Supporting Information for

Melamine-Induced Synthesis of a Structurally Perfect Kagomé Antiferromagnet

Yongbing Shen*[a], Kunihisa Sugimoto[b], Satoshi Yamashita[c], Takefumi Yoshida[d], Yasuhiro Nakazawa[c], Brian K. Breedlove[a], Haitao Zhang[e] and Masahiro Yamashita*[a,f]

[a] Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aza-Aoba, Aramaki, Sendai 980-8578, Japan. +81227956544;

[b] Diffraction & Scattering Division, Japan Synchrotron Radiation Research Institute (ASRI) 1-1-1 Kouto, Sayo-Cho, Sayo-gun, Hyogo 679-5198, Japan

[c] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

[d] Innovation Research Center for Fuel Cells, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

[e] Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

[f] School of Materials Science and Engineering, Nankai University, Tianjin 300350, China.

Experimental Procedures

General procedure. $Cu(BF_4)_2$, $(NH_4)_2(SiF_6)$, Melamine, 4,4′-bipyridine and solvents were purchased commercially without further purification before use.

Synthesis of $\{[Cu_3(bpy)_6](SiF_6)_3(melamine)_8\}_n$. 1.0 mmol Melamine, 0.75 mmol 4,4′-bipyridine dissolved in 15 mL ethanol; 1.5 mmol $Cu(BF_4)_2$ and 1.5 mmol $(NH_4)_2(SiF_6)$ were dissolved in 15 mL distilled H_2O. The two components are slowly mixed and the resulting mixture was stirred for 30 min; then transferred to a Teflon reactor, sealed, and heated at 150ºC in an oven for 72 hours. After slow cooling to room temperature for 24 hours and keeping it for another 72 hours, light blue powder and a small amount of hexagonal prism-like single-crystals were obtained. The well-shaped single-crystals were mechanically isolated and washed by ethanol and water, finally dried in air. CHN analysis: Cal: C (39.37%), H (3.78%), N (32.79%); Exp: C (38.12%), H (4.34%), N (31.58%). IR spectrum in Figure S7.

Physical characterization. Measurements of compound **1** at different temperatures were performed using a PILATUS3 X CdTe 1M detector (DECTRIS) at the SPring-8/BL02B1 beamline in Japan. The wavelength (λ = 0.4132 Å) was selected using Si (311) monochromator crystals. The crystal structures were solved by Olex2 software[1]. The heat capacity measurements were performed on a small pellet (0.2-0.4 mm thickness, 1.5 mm diameter and 0.7-1.4 mg weight) by using PPMS with two different calorimetry cells mounted on ^{3}He and ^{4}He cryostats for cooling the temperatures. The magnetic properties were collected by using a Quantum Design SQUID magnetometer MPMS in the temperature range of 1.8–300 K. The alternate current (*ac*) magnetic susceptibility was measured at zero fields in selected 1.8–20 K in various frequencies (10-1000Hz).

Table S1. Crystallographic parameters of **1** at 300 K.

Compound	**$\{[Cu_3(bpy)_6](SiF_6)_3(melamine)_8\}_n$**
Formula	$C_{84}H_{196}N_{60}Si_3F_{18}$
Crystal system	Hexagonal
Space group	*P*6/*mcc*
***a* (Å)**	22.0326(2)
***b* (Å)**	22.0326(2)
***c* (Å)**	17.1446(3)
***γ* (°)**	120
***V* (Å³)**	7207.58(18)
Index range	$-35 < h < 35$ $-38 < k < 39$ $-30 < l < 30$
***F* (000)**	2712
Wavelength (Å)	0.4132
θ_{min} (°), θ_{max} (°)	3.03, 29.17
GOF on F^2	1.165
R_1 /wR_2 (gt)	0.0644/0.0809
***T* (K)**	300

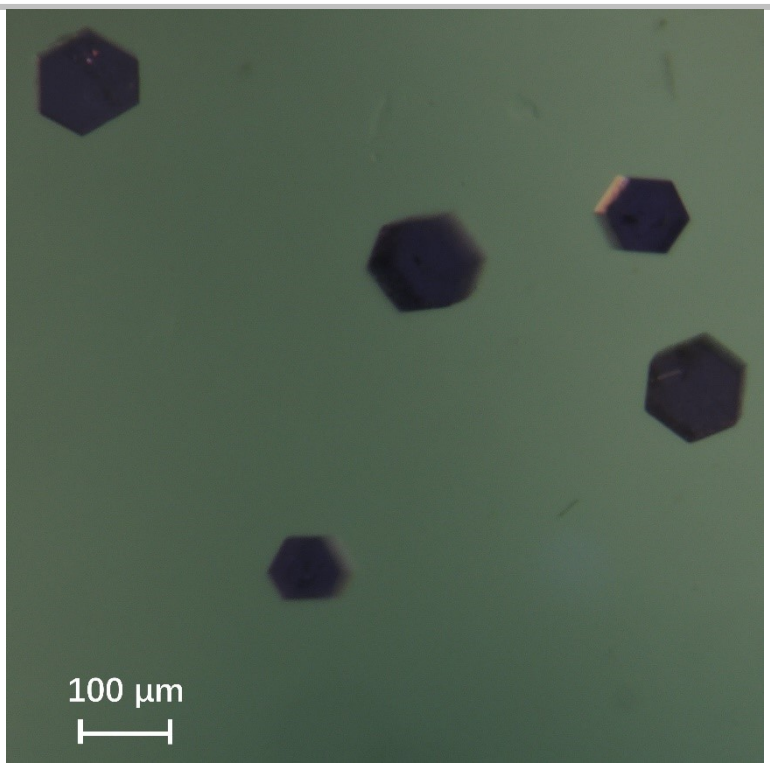


Figure S1. The single-crystal morphology: hexagonal prism-like crystals.

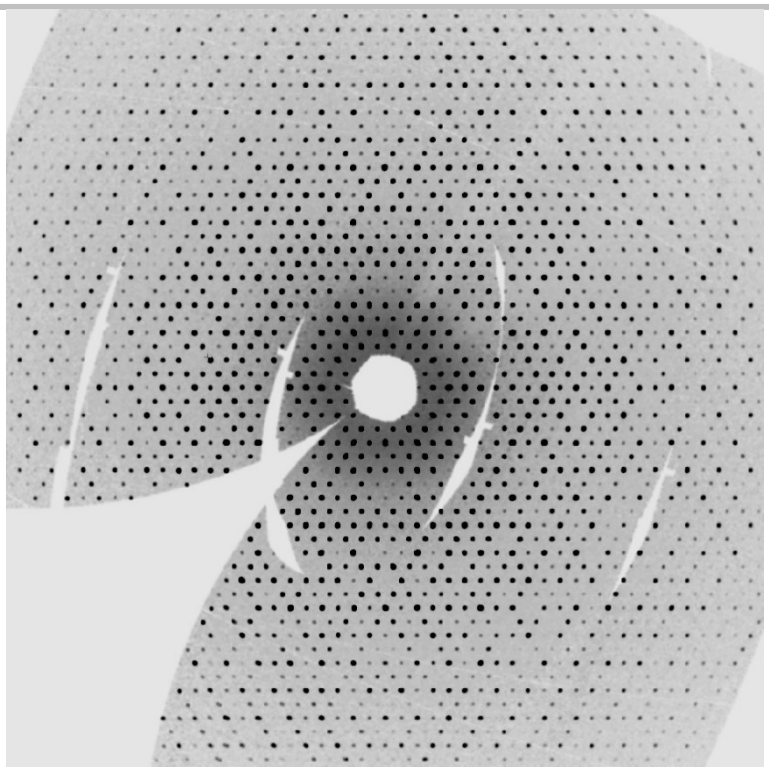


Figure S2. Unwarping single-crystal diffraction images at 300 K by using synchrotron X-ray.

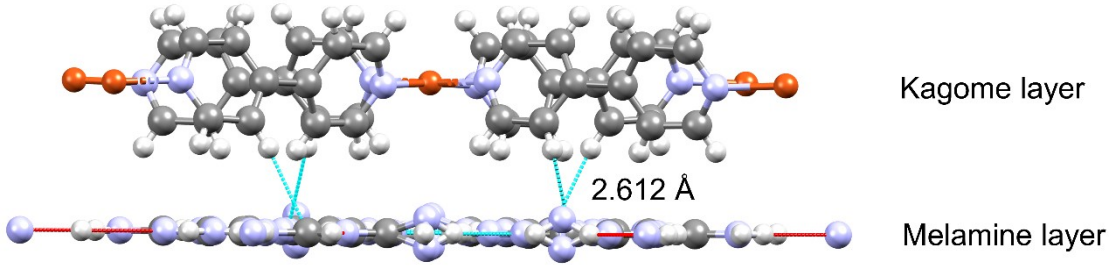


Figure S3. The short contacts between melamine and bpy ligands.

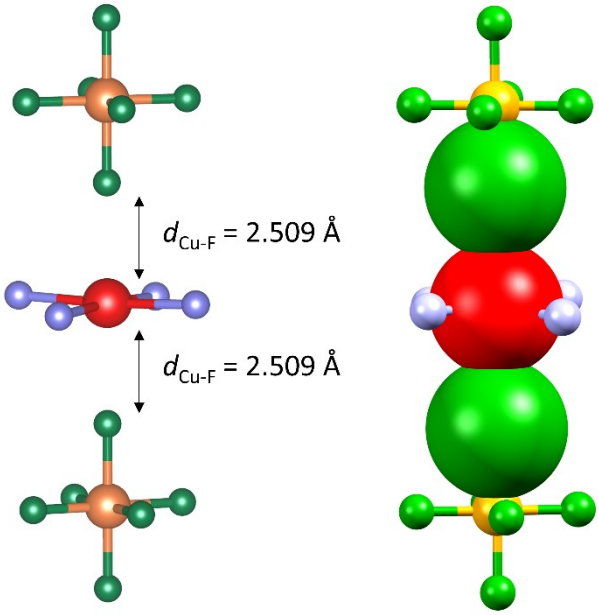


Figure S4. The linear arrangement of Cu···SiF_6. The distance between Cu and F is 2.509 Å, which is slightly smaller than their VdW radii (right figure: space fill mode).

Table S2. Temperature-dependence of unit-cell parameters

***T* (K)**	**300**	**200**	**100**	**80**	**50**	**20**
***a* (Å)**	22.0326(2)	22.0326(2)	22.0042(2)	22.0042(2)	22.0042(2)	21.9827(3)
***b* (Å)**	22.0326(2)	22.0326(2)	22.0042(2)	22.0042(2)	22.0042(2)	21.9827(3)
***c* (Å)**	17.1446(3)	17.1446(3)	16.8320(2)	16.8320(2)	16.8320(2)	16.8317(5)
***γ* (°)**	120	120	120	120	120	120

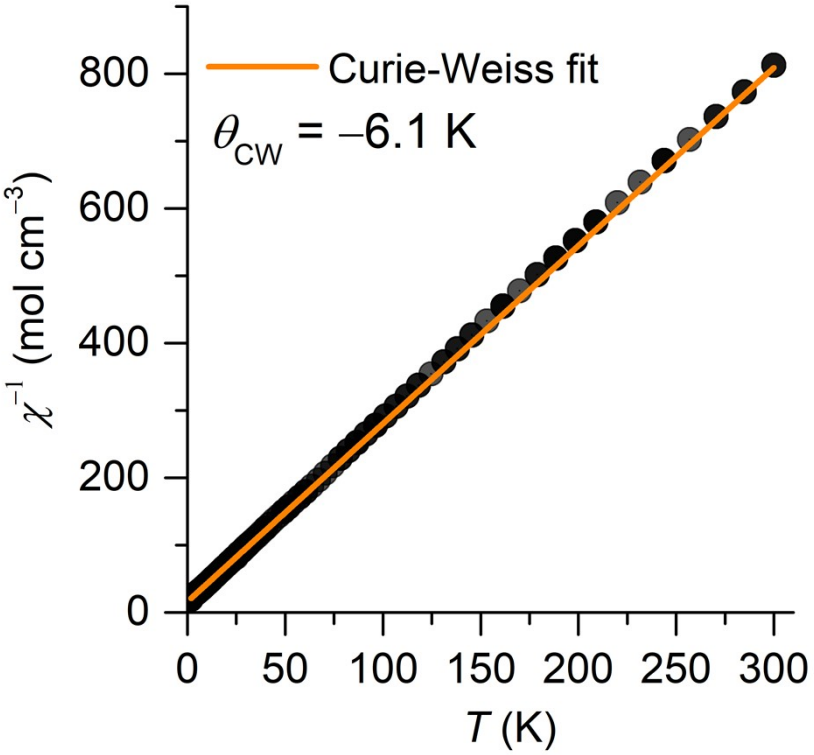
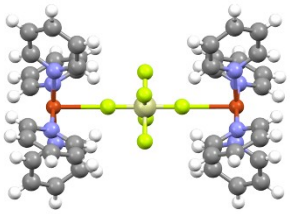


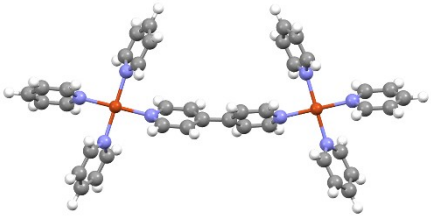
Figure S5. Temperature dependence of reciprocal magnetic susceptibility (χ^{-1}-T) in 1.8-300 K in 1000 field. The brown curve was the best fit by using Curie-Weiss law, yielding a small negative Weiss temperature.

Model system: $[Cupy_4]_2^{4+}(SiF_6)^{2-}$



Interlayer Cu-Cu interaction
J'' = 0.017 cm^{-1}

Model system: $[Cupy_3]_2^{4+}$(bipy)



Intralayer Cu-Cu interaction
J' = -1.1 cm^{-1}.

Noodleman computed magnetic exchange coupling parameters by using broken symmetry unrestricted Hartree-Fock (BS-UHF) solutions for low-spin states

$$J = \frac{-[E(HS) - E(BS)]}{s_{max}^2}$$

Where E(BS) is the energy of the low-spin solution, E(HS) is the high-spin energy, and s_{max} is the total spin of the high-spin state. This assumes that the broken symmetry state is an equal mixture of the lowest and highest spin states, which is strictly valid only for broken symmetry determinants with two s= ½ centres in the weak overlap limit.

$[Cupy_4]^{2+}{}_2(SiF_6)^{2-}$	E(AFM) / eV	E(FM) / eV	E (AFM-FM) eV	E / cm^{-1}	J'' / cm^{-1}
B3LYP/ def2TZVP	-167525.6067141700	-167525.6067147100	5.4002×10^{-7}	4.3556×10^{-3}	0.017422
$[Cupy_3]^{2+}{}_2$(bipy)	E(AFM) / eV	E(FM) / eV	E (AFM-FM) / eV	E / cm^{-1}	J' / cm^{-1}
B3LYP/ def2TZVP	-143275.2130470700	-143275.2130127800	-3.4290×10^{-5}	-0.27657	-1.1063

Figure S6. The exchange models and the calculated J values.

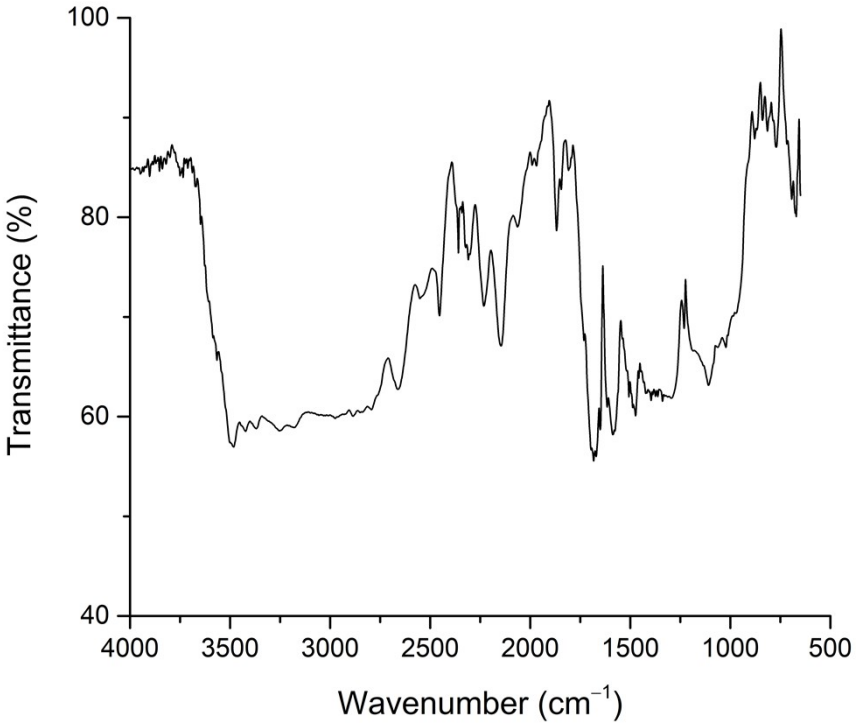


Figure S7. IR spectrum.

References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*, 2009, **42**, 339-341.

Author Contributions

Y.S. conceived and designed the project. Y.S. synthesised, characterised, and analysed all compounds.

K.S. measured crystal structures. S.Y. and Y.N. measured heat capacity. H.Z. performed calculations.

Y.S. wrote the paper with input from M.Y. and B.K.B.