

## Electronic Supplementary Information

### **A heterospin pressure sensor**

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## 1ESI. Preparation of [Cu(hfac)<sub>2</sub>NN-PzMe]

The commercially available reagents and the solvent were used as received. The seed crystals of the “head-to-tail-2” modification of the [Cu(hfac)<sub>2</sub>NN-PzMe] complex and the nitronyl nitroxide 2-(1-methyl-1*H*-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (NN-PzMe) were prepared as described elsewhere.<sup>1,2</sup>

Hexane (10 mL) was added to a mixture of Cu(hfac)<sub>2</sub> (0.191 g, 0.4 mmol) and NN-PzMe (0.095 g, 0.1 mmol) in acetone (2 mL). The surface of the solution was swept with an air flow until the volume of the reaction mixture decreased to ~7 mL. Then the [Cu(hfac)<sub>2</sub>NN-PzMe] “head-to-tail-2” seed crystals were added. After the mixture was kept in an open flask at 5 °C for 48 h, navy-blue needle crystals were filtered off, washed with cold hexane, and dried in air. Yield 260 mg, 91%. Anal. Found: C, 35.6; H, 3.0; N, 7.9; F, 31.9%. Calc. for CuC<sub>21</sub>H<sub>19</sub>N<sub>4</sub>O<sub>6</sub>F<sub>12</sub>: C, 35.3; H, 2.7; N, 7.8; F, 31.9.

## 2ESI. X-ray Crystallography

The intensity data for the single crystals of [Cu(hfac)<sub>2</sub>NN-PzMe] were collected on a SMART APEX CCD (Bruker AXS) automated diffractometer with a Helix (Oxford Cryosystems) open flow helium cooler and D8 QUEST (Bruker AXS) using the standard procedure (Mo and Cu K $\alpha$  radiation). The structures were solved by direct methods and refined by the full-matrix least-squares procedure anisotropically for non-hydrogen atoms. The positions of all H atoms were calculated geometrically and included in the refinement as riding groups. All calculations were fulfilled with the SHELXTL 6.14 program package. Since the thermally induced structural transitions that occurred in the solid led to partial decomposition of the single crystals and a loss of their quality, an X-ray diffraction analysis could not be performed in the whole temperature range for the same crystal. The structural data obtained in the experiments performed for the same single crystal at 306 K and 296 K before and after its thermal treatment for 10 min at 350 K. The results of structural studies at 296 K, 150 K, and 120 K were obtained for other single crystals from the same batch (Table S1). CCDC 1053800-1053804 contain crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Table S2 and Scheme S1 presents the temperature dynamics for selected structural parameters in comparison with the data obtained previously<sup>1-4</sup> for [Cu(hfac)<sub>2</sub>NN-PzMe].

**Table S1.** Crystal data and experimental details

<i>Formula</i>	CuC <sub>21</sub> H <sub>19</sub> N <sub>4</sub> O <sub>6</sub>				
<i>FW</i> , g/mol	714.94				
<i>T</i> , K	306(2)*	306(2)**	296(2)***	150(2)	120(2)
<i>Crystal system</i>	<i>triclinic</i>	<i>monoclinic</i>		<i>triclinic</i>	
<i>Space group</i> , <i>Z</i>	<i>P</i> -1, 4	<i>P</i> 2 <sub>1</sub> / <i>n</i> , 4		<i>P</i> -1, 4	
<i>a</i> , Å	12.2761(6)	12.276(10)	12.304(1)	12.0934(12)	11.9822(13)
<i>b</i> , Å	15.8132(7)	16.180(13)	16.188(2)	15.3697(17)	15.0665(18)
<i>c</i> , Å	15.8350(8)	15.724(13)	15.610(2)	15.9466(15)	15.8827(18)
<i>α</i> , °	84.871(2)	108.76(2)	108.424(7)	84.159(7)	81.337(7)
<i>β</i> , °	74.034(2)			74.197(6)	76.852(6)
<i>γ</i> , °	87.117(2)			87.610(7)	85.591(6)
<i>V</i> , Å <sup>3</sup>	2942.5(2)	2957(4)	2949.9(6)	2836.9(5)	2757.6(5)
<i>ρ</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.614	1.606	1.608	1.674	1.722
<i>λ</i> , Å	0.71073 (Mo, Kα)	0.71073 (Mo, Kα)	0.71073 (Mo, Kα)	1.54178 (Cu, Kα)	1.54178 (Cu, Kα)
<i>Crystal size</i> , mm×mm×mm	0.30×0.08×0.08	0.30×0.08×0.08	0.20×0.04×0.03	0.18×0.05×0.04	0.22×0.04×0.03
<i>μ</i> , mm <sup>-1</sup>	0.860	0.856	0.858	2.237	2.301
<i>θ</i> <sub>max</sub> , °	28.303	28.520	28.367	67.206	66.00
<i>I</i> <sub>hkl</sub> coll / uniq <i>R</i> <sub>int</sub>	74357 / 14542 0.0630	37855 / 7329 0.1675	26464 / 7255 0.0778	10031 / 7363 0.0823	26813 / 9439 0.0779
<i>N</i>	999	506	478	820	820
<i>Goof</i>	1.049	0.961	0.793	1.043	1.052
<i>R</i> 1 / <i>wR</i> 2 ( <i>I</i> >2σ <sub><i>I</i></sub> )	0.0656 / 0.1074	0.0788 / 0.1069	0.0463 / 0.0944	0.0853 / 0.2399	0.0910 / 0.2394
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.1670 / 0.1337	0.2613 / 0.1491	0.1482 / 0.1176	0.1393 / 0.2773	0.1154 / 0.2677
Residual electron density <i>max</i> / <i>min</i> , e·Å <sup>-3</sup>	0.351 / -0.284	0.319 / -0.210	0.441 / -0.356	0.974 / -0.659	1.501 / -1.067

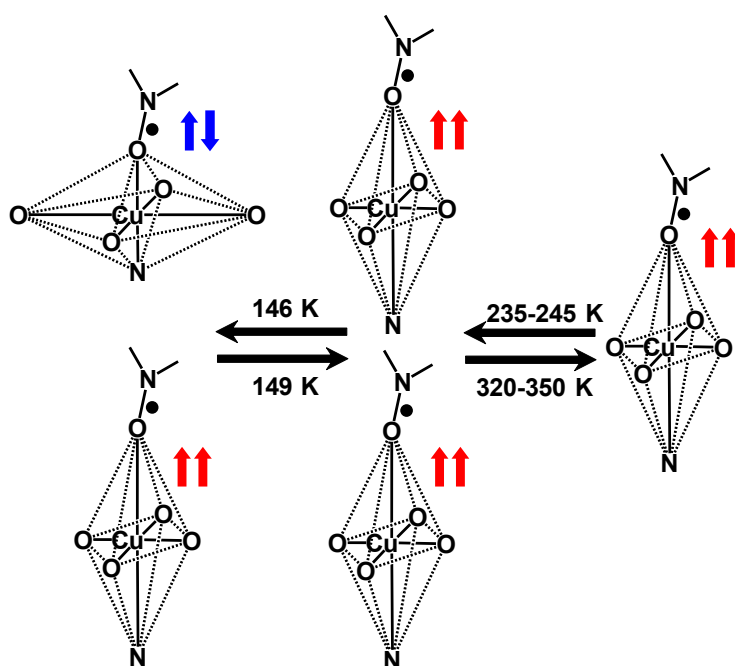
Data collected at 306 K for the same crystal before\* and after\*\* thermal treatment 350 K.

Data collected at 296 K after thermal treatment to 350 K\*\*\* for another crystal.

**Table S2.** Selected data for [Cu(hfac)<sub>2</sub>NN-PzMe] at different temperatures

<i>T</i> , K	Cu-O, Å	Cu-N, Å	Cu-O <sub>hfac</sub> , Å	∠Cu-O-N, °	O <sub>NO</sub> ...O <sub>NO</sub> , Å
293 <sup>1</sup>	2.487(4)	2.326(5)	1.941(3)-1.963(4)	139.3(3)	4.098(9)
293 <sup>2</sup>	2.507(7) 2.508(7)	2.298(7) 2.322(8)	1.937(8)-1.968(6) 1.930(6)-1.963(6)	130.0(6) 149.9(6)	4.49(1) 3.95(1)
306*	2.500(3) 2.521(3)	2.314(3) 2.336(3)	1.951(3)-1.966(2) 1.932(2)-1.961(2)	130.2(2) 150.1(2)	4.492(4) 3.948(6)
306**	2.483(4)	2.317(4)	1.944(4)-1.969(3)	139.7(3)	4.091(8)
296***	2.485(2)	2.311(3)	1.937(2)-1.960(2)	139.8(2)	4.093(5)
293 <sup>2,3</sup>	2.484(5)	2.329(5)	1.937(4)-1.962(4)	139.4(4)	4.10(1)
160 <sup>4</sup>	2.480(2) 2.479(2)	2.301(2) 2.304(2)	1.955(2)-1.978(2) 1.939(2)-1.971(6)	128.1(2) 151.7(2)	4.393(3) 3.814(4)
150	2.469(6) 2.454(8)	2.315(8) 2.296(9)	1.958(6)-1.981(6) 1.936(6)-1.984(6)	128.7(5) 151.6(6)	4.37(1) 3.80(1)
140 <sup>3</sup>	1.977(8) 2.448(8)	2.004(9) 2.340(10)	2.288(7) 2.250(8) 1.977(8) 2.010(9) 1.941(8)-1.968(7)	125.9(6) 150.9(6)	4.35(1) 4.00(1)
120	1.995(4) 2.428(5)	2.031(5) 2.327(5)	2.258(4) 2.315(4) 1.987(4) 2.001(4) 1.930(4)-1.976(4)	123.0(3) 151.8(4)	4.375(7) 3.971(8)

Data collected at 306 K for the same crystal before\* and after\*\* thermal treatment 350 K.  
Data collected at 296 K after thermal treatment to 350 K\*\*\* for another crystal.

**Scheme S1**

### 3ESI. Magnetic susceptibility measurements

The magnetic susceptibility measurements were performed using an MPMS-5 SQUID magnetometer in the temperature range 2-350 K in a magnetic field of 5 kOe. The high-temperature limit of measurements was set at  $\sim 350$  K to avoid the sample decomposition. The temperature dependence of magnetic susceptibility was measured at a pressure of  $10^{-4}$  GPa  $\leq P \leq 0.6$  GPa in an LPC-15 (ElectroLAB, Japan) copper-beryllium high-pressure cell of piston-cylinder type using Daphne 7373 oil as a hydrostatic pressure-transmitting medium as described elsewhere.<sup>5</sup> Magnetic susceptibility measurements of samples [Cu(hfac)<sub>2</sub>NN-PzMe] under applied pressure of  $10^{-4}$  GPa and 0.03-0.06 GPa for the data shown in Figure 4 were carried out at a rate of 1K/min in the temperature region associated with magnetic anomaly (c.a.  $T_a \pm 20$ -30 K) and 5 K/min in the rest of the temperature range both the cooling and warming modes. The rate of warming-cooling modes at applying very low pressures  $10^{-4}$ -0.03 GPa are shown in the footnotes to Table S3. Rate did not vary at monitoring magnetic behavior of the sample in second and third warming-cooling cycles in order to avoid changes in the conditions of the experiment. Measurements in all cases were performed in the settle scan temperature mode of SQUID. The experimental data were corrected for the contribution of the high-pressure cell to the total magnetization. The molar susceptibility was additionally corrected for diamagnetism of atoms using Pascal's additive scheme. The critical temperatures  $T_{a\uparrow}$  and  $T_{a\downarrow}$  were determined as the maximum of the derivative on the curves  $d\mu_{\text{eff}}/dT$ ; for smooth transitions (at a pressure of less than 0.03 GPa),  $T_{a\uparrow}$  and  $T_{a\downarrow}$  were evaluated as the temperature values corresponding to 2.3  $\beta$  (Fig. S1). The critical temperatures  $T_{a\uparrow}$  and  $T_{a\downarrow}$ , the widths of the hysteresis loop  $\Delta T_a$ , and the effective magnetic moments at 300 K  $\mu_{\text{eff}@300K}$  corresponding to different applied pressures are indicated in Table S3. The applied pressure was evaluated from the transition temperature of high-purity Sn to the superconducting state. For Sn, the dependence  $T_s(P)$  at pressures below 1.0 GPa is determined by the equation  $T_s(P) = T_s(P_0) - a \cdot P$ , where  $a = 0.495$  K·GPa<sup>-1</sup>, and  $P_0$  is the starting atmospheric pressure.<sup>6</sup> The accuracy of pressure calibration in this case is  $\pm 0.025$  GPa. A correction for the internal decrease of the pressure of the liquid or solidified oil cooled from 300 to 2 K (0.15–0.17 GPa for oil medium Daphne 7373<sup>7</sup>) was not applied.

**Table S3.**  $T_{a\uparrow}$ ,  $T_{a\downarrow}$ ,  $\Delta T_a$  [K], and  $\mu_{\text{eff}@300K}$  [ $\beta$ ] at different external pressures  $P$  [GPa] for two different batches of the  $[\text{Cu}(\text{hfac})_2\text{NN-PzMe}]$  complex

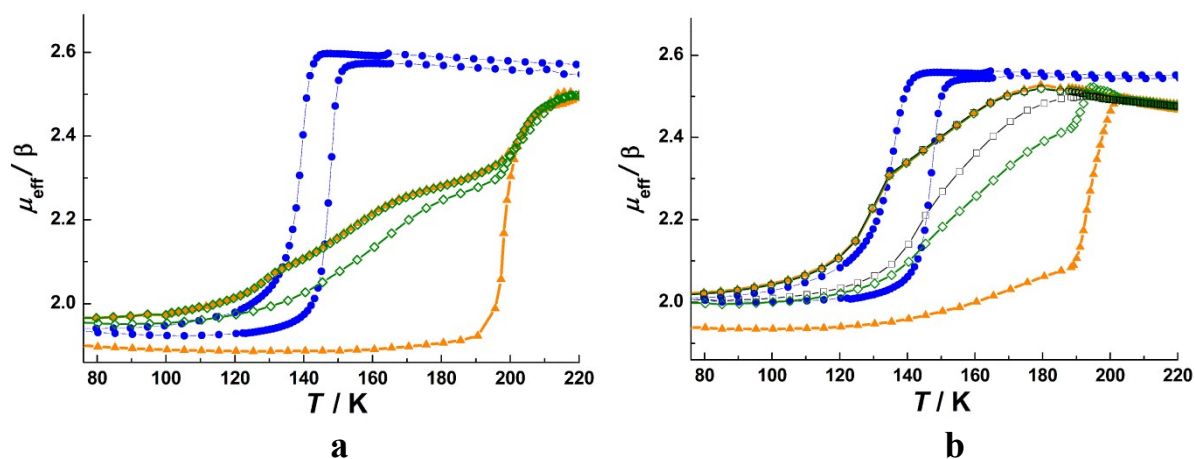
1 <sup>st</sup> batch					2 <sup>nd</sup> batch				
$P$	$T_{a\uparrow}$	$T_{a\downarrow}$	$\Delta T_a$	$\mu_{\text{eff}@300K}$	$P$	$T_{a\uparrow}$	$T_{a\downarrow}$	$\Delta T_a$	$\mu_{\text{eff}@300K}$
<i>regular capsule</i>									
$10^{-4}$	149	146	3	2.53	$10^{-4}$	149	146	3	2.52
<i>pressure cell</i>									
$10^{-4}$	148	140	8	2.55	$10^{-4}$	147	136	11	2.52
< 0.03 (1 <sup>st</sup> cycle)*	175	135	40	2.50	< 0.03 (1 <sup>st</sup> cycle)***	193	130	63	2.45
< 0.03 (2 <sup>nd</sup> cycle)*	152	135	18	2.50	< 0.03 (2 <sup>nd</sup> cycle)***	167	130	37	2.46
< 0.03 (1 <sup>st</sup> cycle)**	198	185	13	2.48	< 0.03 (3 <sup>rd</sup> cycle)***	154	130	24	2.45
< 0.03 (2 <sup>nd</sup> cycle)**	196	185	11	2.48	< 0.03 (1 <sup>st</sup> cycle)****	166	130	36	2.44
0.03	238	232	6	2.46	0.03	224	218	6	2.42
0.04	253	248	5	2.48	0.10	258	254	4	2.32
0.07	269	266	3	2.40	0.11	283	277	5	2.27
0.13	293	290	3	2.23	0.21	-	-	-	1.96
0.14	312	312	0	2.07					
0.32	-	-	-	1.97					

\* the warming-cooling rate was 2 K/min in the temperature range 120-215 K and 5 K/min in the rest of the temperature range (Figure 7);

\*\* the rate was 1 K/min in the temperature ranges 196-235 K (in the warming mode) и 99-235 K (in the cooling mode) and 5 K/min in the rest of the temperature range (Figure S1, a);

\*\*\* the warming-cooling rate was 1 K/min in the temperature range 189-232 K and 5 K/min in the rest of the temperature range (Figure S1, b);

\*\*\*\* the warming-cooling rate was 5 K/min in over the entire temperature range of 2-350 K.



**Figure S1.** Dependence  $\mu_{\text{eff}}(T)$  for the  $[\text{Cu}(\text{hfac})_2\text{NN-PzMe}]$  samples from different syntheses (**a** and **b**): results of measurements at  $10^{-4}$  GPa (—●—) and at pressures below 0.03 GPa: the first (—▲—) and second (—★—) heating-cooling cycles (batches **a** and **b**) and the third (—□—) heating-cooling cycle (**b**).

**4ESI. REFERENCES**

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