Supplementary Materials: Modification of Cooperativity and Critical Temperatures on a Hofmann-Like Template Structure by Modular Substituent

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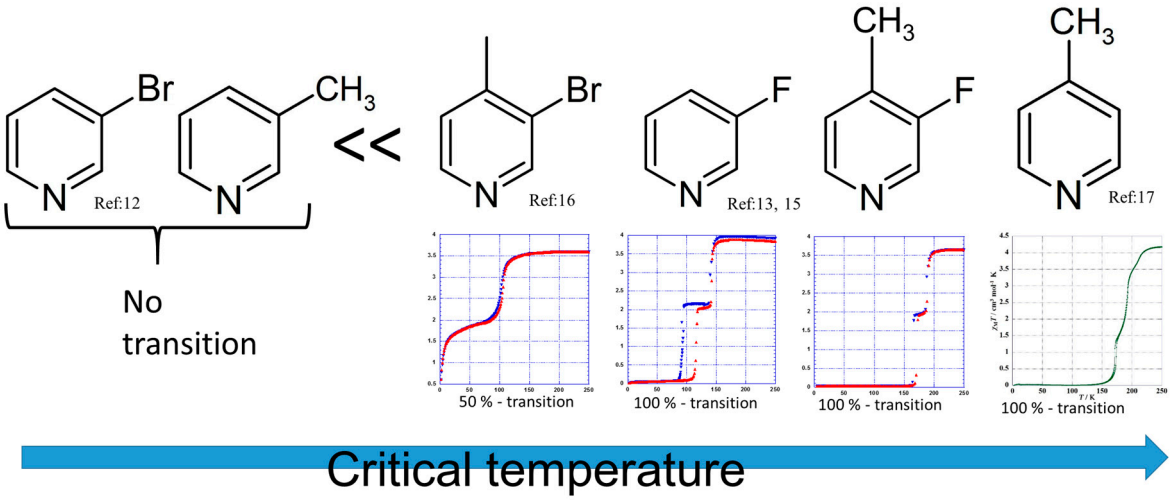

Scheme S1. Critical temperature (T_c) changes depending on the substituent of {Fe(X-py)$_2$[Au(CN)$_2$]$_2$} (X = 3-F-4-Methyl (**1**), 3-Methyl (**2**), 3-F (**3**), 4-Methyl (**4**), 3-Br (**5**) and 3-Br-4-Methyl (**6**))

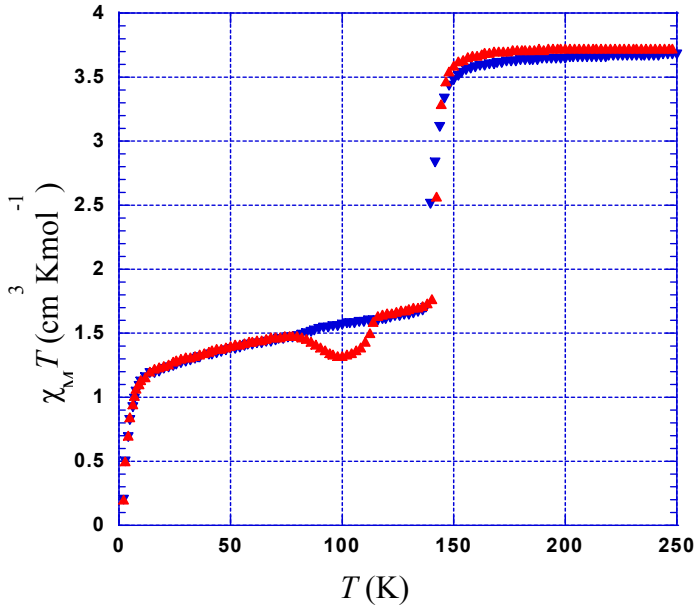

Figure S1. Thermal dependence of spin transition curve for **3**. The samples were cooled from 300 to 2 K and then warmed again to 300 K in the cooling mode at rates of 2 K·min^{-1} and warming mode at rates of 2 K·min^{-1}

Table S1. Crystal data and structure refinement for compounds **1** and **2**.

Crystal data	**1** (293 K)	**1** (180 K)	**1** (90 K)	**2** (293 K)
Empirical formula	$C_{16}H_{12}Au_2F_2FeN_6$	$C_{16}H_{12}Au_2F_2FeN_6$	$C_{16}H_{12}Au_2F_2FeN_6$	$C_{16}H_{14}Au_2FeN_6$
FW	776.10	776.10	776.10	740.11
Temperature (K)	293(2)	180(2)	90(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.9889(14)	9.701(10)	9.8320(9)	9.3741(5)
b (Å)	14.967(2)	14.496(16)	14.3623(13)	14.5078(8)
c (Å)	14.422(2)	14.009(15)	13.9396(13)	15.1866(8)
α (°)				
β (°)	91.675(3)	91.526(3)	91.5485(3)	106.8850(10)
γ (°)				
V (Å^3)	2155.2(5)	1969(4)	1967.7(3)	1976.30(18)
Z	4	4	4	4
Absorption coefficient (mm^{-1})	14.273	15.620	15.633	15.544
d(calc.) (Mg/m^3)	2.392	2.618	2.620	2.487
F(000)	1408	1408	1408	1344
Crystal size (mm^{-3})	0.12 × 0.11 × 0.10	0.10 × 0.10 × 0.08	0.12 × 0.11 × 0.10	0.40 × 0.35 × 0.30
Reflections collected	11249	7760	14056	14562
Independent reflections	3837 [R(int) = 0.0445]	2773 [R(int) = 0.0823]	5866 [R(int) = 0.0335]	4901 [R(int) = 0.0278]
Final R indices [I>2sigma(I)]	R = 0.0296, wR = 0.0487	R = 0.1058, wR = 0.2287	R = 0.0281, wR = 0.526	R = 0.0258, wR = 0.0675
R indices (all data)	R = 0.0574, wR = 0.0565	R = 0.1421, wR = 0.2455	R = 0.0526, wR = 0.0550	R = 0.0327, wR = 0.0714

$R = (\Sigma||Fo| - |Fc||)/\Sigma|Fo|$

$wR = \{\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2\}^{1/2}$

Table S2. Selected Bond Lengths for **1** and **2**.

1 (293 K)	**1** (180 K)	**1** (90 K)	**2** (293 K)
Bond lengths (Å)	Bond lengths (Å)	Bond lengths (Å)	Bond lengths (Å)
Fe(1)-N(1):2.219(6)	Fe(1)-N(1):2.11(4)	Fe(1)-N(1):2.013(4)	Fe(1)-N(1):2.247(4)
Fe(1)-N(2):2.220(6)	Fe(1)-N(2):2.03(4)	Fe(1)-N(2):2.002(4)	Fe(1)-N(2):2.244(4)
Fe(1)-N(3):2.142(7)	Fe(1)-N(3):2.05(5)	Fe(1)-N(3):1.942(4)	Fe(1)-N(3):2.164(4)
Fe(1)-N(4):2.153(6)	Fe(1)-N(4):2.10(4)	Fe(1)-N(4):1.944(4)	Fe(1)-N(4):2.162(4)
Fe(1)-N(5):2.160(7)	Fe(1)-N(5):1.97(4)	Fe(1)-N(5):1.934(4)	Fe(1)-N(5):2.159(4)
Fe(1)-N(6):2.148(6)	Fe(1)-N(6):2.11(4)	Fe(1)-N(6):1.936(4)	Fe(1)-N(6):2.158(4)
Au(1)-C(13):1.981(8)	Au(1)-C(13):1.88(2)	Au(1)-C(13):1.996(5)	Au(1)-C(13):1.979(5)
Au(1)-C(14):1.984(8)	Au(1)-C(14):1.83(6)	Au(1)-C(14):1.988(5)	Au(1)-C(14):1.979(5)
Au(2)-C(15):1.992(8)	Au(2)-C(15):1.91(3)	Au(2)-C(15):1.992(5)	Au(2)-C(15):1.982(5)
Au(2)-C(16):1.967(8)	Au(2)-C(16):1.99(8)	Au(2)-C(16):1.991(5)	Au(2)-C(16):1.979(5)