

Argentophilicity Induced Anomalous Thermal Expansion Behavior in 2D Silver Squarate

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Table S1 Crystallographic data of compound Ag_sq

Name	Ag_sq
Empirical formula	C ₄ H ₃ O ₅ Ag
Formula weight	238.93
Crystal system	Monoclinic
Space group	<i>C2/c</i>
a/Å	13.358(3)
b/Å	8.2296(9)
c/Å	11.1054(16)
α/°	90
β/°	118.508(17)
γ/°	90
Volume/ Å ³	1072.8(4)
Z	8
ρ _{cal} g/cm ³	2.934
2θ range	6.53~70.1
Independent reflections	2016
Goodness-of-fit on F ²	1.267
Final R indexes [I >=2σ(I)]	R ₁ =0.1023 wR ₂ =0.2693
Final R indexes [all data]	R ₁ =0.1059 wR ₂ =0.2782
CCDC	2014485

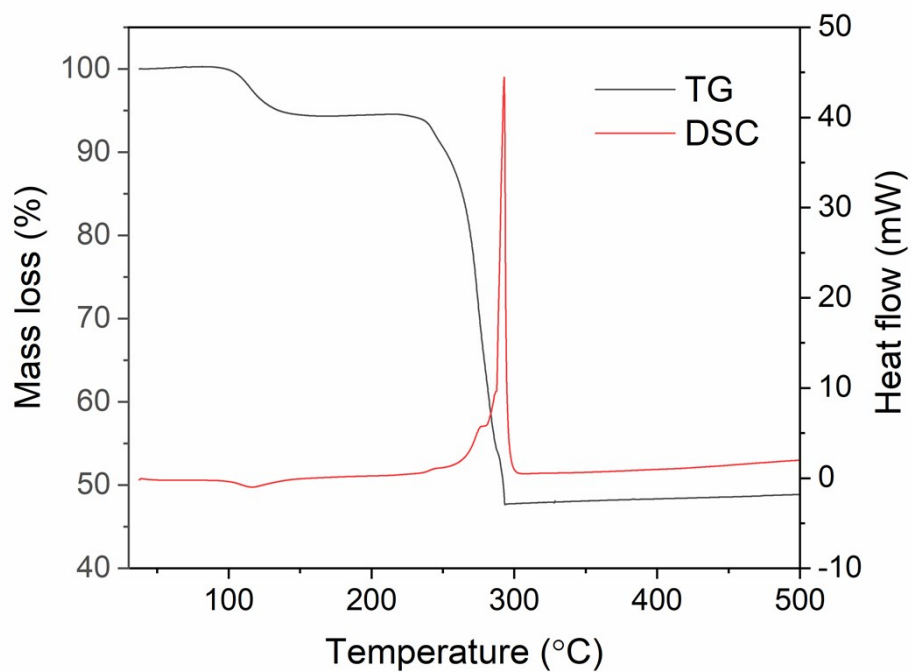


Figure S1 TG-DSC curves of Ag_sq in air.

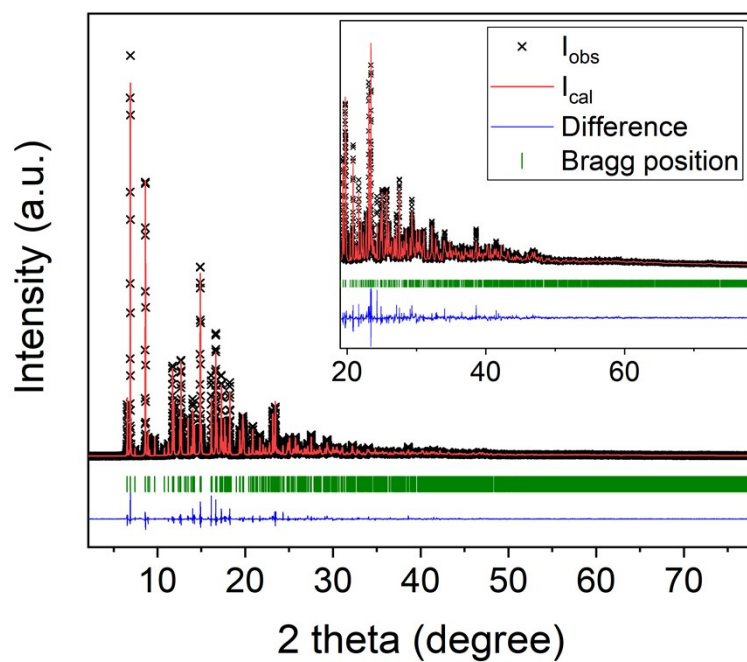


Figure S2 Rietveld refinement of the high resolution synchrotron X-ray powder diffraction pattern of Ag_sq at 300K ($R_p = 5.05\%$, $wR_p = 7.52\%$)

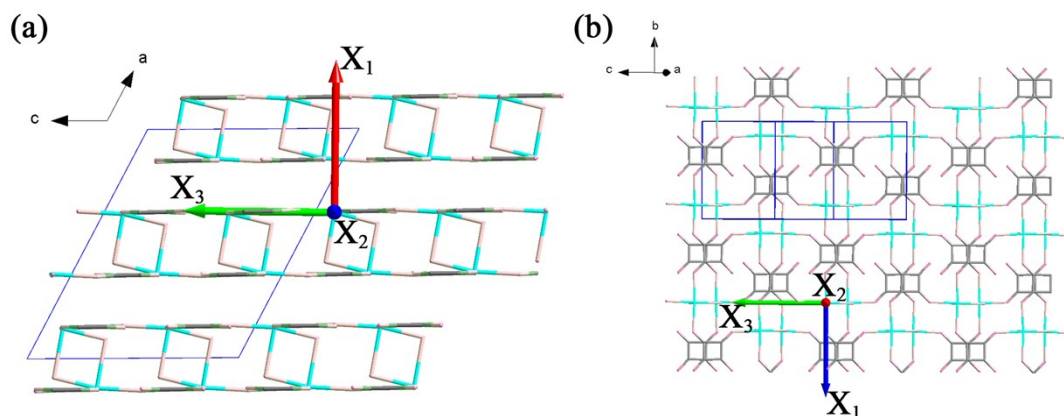


Figure S3 Illustration of the three principal axes

Table S2 Some representative 2D materials with NTE.

Name	CTE (MK ⁻¹)	Temperature range (K)	Reference
Ag_sq	-6.1(2)	100~300	This work
Graphene	-8.0	200~400	1
Silicene	-5.3	-	2
Germanene	-2.1	-	2
Blue phosphorene	-4.2	-	2
Boron nitride	-2.9 (at 293K)	0~770	3

Table S3 Proton conductivities of some representative compounds

Name	Conductivity (S cm ⁻¹)	Condition	References
Ag_sq	1.4×10^{-4}	80°C, 99% R. H.	This work
Ferrous Oxalate Dihydrate	1.3×10^{-4}	25°C, 98% R. H.	4
(N ₂ H ₅)[CeEu(C ₂ O ₄) ₄ (N ₂ H ₅)]·4H ₂ O	3.42×10^{-4}	RT, 98% R. H.	5
Cu ₄ (L) ₂ (OH) ₂ (DMF) ₂			
L = 5-sulfoisophthalic acid	7.4×10^{-4}	95°C, 95% R. H.	6
monosodium salt			
β-PCMOF2	1.3×10^{-3}	85°C, 90% R. H.	7
PCMOF10	3.55×10^{-2}	70°C, 95% R. H.	8

Ca-PiPhA-NH ₃	6.6×10^{-2}	24°C, 98% R. H	9
LiCl@[Ca(C ₄ O ₄)(H ₂ O)]	1.8×10^{-2}	25°C, 40% R. H	10

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