

Supporting Information

Intramolecular Ferromagnetic Radical–Cu^{II} Coupling in a Cu^{II} Complex Ligated with Pyridyl-Substituted Triarylmethyl Radicals

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General method

Solvents and reagents were used as received from commercial sources unless otherwise noted. (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (PyBTM) was prepared according to previously reported protocol.¹ Elemental analysis measurements were performed by the elemental analysis center of the university of Tokyo. ESI-TOF mass spectra were recorded using a Waters Micromass ZQ4000 spectrometer. UV-vis absorption spectra were recorded with a JASCO V-570 spectrometer. Steady-state emission spectra were measured with a HITACHI F-4500 spectrometer. Sample solutions were bubbled with argon before measurements. Absolute photoluminescent quantum yields were measured with a Hamamatsu Photonics C9920-02G.

Synthesis of Cu^{II}(hfac)₂(PyBTM)₂

Under a nitrogen atmosphere, Cu^{II}(hfac)₂·nH₂O (50.3 mg, 0.098 mmol for n = 2) was dissolved in dry hexane (33 mL) under reflux. PyBTM (108.2 mg, 0.208 mmol) in dry dichloromethane and dry hexane (1 ml and 4 ml) was added dropwise to the solution at 70°C, and stirred for 1.5 hrs. The resulting suspension was kept overnight at −30°C. The deep-red precipitate was filtered, washed with hexane, and dried in vacuo. Recrystallization from dichloromethane–hexane afforded Cu^{II}(hfac)₂(PyBTM)₂ (70 mg, 0.046 mmol) in 47% yield. Anal. calcd for C₄₆H₁₄Cl₁₆F₁₂N₂O₄Cu: C, 36.41; H, 0.93; N, 1.85. Found: C, 36.28; H, 1.03; N, 1.91. MS (ESI-TOF+) *m/z* 1310 [Cu^{II}(hfac)(PyBTM)₂]⁺. A deep red crystal suitable for single crystal X-ray diffraction study was obtained by recrystallization from dichloromethane–hexane.

Synthesis of Zn^{II}(hfac)₂(PyBTM)₂

Under a nitrogen atmosphere, Zn^{II}(hfac)₂·2H₂O (53.0 mg, 0.103 mmol) was dissolved in dry hexane (48 mL) and dry dichloromethane (3 ml) under reflux. PyBTM (131.0 mg, 0.251 mmol) dissolved in dry dichloromethane and dry hexane (1.5 ml and 4 ml) was added dropwise to solution at 100°C, and stirred for 1 hr. The resulting suspension was kept overnight at −30°C. The deep-red precipitate was filtered, washed with hexane, and dried in vacuo. Recrystallization from dichloromethane–hexane afforded Zn^{II}(hfac)₂(PyBTM)₂ (82 mg, 0.054 mmol) in 52% yield. Anal. Calcd for C₄₆H₁₄Cl₁₆F₁₂N₂O₄Zn: C, 36.37; H, 0.93; N, 1.84. Found: C, 36.20; H, 1.05; N, 1.74. MS (ESI-TOF+) *m/z* 1313 [Zn^{II}(hfac)(PyBTM)₂]⁺. A deep red crystal suitable for single crystal X-ray diffraction study was obtained by recrystallization from dichloromethane–hexane.

DFT Calculations:

The calculations were carried out using the Gaussian09 program package.² The geometry of each complex was extracted from the crystallographic data. Single-point calculations were performed assuming either doublet or quartet states for Cu^{II}(hfac)₂(PyBTM)₂ and singlet or triplet states for Zn^{II}(hfac)₂(PyBTM)₂, at the (u)B3LYP level of theory³ with LANL2DZ (Hay-Wadt ECP) basis set⁴ for the Cu atom and the 6-31G(d) basis set⁵ for the other atoms. The intramolecular exchange interactions were considered within the broken-symmetry framework proposed by Yamaguchi and co-workers.⁶

Single crystal X-ray diffraction

Diffraction data for X-ray analysis were collected at 113 K with an AFC10 diffractometer coupled with a Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator producing graphite-monochromated MoK α radiation ($\lambda = 0.7107 \text{ \AA}$). Lorentz polarization and numerical absorption corrections were performed with the program *Crystal Clear 1.3.6*. Structures were solved by the direct method using SIR92⁷ and refined against F^2 using SHELXL-2013.⁸ One of two CF₃ groups in each complex was disordered into two positions, in which the fluorine atoms with higher occupancy were refined anisotropically, and those with lower occupancy were refined isotropically. All the other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in idealized positions and were refined using a riding model with fixed thermal parameters. The crystallographic data are listed in Table S1. The cif files (CCDC No. 1050831 for the Cu^{II} complex and No. 1050832 for the Zn^{II} complex) can be obtained free of charge from The Cambridge Crystallographic via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements by SQUID.

The temperature dependence of the magnetic susceptibility of complexes was measured with a Quantum Design MPMS SQUID magnetometer. Aluminum foil was used as a sample container, whose magnetic contribution was subtracted as background by measuring its own magnetic susceptibilities in every measurement. The diamagnetic correction χ_{dia} for the sample was carried out with Pascal's constants. χ_{dia} : $7.04 \times 10^{-4} \text{ emu}\cdot\text{mol}^{-1}$ for Cu^{II}(hfac)₂(PyBTM)₂; $7.06 \times 10^{-4} \text{ emu}\cdot\text{mol}^{-1}$ for Zn^{II}(hfac)₂(PyBTM)₂.

ESR spectroscopy.

ESR spectra were recorded with a JEOL JES-FA200 spectrometer with X-band microwave at room temperature. Observed g-values were calibrated with the $\text{Mn}^{2+}/\text{MgO}$ standard. Powdered samples charged in a 5 mm ϕ sample tube were used for measurements. In the measurements of $\text{Cu}^{\text{II}}(\text{hfac})_2(\text{PyBTM})_2$, the contribution from the sample tube and air was subtracted as background.

Table S1. Crystallographic Data

	Cu^{II}(hfac)₂(PyBTM)₂	Zn^{II}(hfac)₂(PyBTM)₂
Empirical formula	C ₄₆ H ₁₄ Cl ₁₆ CuF ₁₂ N ₂ O ₄	C ₄₆ H ₁₄ Cl ₁₆ F ₁₂ N ₂ O ₄ Zn
<i>F</i> _w / g mol ⁻¹	1517.33	1519.16
Crystal dimension (mm)	0.3 × 0.2 × 0.2	0.2 × 0.15 × 0.05
<i>T</i> (K)	113	113
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	9.107(2)	9.092(3)
<i>b</i> (Å)	14.594(4)	14.604(4)
<i>c</i> (Å)	20.758(5)	21.017(7)
<i>α</i> (°)	96.054(4)	97.123(3)
<i>β</i> (°)	94.587(4)	94.549(4)
<i>γ</i> (°)	90.641(4)	90.761(4)
<i>V</i> (Å ³)	2734(1)	2759(1)
<i>Z</i>	2	2
<i>λ</i> (Å)	0.7107	0.7107
<i>μ</i> (Mo K α) (mm ⁻¹)	1.269	1.307
ρ_{calc} (g/cm ³)	1.843	1.828
<i>R</i> ₁ ^a	0.0794	0.0586
<i>wR</i> ₂ ^b	0.2052	0.1371
<i>GOF</i> ^c	1.169	1.128

(a) $R_1 = \Sigma ||F^o| - |F^c|| / \Sigma |F^o|$ ($I > 2\sigma(I)$). (b) $wR_2 = [\Sigma (w(F^{o2} - F^{c2})^2 / \Sigma w(F^{o2})^2)]^{1/2}$ ($I > 2\sigma(I)$). (c) $GOF = [\Sigma (w(F^{o2} - F^{c2})^2 / \Sigma (N^t - N^p)^2)]^{1/2}$.

Table S2. Calculated parameters of $M(\text{hfac})_2(\text{PyBTM})_2$ using broken-symmetry DFT methods

metal ion ^[1]	S_{total}	E (au)	$\langle S^2 \rangle_{\text{calc}}$	J/k_B (K) ^[2]
Cu1	3/2 (HS)	-10928.68748602	3.7511	20.6
	1/2 (LS)	-10928.68730070	0.905	
Cu2	3/2 (HS)	-10928.69264466	3.7511	47.1
	1/2 (LS)	-10928.69221800	0.893	
Zn1	1 (HS)	-12511.82499826	2.0012	-0.078
	0 (LS)	-12511.82499867	0.338	
Zn2	1 (HS)	-12511.84309829	2.0011	-0.062
	0 (LS)	-12511.84309862	0.330	

[1] There are two crystallographically independent $M(\text{hfac})_2(\text{PyBTM})_2$ complexes in crystals.

[2] $J = ({}^{\text{LS}}E - {}^{\text{HS}}E) / ({}^{\text{HS}}\langle S^2 \rangle_{\text{calc}} - {}^{\text{LS}}\langle S^2 \rangle_{\text{calc}})$. J/k_B is shown in Kelvin unit.

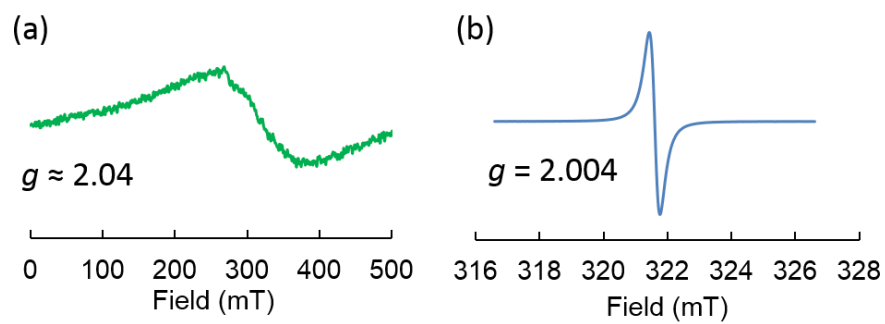


Figure S1. ESR spectra of powdered $\text{M}(\text{hfac})_2(\text{PyBTM})_2$ ($\text{M} = \text{Cu}^{\text{II}}$ (a); Zn^{II} (b)) at room temperature.

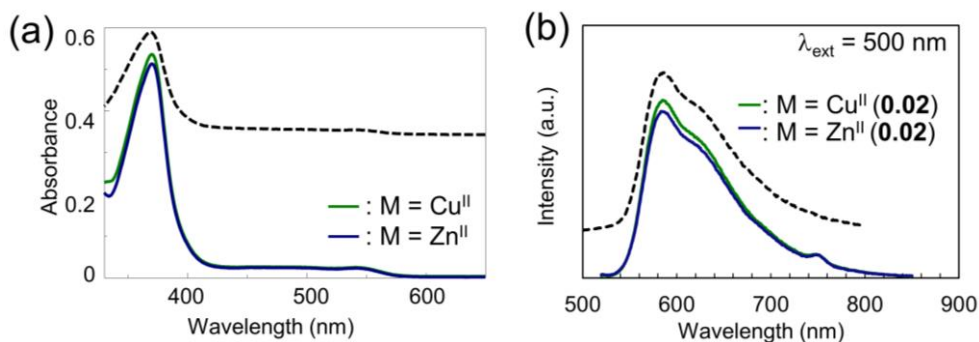


Figure S2. Absorption (a) and emission (b) spectra of $M(\text{hfac})_2(\text{PyBTM})_2$ ($M = \text{Cu}^{\text{II}}$ (green); Zn^{II} (blue)) in CH_2Cl_2 (0.01 mM) at room temperature. Values in parentheses in (b) indicate absolute photoluminescent quantum yields. Dotted lines indicate the spectra of PyBTM in CH_2Cl_2 , which are shifted upward for clarity. Both the absorption and emission spectra of $M(\text{hfac})_2(\text{PyBTM})_2$ are nearly identical with those of PyBTM. The emission of $M(\text{hfac})_2(\text{PyBTM})_2$ solution may result from free PyBTM dissociated in the ground or excited states.

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