

Electronic Supplementary Information

Orthogonality of Jahn–Teller axes in a dinuclear Cu(II) complex bridged by one F⁻ anion

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Synthesis of [Cu₂F(BF₄)₃(4-phpy)₇] (1). The single crystals of **1** were obtained by the standard diffusion method in an H-shaped cell (~ 50 mL). EtOH solution (~2 mL) of Cu(BF₄)₂·6H₂O (86 mg) and toluene solution (2 mL) of 4-phpy (155 mg) were introduced into opposite sides of the H-shaped cell, and pure EtOH was introduced into the diffusion cell slowly. After one month, blue single crystals were obtained, which were filtered, washed with EtOH, and dried in air. Yield: 66 mg (36 %). Phase purity was checked by powder X-ray diffraction and elemental analysis. Anal. Calcd for **1**: C, 61.95; H, 4.25; N, 6.57; F, 16.54 %. Found: C, 61.95; H, 4.21; N, 6.52; F, 16 %.

X-ray Structural Analysis. X-ray diffraction measurement on **1** was performed using a Rigaku Mercury CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.7173 \text{ \AA}$). The data were corrected for Lorentz and polarization effects. The structure was solved using direct methods (SIR2004)^{S1} and expanded using Fourier techniques.^{S2} All nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were refined using the riding model. The refinements were carried out using full-matrix least-squares techniques on F^2 . All calculations were performed using the CrystalStructure crystallographic software package.^{S3} The crystallographic data in CIF format are available from the Cambridge Crystallographic Data Centre, CCDC reference number 759805.

Calculations. The DFT calculations were performed with the B3LYP/LanL2DZ basis set (Spin: Triplet) using the package Gaussian 03, revision E.01. A natural population analysis (NPA) was used to obtain the charge distribution.^{S4,S5} The atomic coordinate of **1** based on the X-ray crystal structural analysis was used for the calculations.

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- S2. *DIRDIF-94*; P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israe., J. M. M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.
- S3. *Crystal Structure Analysis Package, Crystal Structure 3.7.0*; Rigaku and Rigaku/MSK: The Woodlands, TX, 2000-2005.
- S4. A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1983, **78**, 4066.
- S5. A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735.

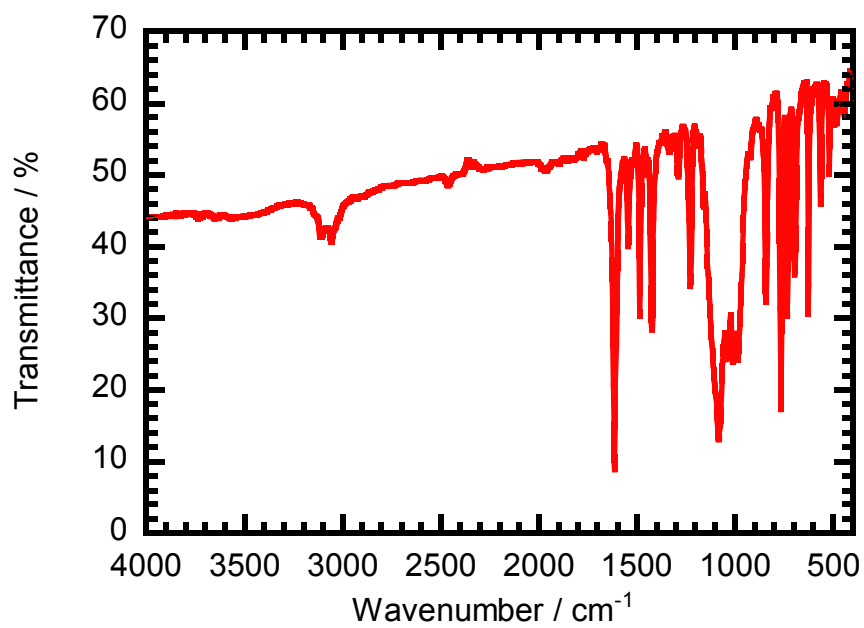


Fig. S1. IR spectra of **1** (KBr pellet).

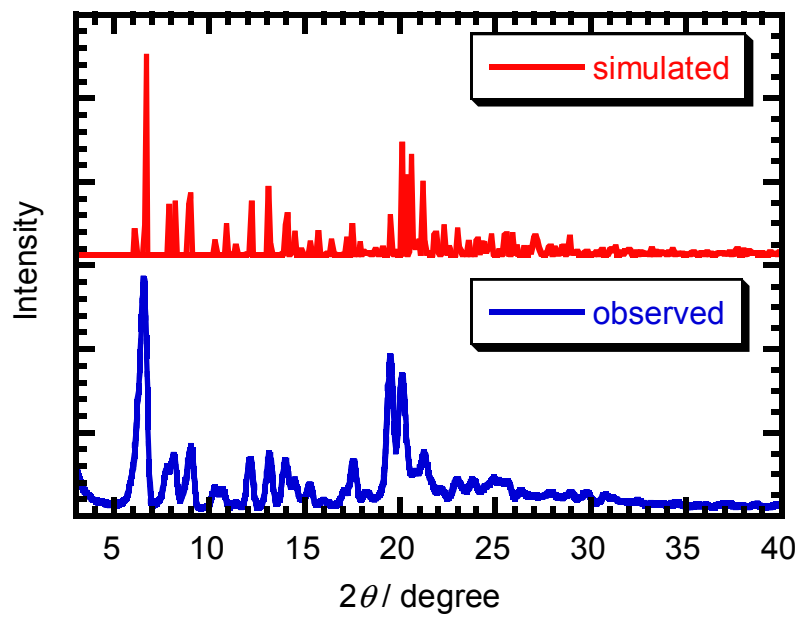


Fig. S2. The simulated and observed XRD patterns of **1**.

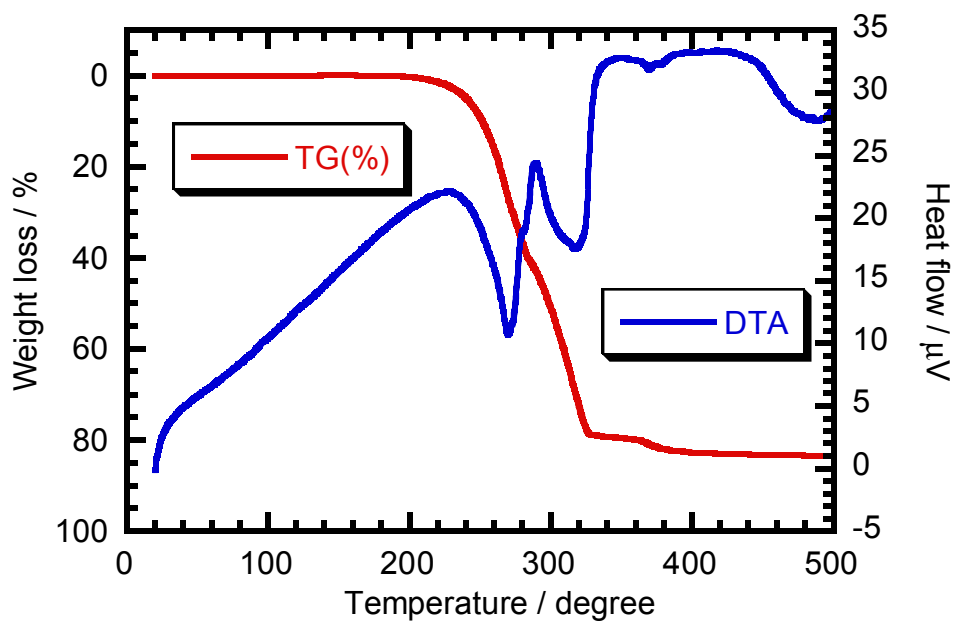


Fig. S3. TG–DTA curve of **1** under N₂ flow.

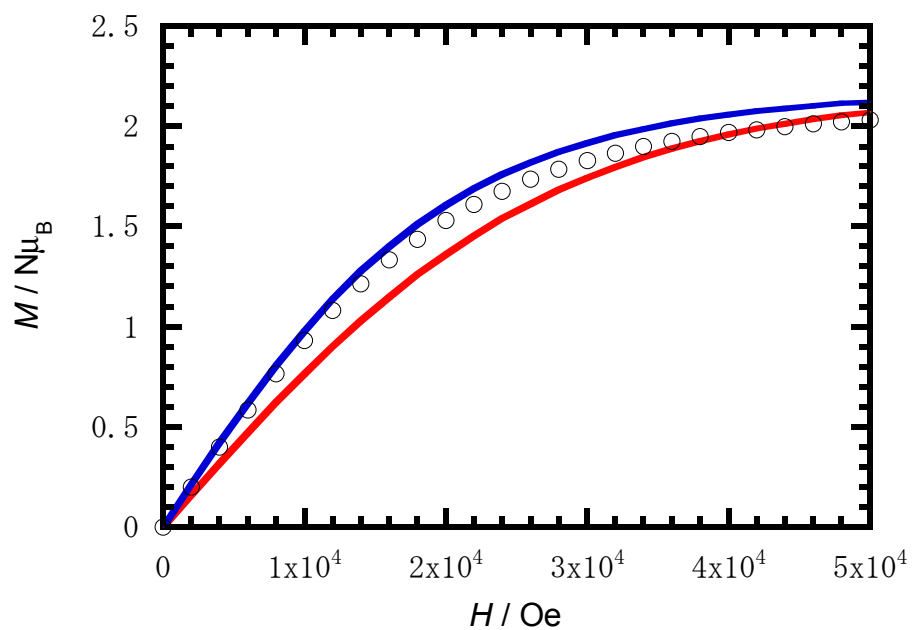


Fig. S4. Field (H) dependence of magnetization (M) of **1** at 2 K. The red and blue lines represent simulation curves with $S = 1/2 + 1/2$ (paramagnetic system with no interaction) and $S = 1$, respectively, where the g value that was experimentally obtained was used in the simulations.

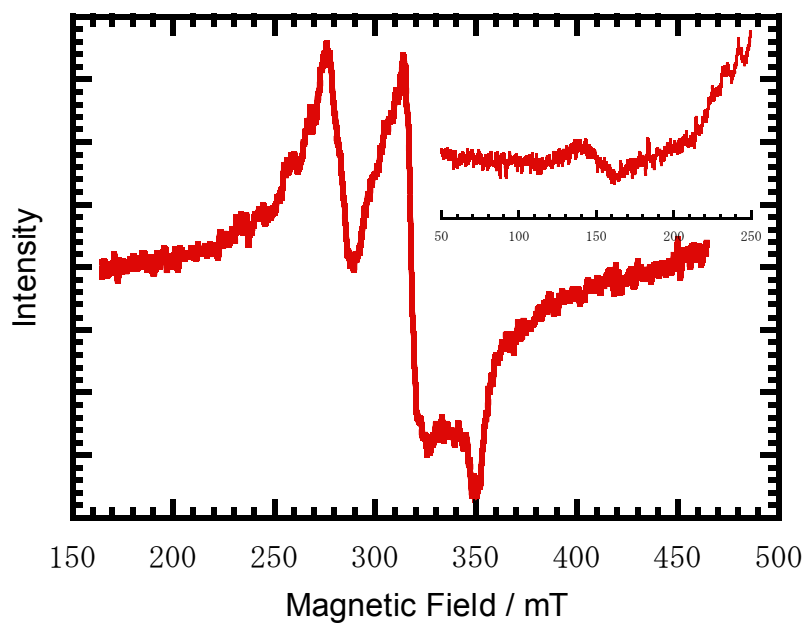


Fig. S5. ESR spectra of **1** (microcrystals) at 297 K.

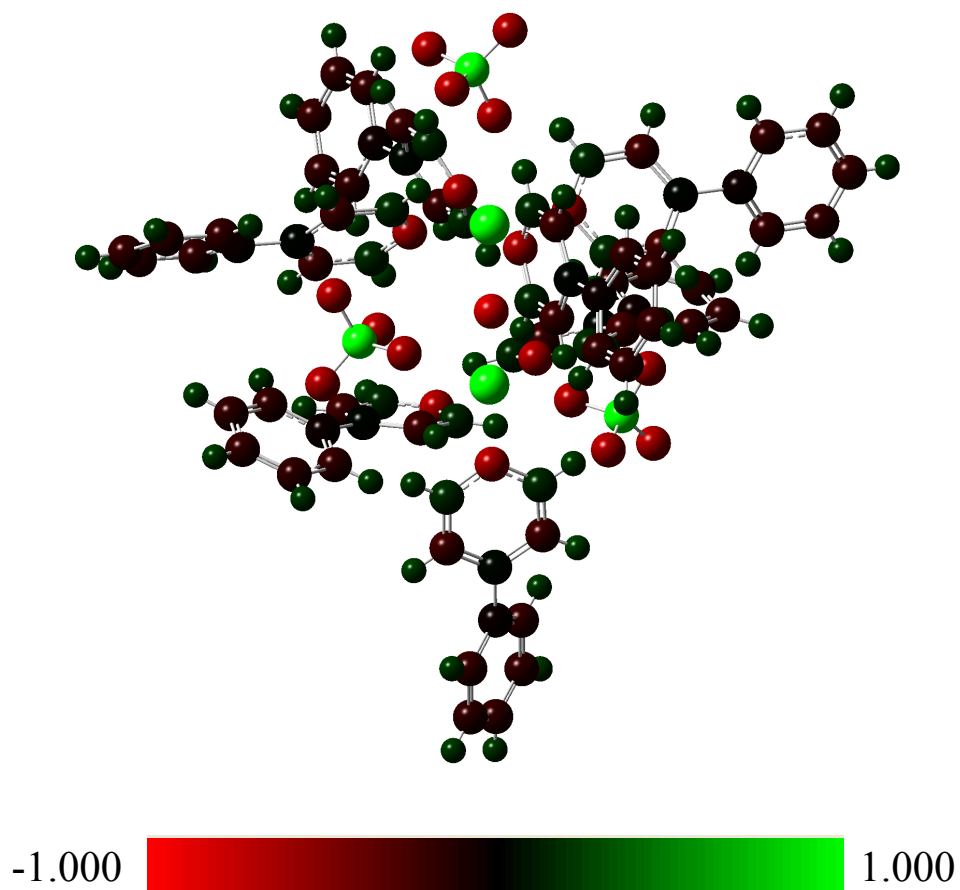


Fig. S6. Visualized charge distribution of **1**.

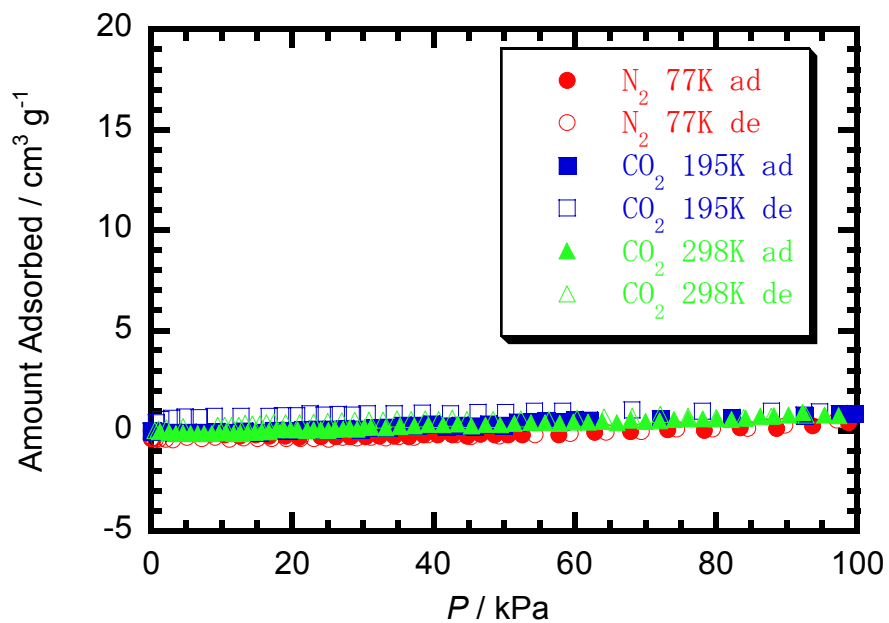


Fig. S7. Adsorption (filled symbols) and desorption (open symbols) isotherms for N₂ at 77 K (circle, red), CO₂ at 195 K (square, blue) and 298 K (triangle, green), on **1**.

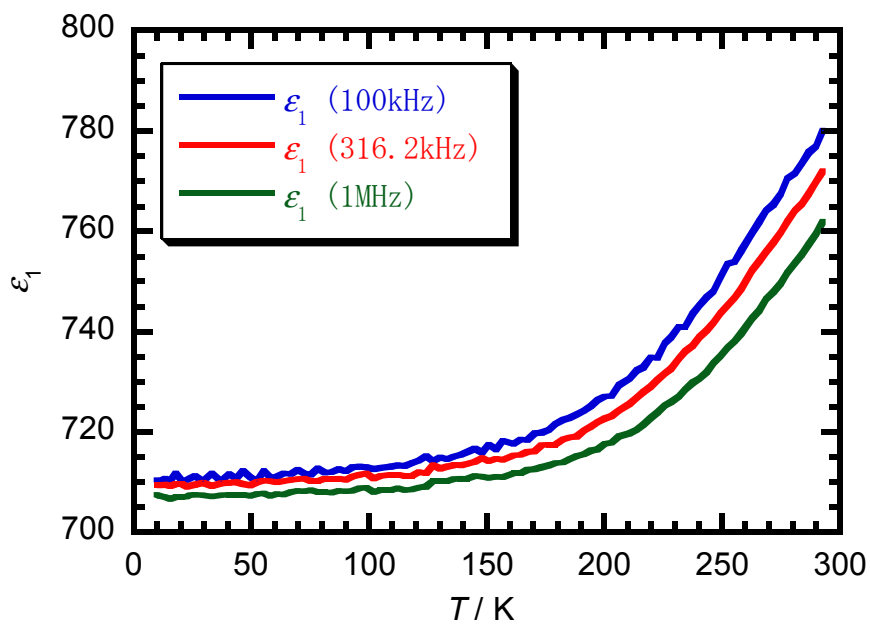


Fig. S8. Temperature-dependent dielectric constants (ϵ_1) of **1**. The electric field was applied along the *c*-axis.