

Electronic Supporting Information for

1-Phenyl-3-(pyrid-2-yl)-benzo[e][1,2,4]-triazinyl: The First “Blatter Radical” for Coordination Chemistry

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Section S1 Synthetic Details

General Methods and Procedures. The reagents sodium nonahydrate, sulfur, aniline, phenyl hydrazine, 1,8-diazabicycloundec-7-ene, and 10% palladium on carbon were obtained from Sigma-Aldrich and were used as received. The solvents used (chloroform, dichloromethane, absolute ethanol, and pentane) were of at least reagent grade. All reactions were performed in air unless otherwise stated. Infrared spectra (solid state) were recorded on a Bruker Alpha Platinum-ATR FTIR spectrometer at 2 cm^{-1} resolution. ^1H NMR spectra were run on a Bruker Avance 300 MHz NMR spectrometer. Elemental analyses were performed by Elina Hautakangas (University of Jyväskylä) & MHW Laboratories (Arizona, USA), whereas cyclic voltammetry was performed by Dr. Robert Reed (University of Guelph).

Preparation of N-phenylpyridine-2-carbothioamide. The procedure was performed as found in the literature.¹ However, the purification step was modified. Instead of performing multiple columns to remove impurities, one large dichloromethane plug followed by one pentane plug was used to afford pure yellow crystalline material. Yield 80 %; all spectral data the same as reported.

Preparation of N-N'-diphenylpicolinohydrazoamide. A modification to a known procedure was used.² Instead of a neat reaction, a small amount of absolute ethanol was added and the solution was refluxed overnight. A small silica plug with dichloromethane, followed by 1:1 dichloromethane:methanol afforded pure off-colourless crystalline material. Yield 35 %; all spectral data the same as reported.³

Preparation of 1-phenyl-3(pyridin-2-yl)-benzo[e][1,2,4]triazolyl (1). 1,8-diazabicycloundec-7-ene (230 mg, 1.53 mmol) and 10% Pd/C (20 mg) were added to a stirred solution of the amidrazone (354 mg, 1.22 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature for 30 hours until thin layer chromatography (1:20 methanol:dichloromethane) showed the absence of starting material and the presence of a new fast-running dark compound. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (1:20 methanol:dichloromethane) followed by recrystallization from toluene to afford plate green-black crystals of **1**. Yield: 178 mg (51 %). Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{N}_4$: C, 75.77; H, 4.59; N, 19.64. Found: C, 75.55; H, 4.65; N, 19.6. IR(cm^{-1}): 3061 (m), 3044 (m), 3029 (m), 3006 (m), 2100 (s), 2026 (w), 1947 (w), 1906 (w), 1866 (w), 1819 (w), 1780 (w), 1709 (w), 1633 (w), 1579 (s), 1569 (s), 1492 (s), 1480 (s), 1472 (s), 1452 (s), 1434 (m), 1382 (s), 1330 (m), 1307 (m), 1272 (m), 1257 (m), 1241 (m), 1210 (m), 1162 (w), 1147 (w), 1118 (w), 1118 (w), 1098 (m), 1073 (m), 1045 (w), 1025 (m), 993 (w), 935 (m), 891 (w), 880 (w), 845 (w), 837 (w), 787 (s), 756 (s), 737 (s), 701 (s), 679 (s), 623 (m), 616 (m), 599 (m), 570 (m), 552 (m), 517 (m), 493 (m), 472 (m), 426 (m).

Preparation of Cu(1)(hfac)₂ (3). A solution of Cu(hfac)₂·2H₂O (69.0 mg, 0.0135 mmol) in chloroform (5 mL) was slowly added to a solution of **1** (38.0 mg, 0.0135 mmol) in chloroform (5 mL). The solution changed from dark red to purple and was stirred for 1 hour. The solvent was evaporated under reduced pressure and the purple powder was crystallized by slow diffusion of pentanes into a chloroform solution to give large purple blocks of **3**. Yield: 26 mg (25 %). Anal. Calcd. for $\text{C}_{28}\text{H}_{15}\text{N}_4\text{O}_4\text{F}_{12}\text{Cu}$: C, 44.08; H, 1.98; N, 7.34. Found: C, 44.03; H, 2.22; N, 7.30. IR(cm^{-1}): 2924 (w), 2854 (w), 1655 (s), 1609 (w), 1590 (w), 1570 (w), 1550 (m), 1525 (m), 1512 (w), 1483 (w), 1455 (w), 1423 (w), 1363 (w), 1338 (w), 1315 (w), 1289 (w), 1256 (s), 1193 (s), 1132 (vs), 1084 (s), 1053 (m), 1029 (m), 998 (w), 983 (w), 945 (w),

925 (w), 885 (w), 861 (w), 840 (w), 807 (w), 794 (m), 773 (m), 757 (m), 748 (m), 699 (m), 664 (s), 627 (m), 606 (w), 579 (m), 531 (m), 508 (m), 476 (w), 444 (w), 425 (w).

Section S2 Cyclic Voltammetry

Cyclic voltammetry was performed using a BASi epsilon potentiostat, with scans of 100 mV/s on solutions of **1** in dichloromethane containing 0.1 M tetra-n-butyl-ammonium hexafluorophosphate. Potentials were scanned with respect to quasi-reference electrode in a single compartment cell fitted with Pt electrodes, and referenced to $\text{Fc}^*/\text{Fc}^{*+}$ couple vs. SCE.

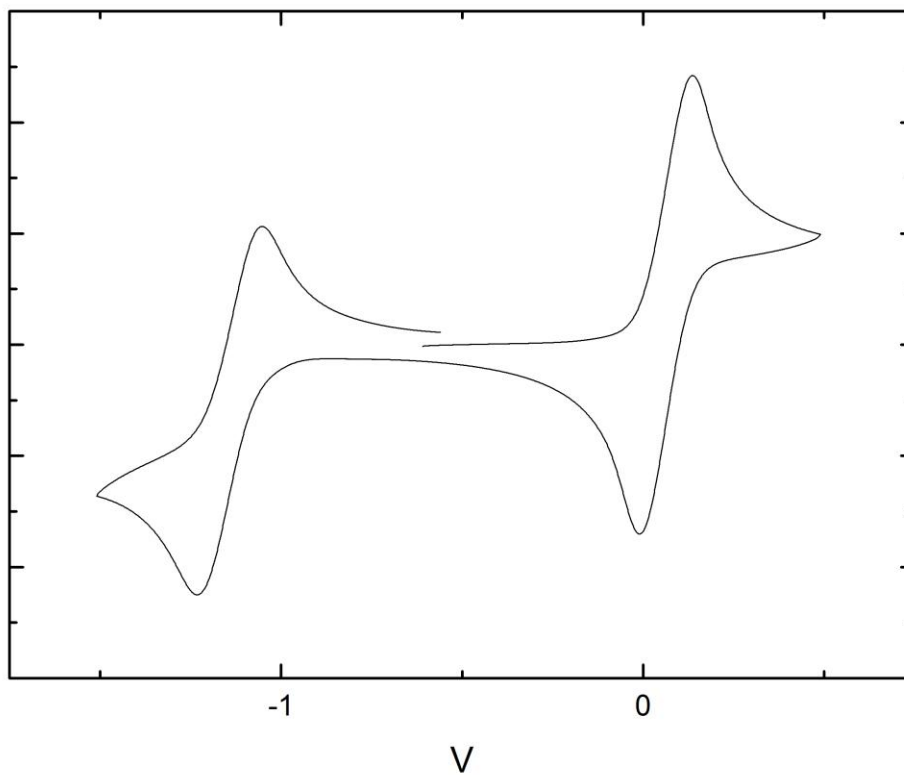


Figure S1 – Cyclic voltammogram of **1** in DCM (vs. SCE).

Section S3 Electron Paramagnetic Resonance Spectroscopy

The EPR spectrum of **1** (top) was recorded in dichloromethane on a Magnettech GmbH MiniScope 200 X-Band spectrometer at room temperature. Hyperfine coupling constants were obtained by spectral simulation (bottom) using PEST WinSIM 2002.

Parameters: $a_{N1} = 6.43$ G, $a_{N2} = 4.29$ G, $a_{N3} = 3.92$ G, $g = 2.0040$, $\Delta H(\text{linewidth, l.w.}) = 2.01$ G, $G.O.F. = 99.997\%$

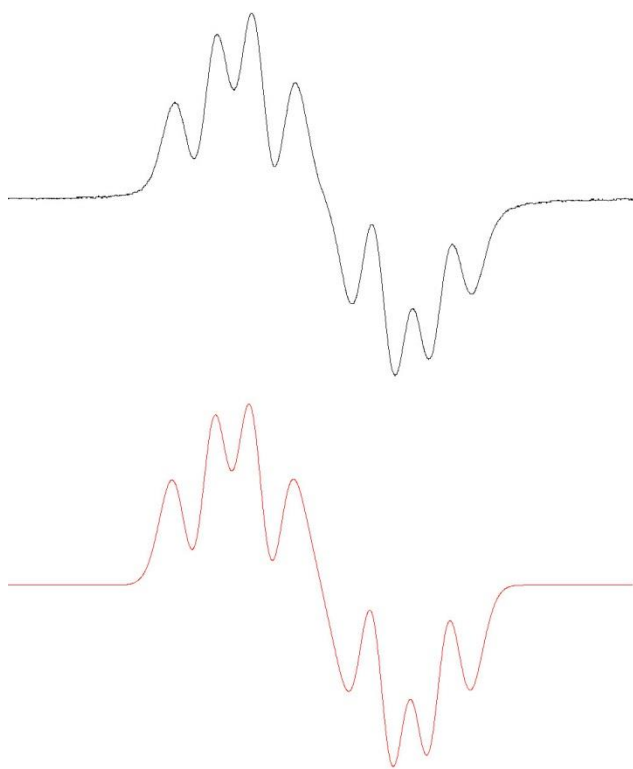


Figure S2 – EPR spectrum of **1** in DCM.

Section S4 X-ray Crystallography

Methods: All single crystal X-ray data were collected with Agilent SuperNova diffractometer equipped with multilayer optics monochromated dual source (Cu and Mo) and Atlas detector, using Cu K $_{\alpha}$ (1.54184 Å) radiation at temperatures of 123 K (**1** and **3**) and 293 K (**3**). Data acquisitions, reductions and analytical face-index based absorption corrections were made using program CrysAlis^{PRO}.⁴ The structures were solved with either ShelXS⁵ or Superflip⁶ programs and refined on F^2 by full matrix least squares techniques with the ShelXL⁵ program in Olex² (v.1.2) program package.⁷ All hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 larger than the respective host atoms. A list of selected bonding parameters and intermolecular distances is presented in Tables S1 (**1**), S2 (low temperature and room temperature data for **3**), and S3 (intermolecular distances for **3** at low and room temperature).

Additional measurements: Variable temperature measurements of the unit cell of **3** were carried out at several temperatures between 103 K and 293 K in order to determine the reversibility of the single crystal to single crystal phase transition between the low (LT) and room temperature (RT) phases. Cooling a crystal of **3** from RT to 193 K induced a change in the unit cell parameters corresponding to the phase transition from RT to LT structure. No additional changes (other than small isotropic contraction) were observed by further cooling the crystal down to 103 K. Subsequent heating of the crystal back to room temperature lead to reversible transition from LT phase back to RT phase with no visible deterioration of the crystal quality.

Table S1. Crystallographically derived and DFT optimized bond distances (Å) of **1**

		2	
		Exptl.	Calc.
N2	N1	1.362(1)	1.344
N1	C10	1.386(2)	1.387
N1	C11	1.441(2)	1.417
C10	C5	1.414(2)	1.415
C5	N4	1.376(2)	1.360
N4	C3	1.334(2)	1.323
C3	N2	1.341(2)	1.327
C3	C17	1.494(2)	1.491
C17	N22	1.340(2)	1.330
N22	C21	1.340(2)	1.325
C21	C20	1.387(2)	1.388
C20	C19	1.379(2)	1.385
C19	C18	1.386(2)	1.383
C18	C17	1.395(2)	1.394

Table S2. Selected bond distances (Å) of **3** taken from single crystal X-ray data measured at 123 K (LT) and 293 K (RT)

		3 (RT)	3 (LT) Complex A	3 (LT) Complex B
Cu1	O1	2.290(3)	2.317(2)	2.343(2)
Cu1	O2	1.936(3)	1.957(1)	1.944(1)
Cu1	O3	2.302(3)	2.298(2)	2.302(1)
Cu1	O4	2.035(3)	1.999(1)	2.013(1)
Cu1	N4	2.037(3)	2.024(2)	2.032(2)
Cu1	N22	1.978(3)	1.990(2)	1.988(2)
N2	C3	1.314(4)	1.322(2)	1.322(3)
C3	N4	1.342(4)	1.339(2)	1.340(3)
N22	C5	1.389(5)	1.381(3)	1.382(2)
C5	C10	1.402(5)	1.421(3)	1.426(3)
C10	N1	1.385(5)	1.394(2)	1.391(3)
N1	N2	1.362(5)	1.361(3)	1.359(2)

Table S3. Selected intermolecular distances (Å) between the adjacent units of **3** at 123K (LT) and 293 K (RT)^a

		3 (RT)		3 (LT)	
N2	N22'	3.850(5)	N2A	N22B	3.786(3)
N1	C21'	3.926(6)	N1A	C21B	3.917(3)
C10	C20'	3.637(6)	C10A	C20B	3.682(3)
C5	C19'	3.479(6)	C5A	C19B	3.534(3)
N4	C18'	3.631(5)	N4A	C18B	3.629(3)
C3	C17'	3.728(5)	C3A	C17B	3.681(3)
C17	C3'	3.728(5)	C17A	C3B	3.653(3)
N22	N2'	3.850(5)	N22A	N2B	3.745(3)
C21	N1'	3.926(6)	C19A	N1B	3.832(3)
C20	C10'	3.637(6)	C20A	C10B	3.564(3)
C19	C5'	3.479(6)	C19A	C5B	3.428(3)
C18	N4'	3.631(5)	C18A	N4B	3.572(3)

^a Symmetry code for (') = 1-x, 1-y, 1-z.

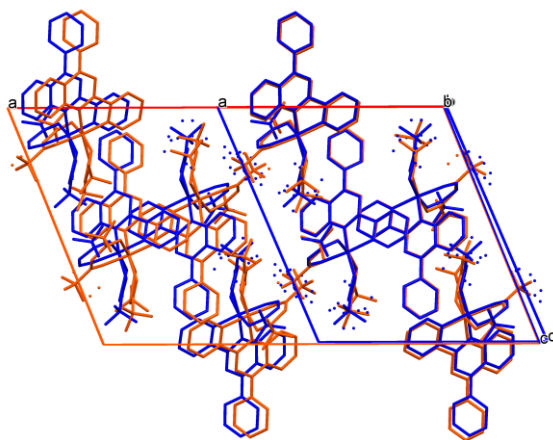


Figure S3 – Overlay of the **3** (RT) and **3** (LT) structures viewed along the crystallographic *b*-axis.

Table S4. Crystallographic data for structures **1**, **3 (RT)** and **3 (LT)**

	1	3 (RT)	3 (LT)
Empirical formula	C ₁₈ H ₁₃ N ₄	C ₂₈ H ₁₅ F ₁₂ N ₄ O ₄ Cu	C ₂₈ H ₁₅ F ₁₂ N ₄ O ₄ Cu
Formula weight	285.32	762.98	762.98
Temperature/K	123.01(10)	293.00(10)	123.01(10)
Crystal system	monoclinic	Monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	8.8690(4)	15.5585(3)	29.6356(7)
<i>b</i> /Å	10.0658(4)	12.6810(2)	12.6090(3)
<i>c</i> /Å	15.5522(6)	17.3525(3)	17.3227(4)
α /°	90	90	90
β /°	95.733(4)	113.140(2)	111.937(2)
γ /°	90	90	90
Volume/Å ³	1381.44(10)	3148.19(10)	6004.4(3)
<i>Z</i>	4	4	8
ρ_{calc} /mg/mm ³	1.372	1.610	1.688
m/mm ⁻¹	0.671	2.018	2.116
<i>F</i> (000)	596.0	1520.0	3040
Crystal size/mm ³	0.23 × 0.11 × 0.07	0.19 × 0.17 × 0.10	0.1890 × 0.1649 × 0.0908
2 Θ range for data collection	10.484 to 137.976°	8.908 to 134°	7.336 to 133.998°
Index ranges	-8 ≤ <i>h</i> ≤ 10, -12 ≤ <i>k</i> ≤ 12, -17 ≤ <i>l</i> ≤ 18	-17 ≤ <i>h</i> ≤ 18, -15 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 20	-24 ≤ <i>h</i> ≤ 35, -13 ≤ <i>k</i> ≤ 15, -20 ≤ <i>l</i> ≤ 20
Reflections collected	4668	10419	20782
Independent reflections	2553 [R(int) = 0.0165]	5578 [R(int) = 0.0170]	10654 [R(int) = 0.0246]
Data/restraints/parameters	2553/0/199	5578/58/470	10654/114/911
Goodness-of-fit on <i>F</i> ²	1.020	1.065	1.024
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0354, <i>wR</i> ₂ = 0.0940	<i>R</i> ₁ = 0.0633, <i>wR</i> ₂ = 0.1816	<i>R</i> ₁ = 0.0362, <i>wR</i> ₂ = 0.0937
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.1007	<i>R</i> ₁ = 0.0726, <i>wR</i> ₂ = 0.1945	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.1000
Largest diff. peak/hole / e Å ⁻³	0.18/-0.16	0.52/-0.55	0.49/-0.48

Section S5 Magnetic Measurements

The magnetic measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on finely ground crystalline samples of **1** and **3** (28.42 and 28.40 mg respectively) sealed in a polyethylene bag ($3 \times 0.5 \times 0.02$ cm). The data were corrected for the sample holder and the diamagnetic contributions.

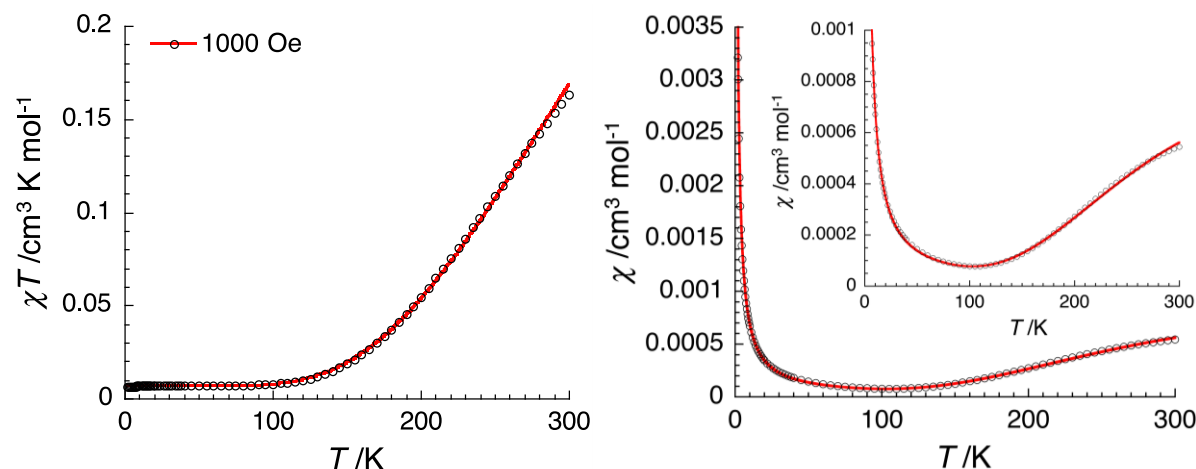


Figure S4 - Temperature dependence of the χT product (left) and χ (right) for **1** at 1000 Oe (with χ defined as molar magnetic susceptibility equal to M/H per mole of **1**). Black circles indicate measured data; red line represents the best fit obtained with the $S = \frac{1}{2}$ dimer model described in the main text.

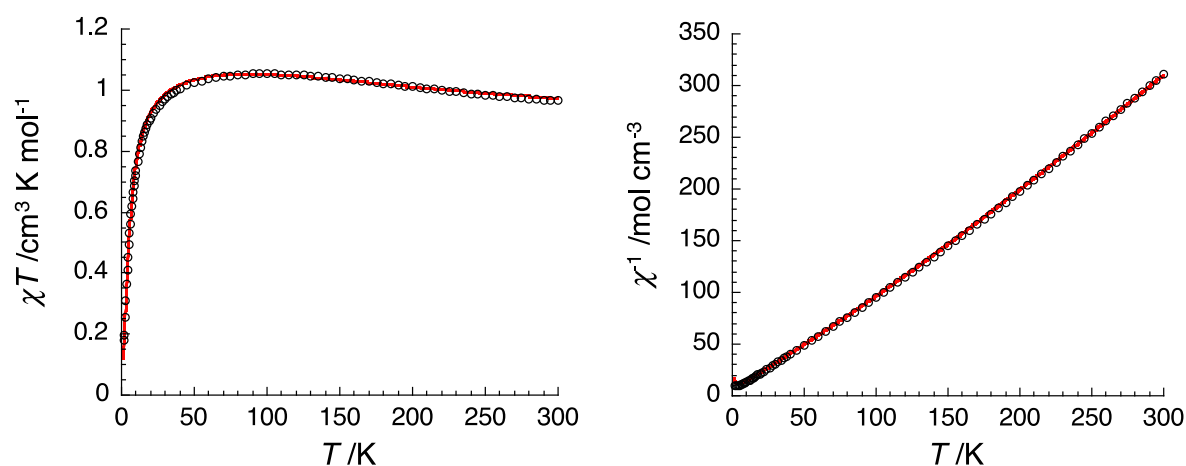
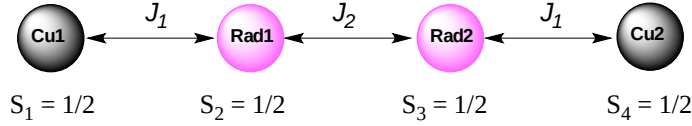


Figure S5 - Temperature dependence of the χT product (left) and $1/\chi$ (right) for **3** at 1000 Oe (with χ defined as molar magnetic susceptibility equal to M/H per mole of **3**). Black circles indicate measured data; red line represents the best fit obtained with the model described in the main text and below.

Model to describe the magnetic properties of complex 3 with the following spin and interaction topology:



On the basis of the crystal structure of **3** and the presence of Cu(**1**)(hfac)₂ pairs stabilized by weak radical-radical interactions, the magnetic model was built considering the following isotropic Heisenberg spin Hamiltonian for four spins as shown in the scheme above and in Figure 4:

$$H = -2J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - 2J_2(S_2 \cdot S_3)$$

In the weak field approximation, the analytical expression of the magnetic susceptibility (per Cu(**1**)(hfac)₂ unit) can be estimated applying the van Vleck equation:

$$\chi = \frac{Ng^2\mu_B^2}{2k_B T} \times \left[10 \exp\left(\frac{-E_1}{k_B T}\right) + 2 \exp\left(\frac{-E_2}{k_B T}\right) + 2 \exp\left(\frac{-E_3}{k_B T}\right) + 2 \exp\left(\frac{-E_4}{k_B T}\right) \right] / Z,$$

where

$$Z = 5 \exp\left(\frac{-E_1}{k_B T}\right) + 3 \left[\exp\left(\frac{-E_2}{k_B T}\right) + \exp\left(\frac{-E_3}{k_B T}\right) + \exp\left(\frac{-E_4}{k_B T}\right) \right] + \exp\left(\frac{-E_5}{k_B T}\right) + \exp\left(\frac{-E_6}{k_B T}\right)$$

$$E_1 = -J_1 - \frac{1}{2}J_2$$

$$E_2 = J_1 - \frac{1}{2}J_2$$

$$E_3 = \frac{1}{2}J_2 + (J_1^2 + J_2^2)^{1/2}$$

$$E_4 = \frac{1}{2}J_2 - (J_1^2 + J_2^2)^{1/2}$$

$$E_5 = J_1 + \frac{1}{2}J_2 + (4J_1^2 - 2J_1J_2 + J_2^2)^{1/2}$$

$$E_6 = J_1 + \frac{1}{2}J_2 - (4J_1^2 - 2J_1J_2 + J_2^2)^{1/2}.$$

Section S6 Computational Details

All calculations were performed with the Turbomole 6.3⁸ and Gaussian 09⁹ program packages using the PBE1PBE density functional¹⁰ and Ahlrichs def2-TZVP basis sets.¹¹ The program gOpenMol was used for all visualizations of computational data.¹² The geometry of **1** was optimized and the nature of the located minimum confirmed by full vibrational analysis. The geometries of the metal complex **3** were taken from single crystal X-ray diffraction data and were used without further geometry optimizations. All CF₃ groups were replaced with CH₃ groups (for reasons of computational efficiency) and the C–H bond lengths were normalized to distances determined via neutron diffraction (1.083 Å for aromatic hydrogens and 1.070 Å for methyl hydrogens). The effect of the CF₃ to CH₃ replacement was studied by performing a set of test calculations using the room temperature structure of **3**, which indicated that replacement of fluorine with hydrogen has an insignificant effect to both the spin density and the magnetic coupling.

The exchange couplings in the solid-state were determined using the broken symmetry (BS) approach by Noodleman.¹³ For density functional theory and when the low spin broken symmetry state represents the singlet state sufficiently well, the equation by Ruiz *et al.* can be used:¹⁴

$$2J = 2(E_{BS} - E_{HS}) / (S(S + 1)),$$

where $S = S_1 + S_2$ and $S_1 = S_2$.

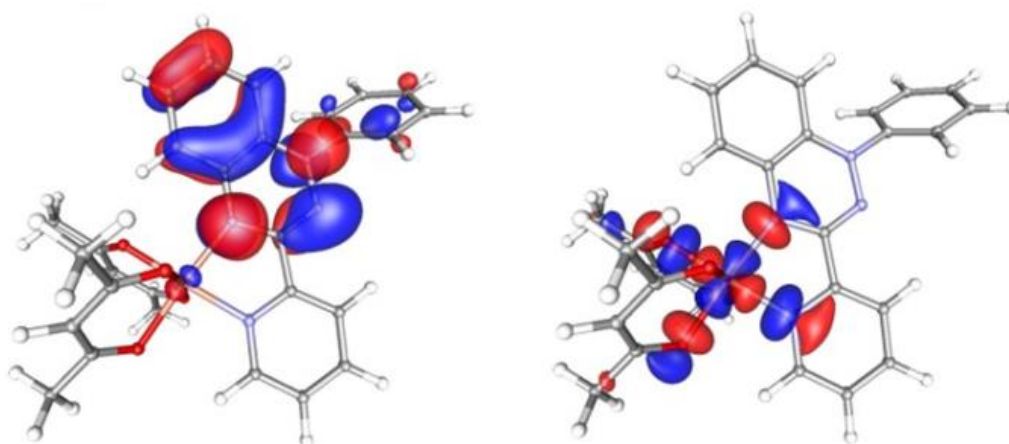


Figure S6 - Isosurface plots of the two magnetic orbitals of **3** showing the unpaired electron localized on the radical ligand (left) and on the copper(II) site (right).

1...1

	Energy (Hartree)	$\langle S^2 \rangle$
HS	-1823.377723	2.042299
BS	-1823.379845	0.968324

$$J = (-1823.379845 + 1823.377723) / (1(1+1)) = -335.038 \text{ K} \quad (1 \text{ Hartree} = 320\,000 \text{ K})$$

3 (RT)

	Energy (Hartree)	$\langle S^2 \rangle$
HS	-3242.172615	2.021139
BS	-3242.171849	1.018337

$$J = 121.023 \text{ K}$$

3 (LT, complex 1)

	Energy (Hartree)	$\langle S^2 \rangle$
HS	-3242.184483	2.021333
BS	-3242.183702	1.019414

$$J = 123.222 \text{ K}$$

3 (LT, complex 2)

	Energy (Hartree)	$\langle S^2 \rangle$
HS	-3242.180599	2.021097
BS	-3242.179850	1.018278

$$J = 118.236 \text{ K}$$

3...3 (RT)

	Energy (Hartree)	$\langle S^2 \rangle$
HS	-6484.365869	6.040164
BS	-6484.365891	2.039885

$$J = (-6484.365891 + 6484.365869) / (2(2+1)) = -1.114 \text{ K}$$

3...3 (LT)

	Energy (Hartree)	$\langle S^2 \rangle$
HS	-6484.379953	6.040288
BS	-6484.379976	2.039994

$$J = -1.188 \text{ K}$$

The calculated spin density of **1** (see Figure 1) was used to theoretically determine its hyperfine coupling constants. The analysis shows strong coupling to N1 (4.94 G), N2 (3.59 G) and N4 (4.03 G) along with a significantly smaller coupling to N22 (-0.31 G). The calculations also indicate smaller couplings to the ^1H nuclei on the benzo-fused aromatic ring along with the phenyl ring on N1. However, these are obscured in the experimental spectrum due to the broad linewidth.

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