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$BaCu(OH)_3Cl$: A new one-dimensional Mott insulator with a CuO_2 chessboard layer

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Table S1 Atomic displacement parameters (Å^2) for $BaCu(OH)_3Cl$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.0083(2)	0.0329(2)	0.0085(2)	0.000	0.00170(13)	0.000
Cu1	0.0172(4)	0.0107(3)	0.0081(3)	0.0026(3)	0.0015(3)	0.0000(2)
Cl1	0.0137(7)	0.0189(7)	0.0128(6)	0.000	0.0017(5)	0.000
O1	0.017(2)	0.015(2)	0.012(2)	0.000	0.0013(17)	0.000
O2	0.0246(16)	0.0127(14)	0.0099(13)	−0.0010(12)	−0.0001(12)	−0.0008(11)

Table S2 Hydrogen-bond geometry (Å, °) for $BaCu(OH)_3Cl$

D−H···*A*	*D*−H	H···*A*	*D*···*A*	*D*−H···*A*
O2−H2···Cl1^{v}	0.83(2)	2.93(5)	3.410(3)	119(5)

Symmetry codes: (v) −x+1, −y+1, −z+1.

Table S3 Selected bond lengths and angles for $BaCu(OH)_3Cl$

Atoms	Dis. (Ang.)	Atoms	Dis. (Ang.)
Ba1−O2	2.693(3)	Ba1−Cl1^{iv}	3.4739(7)
Ba1−O2^{i}	2.693(3)	Ba1−Cl1^{v}	3.4739(7)
Ba1−O2^{ii}	2.712(3)	Cu1−O2^{viii}	1.889(3)
Ba1−O2^{iii}	2.712(3)	Cu1−O2	1.889(3)
Ba1−O1	2.864(4)	Cu1−O1	1.992(2)
Ba1−Cl1	3.1917(18)	Cu1−O1^{viii}	1.992(2)
Ba1−Cl1^{iii}	3.2012(15)	Cu1−O1−Cu1^{vi}	113.8(2)
O2^{viii}−Cu1−O2	180.0	Cu1−O1−Ba1	99.11(13)
O2^{viii}−Cu1−O1	92.39(15)	Cu1^{vi}−O1−Ba1	99.11(13)
O2−Cu1−O1	87.61(15)	Cu1−O1−H1	101(3)
O2^{viii}−Cu1−O1^{viii}	87.61(15)	Cu1^{vi}−O1−H1	101(3)
O2−Cu1−O1^{viii}	92.39(15)	Ba1−O1−H1	142(6)
O1−Cu1−O1^{viii}	180.0	Cu1−O2−Ba1	108.07(13)
Cu1−O2−H2	105(5)	Cu1−O2−Ba1^{vii}	119.55(14)
Ba1−O2−H2	116(4)	Ba1^{vii}−O2−H2	109(5)

Symmetry codes: (i) x, $-y+1/2$, z; (ii) $x-1$, $-y+1/2$, z; (iii) $x-1$, y, z; (iv) $-x+1$, $-y$, $-z+1$; (v) $-x+1$, $-y+1$, $-z+1$; (vi) $-x+1$, $y-1/2$, $-z$; (vii) $x+1$, y, z; (viii) $-x+1$, $-y+1$, $-z$.

Table S4 Bond valence sums (BVS) for $BaCu(OH)_3Cl$

atoms	Ba1	Cu1	BVS
O1	0.212	0.429 (×2)	1.070
O2	0.336 (×2)*, 0.319 (×2)	0.567 (×2)	1.223
Cl1	0.258, 0.251, 0.120 (×2)	——	0.749
BVS	2.27	1.992	

* (×n) for the sum of columns;

Table S5 Magnetic susceptibility fitting formula and the corresponding parameters

$$\chi_{fit}(T)= \chi_0 + C_{imp} / (T - \theta_{imp}) + \chi^*_{chain}(T) \; ; \; \chi^*_{chain}(T) = \frac{Ng^2U_B^2}{4K_BT}\frac{1+\sum_{n=1}^{5} N_n/t^n}{1+\sum_{n=1}^{6} D_n/t^n}$$

N_1 = - 0.05384	N_2 = 0.09740	N_3 = 0.01447	N_4 = 0.00139	N_5 = 0.00011
D_1 = 0.44616	D_2 = 0.32048	D_3 = 0.13304	D_4 = 0.03718	D_5 = 0.00281
D_6 = 0.00026				

The experimental magnetic susceptibility data of the title compound in the temperature range from 2 to 300 K were well fitted using a model for the S = 1/2

Heisenberg antiferromagnetic (HAFM) uniform spin chain with the consideration for diamagnetic corrections and impurities:[1, 2]

$\chi_{fit}(T) = \chi_0 + C_{imp} / (T - \theta_{imp}) + \chi^*_{chain}(T)$,

where $\chi^*_{chain}(T)$ (see below) is the spin susceptibility of the uniform S = 1/2 chain parameterized by Johnston et al.[1], and χ_0 is the temperature independent susceptibility. The Curie constant (C_{imp}) and Curie-Weiss temperature (θ_{imp}) are related to intrinsic and extrinsic impurity contributions, which give rise to a low-temperature upturn in $\chi(T)$. The fitted parameters are χ_0 = -1.8(1) $\times 10^{-4}$ cm^3 mol^{-1}, g (the Landè factor) = 2.01(1).

The intrachain coupling constant of J/k_B = 135.7(6) K, which is deduced from the magnetic susceptibility data, is consistent with the expected value of the broad local maximum at T_{max} = 70 K for a 1D AFM uniform Heisenberg chain model: *i.e.*, T_{max} = ~ 0.641×J/k_B, and χ_{max} T_{max} = ~ 0.0353 g^2.[1] Other parameters are C_{imp}= 7.6(1)$\times 10^{-3}$ cm^3 K mol^{-1} and θ_{imp}= -2.9(1) K, which suggest the presence of ~0.76 wt% Cu oxides as impurities.

The spin susceptibility of the uniform S = 1/2 chain, $\chi^*_{chain}(T)$, is given by the following equation:

$$\chi^*_{chain}(T) = \frac{Ng^2U_B^2}{4K_BT} \frac{1 + \sum_{n=1}^{5} N_n/t^n}{1 + \sum_{n=1}^{6} D_n/t^n}$$

where N, g, U_B, and k_B are the Avogadro number, Landè factor, Bohr magneton, and Boltzmann constant, respectively, and $t = k_BT / J$; $\chi^*_{chain}(T)$ and the corresponding parameters are summarized in Table S5.

References:

1. D. C. Johnston, R. K. Kremer, M. Troyer, X. Wang, A. Klumper, S. L. Bud'ko, A. F. Panchula and P. C. Canfield, *Phys Rev B*, 2000, **61**, 9558-9606.
2. M. Fujisawa, H. Kikuchi, Y. Fujii, S. Mitsudo, A. Matsuo and K. Kindo, in *International Conference on Frustration in Condensed Matter*, eds. H. A. Katori, H. Kawamura, T. H. Arima and S. Fujiyama, Iop Publishing Ltd, Bristol, 2011, vol. 320.

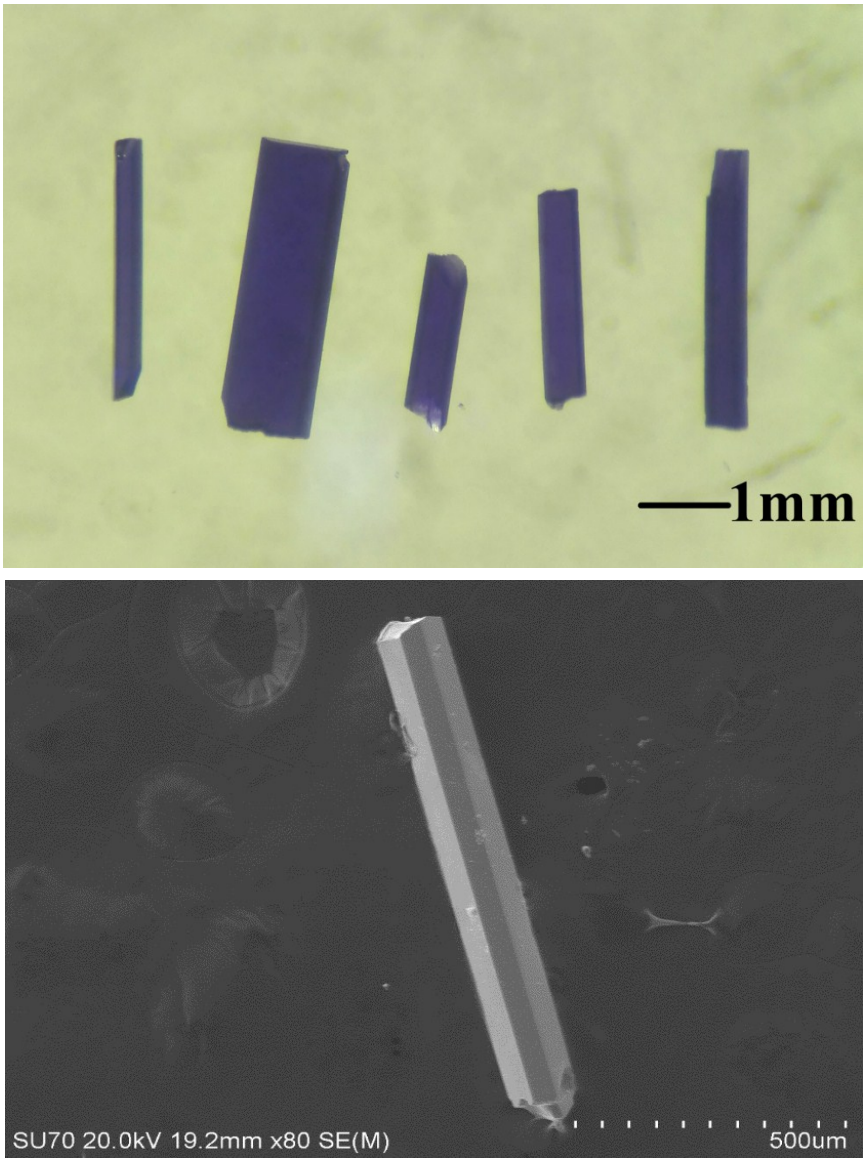
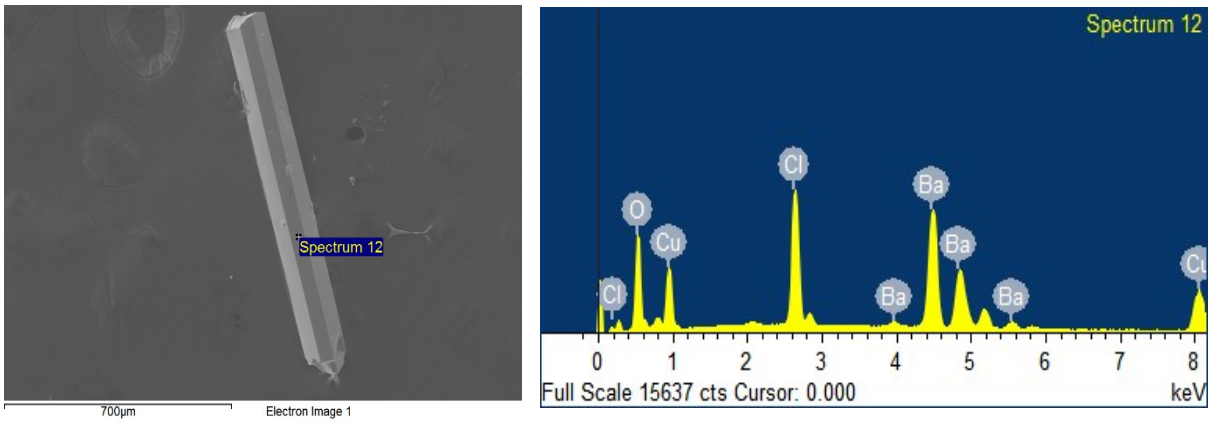


Figure S1. Crystal morphologies of $BaCu(OH)_3Cl$ (upper: optical microscope photograph; bottom: scanning electron microscopy (SEM) image)



Element	Weight%	Atomic%
O K	19.04	53.61
Cl K	12.89	16.38
Cu K	20.15	14.29
Ba L	47.92	15.72
Totals	100.00	

Figure S2. EDX spectrum and composition of $BaCu(OH)_3Cl$

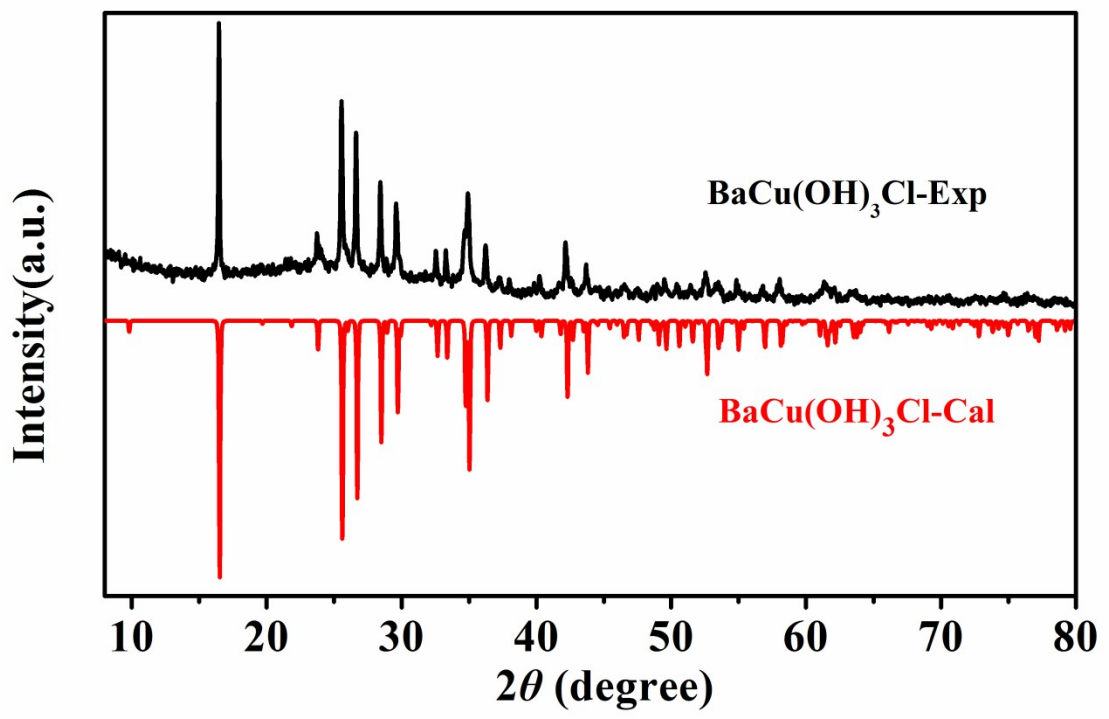


Figure S3. Experimental and calculated PXRD patterns of $BaCu(OH)_3Cl$

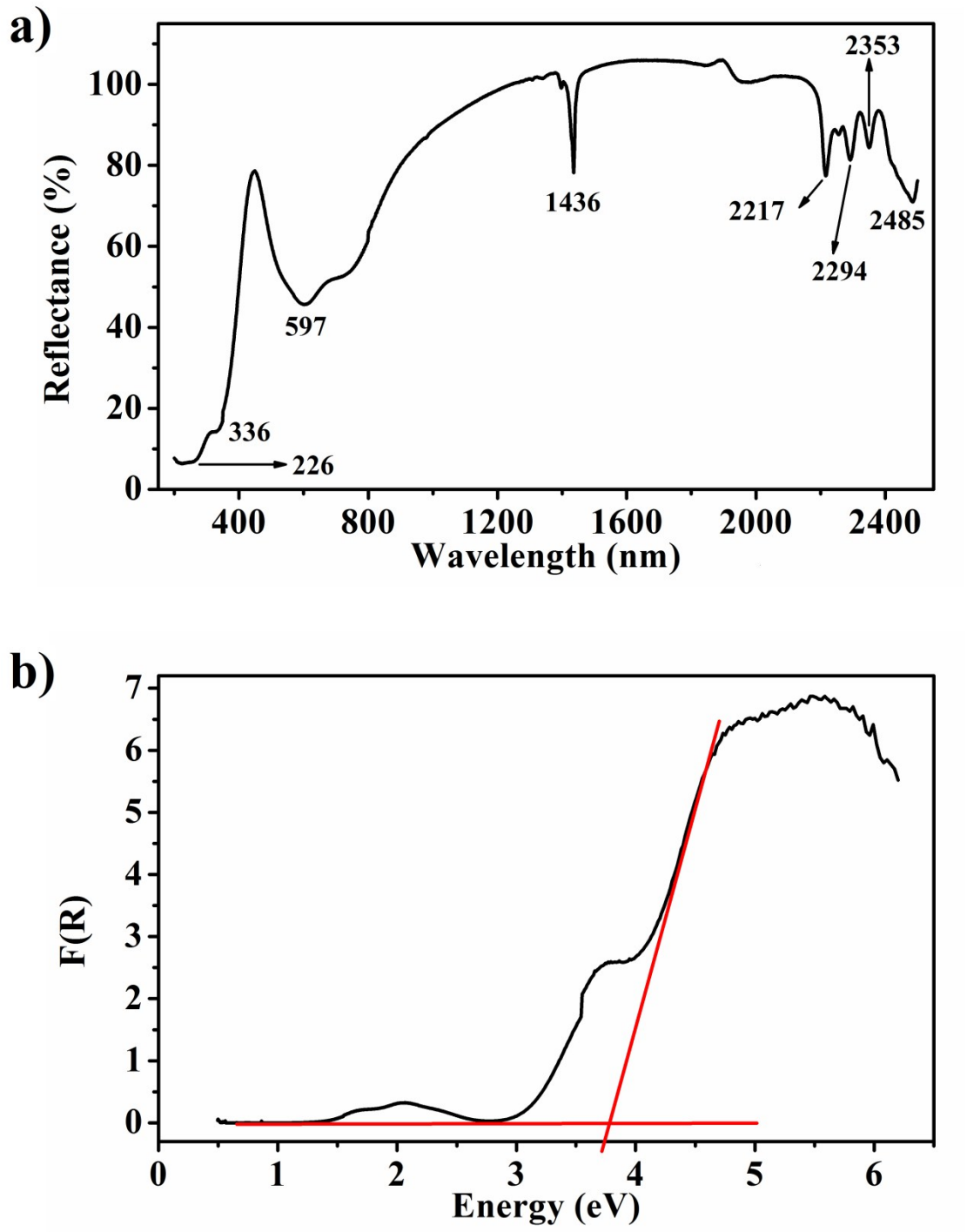


Figure S4. UV-Vis-NIR diffuse reflectance spectrum of $BaCu(OH)_3Cl$ (a) and its plot of absorption (K/S) data based on the Kubelka–Munk function (b).

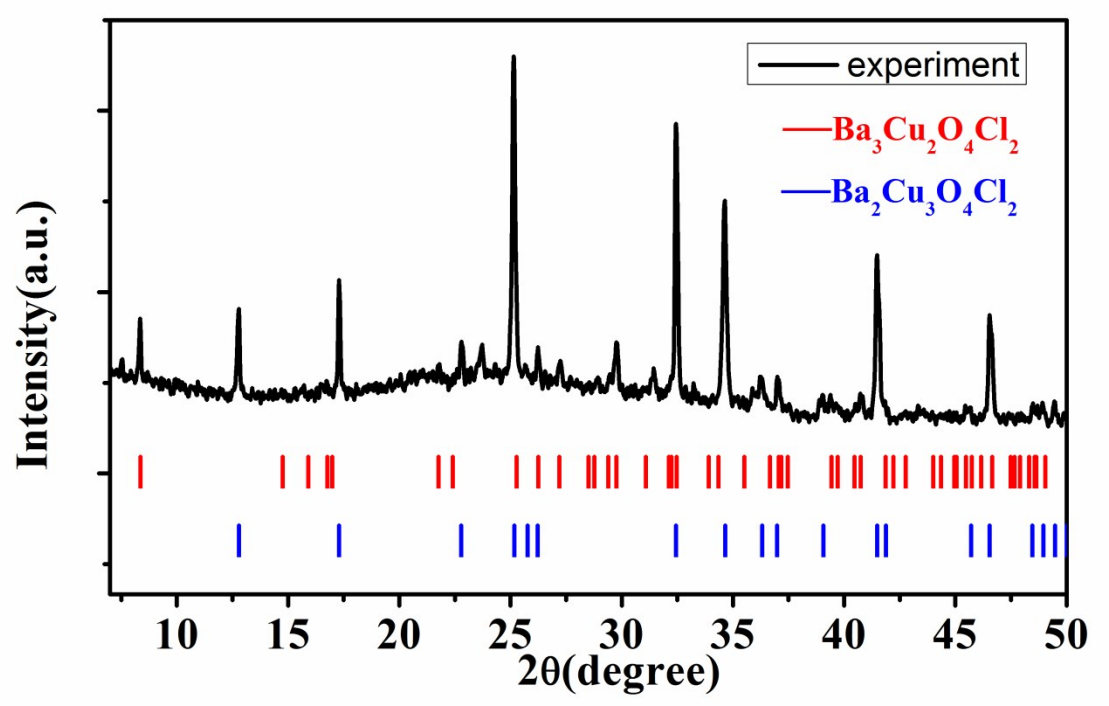


Figure S5. The PXRD pattern of the solid residual from $BaCu(OH)_3Cl$ after TG-DSC analysis

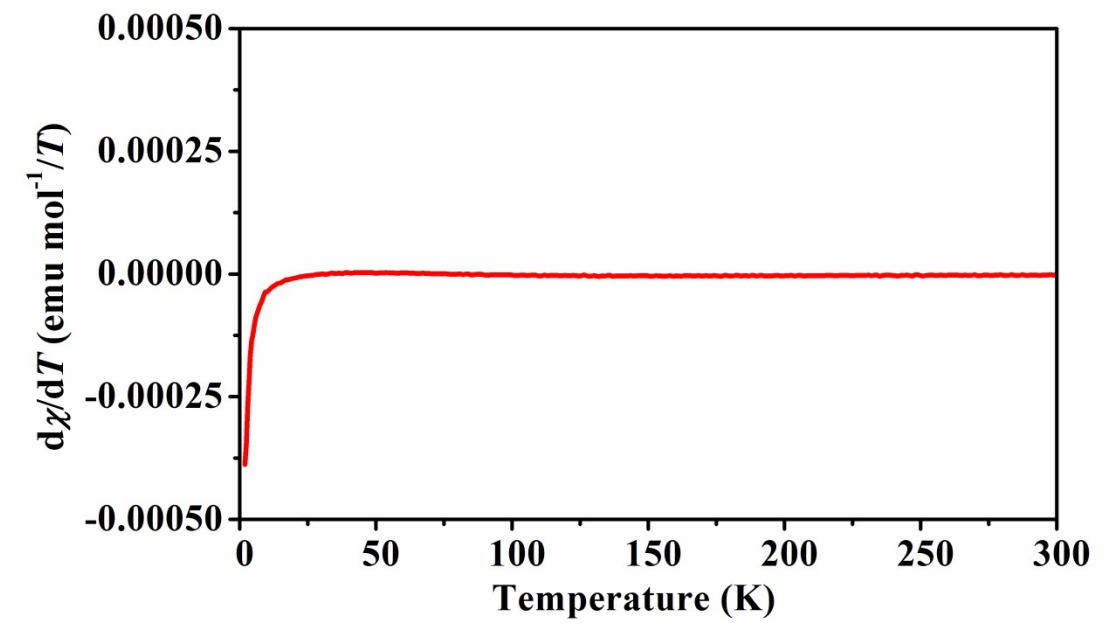


Figure S6 The derivative curve (dχ/dT versus T) for magnetic susceptibility of $BaCu(OH)_3Cl$

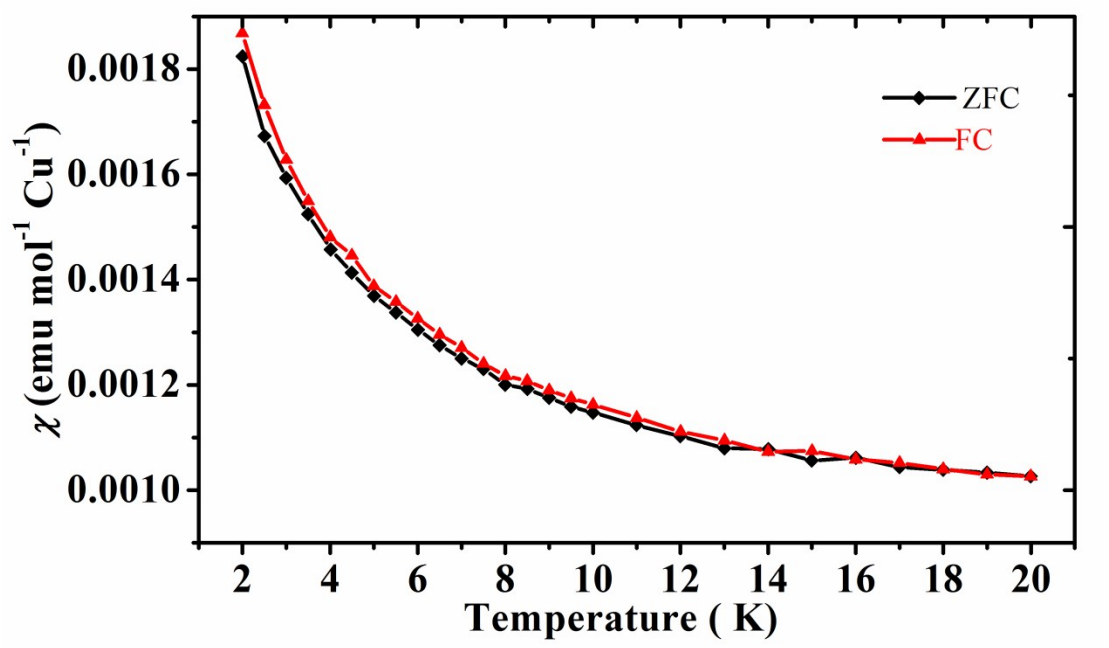


Figure S7 Comparison of magnetic susceptibility of $BaCu(OH)_3Cl$ under FC and ZFC