Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Heterometallic chalcogenide oligomers as building blocks for an environmentally-friendly, low-cost, solar cells fabrication.

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S1- h- s oligomers formation domains.

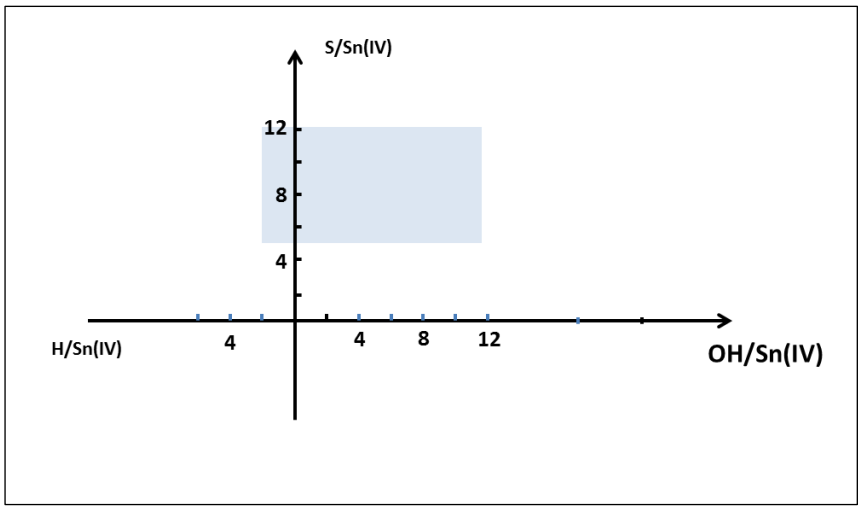

Figure S1a. h-s $(Sn_a–S_c)^{t-}$ oligomers formation domain. s denotes $[S^{2-}]/[Sn^{4+}]$ molar ratio and h = [H]/ $([Sn^{4+}])$ or [OH]/$([Sn^{4+}])$ molar ratios. [H], [OH] being the molar concentration in the metallic solution. The h-s formation domain is determined at $^{-}[Sn^{4+}]$ = 0.1M. Blue area depicts the as-synthesized limpid solutions.

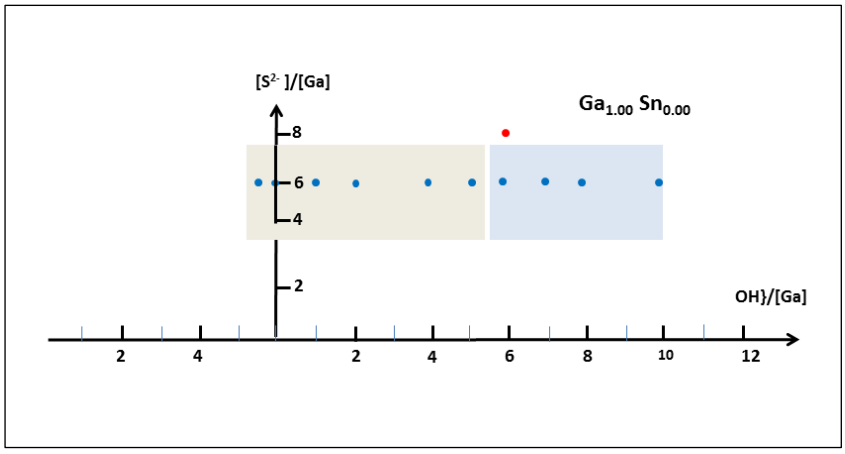

Figure S1b. Figure S1b: h-s $(Ga_a–S_c)^{t-}$ oligomers formation domain. s denotes $[S^{2-}]/[Ga^{3+}]$ molar ratio and h = [H]/ $([Ga^{3+}])$ or [OH]/$([Ga^{3+}])$ molar ratios. [H], [OH] being the molar concentration in the metallic solution. The h-s formation domain is determined at $^{-}[Ga^{3+}]$ = 0.1 M. The colored areas depict the domain of limpid oligomer solutions. Blue area: as-synthesized limpid solutions. Grey area: limpid solutions in low ionic strength conditions

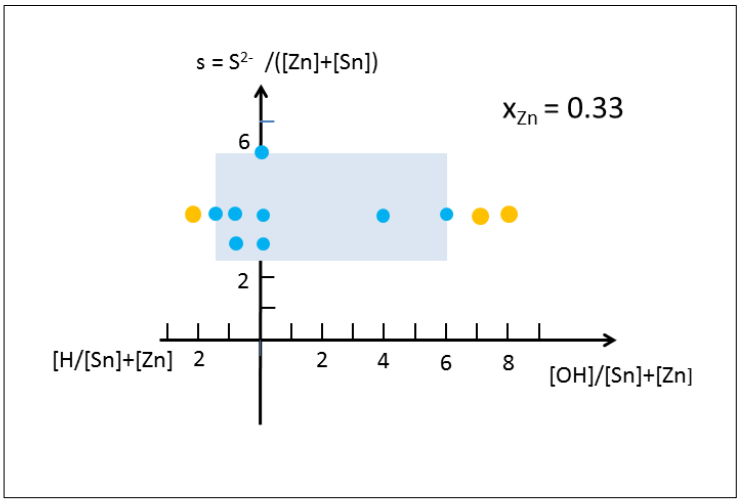

Figure S1c. Typical $(Sn_a–Zn_b–S_c)^{t-}$ oligomers formation domain, x_{Zn}= 0.33. s denotes $[S^{2-}]/[Sn^{4+}]+[Zn^{2+}]$ molar ratio and h = [H]/ $([Sn^{4+}]+[Zn^{2+}])$ or $[OH]/([Sn^{4+}]+[Zn^{2+}])$. [H], [OH] being the molar concentration in the metallic solution. Total metal concentration of the reaction mixtures is 0.1 M. The blue area represents the oligomer formation domain. pH values were ranging from 8.6 ([H]/[Sn]+[Zn] = 1.5) to 11.6 ([OH]/[Zn]+[Sn] = 6).

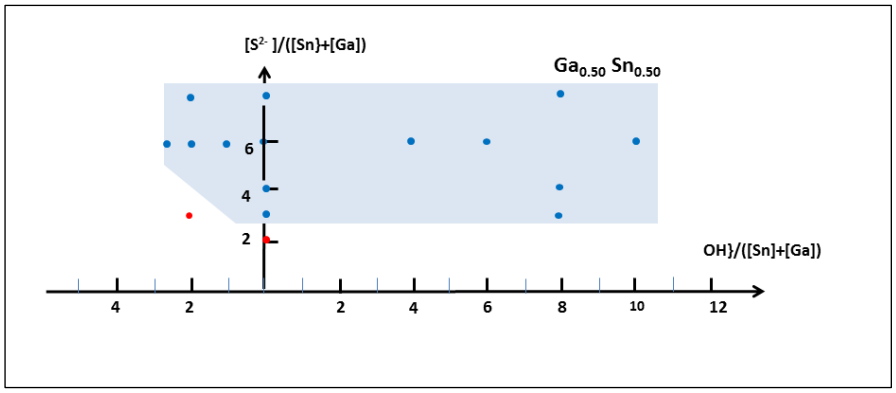

Figure S1d. Typical $(Sn_a–Ga_b–S_c)^{t-}$ oligomer formation domain, x_{Ga}= 0.5, showing successful preparation of limpid dispersions in a large range of [OH]/ ([Sn]+[Ga]) values, ([Sn]+[Ga]) = 0.1 M.

S2- ESI-MS spectrum of $(Sn_a–S_c)^{t-}$ prepared in highly basic pH

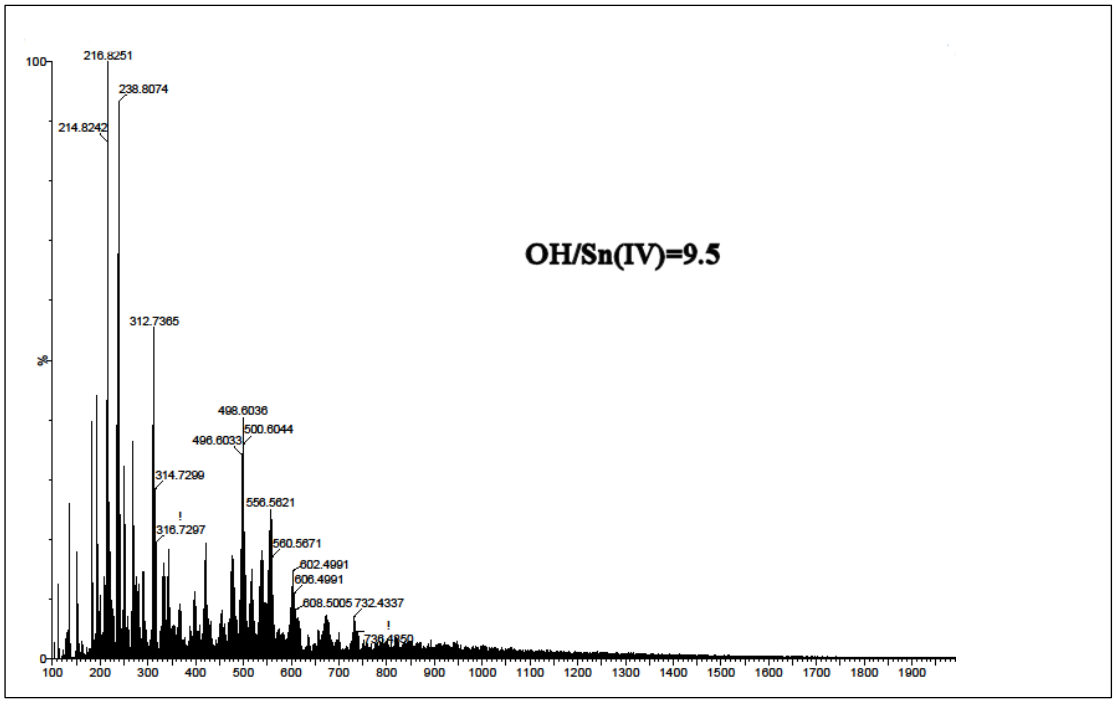

Figure S2. Negative ion ESI-MS experimental spectrum of $(Sn_aZn_bS_c)^{t-}$ oligomer, x $_{Zn}$=0, Sn(IV)= 0.1M and OH/Sn= 9.5 molar. The OH/Sn ratio was adjusted using NaOH. We can observe m/z= 398.4 $(Sn_2S_5H)^-$, m/z= 420.4 $(Sn_2S_5Na)^-$ m/z= 581 $(Sn_3S_7H)^-$, m/z= 602.5 $(Sn_3S_7Na)^-$. On can note that $(Sn_4S_{10}H_3)^-$ tetramers m/z= 798.3 are not observed in highly basic conditions.

S3- Confirmation of chemical composition. Comparison of ESI-MS experimental isotopic distribution with theoretical spectra.

S3-1- Monometallic oligomers

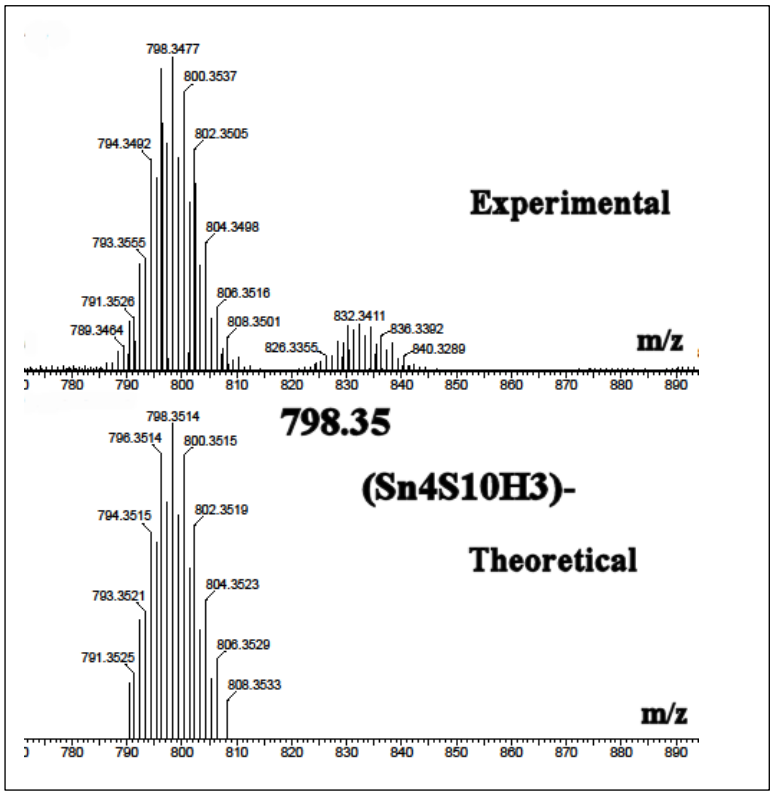

Figure S3a. Confirmation of chemical composition for m/z= 798.35 $(Sn_4S_{10}H_3)^-$, detected by ESI-MS.

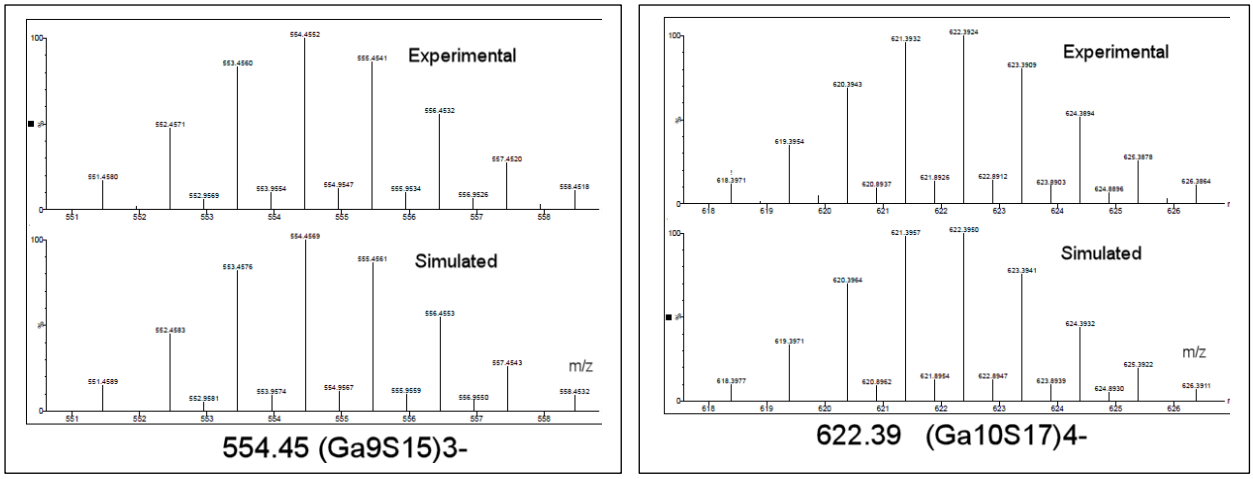

Figure S3b. Confirmation of chemical composition (A) for m/z= 554.45 $(Ga_9S_{15})^{3-}$, (B) for m/z= 622.39 $(Ga_{10}S_{17})^{4-}$, detected by ESI-MS.

3-2-($Sn_aZn_bS_c)^{t-}$ et ($Sn_aZn_bSe_c)^{t-}$ oligomers.

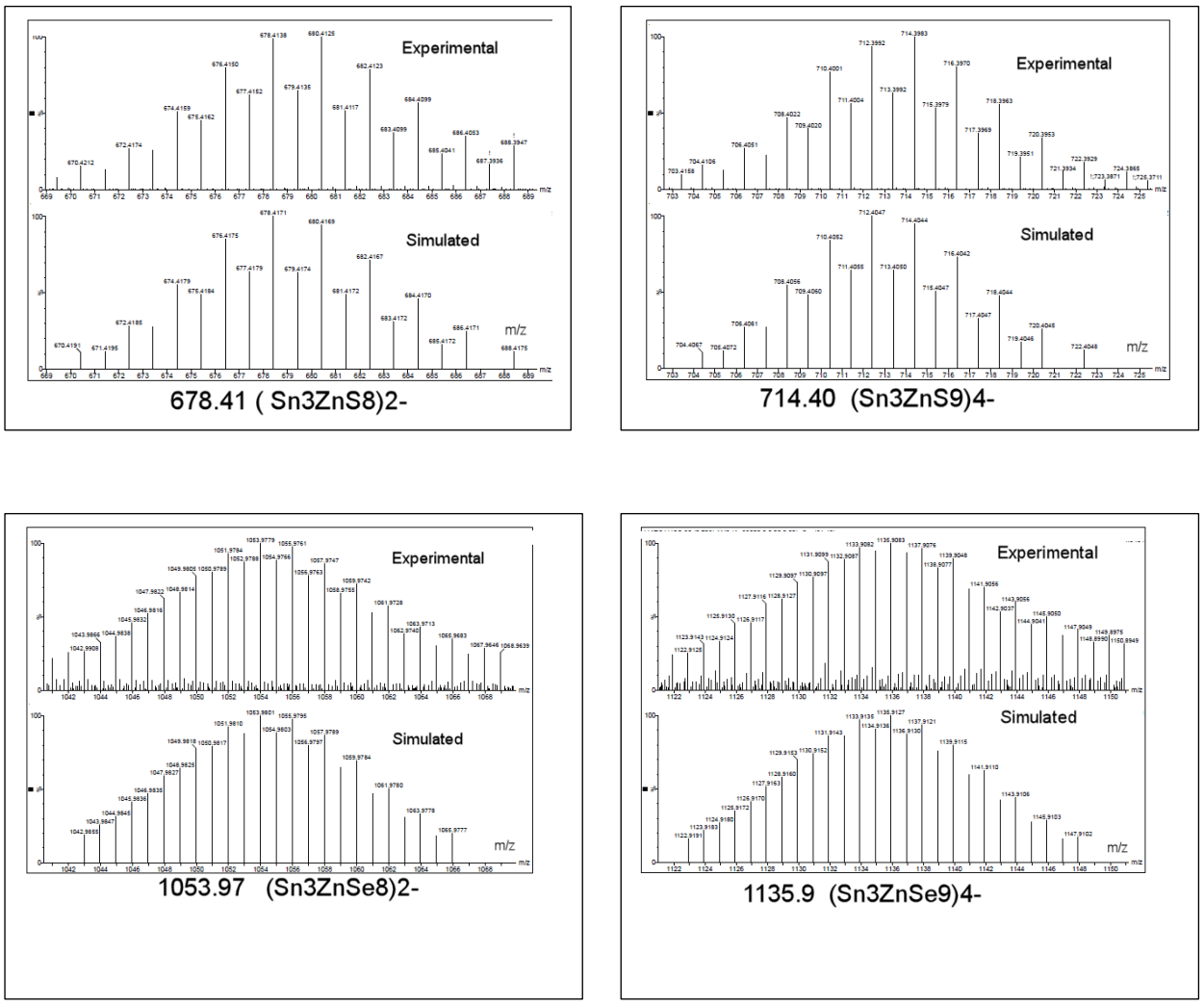

Figure S3c. Confirmation of chemical composition (A) for m/z = 678.41 $(Sn_3\ Zn_1S_8)^{2-}$, (B) for m/z = 714.40 $(Sn_3\ Zn_1S_9)^{4-}$ (C) for m/z = 1053.97 $(Sn_3\ Zn_1Se_8)^{2-}$, (D) for m/z = 1135.9$(Sn_3\ Zn_1Se_9)^{4-}$detected by ESI-MS.

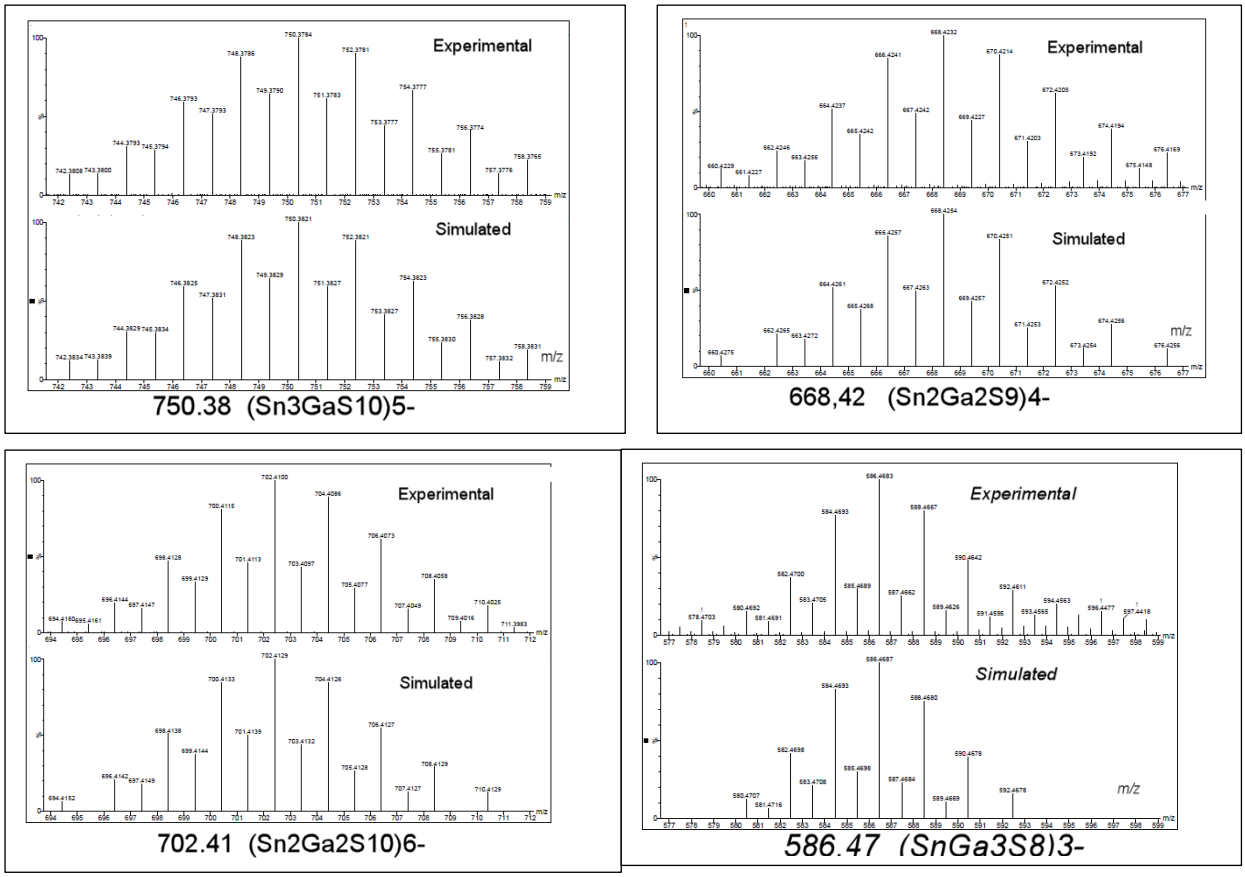

Figure S3d. Confirmation of chemical composition (A) for m/z = 750.38 $(Sn_3\ Ga_1S_{10})^{5-}$, (B) for m/z = 668.42 $(Sn_2\ Ga_2S_9)^{4-}$ (C) for m/z = 702.41 $(Sn_2\ Ga_2S_{10})^{6-}$, (D) for m/z = 586.47 $(Sn\ Ga_3S_8)^{3-}$detected by ESI-MS.

S4- $(Sn_a–Zn_b–S_c)^{t-}$ oligomers-capped ZnS colloids

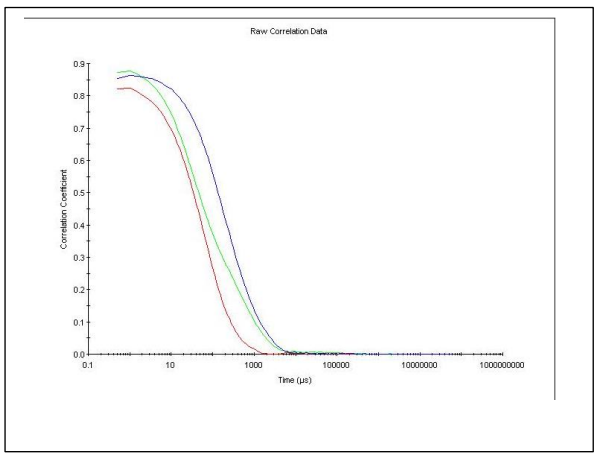

Figure S4. Correlogramms recorded by dynamic light scattering on Sn(IV)-Zn(II)-S dispersions showing monodisperse size distribution for $0.2 < x_{Zn} < 0.50$ and an increase

average hydrodynamic diameter with x_{Zn}. Corresponding hydrodynamic diameters of 4.25 nm, 5.5 nm and 18.5 nm were respectively determined for x_{Zn}= 0.5 (s= 6, red curve) x_{Zn}= 0.66 (s= 4, green curve) x_{Zn}= 0.66 (s= 6, Blue curve).

S5- DFT results.

Oligomers	Frequency, cm^{-1} (Raman Scattering Activity >20 $a^4.amu^{-1}$)
$(Sn_4S_{10})^{4-}$	70.4(22) 72.6(22) 96.7(33) 98.4(34) 99.0(32) 133.0(99) 287.2(88) **287.7**(318) **289.5**(63) 301.2(29) 302.9(26) **338.8**(46) **339.4**(47) **340.5**(47) **386.0**(92) **386.5**(92) **387.0**(88) **393.9**(408) Main peak: **390**
*$(Sn_3GaS_{10})^{5-}$	74.3(22) 98.9(23) 99.8(29) 108.5(32) **140.6**(74) 274.2(34) **287.6**(315) 292.2(33) 293.9(47) 321.5(35) 324.0(40) **350.8**(375) **372.8**(113) **375.4**(102) **377.0**(204) **388.2**(151) Main peak: **372**
*$(Sn_2Ga_2S_{10})^{6-}$	105.2(32) 147.0(63) 272.3(52) **279.1**(57) **281.9**(118) **298.0**(70) 303.7(32) 327.9(27) 330.3(38) **337.8**(387) 351.1(91) **359.6**(120) **361.3**(210) **374.3**(106) Main peak **343**
$(SnGa_3S_{10})^{7-}$	100.7(22) **148.9**(57) 258.9(21) **277.6**(118) 294.6(45) **325.6**(355) **330.3**(98) **333.2**(88) **341.0**(138) **349.4**(63) 353.4(57) Main peak: **329**
$(Ga_4S_{10})^{8-}$	151.9(58) 267.2(27) 277.8(45) **280.7**(110) 295.2(21) 310.1(55) **312.7**(78) **314.8**(68) 330.0(32) 330.7(76) Main peak: **310**

Table S5. Calculated Raman shift and scattering activities of $(Sn_aGa_bS_c)^{t-}$ adamantane –like structures. * denote oligomers observed by mass spectrometry. The frequency of main peak has been determined by convoluting Lorentzian functions whose amplitudes are proportional to computed Raman activity intensities and a half-band width of 20 cm^{-1}. Increase of the number of substituted Ga cations into the adamantane-like structure clearly results in a decrease of the frequency of the Raman main peak.

Cartesian Coordinates of DFT-Optimized Compounds and There Related Energies. 8

$[SnSe_3]^{2-}$

4
scf done: -31.991577

Sn	0.490921	-0.248044	-0.371230
Se	2.665337	-0.086782	0.764849
Se	-0.673701	-2.409616	-0.493915
Se	-0.519382	1.752668	-1.382976

$[SnSe_4]^{4-}$

5
scf done: -41.679006

Sn	0.301056	-0.119670	0.178351
Se	-0.726686	0.404852	2.464426
Se	2.854166	-0.179276	0.384191
Se	-0.534169	-2.404561	-0.628920
Se	-0.386572	1.684144	-1.503468

$[Sn_2Se_5]^{2-}$

12
scf done: -3423.503759

Zn	0.035128	-0.286652	-0.477250
S	2.229832	0.321887	-0.811671
S	-0.952851	-2.353384	-0.739872
S	-1.600291	1.571050	-0.925008
Sn	2.313362	0.145488	-3.212983
Sn	-0.815405	-2.556558	-3.137441
Sn	-1.273261	1.134293	-3.174278
S	4.335352	0.635105	-4.208283
S	0.698452	1.900482	-4.221145
S	-1.607630	-4.516353	-4.057786
S	1.425335	-2.009264	-4.020390
S	-2.332433	-0.725598	-4.171111

lin-$[Sn_4Se_{10}]^{4-}$

14
scf done: -108.676640

Sn	0.072410	-0.194489	-0.198413
Se	-0.621784	0.367216	2.323374
Se	2.679248	-0.169226	0.404535
Se	-0.653946	-2.490249	-0.802350
Se	-0.490592	1.707229	-1.691116
Sn	1.881709	0.351512	2.761370
Se	2.850891	2.490727	3.839126
Se	2.692145	-1.263953	4.609212

Sn	3.661303	0.875266	5.686982
Se	2.863717	1.396005	8.043802
Se	6.164787	0.859571	6.125023
Sn	5.470544	1.421292	8.646794
Se	6.033535	-0.480410	10.139521
Se	6.196875	3.717062	9.250724

ada-$[Sn_4Se_{10}]_{4-}$

14
scf done: -108.694776

Sn	-0.045393	-0.196485	0.035593
Se	-0.042109	-0.122814	2.509769
Se	2.370392	0.244251	-0.775517
Se	-0.850539	-2.540276	-0.699554
Se	-1.654386	1.639547	-0.815407
Sn	2.307541	0.158294	-3.358562
Sn	-0.831520	-2.548833	-3.285153
Sn	-1.610370	1.523236	-3.398117
Se	4.598545	0.573143	-4.199431
Se	0.764593	2.008064	-4.300225
Se	-1.603016	-4.774766	-4.045891
Se	1.562830	-2.174962	-4.187928
Se	-3.132941	3.269215	-4.270786
Se	-2.458141	-0.773759	-4.230101

ada-$[Sn_3ZnSe_9]^{4-}$

13
scf done: -323.075542

Zn	-0.026327	-0.218036	-0.582476
Se	2.391762	0.260094	-0.683679
Se	-0.846429	-2.547937	-0.600183
Se	-1.689017	1.621990	-0.725405
Sn	2.336592	0.169684	-3.221688
Sn	-0.846383	-2.569038	-3.140102
Sn	-1.634335	1.552683	-3.260409
Se	4.564965	0.555783	-4.269535
Se	0.757716	1.998328	-4.195419
Se	-1.599263	-4.738968	-4.108279
Se	1.544353	-2.154260	-4.090127
Se	-3.103054	3.247253	-4.347079
Se	-2.430792	-0.764000	-4.149377

ada-$[Sn_3Zn_2Se_8]^{4-}$

12
scf done: -537.441905

Zn	-0.108019	-0.394546	-0.590756	10
Se	2.334172	0.184271	-0.748642	
Se	-0.894929	-2.694482	-0.563477	
Se	-1.666603	1.576438	-0.777666	
Sn	2.328744	0.077750	-3.302088	
Zn	-0.616565	-1.916775	-2.861563	
Sn	-1.684989	1.470255	-3.331981	
Se	4.579428	0.644031	-4.251431	
Se	0.734367	1.937715	-4.240725	
Se	1.526210	-2.204890	-4.112203	
Se	-3.065491	3.303781	-4.340378	
Se	-2.447274	-0.831005	-4.144570	

ada-$[Sn_4S_{10}]^{4-}$

14

scf done: -3996.440783

Sn	-0.045571	-0.197010	-0.037223
S	-0.043359	-0.134519	2.282352
S	2.230653	0.202809	-0.876754
S	-0.809341	-2.405273	-0.802876
S	-1.548658	1.540028	-0.915683
Sn	2.238132	0.148943	-3.333293
Sn	-0.808434	-2.486001	-3.260757
Sn	-1.564648	1.469116	-3.375210
S	4.385564	0.542027	-4.119568
S	0.718189	1.878043	-4.193990
S	-1.530426	-4.571688	-3.976479
S	1.466521	-2.058404	-4.093282
S	-2.992447	3.104519	-4.195710
S	-2.320688	-0.748736	-4.122837

lin-$[Sn_4S_{10}]^{4-}$

14

scf done: -3996.415696

Sn	0.155596	-0.167751	-0.060806
S	-0.448613	0.386829	2.397748
S	2.661039	-0.113633	0.595367
S	-0.492176	-2.348647	-0.556529
S	-0.339933	1.646592	-1.433553
Sn	1.905546	0.369671	2.809935
S	2.841309	2.372838	3.876938
S	2.701807	-1.146047	4.571345
Sn	3.637521	0.857128	5.638377
S	2.881917	1.340431	7.852908
S	5.991659	0.839999	6.050677
Sn	5.387321	1.394540	8.509212
S	5.882790	-0.419823	9.881952

S	6.035060	3.575427	9.005013	11

ada-$[Ga_4S_{10}]^{8-}$

14
scf done: -4289.678285

Ga	-0.048278	-0.199922	-0.145783
S	-0.054905	-0.141517	2.154112
S	2.141572	0.197329	-0.945958
S	-0.771605	-2.330249	-0.865324
S	-1.517591	1.461282	-0.968514
Ga	2.137752	0.126645	-3.308676
Ga	-0.771182	-2.390024	-3.226804
Ga	-1.495285	1.408863	-3.333297
S	4.270751	0.497995	-4.092348
S	0.698386	1.821816	-4.126460
S	-1.500104	-4.461899	-3.911871
S	1.420916	-2.009943	-4.024927
S	-2.938501	3.018885	-4.127960
S	-2.196441	-0.715407	-4.097499

lin-$[Ga_4S_{10}]^{8-}$

14
scf done: -4289.688653

Ga	0.318252	-0.121248	0.143820
S	-0.368930	0.381423	2.440665
S	2.676240	-0.148305	0.785876
S	-0.410283	-2.192581	-0.538369
S	-0.146887	1.623550	-1.275987
Ga	1.903319	0.351485	2.914798
S	2.772330	2.298780	3.919606
S	2.628682	-1.104489	4.622407
Ga	3.551458	0.835839	5.593632
S	2.888467	1.288420	7.769466
S	5.844862	0.843149	5.944535
Ga	5.279313	1.363529	8.265452
S	5.913362	-0.309381	9.702483
S	5.950658	3.477385	8.850199

ada-$[Sn_3GaS_{10}]^{5-}$

14
scf done: -4069.772394

Ga	-0.044505	-0.197220	-0.054129
S	-0.060936	-0.135415	2.167095
S	2.154278	0.197562	-0.862551
S	-0.765354	-2.335639	-0.789762
S	-1.502419	1.476384	-0.896406
Sn	2.224056	0.145687	-3.278747

Sn	-0.801077	-2.472845	-3.203963	12
Sn	-1.555729	1.462848	-3.314713	
S	4.368609	0.535689	-4.127189	
S	0.711045	1.857243	-4.219975	
S	-1.530305	-4.555076	-3.980774	
S	1.456577	-2.048429	-4.121530	
S	-2.976341	3.099144	-4.197472	
S	-2.302412	-0.746077	-4.141194	

ada-$[Sn_2Ga_2S_{10}]^{6-}$

14
scf done: -4143.088763

Ga	0.003219	-0.187702	-0.086636
S	-0.068826	-0.141748	2.157065
S	2.130449	0.202744	-0.950363
S	-0.789343	-2.335521	-0.788285
S	-1.532111	1.462330	-0.895661
Ga	2.212393	0.146276	-3.276082
Sn	-0.750248	-2.453037	-3.214775
Sn	-1.497326	1.462030	-3.325666
S	4.276518	0.505476	-4.090434
S	0.748743	1.808991	-4.186581
S	-1.526651	-4.547493	-3.977917
S	1.467274	-1.979334	-4.088081
S	-2.970596	3.091084	-4.190593
S	-2.328008	-0.750241	-4.107300

ada-$[SnGa3S_{10}]^{7-}$

14
scf done: -4216.390241

Sn	-0.041044	-0.199942	-0.125233
S	-0.028077	-0.139940	2.257084
S	2.222078	0.212197	-0.941285
S	-0.813247	-2.390412	-0.874442
S	-1.559516	1.509799	-0.981879
Ga	2.145975	0.130566	-3.357426
Ga	-0.783706	-2.399588	-3.289969
Ga	-1.503685	1.407879	-3.399426
S	4.267447	0.500555	-4.082329
S	0.699740	1.828519	-4.091419
S	-1.493000	-4.467480	-3.911495
S	1.413102	-2.001511	-4.002732
S	-2.931792	3.015111	-4.141405
S	-2.218788	-0.721897	-4.079354

S6- TGA and XRD obtained after thermal decomposition of the hetero-metallic chalcogenide oligomers. 13

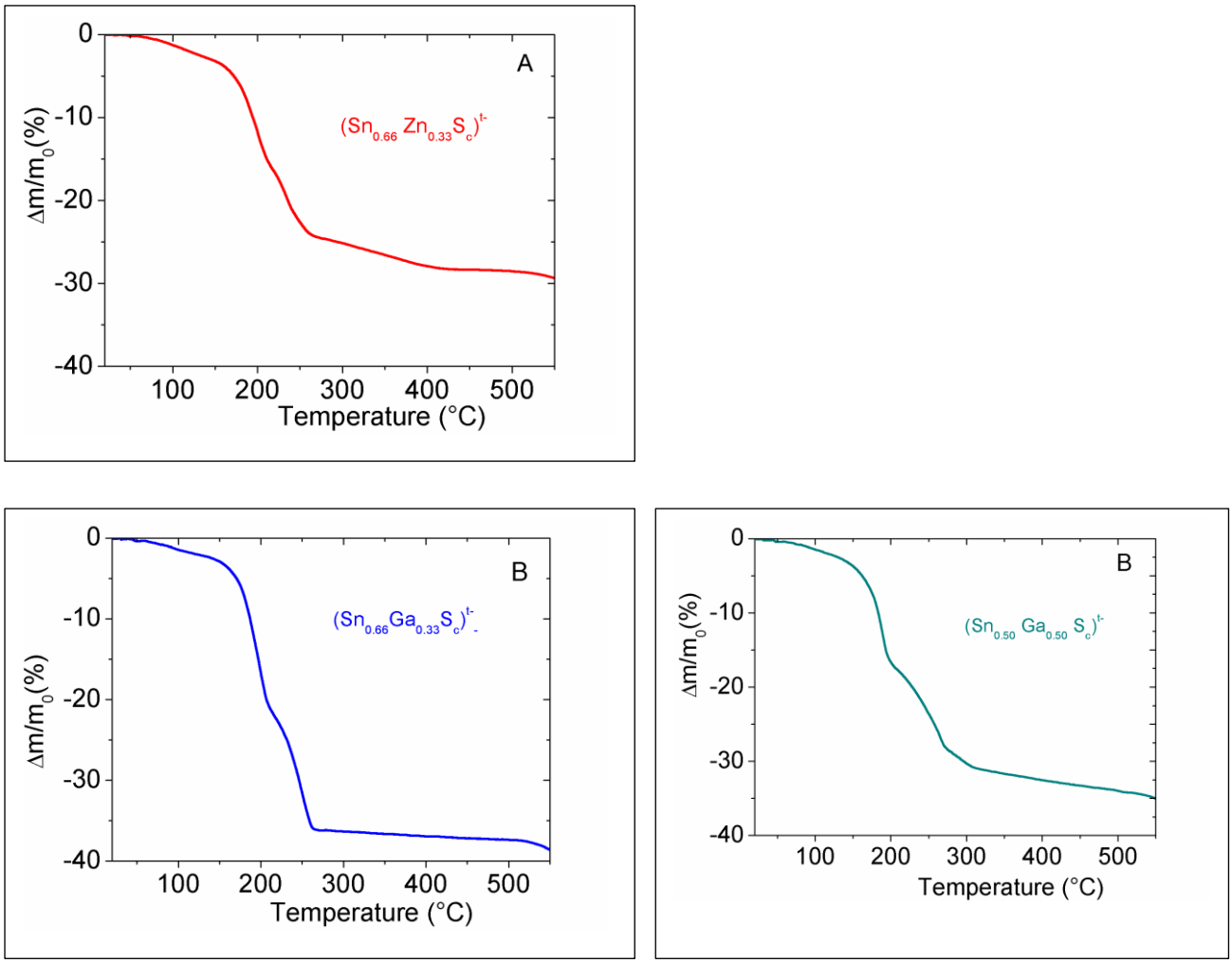

Figure S6-a: TGA curves recorded on (A): NH_4Cl-$(NH_4)_2S$-$(Sn_aZn_bS_c)^{t-}$ and (B): NH_4Cl-$(NH_4)_2S$-$(Sn_aGa_bS_c)^{t-}$ solid samples showing two decomposition temperatures occurring at T< 250 °C. $(Sn_aZn_bS_c)^{t-}$ oligomers were prepared at x_{Zn}= 0.33, ([Zn]+[Sn])= 0.2M, s= $(NH_4)_2S$/([Sn]+[Sn])= 6). $(Sn_aGa_bS_c)^{t-}$ oligomers were synthesized at x_{Ga}= 0.33 (Sn+Ga= 0.40M, s= 6) and x_{Ga}= 0.50 (Sn+Ga= 0.35M, s= 6). The solid samples were collected after evaporating the oligomer solutions at room temperature during 16 h, centrifugation at 4500 rpm, 10 min and drying at 30 °C under air atmosphere. TGA curves were recorded under N_2 at heating rate v= 0.5 °C min^{-1}.

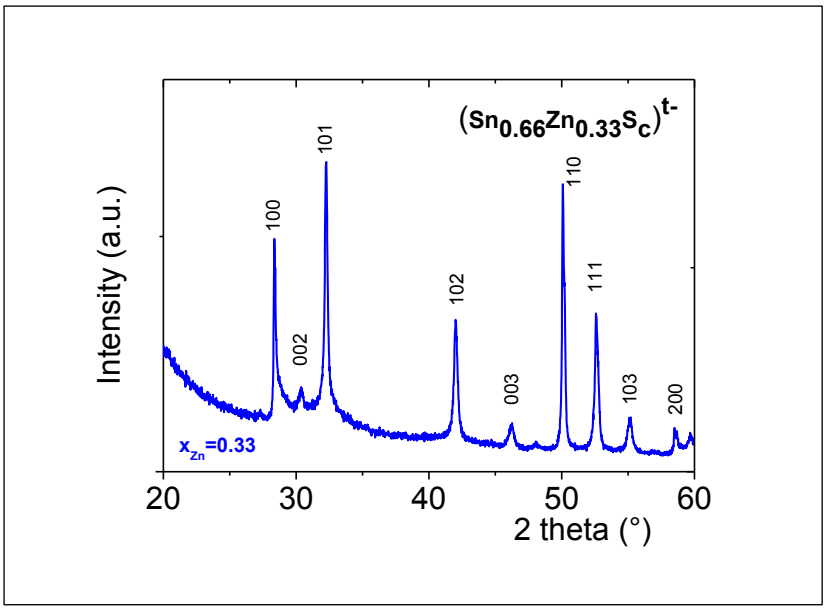

Fig S6-b: X-ray diffractogram recorded on $(Sn_aZn_bS_c)^{t-}$, x_{Zn}= 0.33 solid oligomer after calcination at 550 °C 2h under N_2. Decomposition into the parent metal chalcogenides is observed resulting for x_{Zn}=0.33 in the formation of a SnS_2 solid solution (Hexagonal , 00-022-0951).

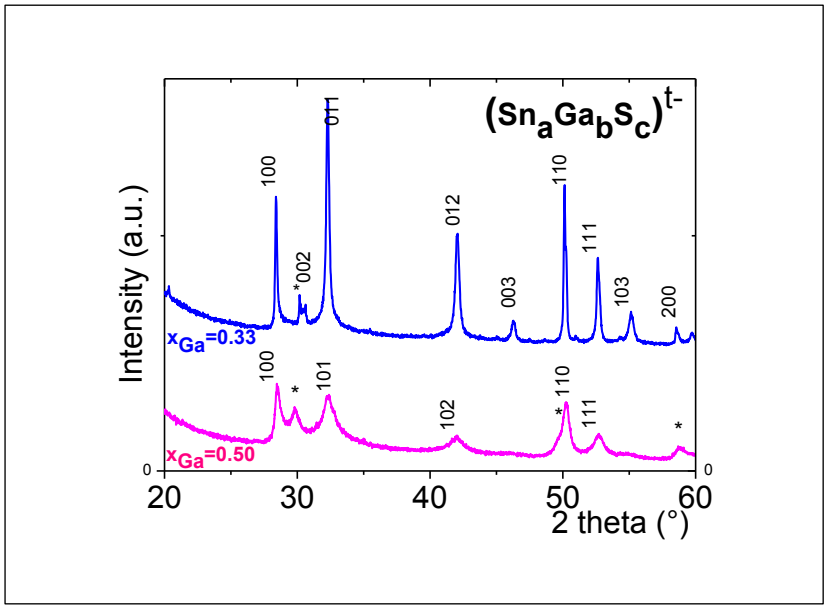

Fig S6-c: X-ray diffractogram recorded on $(Sn_aGa_bS_c)^{t-}$, x_{Ga} = 0.33 and x_{Ga}= 0.55 solid oligomers after calcination at 550 °C 2h under N_2. $Sn_{1,x}Ga_xS_2$ solid solution (SnS_2 Hexagonal, 01-089-2358) and trace of Ga_2S_3 (Cubic, 03-065-7839) are observed for the sample prepared at x_{Ga}= 0.33 while Ga_2S_3 (Cubic, 00-043-0916) and SnS_2 (Hexagonal, 00-040-1467) structures are identified at x_{Ga}= 0.50. Note the better crystallization of the sample prepared at x_{Ga}= 0.33.

S7- Low-chloride hetero-metallic oligomers solutions preparation for infiltration **15**

The $(Sn_a–Zn_b–S_c)^{t-}$ hetero-metallic oligomers were used as composition additives to fine tune the Cu non stoichiometry of CZTS nanocrystals films. To avoid chloride contamination of CZTS nanocrystals films, a procedure was developed for the synthesis of low-chloride hetero-metallic oligomers solutions. Oligomer solutions with concentration close to the solubility limit as indicated in the oligomers formation domain were prepared. Room-temperature evaporation under stirring of these solutions yields super-saturated oligomers solutions which precipitate with time (t= 16 h). The solid precipitate was isolated and re-dispersed in a diluted $(NH_4)_2S$ solution producing low chloride oligomer solutions displaying total metal cations concentration larger than 0.5 M. In a typical synthesis, a 0.2 M solution of $(Sn_a–Zn_b–S_c)^{t-}$, x_{Zn}= 0.33, oligomers are prepared at 0.2 M ([Sn]+[Zn]). The oligomer solution is evaporated at room temperature overnight under stirring. The solid precipitate (4.16 g) is isolated by centrifugation at 4500 rpm. The $(Sn_a–Zn_b–S_c)^{t-}$ oligomer solution is obtained by re-dissolution in 0.02 M $(NH_4)_2S$ solution.

S8- Solar cells characteristics

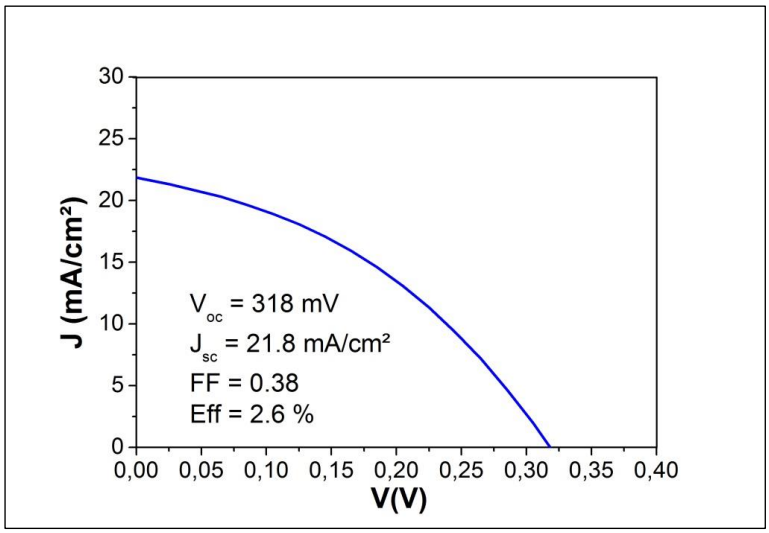

Figure S8. Current voltage curve and solar cell characteristics for the Mo/CZTSSe/CdS/ ZnO: ZnO/Al cell.