Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Slow Magnetic Relaxation in a Mononuclear 8-Coordinate Fe(II) Complex

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Experimental section

Synthesis

Materials and physical measurements

IR spectra were obtained as KBr discs using a Nicolet 360 FT-IR spectrophotometer. Elemental analysis was performed using an Elementar Vario EL Analyzer. Variable-temperature magnetic susceptibility, ac magnetic susceptibility, and field dependence of magnetization were measured on a Quantum Design MPMS XL-5 SQUID system. Background corrections were done by experimental measurement on the sample holder. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

X-ray crystallography

Crystals suitable for X-ray diffraction analysis were obtained for **1**. X-ray diffraction data were collected at 100 K on an Oxford CCD or a NONIUS Kappa CCD diffractometer using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) for **1** in the ω-scan mode. Absorption corrections were done by the multiscan method. The structures were resolved by the heavy-atom Patterson method or direct methods and refined by full-matrix least-squares using SHELX-97 and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. H atoms were generated by the program SHELXL-97. The positions of H atoms were calculated on the basis of riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.

Computational Details

All calculations were done with MOLCAS 8.0 and are of CASSCF/CASPT2/RASSI/SINGLE_ANISO type. The structure used for calculation is $[FeII(L1)2]^{2+}$, two perchlorate ions were omitted for they lie far from Fe^{2+} and are not coordinate with Fe^{2+}. No geometry optimization has been done, all atomic coordinates (except for added hydrogens) were taken directly from the X-ray crystal structure. The basis sets used for the calculations were taken from the basis libraries from MOLCAS package. The basis set of Fe is ano-rcc-vtzp, the coordinated N and O atoms are ano-rcc-vdzp, for other atoms are ano-rcc-vdz. The active space of the complete active space self-consisting field (CASSCF) of calculation of the

Fe include 3d orbitals (CAS 6 in 5). The spin multiplicity considered in the calculation includes 5, 3, 1. CASPT2 was performed after CASSCF with 9 atoms (Fe and four coordinate N and four coordinate O atoms) froze. The RASSI-SO calculations were used to get the low-lying spin-orbit coupling states. At last, SINGLE_ANISO program were used to compute local magnetic properties (energy levels, D tensors, g-tensors, main magnetic axes, local magnetic susceptibility, etc.)

Table S1 Low-lying spin-orbit energies (cm^{-1})

spin-orbit states (RASSI)					
0.000	0.115	34.928	35.414	47.023	2878.482
2885.798	2896.534	2926.325	2928.458	3673.516	3682.622
3692.092	3728.017	3728.868	5542.580	5542.910	5589.161
5600.017	5612.296	6643.072	6644.882	6656.638	6667.952
6669.508	19943.504	19953.963	20004.963	20613.923	20622.086
…					

Synthesis

[Fe^{II}($\mathbf{L_1}$)$_2$](ClO$_4$)$_2$ (**1**). 1,10-phenanthroline-2,9-dicarboxylic acid (PDA) (100 mg, 0.37 mmol) and Fe(ClO$_4$)$_2$·6H$_2$O (134 mg, 0.37 mmol) were added into MeOH (30 ml). The mixture was heated at reflux for 5 h and cooled to room temperature. Red block crystals that were suitable for X-ray crystallography were obtained by slow evaporation of the resulting solution for 1 day. Yield (117 mg, 74%). Elemental analysis (%) calcd for $C_{32}H_{24}Cl_2FeN_4O_{16}$: C, 45.36; H, 2.86; N, 6.61. Found: C, 45.30; H, 2.92; N, 6.58. IR (KBr)/cm^{-1}: ν(C=O) 1698. UV-vis (CH$_3$CN): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) 208 (20860), 236 (33050), 282 (21810), 315sh (8280), 517 (150). ESI-MS: m/z = 324.0 (M^{2+}). μ_{eff} = 5.72 μ_B.

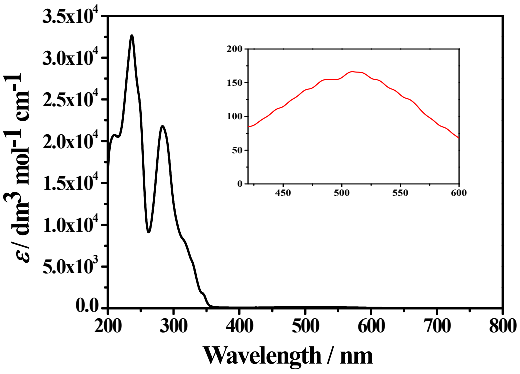

Fig. S1 The UV/vis spectrum of **1** in CH$_3$CN.

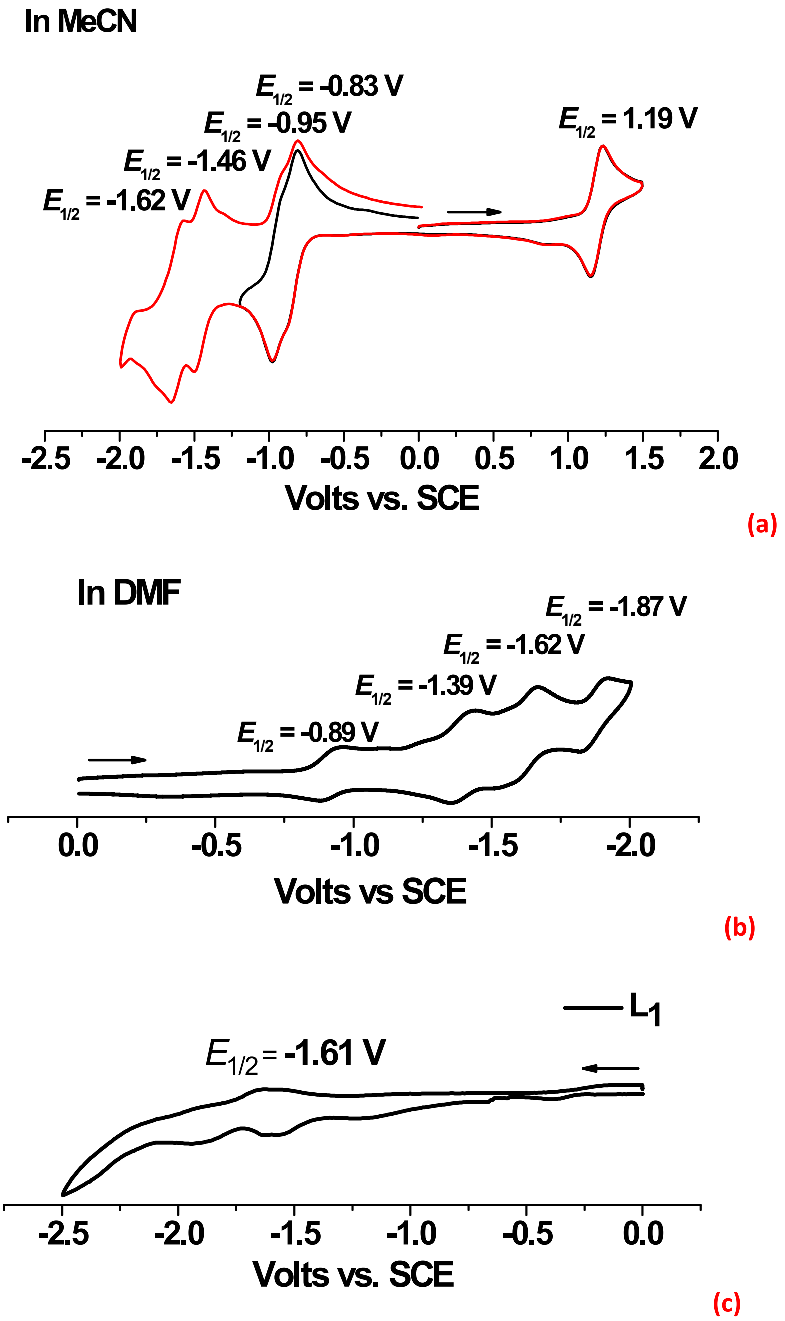

Fig. S2 (a) CV of **1** in MeCN containing 0.1 *M* $^{n}Bu_4NPF_6$; (b) CV of **1** in DMF containing 0.1 *M* $^{n}Bu_4NPF_6$; (c) CV of $\mathbf{L_1}$ in MeCN containing 0.1 *M* $^{n}Bu_4NPF_6$.

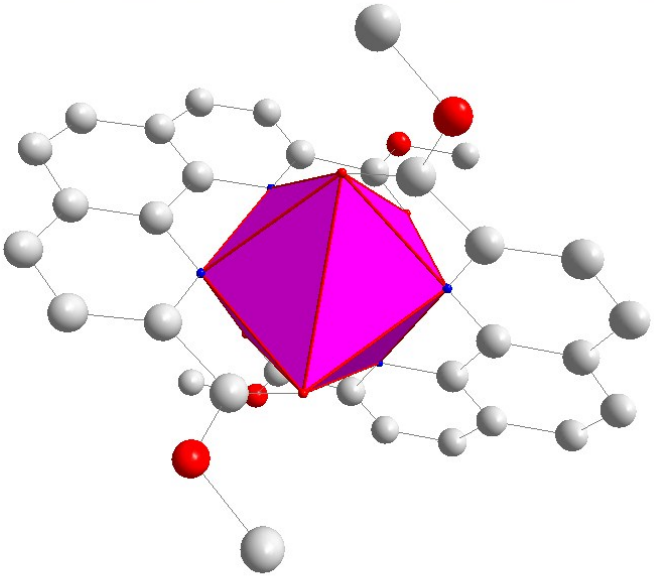

Fig. S3 The perspective view showing that the Fe(II) center is in a distorted bisdisphenoid dodecahedron geometry.

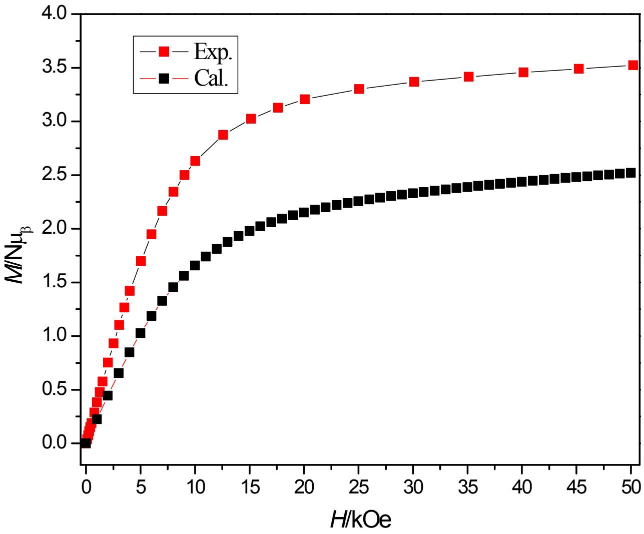

Fig. S4 Magnetization of **1** as a function of applied field at 2.0 K. Red solid squares are experiment results and black solid squares are ab initio calculations results. The difference may cause by the orientation of the sample powder which introduce anisotropy or the limitation of ab initio calculations.