

Supporting Information

A novel method for synthesis of MoSSe using $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_4\text{Se}_3\text{Br}_6]$ complex as the sole precursor

Dang B. Tran,^a Ly T. Le,^a Duc N. Nguyen,^a Quyen T. Nguyen,^a Ta Thi Thuy Nga,^{b,d} Wu-Ching Chou,^b Hoang H. Luc,^c Chung-Li Dong,^d Phong D. Tran^{a*}

^aUniversity of Science and Technology of Hanoi, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam. Email: tran-dinh.phong@usth.edu.vn

^bDepartment of Electrophysics, National Yang Ming Chiao Tung University, Hsinchu City 300093, Taiwan

^cInstitute of Natural Sciences, Hanoi National University of Education, 136 Xuan Thuy, Cau Giay, Hanoi, Vietnam

^dResearch Center for X-ray Science & Department of Physics, Tamkang University, New Taipei City 25137, Taiwan

I. Experimental Details

Synthesis of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$ complex

Ammonium polysulfide solution was prepared by dissolving 25 grams of sulfur powder into 120 mL of hot ammonium sulfide solution (48%). This mixture was stirred at 90°C for 30 minutes to produce a transparent and intense red solution. Subsequently, 6 grams of ammonium heptamolybdate tetrahydrate was dissolved completely in 30 mL of hot DI water. The obtained solution was added into the ammonium polysulfide solution, and the reaction mixture was refluxed for 20 hours at 90°C. When the reaction was over, the resultant dark red solution was

cooled to room temperature. It was then filtered to collect the red powder which was washed carefully with DI water (3 times), ethanol (3 times), carbon disulfide until the sulfur powder was completely removed from solid. The resultant $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$ powder was finally washed with diethyl ether (3 times), dried in vacuum and stored in a glovebox prior to use. Yield: 72% (6 grams).

It is noted that all apparatus was immersed into a Javel solution to eliminate the smell of sulfur-base compounds at the end of synthesis.

Synthesis of $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ complex

1 gram of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$ was dissolved in a concentrated HBr solution. The mixture was stirred and refluxed for 30 minutes at 90°C , then it was cooled down to 60°C . The warm solution was filtered to get the orange solution, followed by adding 1 gram of tetraethylammonium bromide. The obtained solution was stood overnight in fridge, leading to the separation of red crystals. Those crystals were filtered and washed with DI water (3 times), ethanol (3 times), acetonitrile (3 times) and diethyl ether (3 times). The dried product was recrystallized from acetonitrile – ethyl acetate solvent based on the slow diffusion method to collect the single crystal. To do this, one additional equivalence of tetraethylammonium bromide was added into the acetonitrile solution containing $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ before the vapor of ethyl acetate was driven to diffuse through this solution at 4°C . Yield: 50% (860 mg).

Synthesis of $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_4\text{Se}_3\text{Br}_6]$ complex

$\text{Se}=\text{PPh}_3$ was synthesized by refluxing a mixture of triphenyl phosphine and selenium powder with the molar ratio of 1 : 1.2 in acetonitrile. After 4 hours, the hot solution was filtered immediately to collect the white precipitate $\text{Se}=\text{PPh}_3$ and remove the excess of selenium powder. The white solid $\text{Se}=\text{PPh}_3$ separated from the resultant solution at room temperature. It was then collected and recrystallized from acetonitrile. Yield: 90%.

250 mg of $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ was dissolved entirely in acetonitrile (30 mL) until a transparent red-orange solution was formed. In the next step, 340 mg of $\text{Se}=\text{PPh}_3$ powder was added. The

reaction mixture was then refluxed for 1 hour. The obtained solution was cooled down to room temperature before 30mL of toluene was dropped gently on the top of reaction solution. The mixture was stored at 4°C overnight to get the red-brown powder of $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{Se}_3\text{S}_4\text{Br}_6]$. This product was filtered and washed by toluene (3 times), acetonitrile (3 times) and diethyl ether (3 times). The dried product was recrystallized from acetonitrile – toluene solvent based on the slow diffusion method to collect the single needle red crystal. Yield: 87% (230 mg).

Single Crystal X-ray Diffraction

Single Crystal X-ray Diffraction of the $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{Se}_3\text{S}_4\text{Br}_6]$ complex and the $(\text{Et}_4\text{N})_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ reference complex was collected by employing an Oxford-Diffraction XCalibur diffractometer with a Sapphire 3 CCD detector. The crystal was kept at 149(2) K during the data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization.

II. Supplementary Data

Crystal Data of $\text{C}_{16}\text{H}_{40}\text{Br}_6\text{Mo}_3\text{N}_2\text{S}_7$ ($M=1252.20$ g/mol): orthorhombic, space group Pbca (no. 61), $a = 19.0986(11)$ Å, $b = 12.9141(8)$ Å, $c = 29.880(2)$ Å, $V = 7369.7(8)$ Å³, $Z = 8$, $T = 273.15$ K, $\mu(\text{MoK}\alpha) = 7.921$ mm⁻¹, $D_{\text{calc}} = 2.257$ g/cm³, 97429 reflections measured ($5.306^\circ \leq 2\theta \leq 56.77^\circ$), 9191 unique ($R_{\text{int}} = 0.0450$, $R_{\text{sigma}} = 0.0254$) which were used in all calculations. The final R_1 was 0.0310 ($I > 2\sigma(I)$) and wR_2 was 0.0767 (all data).

Crystal Data of $\text{C}_{16}\text{H}_{40}\text{Br}_6\text{Mo}_3\text{N}_2\text{S}_4\text{Se}_3$ ($M=1392.90$ g/mol): orthorhombic, space group Pbca (no. 61), $a = 13.3937(6)$ Å, $b = 13.9303(6)$ Å, $c = 38.2930(11)$ Å, $V = 7144.6(5)$ Å³, $Z = 8$, $T = 149(2)$ K, $\mu(\text{Mo K}\alpha) = 11.052$ mm⁻¹, $D_{\text{calc}} = 2.590$ g/cm³, 16964 reflections measured ($4.35^\circ \leq 2\theta \leq 52.744^\circ$), 7286 unique ($R_{\text{int}} = 0.0906$, $R_{\text{sigma}} = 0.1396$) which were used in all calculations. The final R_1 was 0.0521 ($I > 2\sigma(I)$) and wR_2 was 0.0905 (all data).

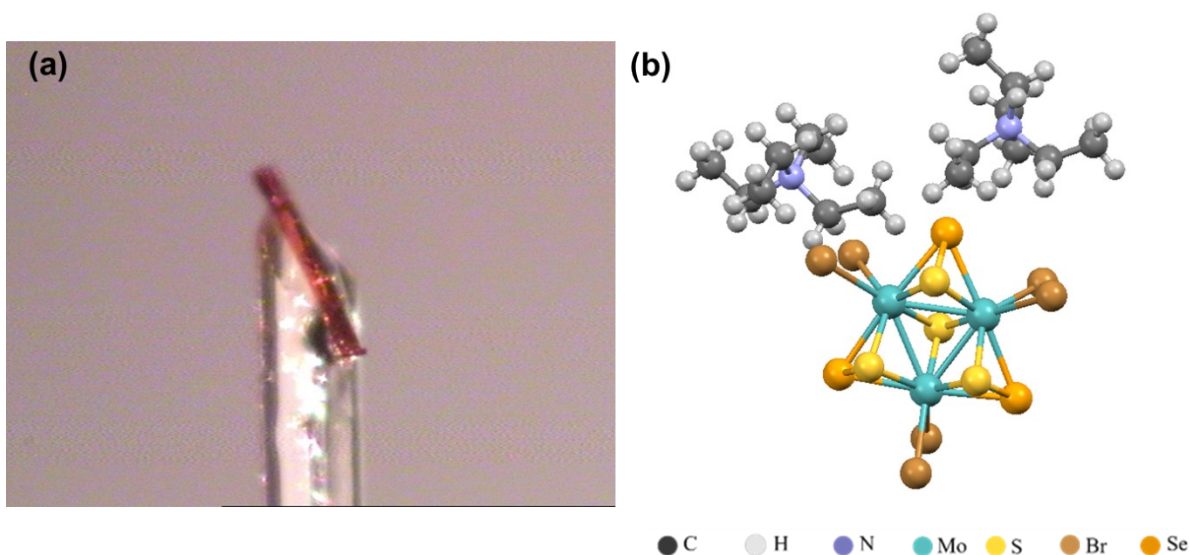


Figure S1. Optical micrograph of $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_4\text{Se}_3\text{Br}_6]$ single crystal (a) and its single structure constructed by single crystal XRD analysis and refinement (b).

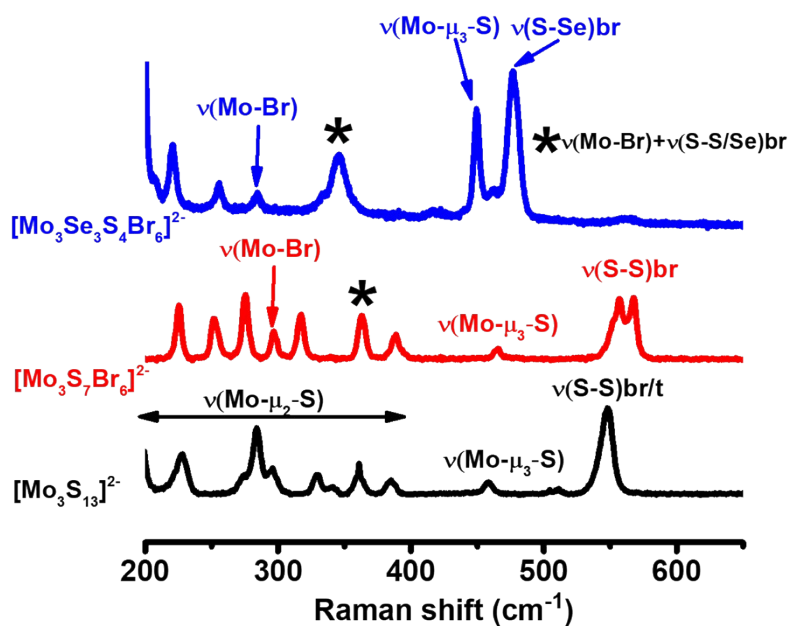


Figure S2. Raman spectra recorded for $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$, $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ and $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_4\text{Se}_3\text{Br}_6]$ complexes using a 532 nm green laser excitation. (“t” and “br” stands for terminal and bridging ligand).

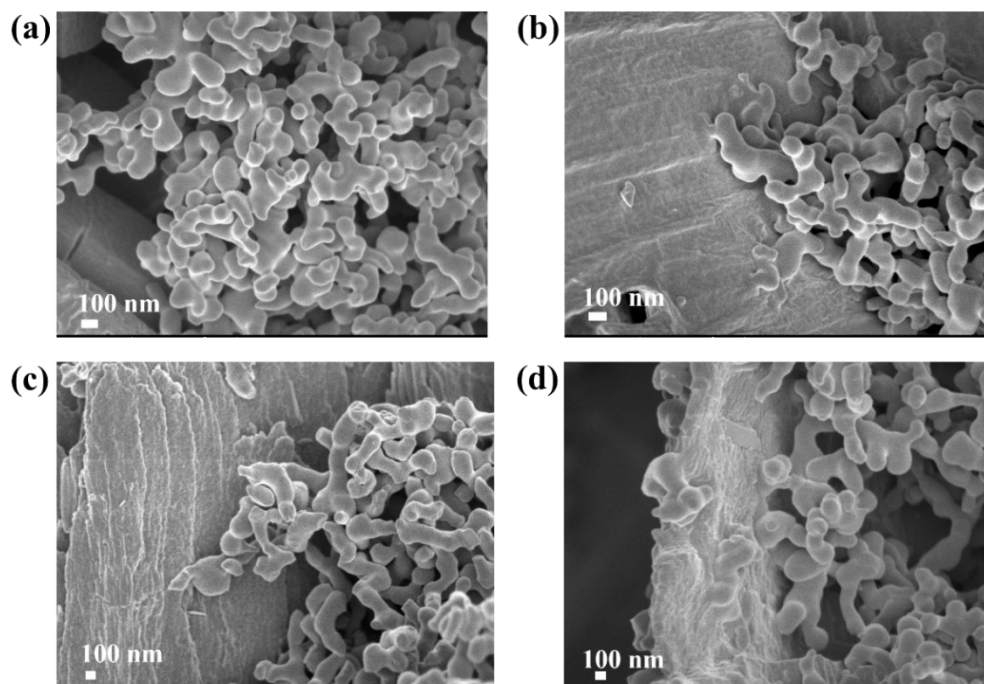


Figure S3. SEM images showing the morphology of (a) [MoSSe]-350, (b) [MoSSe]-450, (c) [MoSSe]-550, and (d) [MoSSe]-650 samples

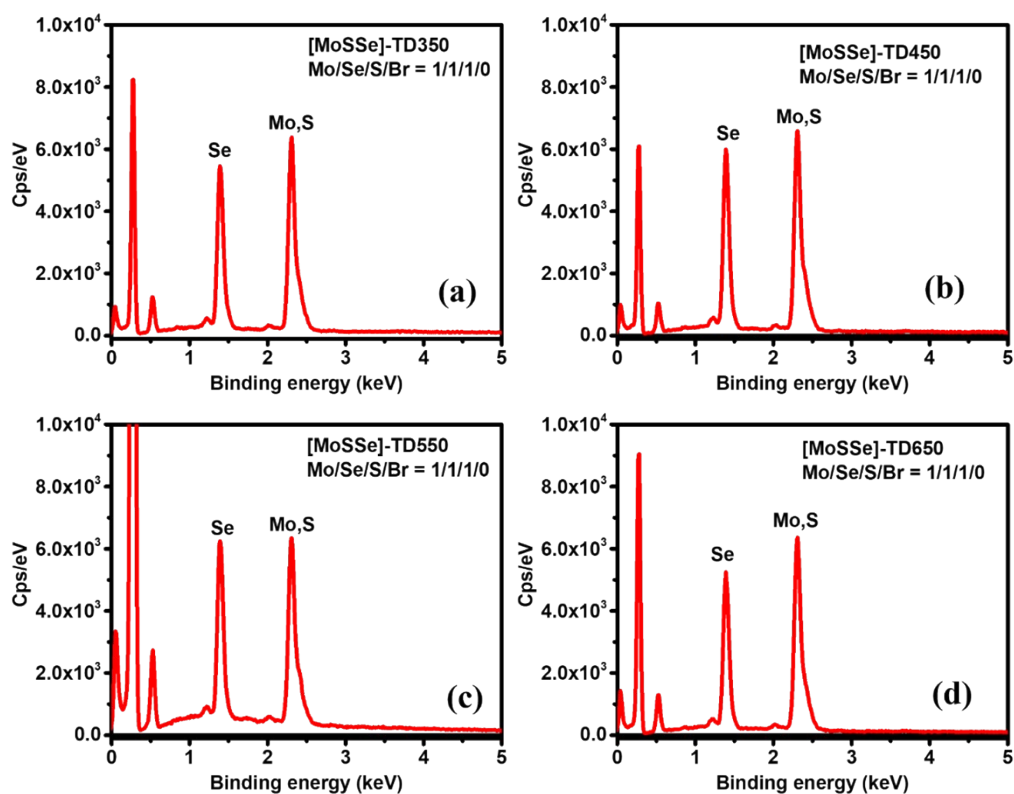


Figure S4. EDS analysis showing the element histograms of (a) [MoSSe]-350, (b) [MoSSe]-450, (c) [MoSSe]-550 and (d) [MoSSe]-650 samples

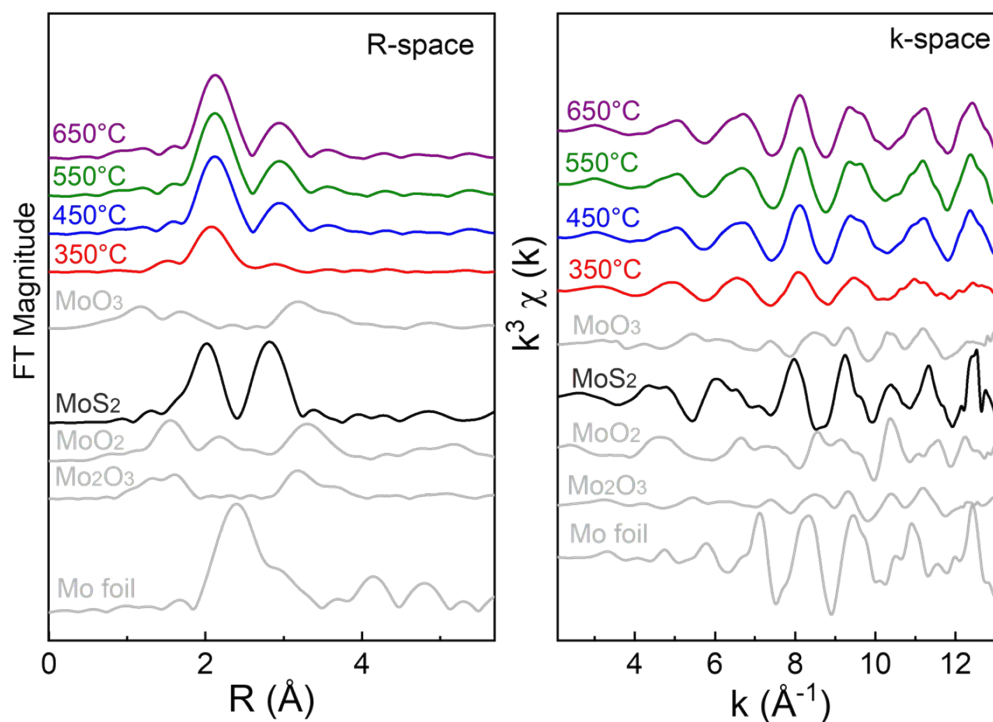


Figure S5. XAS FT-EXAFS (left panel) and corresponding EXAFS $k^3\chi(k)$ oscillations (right panel) of [MoSSe]-X along with various reference samples.

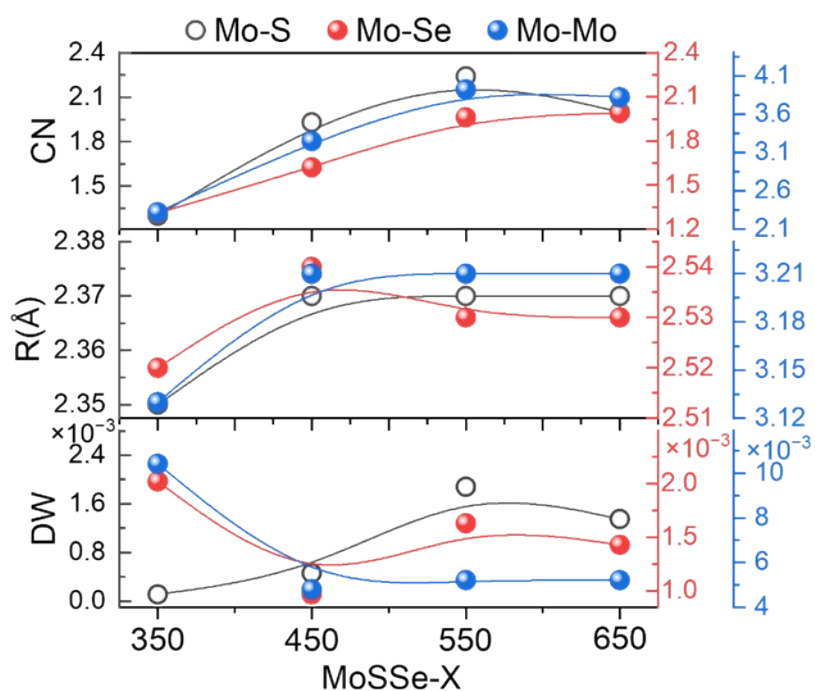


Figure S6. Plotting the coordination number, bond distance and Debye-Waller Factor of MoSSe-X samples obtained from the fitting

Table S1. Key bond length of [Et₄N]₂[Mo₃S₇Br₆] and [Et₄N]₂[Mo₃S₄Se₃Br₆] complexes

Bond	Bond length (Å)	
	[Et ₄ N] ₂ [Mo ₃ S ₇ Br ₆]	[Et ₄ N] ₂ [Mo ₃ S ₄ Se ₃ Br ₆]
Mo-Mo	2.75 – 2.76	2.77 – 2.78
Mo-μ ₃ -S	2.34 – 2.35	2.36
Mo-μ ₂ -S _{ax}	2.35 – 2.49	2.37 – 2.41
Mo-μ ₂ -S _{eq}	2.48 – 2.49	-
Mo-μ ₂ -Se _{eq}	-	2.61 – 2.62
S-S	2.02 – 2.03	-
S-Se	-	2.16 – 2.18
Mo-Br _{cis}	2.60	2.61 – 2.62
Mo-Br _{trans}	2.63 – 2.70	2.66 – 2.67

Table S2. Potential products generated during the thermal decomposition of molybdenum complexes in Ar atmosphere

Complex	Temperature (°C)	Mass loss (%)	Potential products
(NH ₄) ₂ [Mo ₃ S ₁₃]	25-300	4.67	(NH ₄)[Mo ₃ S _{12.5}](s) + 0.5H ₂ S(g) + NH ₃ (g)
	300-800	30.83	[Mo ₃ S ₆](s) + S(g) + 0.5H ₂ S(g) + NH ₃ (g)
[Et ₄ N] ₂ [Mo ₃ S ₇ Br ₆]	25-310	-	-
	310-800	60.16	[Mo ₃ S ₆](s) + 2C(s) + 7C ₂ H ₄ (g) + 6HBr(g) + 2NH ₃ (g) + H ₂ S(g) + H ₂ (g)
[Et ₄ N] ₂ [Mo ₃ S ₄ Se ₃ Br ₆]	25-270	-	-
	270-400	46.34	[Mo ₃ Se ₃ S ₃](s) + 6C•2C ₂ H ₄ (s) + 3C ₂ H ₄ (g) + 6HBr(g) + 2NH ₃ (g)
	400-800	4.21	[Mo ₃ Se ₃ S ₃](s) + 6C(s) + 2C ₂ H ₄ (g)

Table S3. Elemental analysis of [Et₄N]₂[Mo₃S₄Se₃Br₆] complex and [MoSSe]-X products using ICP-OES analysis

Compound	Mo (μg L ⁻¹)/1mg sample	S (μg L ⁻¹)/1mg sample	Se (μg L ⁻¹)/1mg sample	Atomic ratio Mo/S/Se
[Et ₄ N] ₂ [Mo ₃ S ₄ Se ₃ Br ₆]	38100	9350	31000	1/0.74/0.99
[MoSSe]-350	55000	8292	46250	1/0.45/1.02
[MoSSe]-450	87250	19675	74250	1/0.68/1.03
[MoSSe]-550	76538	14615	57308	1/0.57/0.91
[MoSSe]-650	50833	6500	42500	1/0.38/1.02

Table S4. Estimation of S/Se atomic ratio using XPS analysis result

RSF Se3p=2.65*	Concentration extracted from fitted envelopes				S:Se ratio
	S2p 3/2	S2p 1/2	Se3p 3/2	Se3p 1/2	
[MoSSe]-350	31.55	31.77	18.29	18.39	1.726281
[MoSSe]-450	24.76	24.93	25.08	25.22	0.987873
[MoSSe]-550	20.96	25.02	28.58	25.45	0.851009
[MoSSe]-650	19.58	24.16	32.13	24.14	0.777324
RSF Se3p=3.3**	S2p 3/2	S2p 1/2	Se3p 3/2	Se3p 1/2	S:Se ratio
[MoSSe]-350	34.02	34.26	15.86	15.86	2.152585
[MoSSe]-450	27.5	27.69	22.41	22.41	1.23137
[MoSSe]-550	23.46	28.01	25.74	22.79	1.060581
[MoSSe]-650	27.07	22.03	29.08	21.72	0.966535

*Referred from single crystal ZnSe; **Referred from powder CdSe

Table S5. Summary of fitting results obtained for MoSSe-X samples

Sample	Bond	CN = $N \times S_0^2$	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R - factor
MoSSe-350	Mo-S	1.30	2.35	0.00011	10.94	0.019
	Mo-Se	1.31	2.52	0.00202	-1.74	
	Mo-Mo	2.32	3.13	0.01042	-3.68	
MoSSe-450	Mo-S	1.93	2.37	0.00046	10.7	0.011
	Mo-Se	1.62	2.54	0.00097	9.03	
	Mo-Mo	3.25	3.21	0.0048	9.83	
MoSSe-550	Mo-S	2.24	2.37	0.00188	10.12	0.011
	Mo-Se	1.96	2.53	0.00163	8.94	
	Mo-Mo	3.92	3.21	0.00521	9.36	
MoSSe-650	Mo-S	2	2.37	0.00135	9.89	0.016
	Mo-Se	1.99	2.53	0.00143	8.03	
	Mo-Mo	3.82	3.21	0.00521	9.05	