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$Cs_3CuAs_4Q_8$ (Q = S, Se): unique two-dimensional layered inorganic thioarsenates with the lowest Cu-to-As ratio and remarkable photocurrent responses

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Table S3. Structural features of selected quaternary X/Cu/As/Q (X = inorganic cations; Q = chalcogen) system.

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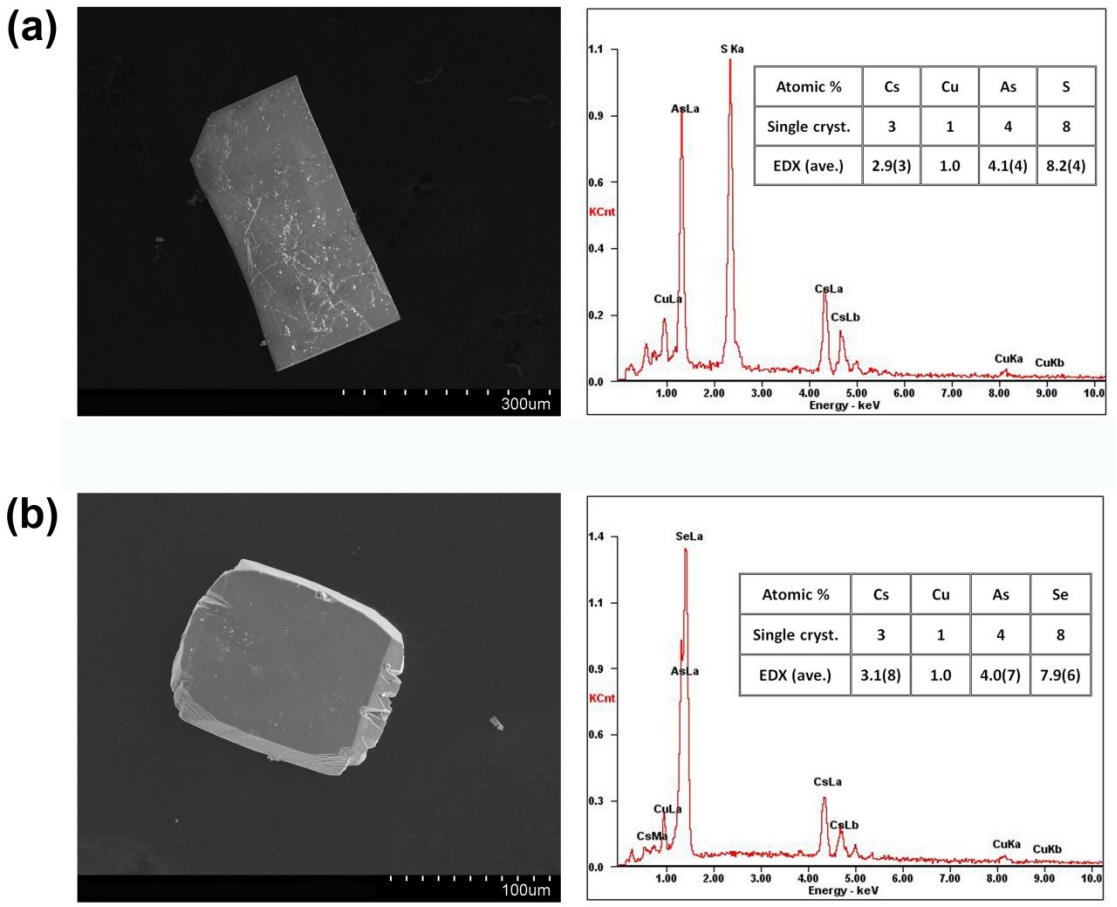
Figures and Tables



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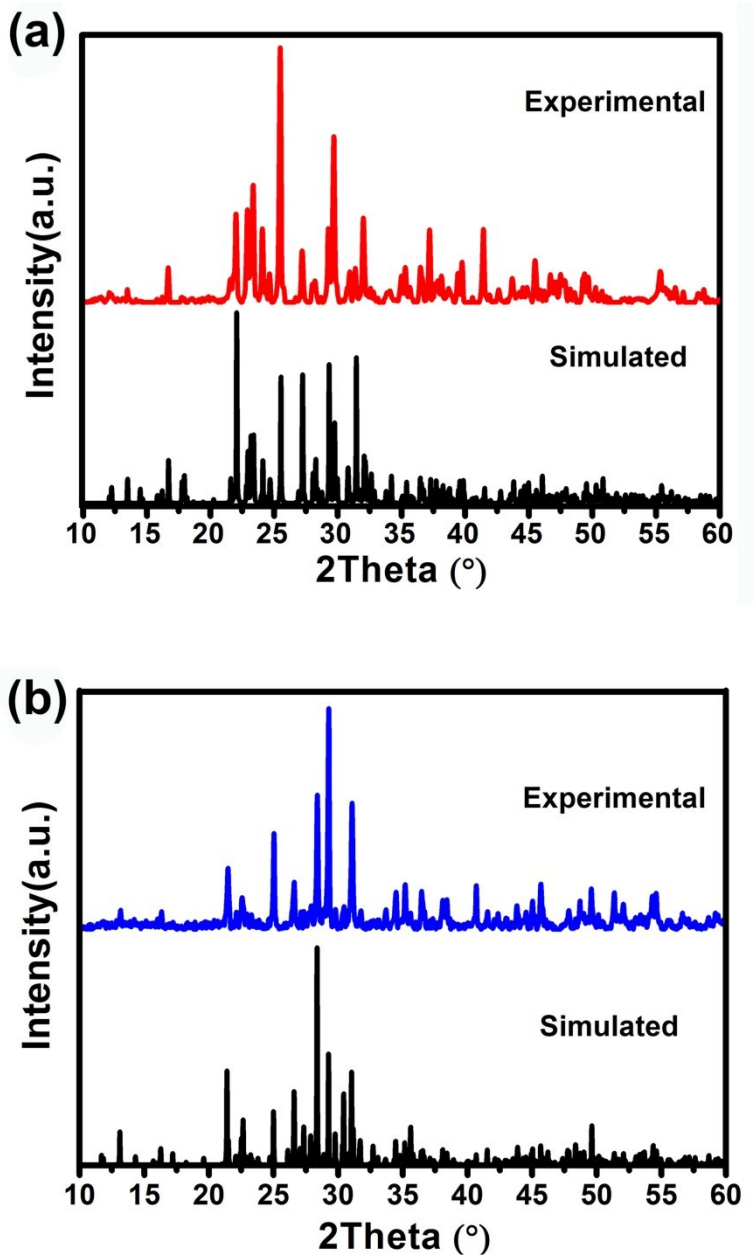


Figure S2. The experimental and simulated powder XRD of of (a) $Cs_3CuAs_4S_8$ and (b) $Cs_3CuAs_4Se_8$.

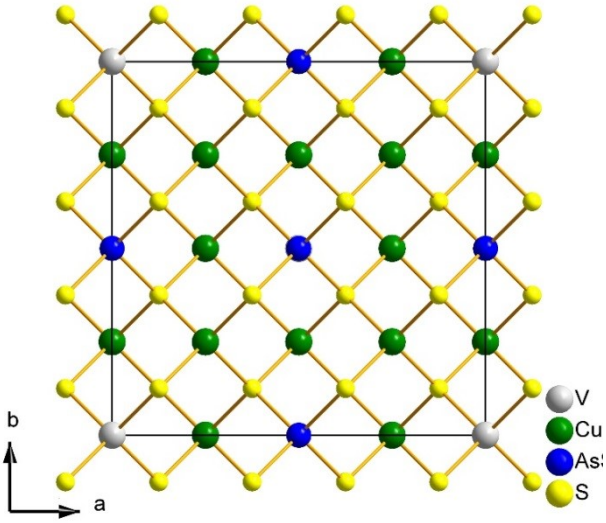


Figure S3. 3D structure of $VCu_{13}As_3S_{16}$ along the *c* direction.

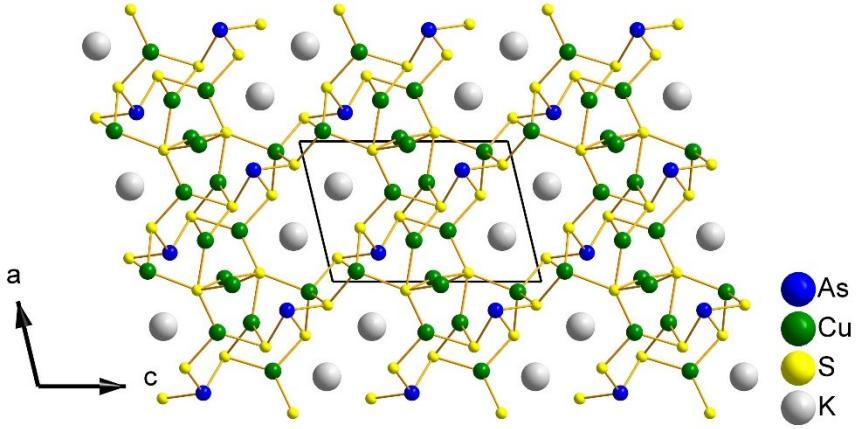


Figure S4. 3D structure of KCu_4AsS_4 along the *b* direction.

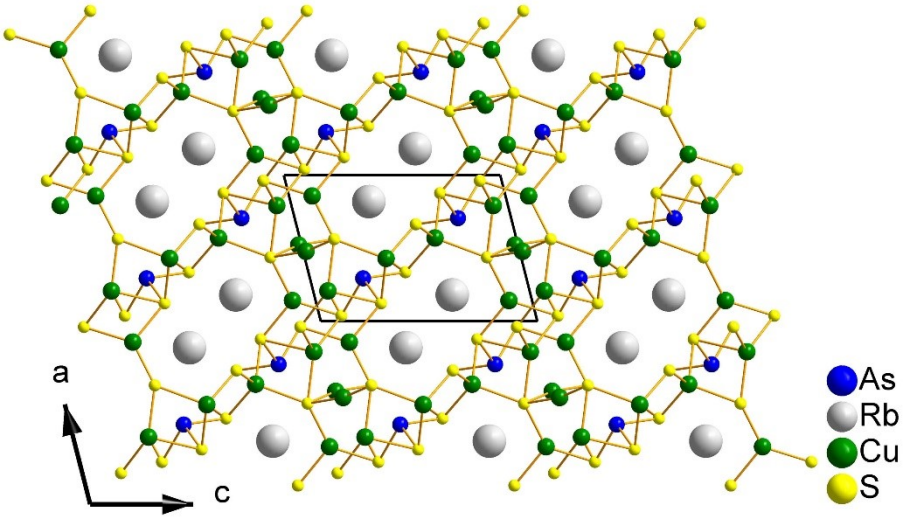
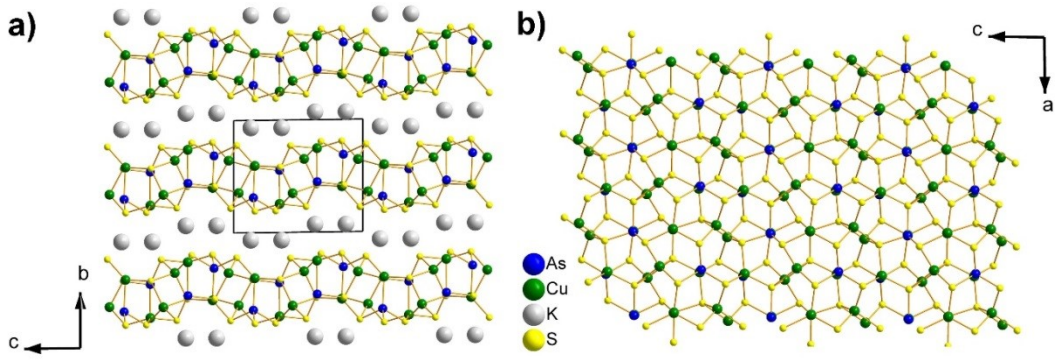


Figure S5. 3D structure of $RbCu_4AsS_4$ along the *b* direction.



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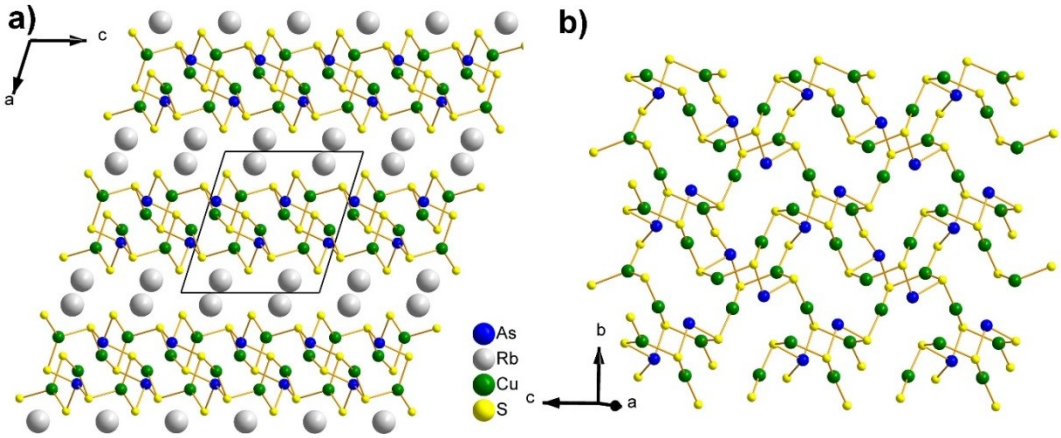

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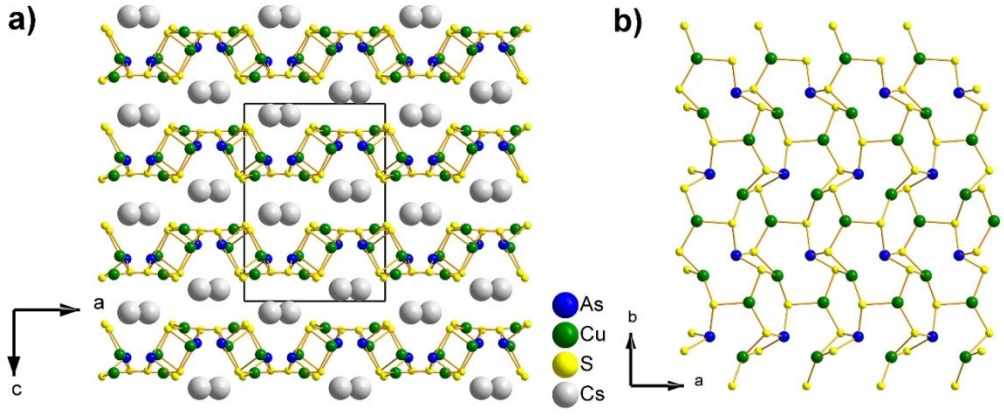
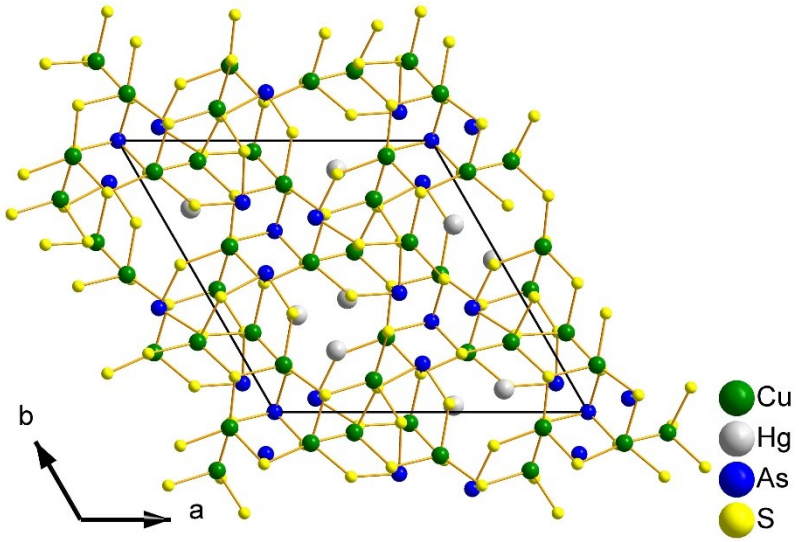


Figure S8. (a) 2D layered structure of $CsCu_2AsS_3$ viewed from *b* direction. (b) $[Cu_2AsS_3]^-$ layer along the *ab* plane.



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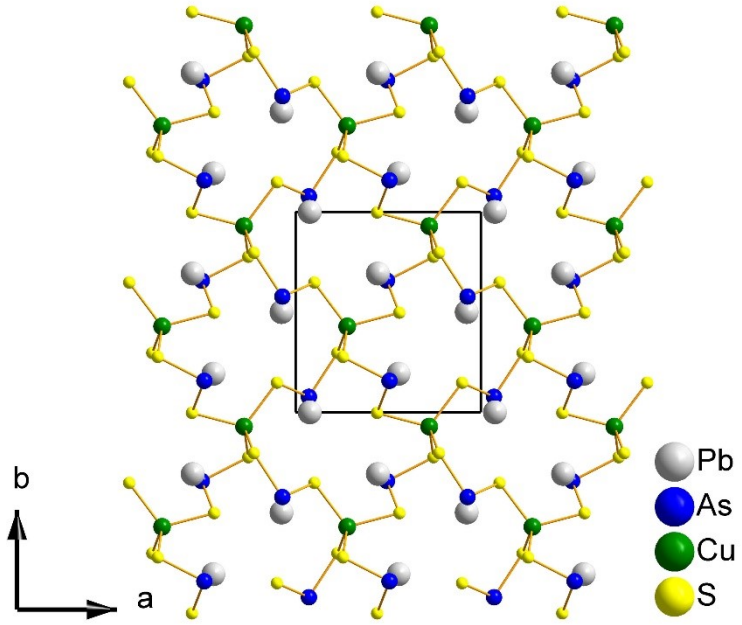

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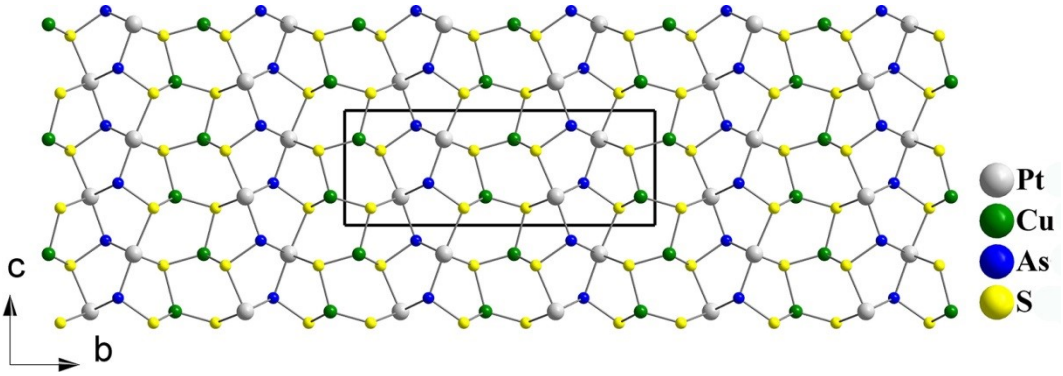

Figure S11. 3D structure of $PtCuAsS_3$ along the *a* direction.

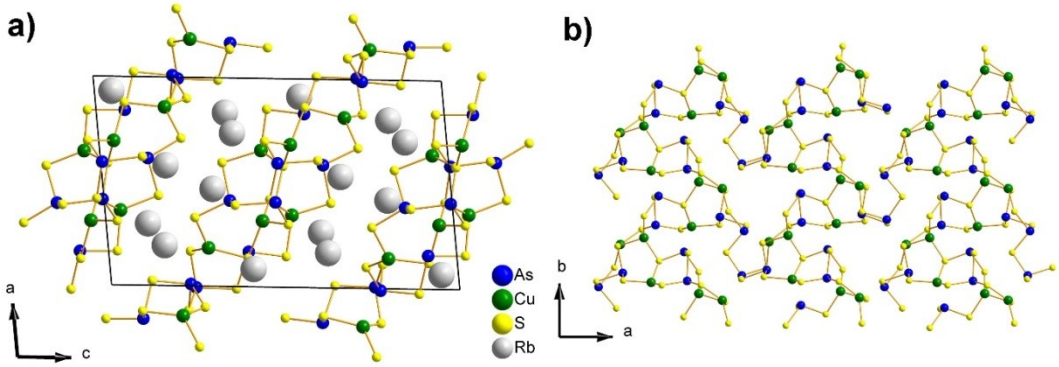

Figure S12. (a) 2D layered structure of $Rb_8Cu_6As_8S_{19}$ along the *b* direction. (b) $[Cu_6As_8S_{19}]^{8-}$ layer in the *ab* plane.

Table S1. Selected bond lengths (Å) for $Cs_3CuAs_4Q_8$ (Q = S, Se).

$Cs_3CuAs_4S_8$		$Cs_3CuAs_4Se_8$	
Cu(1)-As(4)	2.6628(18)	Cu(1)-As(4)	2.615(2)
Cu(1)-S(4)	2.328(3)	Cu(1)-Se(4)	2.4414(15)
Cu(1)-S(5)	2.288(3)	Cu(1)-Se(5)	2.3908(16)
Cu(1)-S(8)	2.298(3)	Cu(1)-Se(8)	2.4136(14)
As(1)-S(2)	2.154(3)	As(1)-Se(2)	2.3039(15)
As(1)-S(3)	2.311(3)	As(1)-Se(3)	2.434(2)
As(1)-S(7)	2.313(3)	As(1)-Se(7)	2.4487(15)
As(2)-S(3)	2.252(3)	As(2)-Se(3)	2.3861(14)
As(2)-S(4)	2.189(3)	As(2)-Se(4)	2.3394(18)
As(2)-S(6)	2.289(3)	As(2)-Se(6)	2.4215(13)
As(3)-S(1)	2.299(3)	As(3)-Se(1)	2.4273(18)
As(3)-S(7)	2.264(3)	As(3)-Se(7)	2.4110(13)
As(3)-S(8)	2.201(3)	As(3)-Se(8)	2.3537(13)
As(4)-S(1)	2.280(3)	As(4)-Se(1)	2.4148(13)
As(4)-S(5)	2.179(3)	As(4)-Se(5)	2.3322(14)
As(4)-S(6)	2.318(3)	As(4)-Se(6)	2.4454(15)
Cs(1)-S(2)	3.513(3)	Cs(1)-Se(2)	3.6485(13)
Cs(1)-S(5)	3.849(3)	Cs(1)-Se(7)	4.3085(13)
Cs(1)-S(6)	3.924(3)	Cs(1)-Se(6)	3.9442(18)
Cs(2)-S(1)	3.688(3)	Cs(2)-Se(1)	3.7381(16)
Cs(2)-S(1)	3.690(3)	Cs(2)-Se(1)	3.7595(15)
Cs(2)-S(1)	4.079(3)	Cs(2)-Se(1)	4.326(2)
Cs(2)-S(2)	3.504(3)	Cs(2)-Se(2)	3.606(2)
Cs(2)-S(2)	3.880(3)	Cs(2)-Se(2)	3.9250(15)
Cs(2)-S(5)	4.159(3)	Cs(2)-Se(5)	4.328(2)

Cs(2)-S(6)	3.636(3)	Cs(2)-Se(6)	3.7384(12)
Cs(2)-S(7)	3.711(3)	Cs(2)-Se(7)	3.9400(14)
Cs(2)-S(7)	3.896(3)	Cs(2)-Se(7)	3.935(2)
Cs(2)-S(8)	3.617(3)	Cs(2)-Se(8)	3.6504(18)
Cs(3)-S(2)	3.477(4)	Cs(3)-Se(2)	3.6005(19)
Cs(3)-S(3)	4.075(3)	Cs(3)-Se(3)	3.7215(12)
Cs(3)-S(3)	3.631(3)	Cs(3)-Se(3)	4.1309(15)
Cs(3)-S(4)	3.885(3)	Cs(3)-Se(4)	3.7162(13)
Cs(3)-S(4)	3.537(3)	Cs(3)-Se(4)	3.9687(16)
Cs(3)-S(8)	3.547(3)	Cs(3)-Se(8)	3.5847(12)
Cs(3)-S(8)	3.506(2)	Cs(3)-Se(8)	3.6184(19)
Cs(3)-S(7)	4.148(3)	Cs(3)-Se(7)	4.341(2)
Cs(4)-S(4)	3.527(3)	Cs(4)-Se(4)	3.6124(11)
Cs(4)-S(5)	3.524(3)	Cs(4)-Se(5)	3.6488(13)
Cs(4)-S(6)	3.583(3)	Cs(4)-Se(6)	3.6866(17)
Cs(4)-S(8)	3.688(3)	Cs(4)-Se(8)	3.8163(11)

Table S2. Selected Bond Angles (deg) for $Cs_3CuAs_4Q_8$ (Q = S, Se).

$Cs_3CuAs_4S_8$		$Cs_3CuAs_4Se_8$	
S(1)-As(4)-S(6)	93.11(11)	Se(1)-As(4)-Se(6)	93.01(5)
S(2)-As(1)-S(3)	99.16(12)	Se(2)-As(1)-Se(3)	98.73(6)
S(2)-As(1)-S(7)	102.99(11)	Se(2)-As(1)-Se(7)	103.37(5)
S(3)-As(1)-S(7)	98.92(12)	Se(3)-As(1)-Se(7)	98.80(6)
S(3)-As(2)-S(6)	98.27(11)	Se(3)-As(2)-Se(6)	97.46(5)
S(4)-As(2)-S(3)	100.14(11)	Se(4)-As(2)-Se(3)	99.45(5)
S(4)-As(2)-S(6)	106.14(11)	Se(4)-As(2)-Se(6)	107.82(6)
S(5)-As(4)-S(1)	104.32(11)	Se(5)-As(4)-Se(1)	103.78(5)
S(5)-As(4)-S(6)	102.93(10)	Se(5)-As(4)-Se(6)	102.46(6)
S(7)-As(3)-S(1)	96.36(11)	Se(7)-As(3)-Se(1)	96.31(6)
S(8)-As(3)-S(1)	101.75(10)	Se(8)-As(3)-Se(1)	101.29(5)
S(8)-As(3)-S(7)	100.64(11)	Se(8)-As(3)-Se(7)	101.24(5)
S(1)-As(4)-Cu(1)	100.25(8)	Se(1)-As(4)-Cu(1)	100.97(5)
S(5)-As(4)-Cu(1)	124.94(9)	Se(5)-As(4)-Cu(1)	125.30(5)
S(6)-As(4)-Cu(1)	124.12(9)	Se(6)-As(4)-Cu(1)	124.07(6)
S(5)-Cu(1)-S(4)	115.04(11)	Se(5)-Cu(1)-Se(4)	116.95(6)
S(5)-Cu(1)-S(8)	121.42(11)	Se(5)-Cu(1)-Se(8)	116.81(6)
S(8)-Cu(1)-S(4)	115.36(11)	Se(8)-Cu(1)-Se(4)	115.45(5)
S(4)-Cu(1)-As(4)	89.66(9)	Se(4)-Cu(1)-As(4)	88.69(6)
S(5)-Cu(1)-As(4)	119.66(8)	Se(5)-Cu(1)-As(4)	122.28(6)
S(8)-Cu(1)-As(4)	88.31(9)	Se(8)-Cu(1)-As(4)	91.15(6)

Table S3. Structural features of selected quaternary X/Cu/As/Q (X = inorganic cations; Q = chalcogen) system.

Compounds	Cu/As ratio	Crystal system	Space group	Structural dimension	Ref.
$VCu_{13}As_3S_{16}$	4.33	Cubic	$P\bar{4}3n$	3D	1
KCu_4AsS_4	4.0	Monoclinic	$P2_1$	3D	2
$RbCu_4AsS_4$	4.0	Monoclinic	$P2_1$	3D	2
KCu_2AsS_3	2.0	Triclinic	$P\bar{1}$	2D	2
$RbCu_2AsS_3$	2.0	Monoclinic	$P2_1/c$	2D	2
$CsCu_2AsS_3$	2.0	Orthorhombic	*Pbca*	2D	3
$Hg_3Cu_6As_4S_{12}$	1.5	Trigonal	*R*3	3D	4
$PbCuAsS_3$	1.0	Orthorhombic	$Pmn2_1$	3D	5
$PtCuAsS_3$	1.0	Monoclinic	*Cc*	3D	6
$Rb_8Cu_6As_8S_{19}$	0.75	Monoclinic	$P2_1$	2D	7
$Cs_3CuAs_4S_8$	**0.25**	**Monoclinic**	**$P2_1/c$ (14)**	**2D**	**This work**
$Cs_3CuAs_4Se_8$	**0.25**	**Monoclinic**	**$P2_1/c$ (14)**	**2D**	**This work**

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