(2)
Fe(1)-O(2)#5	2.0207(18)	Fe(2)-N(1)#5	2.142(2)
O(2)-Fe(1)-O(2)#1	87.53(7)	O(1)-Fe(2)-O(1)#5	98.30(11)
O(2)-Fe(1)-O(2)#2	87.53(7)	O(1)-Fe(2)-O(2)#5	96.09(7)
O(2)#1-Fe(1)-	87 53(7)	O(1)#5-Fe(2)-	159 07(7)
O(2)#2	87.33(7)	O(2)#5	130.97(7)
O(2)-Fe(1)-O(2)#3	133.57(9)	O(1)-Fe(2)-O(2)	158.97(7)
O(2)#1-Fe(1)-	132 28(0)	O(1)#5-Fe(2)-O(2)	96.10(7)
O(2)#3	152.20(9)		
O(2)#2-Fe(1)-	73 98(9)	O(2)#5-Fe(2)-O(2)	74.74(10)
O(2)#3	75.56(5)	0(2)#5-10(2)-0(2)	74.74(10)
O(2)-Fe(1)-O(2)#4	132.28(9)	O(1)-Fe(2)-N(1)	86.85(8)
O(2)#1-Fe(1)-	73 98(9)	O(1)#5-Fe(2)-N(1)	92 54(8)
O(2)#4	75.56(5)	0(1)//5 10(2) 11(1)	J2.54(0)
O(2)#2-Fe(1)-	133 57(9)	O(2)#5-Fe(2)-N(1)	103.51(7)
O(2)#4	155.57(5)		
O(2)#3-Fe(1)-	87 53(7)	O(2)-Fe(2)-N(1)	77.25(7)
O(2)#4	07.55(7)		
O(2)-Fe(1)-O(2)#5	73.99(9)	O(1)-Fe(2)-N(1)#5	92.54(8)
O(2)#1-Fe(1)-	133 57(9)	O(1)#5-Fe(2)-	86.85(8)
O(2)#5	155.57(5)	N(1)#5	
O(2)#2-Fe(1)-	132 28(9)	O(2)#5-Fe(2)- N(1)#5	77.25(7)
O(2)#5	10		
O(2)#3-Fe(1)-	87.53(7)	O(2)-Fe(2)-N(1)#5	103.51(7)
O(2)#5			
O(2)#4-Fe(1)-	87.53(7)	N(1)-Fe(2)-N(1)#5	179.07(11)
O(2)#5			

 Table S3.2.
 Selected bond lengths (Å) and angles (°) for 1*R*.

Symmetry operation: #1 -y,x-y,z;#2 -x+y,-x,z; #3 -x,-x+y,-z+1; #4 y,x,-z+1;#5 x-y,-y,-

z+1.

Fe(1)-O(2)	2.021(2)	Fe(2)-O(1)	1.941(3)
Fe(1)-O(2)#1	2.021(2)	Fe(2)-O(1)#2	1.941(3)
Fe(1)-O(2)#2	2.021(2)	Fe(2)-O(2)	2.009(2)
Fe(1)-O(2)#3	2.021(2)	Fe(2)-O(2)#2	2.009(2)
Fe(1)-O(2)#4	2.021(2)	Fe(2)-N(1)	2.149(3)
Fe(1)-O(2)#5	2.021(2)	Fe(2)-N(1)#2	2.149(3)
O(2)#1-Fe(1)- O(2)#2	87.32(9)	O(1)#2-Fe(2)-O(1)	98.78(17)
O(2)#1-Fe(1)-O(2)	131.85(13)	O(1)#2-Fe(2)-O(2)	95.90(11)
O(2)#2-Fe(1)-O(2)	74.29(13)	O(1)-Fe(2)-O(2)	158.66(11)
O(2)#1-Fe(1)- O(2)#3	134.19(12)	O(1)#2-Fe(2)- O(2)#2	158.66(10)
O(2)#2-Fe(1)- O(2)#3	131.85(13)	O(1)-Fe(2)-O(2)#2	95.90(11)
O(2)-Fe(1)-O(2)#3	87.32(9)	O(2)-Fe(2)-O(2)#2	74.81(13)
O(2)#1-Fe(1)- O(2)#4	74.29(13)	O(1)#2-Fe(2)-N(1)	92.47(11)
O(2)#2-Fe(1)- O(2)#4	134.19(12)	O(1)-Fe(2)-N(1)	86.88(11)
O(2)-Fe(1)-O(2)#4	87.32(9)	O(2)-Fe(2)-N(1)	77.05(10)
O(2)#3-Fe(1)- O(2)#4	87.32(9)	O(2)#2-Fe(2)-N(1)	103.76(10)
O(2)#1-Fe(1)- O(2)#5	87.32(9)	O(1)#2-Fe(2)- N(1)#2	86.88(11)
O(2)#2-Fe(1)- O(2)#5	87.32(9)	O(1)-Fe(2)-N(1)#2	92.47(11)
O(2)-Fe(1)-O(2)#5	134.19(13)	O(2)-Fe(2)-N(1)#2	103.76(10)
O(2)#3-Fe(1)- O(2)#5	74.29(13)	O(2)#2-Fe(2)- N(1)#2	77.05(10)
O(2)#4-Fe(1)- O(2)#5	131.85(13)	N(1)-Fe(2)-N(1)#2	179.00(16)

Table S3.3. Selected bond lengths (Å) and angles (°) for 1S.

Symmetry operation: #1 x-y+1,-y+2,-z+2;#2 -x,-x+y,-z+2; #3 -x+y-1,-x+1,z;#4 -

y+1,x-y+2,z; #5 y-1,x+1,-z+2.

SI 4 Static magnetization



Figure S4.1. Temperature dependence of $\chi_M T$ at H = 1 kOe at 2–300 K (the red solid line represents the best simulation of magnetic susceptibilities calculated by MAGPACK at 20–300 K) and *Mvs.H/T* plots at different temperature (1.8 K, 2.0 K, 3.0 K, and 5.0 K) for the polycrystalline sample of **1***R*.



Figure S4.2. Plot of magnetization (*M*) *vs*. dc magnetic field (*H*) within ± 5 kOe for **1***R* at 0.5 Kin MPMS, an obvious hysteresis loop can be observed.



Figure S4.3. Plot of magnetization (*M*) vs. dc magnetic field (*H*) within ± 5 kOe for **1***R* at 1.2 K in MPMS, no obvious hysteresis loop can be observed.



Figure S4.4. Plot of zero-field cooled (black) and field cooled (red) magnetic susceptibility measurement at 10 Oe for **1***R* below1.6 K.

SI 5 dynamic magnetization



FigureS5.1. Temperature dependence of ac susceptibility at different temperatures from 1 to 1000 Hz for **1***R*.



FigureS5.2. Frequency dependence of ac susceptibility at frequencies from 1 to 1000 Hz for **1***R*.



Figure S5.3. Arrhenius plots for **1***R* obtained from $\chi''vs$. Temperature measurements in the absence of a dc field.

SI6 HFEPR spectra



Figure S6.1. Experimental (black) and simulated (red) HFEPR spectra of **1***R* powder sample at 10 K.



Figure S6.2. The HFEPR spectra of 1R single crystal sample from rotating the magnetic field perpendicular to the *c* axis at 15 K. The angle θ on the right column is defined and the angle between the static field and the crystallographic *a* axis.



Figure S6.3. The face index information of the single crystal sample of 1*R*.