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Reversible phase transition and thermochromic response in two-dimensional organic copper-based perovskites

Gele Teri, Qiang-Qiang Jia, Qing-Feng Luo, Hao-Fei Ni, Da-Wei Fu* and Qiang Guo*

Institute for Science and Applications of Molecular Ferroelectrics, Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Normal University, Jinhua, 321004, People's Republic of China

E-mail: dawei@zjnu.edu.cn; qiangguo@zjnu.edu.cn

Experimental Section

Synthetic procedures

All reagents and solvents employed in this work are readily commercially available without further purification. 4-methoxybenzylamine (98%, Meryer-Shanghai), benzylamine (99%, Aladdin), cupric chloride anhydrous ($CuCl_2$, 98%, Adama-Sahnghai), methanol (CH_3OH, AR, HUSHI-Shanghai) and hydrochloric acid (HCl, AR, HUSHI-Shanghai).

For **$(MBA)_2CuCl_4$** (**1**) crystals, $CuCl_2$ and 4-methoxybenzylamine were mixed in a solution of methanol and HCl at a molar ratio of 2:1. Dark yellow flaky single crystals were obtained by slow evaporation at room temperature.

For **$(BA)_2CuCl_4$** (**2**) crystals, $CuCl_2$ and benzylamine were mixed in the HCl solution at a molar ratio of 2:1. Dark yellow flaky single crystals were obtained by slow evaporation at room temperature.

X-ray single crystal diffraction. Single-crystal X-ray diffraction data were collected by using a Bruker D8 APEX-III diffractometer with Mo-Kα and Cu- Kα radiation (operating at 50 kV and 40 mA). Data reduction and numerical absorption corrections were generated using APEX-III software. Refinement of single crystal data was solved and refined using SHELXT and OLEX 2 software packages, all non-hydrogen atoms were anisotropically manipulated.

Thermal stability. The powders of the two compounds were put in aluminum crucibles and then placed in the differential scanning calorimetry (DSC) instrument for the experiment. The experiment was conducted with heating and cooling rates of 20 $K \cdot min^{-1}$.

Dielectric measurements. The powder was pressed into a sheet, and the dielectric measurement was performed on the Tonghui TH2828A instrument at various temperatures. The frequency range was from 500 Hz to 1 MHz.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) data for two compounds were measured on a D8 Advance 03030502 instrument at room temperature. Diffraction patterns were collected in the 2θ range of 5~55° with a step size of 0.02°.

UV-Vis Measurements. UV-near-infrared-visible (UV-NIR-vis) spectra were obtained on a Cary RF 6000 instrument.

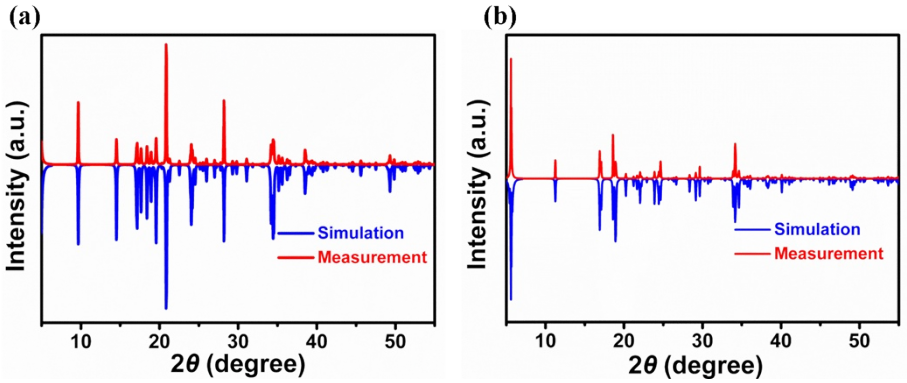

Figure S1. Powder X-ray diffraction (PXRD) patterns for $(MBA)_2CuCl_4$ (**1**) and $(BA)_2CuCl_4$ (**2**).

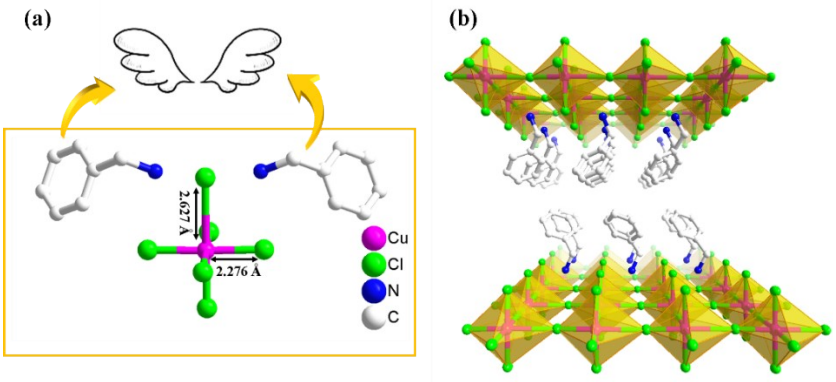

Figure S2. (a and b) Crystal structures of $(BA)_2CuCl_4$ (**2**). For clarity, all H atoms were omitted.

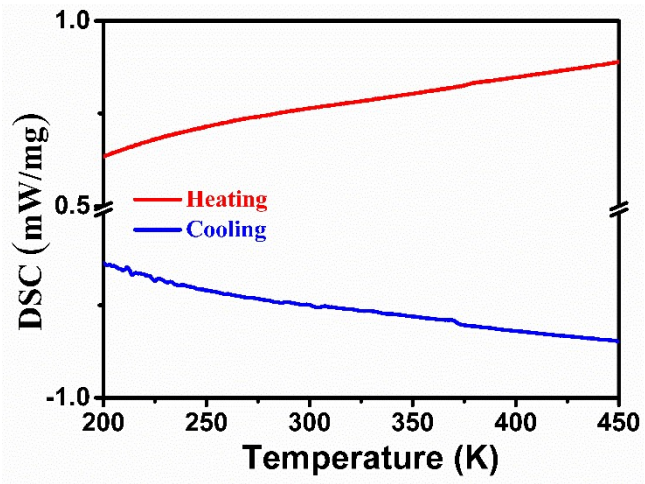

Figure S3. DSC curve of $(BA)_2CuCl_4$ (**2**) in heating-cooling runs.

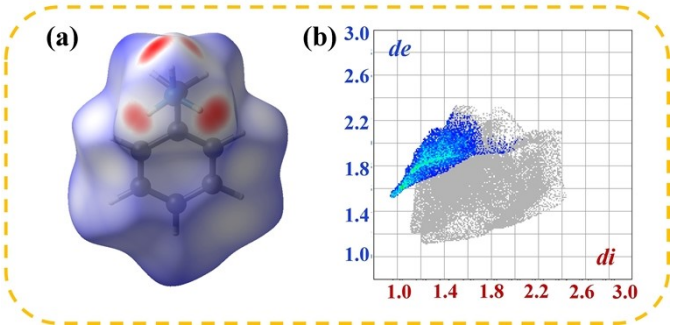

Figure S4. Hirshfeld surface (a) and 2D fingerprint plot (b) for $(BA)_2CuCl_4$ (**2**).

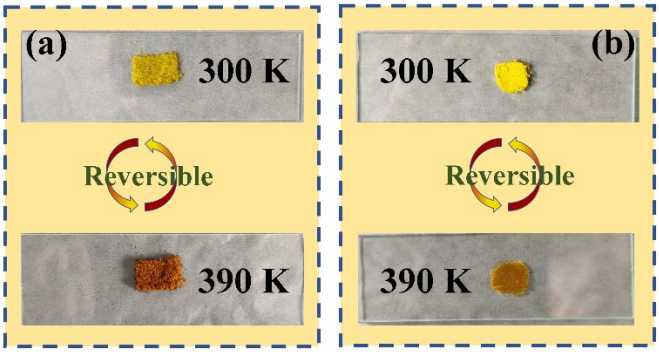

Figure S5. Color changes of (a) $(MBA)_2CuCl_4$ (**1**) and (b) $(BA)_2CuCl_4$ (**2**).

Table S1 Cell parameters for compound **1** at different temperatures.

Temp	273K	293K	313K	333K	353K	373K	393K	413K	432K
a(Å)	10.504	10.539	10.543	10.559	10.579	10.601	10.636	10.672	10.693
b(Å)	36.811	36.831	36.884	36.918	36.971	36.996	37.088	37.206	37.267
c(Å)	5.2766	5.2795	5.2844	5.2855	5.2935	5.2939	5.3083	5.316	5.3299

Table S2 Crystallographic data and structural refinement details of compound **1**

Compounds	$(MBA)_2CuCl_4$	
	LTP	HTP
CCDC Code	2219275	2219276
Formula	$C_{16}H_{24}Cl_4CuN_2O_2$	$C_{16}H_{24}Cl_4N_2O_2Cu$
Fw	481.71	481.71
Temp(K)	273	432
Crystal Syst	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*
a(Å)	10.504(3)	10.693(4)
b(Å)	36.811(14)	37.267(11)
c(Å)	5.2766(9)	5.3299(14)
α/°	90	90
β/°	90	90
γ/°	90	90
V(Å^3)	2040.3(11)	2123.9(12)
Z	4	4
μ(mm^{-1})	6.438	1.543
GOF on F^2	1.077	1.060
R_1	0.0670	0.0516
wR_2	0.1635	0.1400

Table S3 Crystallographic data and structural refinement details of compound **2**

Compound	$(BA)_2CuCl_4$
CCDC Code	2219277
Formula	$C_{14}H_{20}Cl_4N_2Cu$
Fw	421.66
Temp(K)	300
Crystal Syst	Monoclinic
Space group	*Cc*
a(Å)	31.706(5)
b(Å)	5.2429(7)
c(Å)	10.5574(15)
α/°	90
β/°	98.116(6)
γ/°	90
V(Å^3)	1737.4(4)
Z	4
μ(mm^{-1})	1.866
GOF on F^2	1.062
R_1	0.0369
wR_2	0.0865

Table S4 Selected bond lengths /Å and angles/° for compound **1**

Compound **1**			
LTP		HTP	
Cu1-Cl1	2.276(2)	Cu1-Cl0A^{1}	2.294(4)
Cu1-Cl2	2.298(5)	Cu1-Cl1	2.2886(17)
Cu1-Cl3	2.324(5)	Cu1-Cl1^{2}	2.2886(17)
Cu1-Cl4	2.241(4)	Cu1- Cl0A^{3}	2.287(4)
Cu1-Cl5	2.352(6)	Cu1-Cl2	2.311(4)
O1-C5	1.505(17)	Cu1-Cl3	2.325(4)
O1-C8	1.476(18)	Cu1-Cl2	2.275(6)
O1-C5	1.432(11)	O1-C2	1.426(12)
O1-C9	1.476(12)	O1-C15	1.397(8)
N1-C1	1.439(10)	O2-C1	1.42(2)
C1-C2	1.498(11)	O2-C16	1.457(18)
C2-C3	1.361(10)	N1-C009	1.478(19)
C2-C7	1.363(10)	C0-C9	1.67(4)
C3-C4	1.368(12)	C009-C10	1.498(12)
C4-C5	1.366(12)	C15-C13	1.3900
C5-C6	1.398(13)	C15-C5	1.3900
C6-C7	1.362(11)	C13-C11	1.3900
Cl1-Cu1-Cl1^{1}	173.57(10)	C11-C10	1.3900
Cl1-Cu1-Cl2	90.02(6)	C10-C7	1.3900
Cl1^{1}-Cu1-Cl2	90.02(6)	C7-C5	1.3900
Cl1-Cu1-Cl3^{2}	90.44(5)	C16-C14	1.3900
Cl1^{1}-Cu1-Cl3^{2}	90.44(5)	Cl1^{1}-Cu1-Cl0A^{2}	89.92(4)
Cl1^{1}-Cu1-Cl3	89.90(6)	Cl1-Cu1- Cl0A^{2}	89.92(4)

Cl1-Cu1-Cl3	89.90(6)	$Cl1^{1}$-Cu1-Cl1	174.80(8)
$Cl1^{1}$-Cu1-Cl5	93.21(5)	Cl1-Cu1-Cl2	90.43(4)
Cl1-Cu1-$Cl5^{3}$	86.79(5)	$Cl1^{1}$-Cu1-Cl2	90.43(4)
Cl1-Cu1-Cl5	93.21(5)	$Cl1^{1}$-Cu1-Cl3	87.41(4)
Cl2-Cu1-$Cl3^{2}$	171.90(14)	Cl1-Cu1-Cl3	87.41(4)
Cl2-Cu1-$Cl5^{3}$	93.6(2)	$Cl1A^{3}$-Cu1-$Cl0A^{2}$	89.7(2)
Cl2-Cu1-Cl5	88.30(19)	$Cl1A^{3}$-Cu1-$Cl1^{1}$	92.60(4)
$Cl3^{2}$-Cu1-Cl3	173.9(3)	$Cl1A^{3}$-Cu1-Cl1	92.60(4)
$Cl3^{2}$-Cl1-$Cl5^{3}$	94.5(2)	$Cl3^{3}$-Cu1-$Cl2^{2}$	83.58(12)
C8-O1-C5	114(3)	Cl2-Cu1-Cl3	94.9(2)
C5-O2-C9	110.4(10)	C15-O1-C2	117.1(11)
N1-C1-C2	115.1(6)	C1-O2-C16	108(3)
C3-C2-C1	119.3(7)	N2-C0-C9	121(3)
C3-C2-C7	119.6(8)	N1-C009-C10	111.7(10)
C7-C2-C1	121.1(8)	C13-C15-O1	116.2(6)
C2-C3-C4	122.0(8)	C13-C15-C5	120
C5-C4-C3	118.1(10)	C5-C15-O1	123.8(6)
C4-C5-O1	152.4(17)	C15-C13-C11	120
C4-C5-O2	108.5(10)	C11-C10-C009	110.2(7)
C4-C5-C6	120.9(9)	C7-C10-C009	129.6(7)
C6-C5-O1	86.2(15)	C7-C10-C11	120
C6-C5-O2	130.5(9)	C14-C16-O2	126(2)
C7-C6-C5	119.0(9)	C6-C16-O2	114(2)
C6-C7-C2	120.5(9)	C12-C9-C0	150(2)
		C12-C9-C8	120
		C8-C9-C0	90(2)

		C9-C8-C6	120

Symmetry codes: [1]+*X*,3/2-*Y*,+*Z*; [2]+*X*,+*Y*, 1+*Z*; [3]-1/2+*X*,+*Y*, 1/2-*Z*; [4]+*X*,+*Y*, -1+*Z*; [5]-1/2+*X*,+*Y*, 1/2-*Z*;

Table S5 Selected bond lengths /Å and angles/° for compound **2**

Compound **2**			
Cu1-Cl1	2.281(13)	Cl1-Cu1-Cl4	92.37(13)
Cu1-Cl2	2.299(12)	Cl1-Cu1-Cl0A[1]	83.21(13)
Cu1-Cl3	2.2766(19)	Cl1-Cu1-Cl0A[2]	177.38(12)
Cu1-Cl4	2.281(2)	Cl2-Cu1-Cl1A[2]	92.99(14)
N1-C1	1.454(10)	Cl4-Cu1-Cl2	89.72(13)
C1-C2	1.497(8)	Cl4-Cu1-Cl0A[1]	90.67(14)
C2-C3	1.360(8)	Cl4-Cu1-Cl1A[1]	87.91(13)
C3-C4	1.381(9)	C13-C14-C9	121.4(6)
C4-C5	1.358(10)	N2-C8-C9	113.6(5)
C5-C6	1.368(10)	C11-C10-C9	119.5(6)
C6-C7	1.368(9)	C14-C9-C8	121.6(6)
N2-C8	1.448(9)	C14-C9-C10	118.9(5)
C8-C9	1.501(8)	C2-C3-C4	120.3(6)
C9-C10	1.386(9)	C3-C2-C7	119.0(5)
C9-C14	1.380(8)	C3-C2-C1	121.8(6)
C10-C11	1.386(9)	C7-C2-C1	119.2(6)
C11-C12	1.354(10)	C6-C7-C2	119.9(6)
C12-C13	1.391(10)	C14-C13-C12	119.3(6)

	C13-C14	1.363(9)	C12-C11-C10	120.8(6)
Sym	Cl3-Cu1-Cl1	92.35(13)	C7-C6-C5	120.8(6)
metry	Cl3-Cu1-Cl2	89.73(13)	C5-C4-C3	120.7(6)
codes:	Cl3-Cu1-Cl4	175.24(9)	N1-C1-C2	113.6(5)
[1]+*X*,-	Cl3-Cu1-Cl0A[1]	90.46(14)	C4-C5-C6	119.2(6)
1+*Y*,	Cl3-Cu1-ClA[2]	87.40(13)	C11-C12-C13	120.1(6)

+*Z*;

[2]+*X*,-*Y*,1/2+*Z*