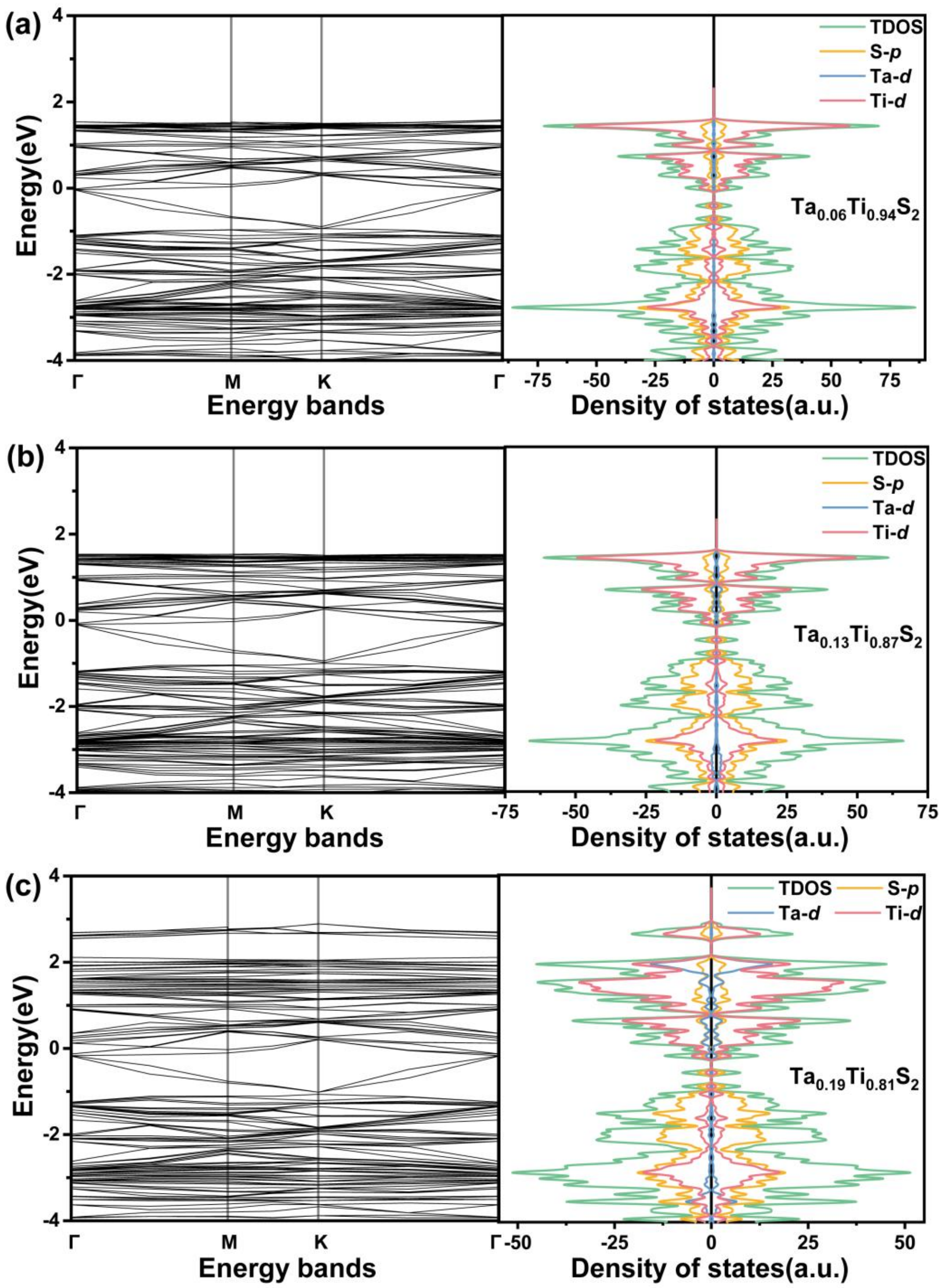
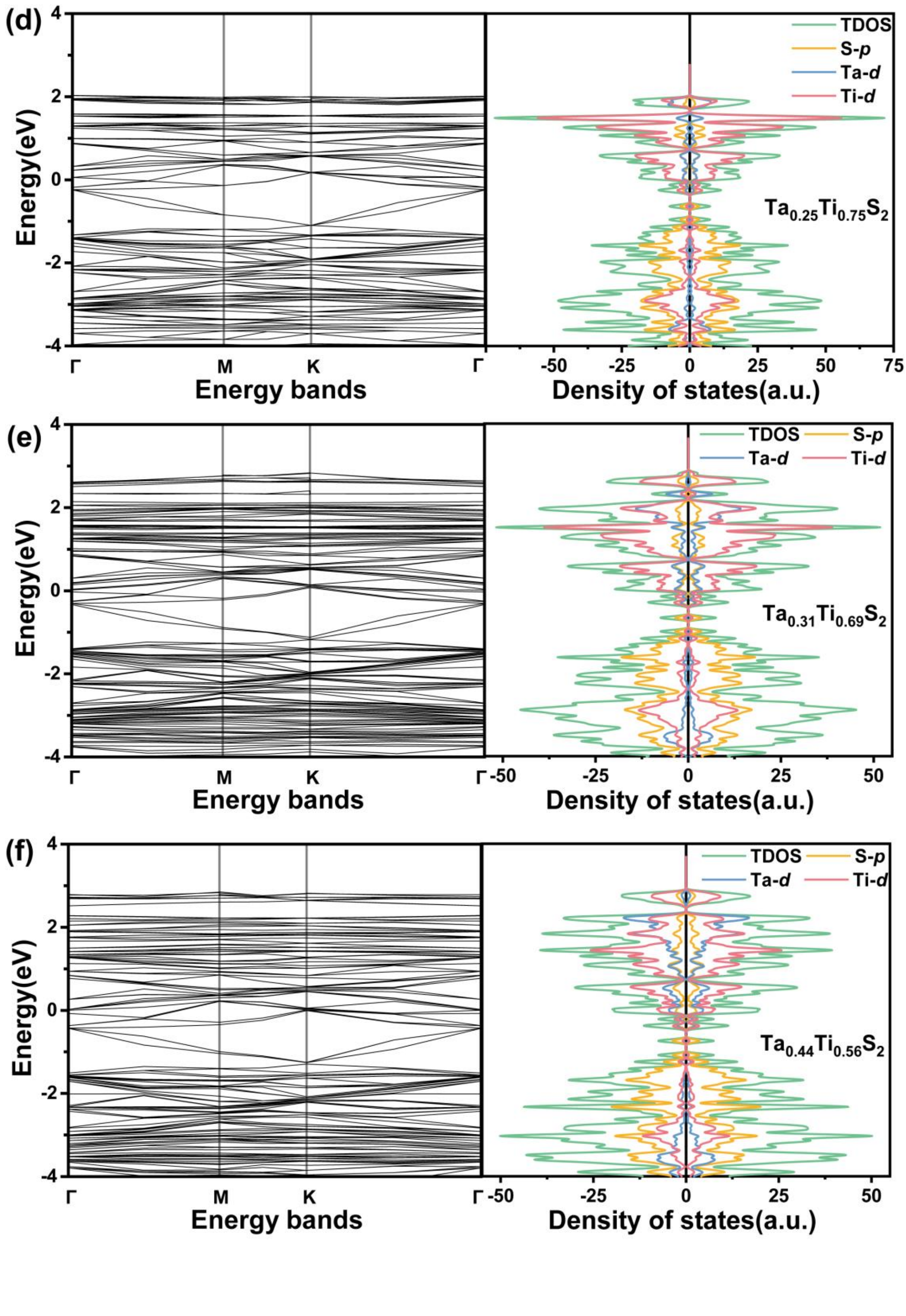
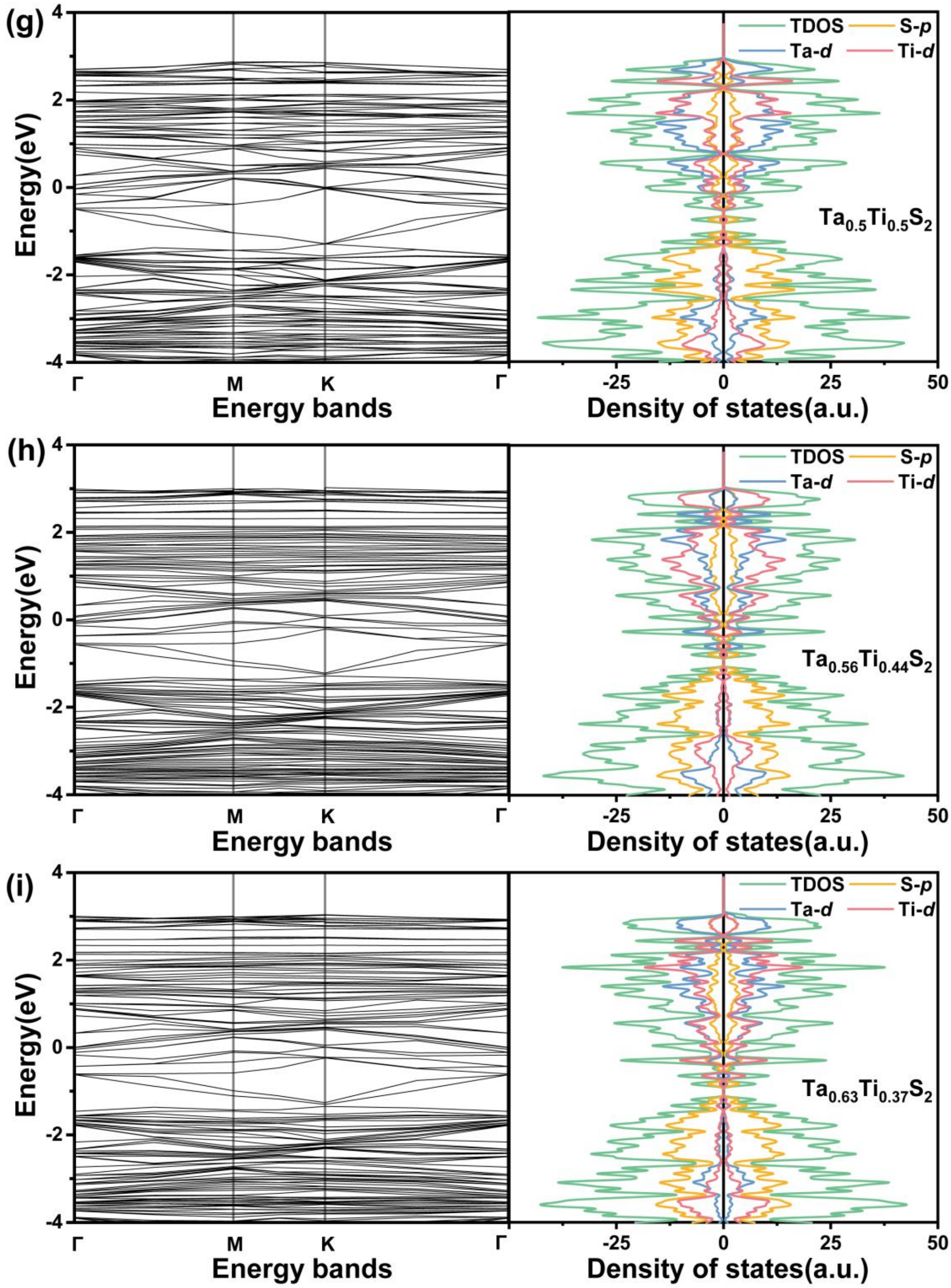
Supplementary Information (SI) for Journal of Materials Chemistry A.

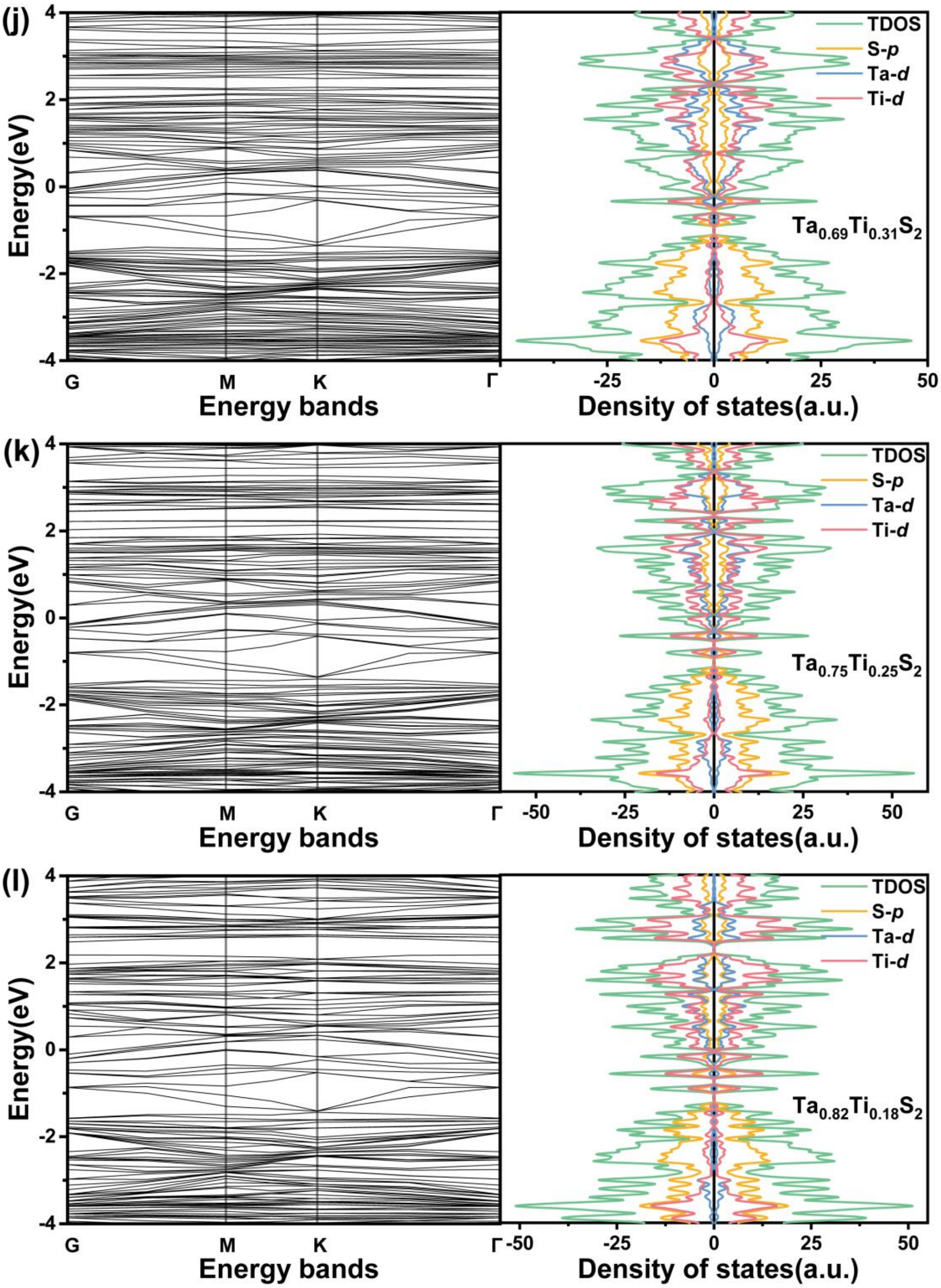
Supporting Information

Density Functional Theory Studies on Tuning $Ta_XTi_{(1-X)}S_2$ For Insoluble Li_2S_2-Li_2S Conversion in Lithium-Sulfur Batteries




(d)
Energy(eV)
Energy bands
Density of states(a.u.)
TDOS
S-p
Ta-d
Ti-d
$Ta_{0.25}Ti_{0.75}S_2$
(e)
Energy(eV)
Energy bands
Density of states(a.u.)
TDOS
S-p
Ta-d
Ti-d
$Ta_{0.31}Ti_{0.69}S_2$
(f)
Energy(eV)
Energy bands
Density of states(a.u.)
TDOS
S-p
Ta-d
Ti-d
$Ta_{0.44}Ti_{0.56}S_2$


(g)
(h)
(i)
TDOS
S-p
Ta-d
Ti-d
Ta0.5Ti0.5S2
Ta0.56Ti0.44S2
Ta0.63Ti0.37S2
Energy(eV)
Γ
M
K
Energy bands
Density of states(a.u.)
-25
0
25
50


(j)
Energy(eV)
Energy bands
Density of states(a.u.)
TDOS
S-p
Ta-d
Ti-d
$Ta_{0.69}Ti_{0.31}S_2$
(k)
Energy(eV)
Energy bands
Density of states(a.u.)
TDOS
S-p
Ta-d
Ti-d
$Ta_{0.75}Ti_{0.25}S_2$
(l)
Energy(eV)
Energy bands
Density of states(a.u.)
TDOS
S-p
Ta-d
Ti-d
$Ta_{0.82}Ti_{0.18}S_2$

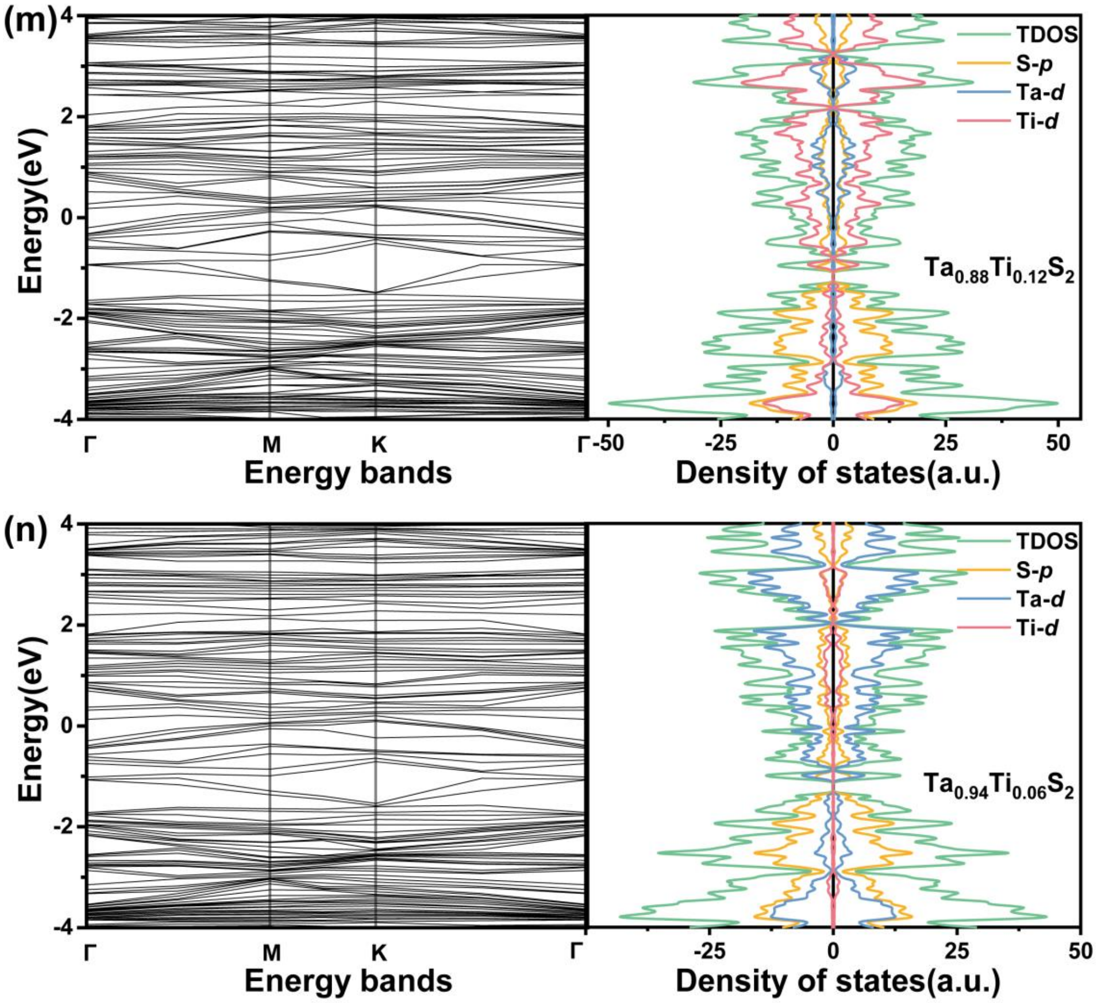


Figure S1. Energy band structure and PDOS of (a)$Ta_{0.06}Ti_{0.94}S_2$ (b)$Ta_{0.13}Ti_{0.87}S_2$ (c)$Ta_{0.19}Ti_{0.81}S_2$ (d)$Ta_{0.25}Ti_{0.75}S_2$ (e)$Ta_{0.31}Ti_{0.69}S_2$ (f)$Ta_{0.44}Ti_{0.56}S_2$ (g)$Ta_{0.5}Ti_{0.5}S_2$ (h)$Ta_{0.56}Ti_{0.44}S_2$ (i)$Ta_{0.63}Ti_{0.37}S_2$(j)$Ta_{0.69}Ti_{0.31}S_2$ (k)$Ta_{0.75}Ti_{0.25}S_2$(l)$Ta_{0.82}Ti_{0.18}S_2$ (m)$Ta_{0.88}Ti_{0.12}S_2$ and (n)$Ta_{0.94}Ti_{0.06}S_2$, respectively.

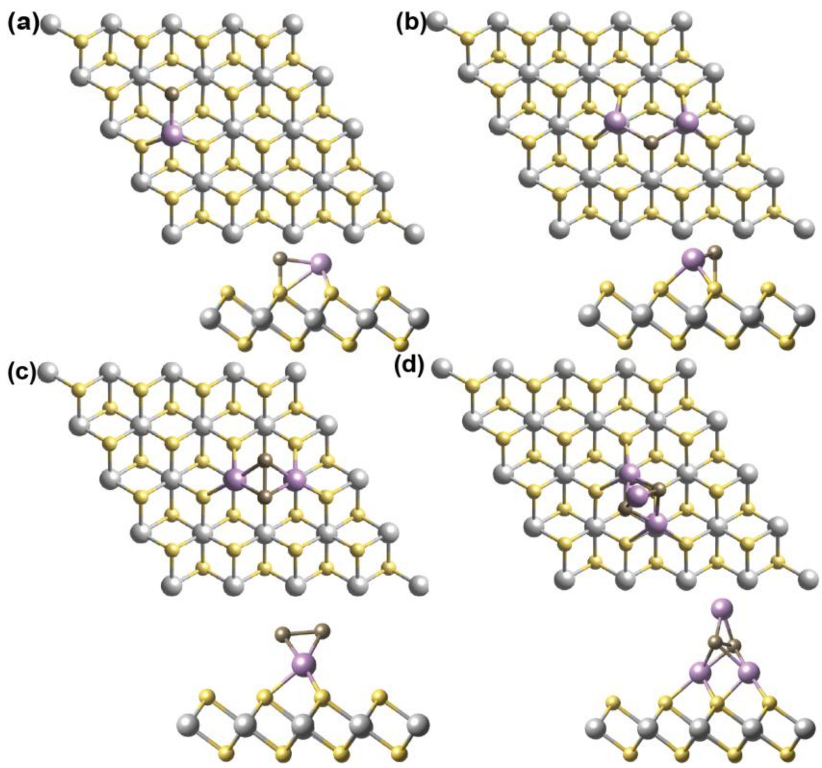


Figure S2. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on TiS_2.The grey, yellow brown and purple atom is Ti, S_{TiS_2}, S_{LiPSs}, and Li respectively.

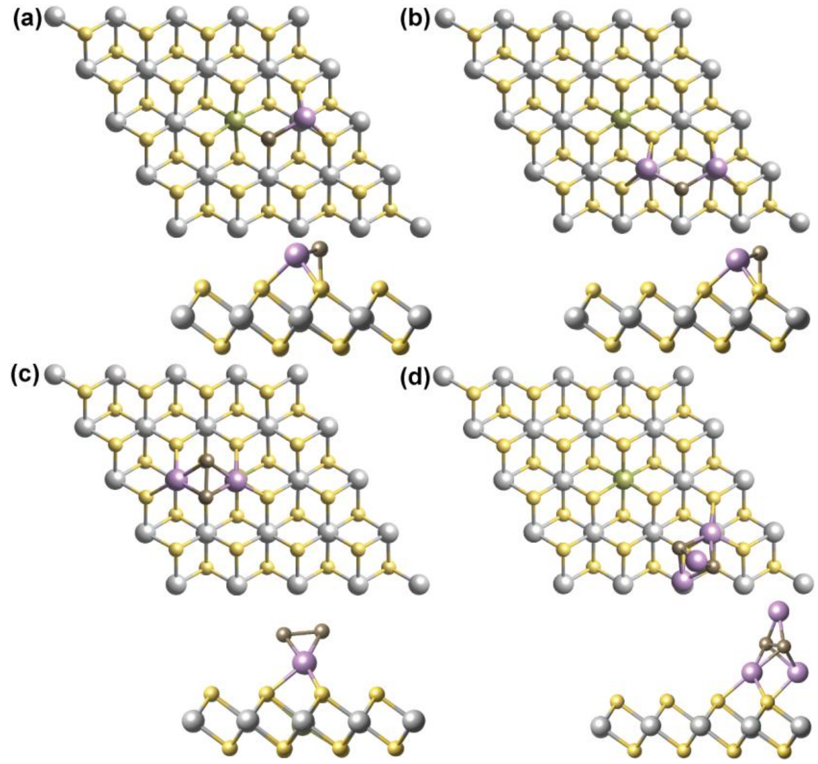


Figure S3. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.06}Ti_{0.94}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.06}Ti_{0.94}S_2}$, S_{LiPSs}, and Li respectively.

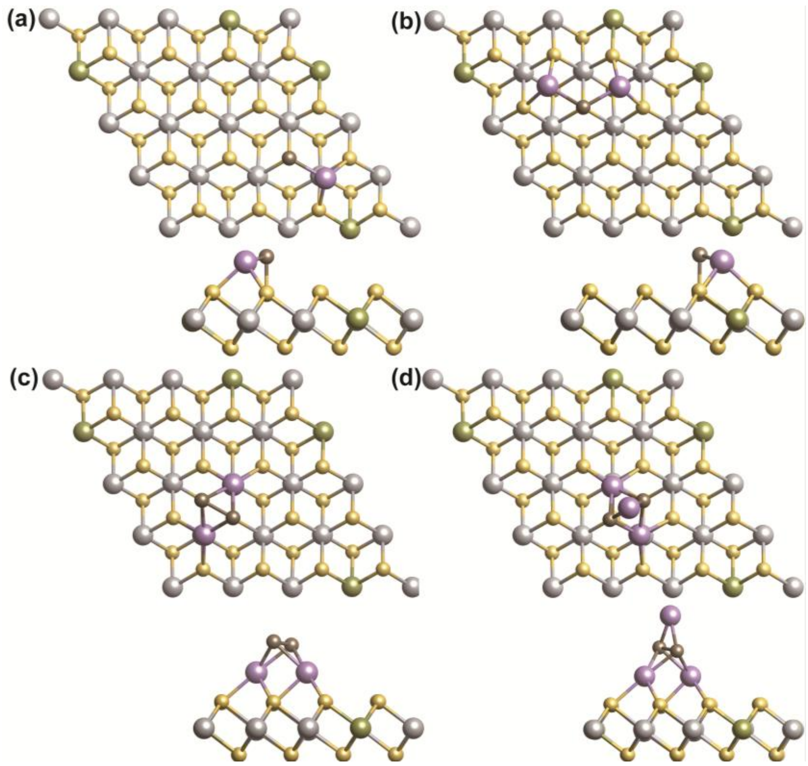


Figure S4. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.13}Ti_{0.87}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.13}Ti_{0.87}S_2}$, S_{LiPSs}, and Li respectively.

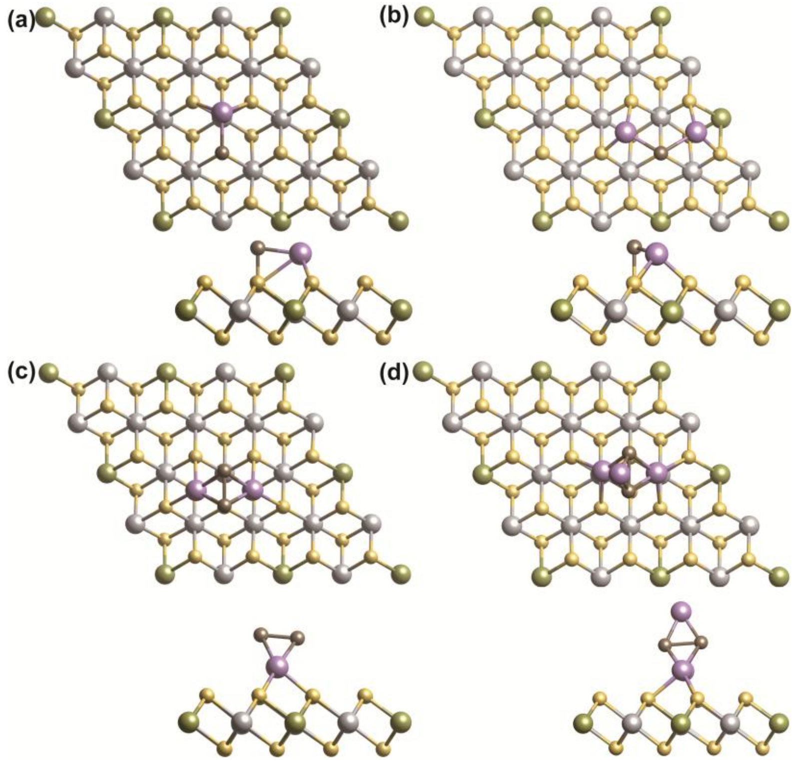


Figure S5. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.19}Ti_{0.81}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.19}Ti_{0.81}S_2}$, S_{LiPSs}, and Li respectively.

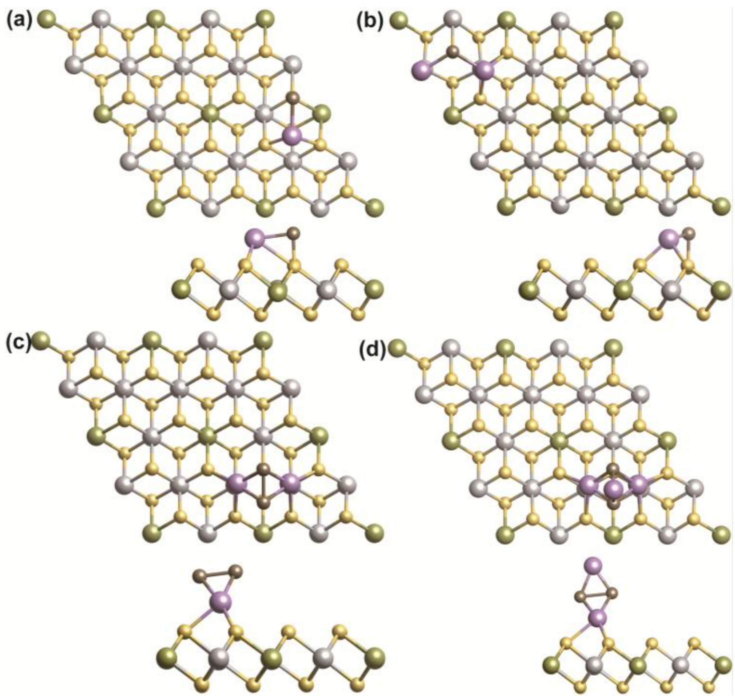


Figure S6. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.25}Ti_{0.75}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.25}Ti_{0.75}S_2}$, S_{LiPSs}, and Li respectively.

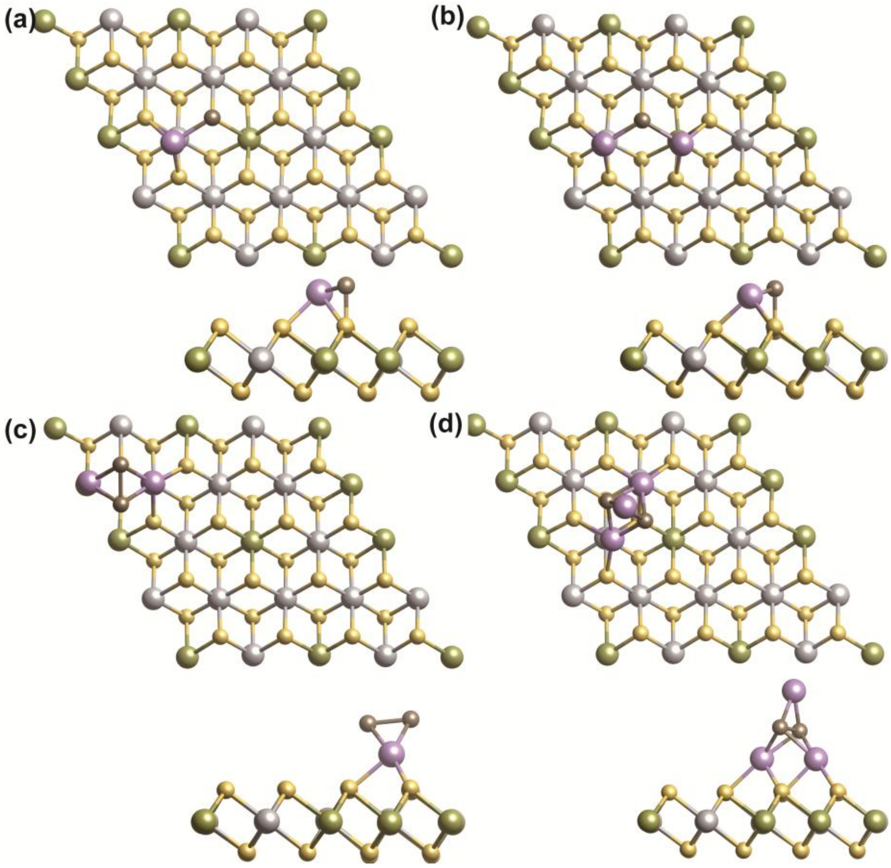


Figure S7. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.31}Ti_{0.69}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.31}Ti_{0.69}S_2}$, S_{LiPSs}, and Li respectively.

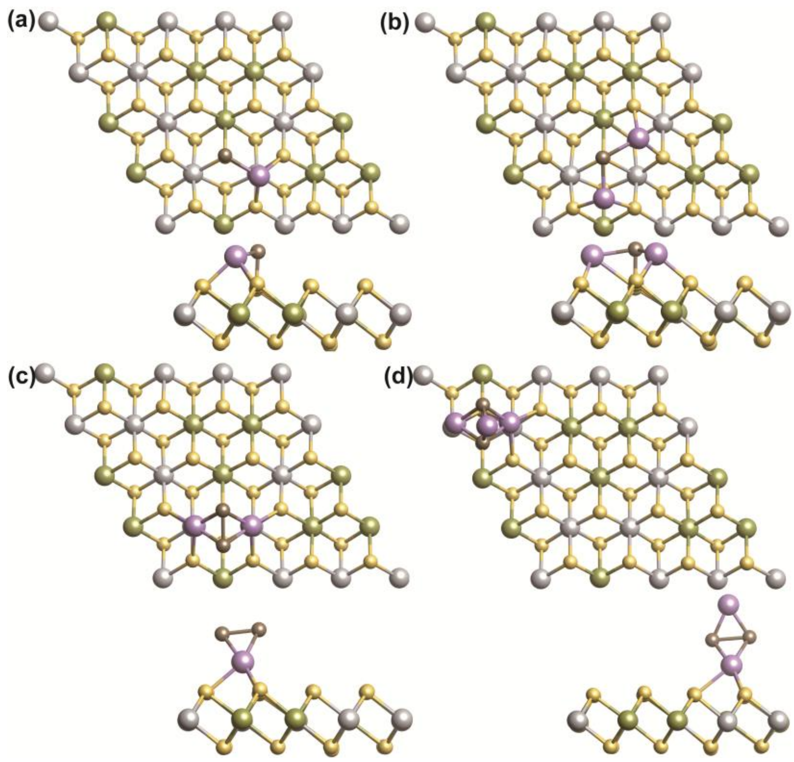


Figure S8. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.44}Ti_{0.56}S_2$ .The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.44}Ti_{0.56}S_2}$, S_{LiPSs}, and Li respectively.

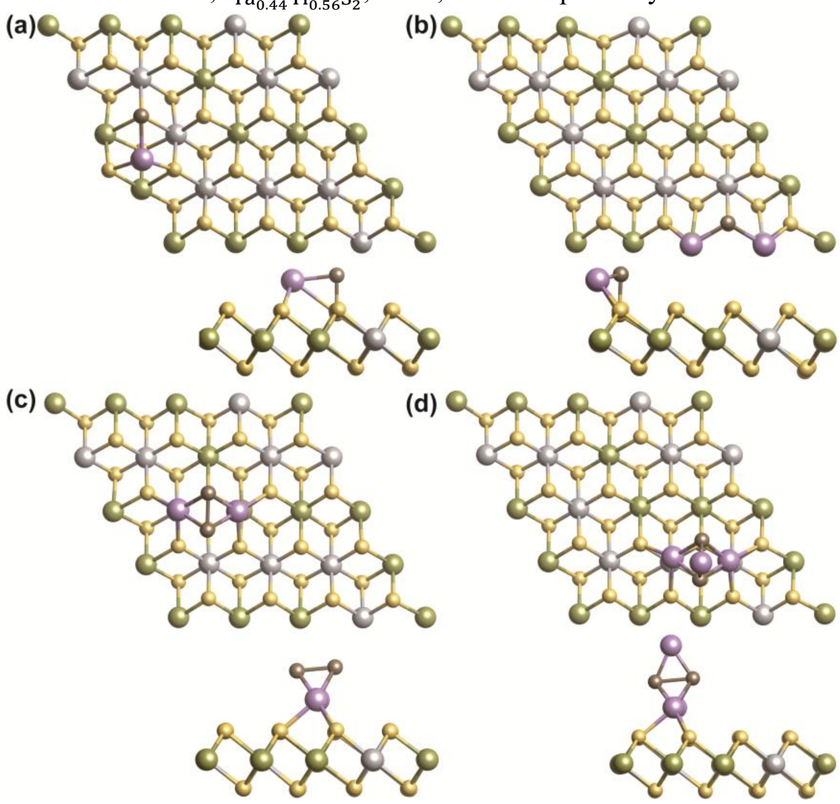


Figure S9. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.5}Ti_{0.5}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.5}Ti_{0.5}S_2}$, S_{LiPSs}, and Li respectively.

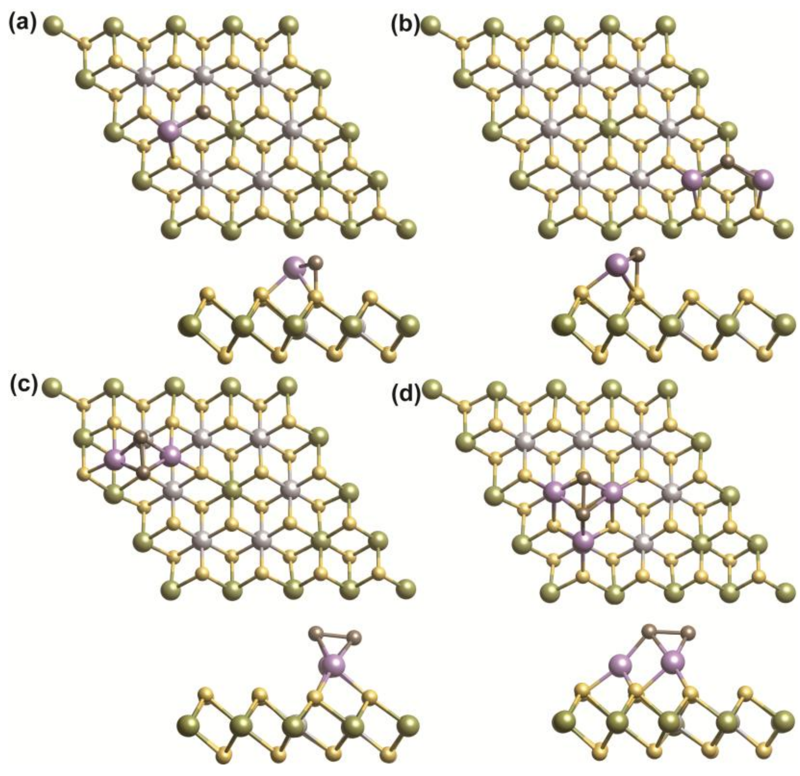


Figure S10. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.56}Ti_{0.44}S_2$ .The grey, green, yellow brown and purple atom is Ti, Ta, $S_{Ta_{0.56}Ti_{0.44}S_2}$, S_{LiPSs}, and Li respectively.

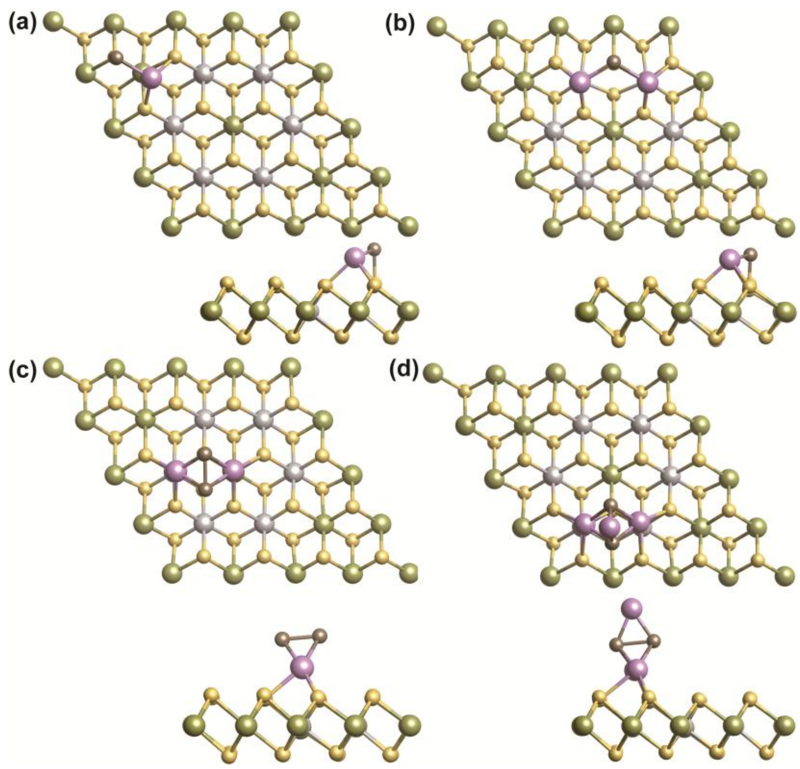


Figure S11. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.63}Ti_{0.37}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta, $S_{Ta_{0.63}Ti_{0.37}S_2}$, S_{LiPSs}, and Li respectively.

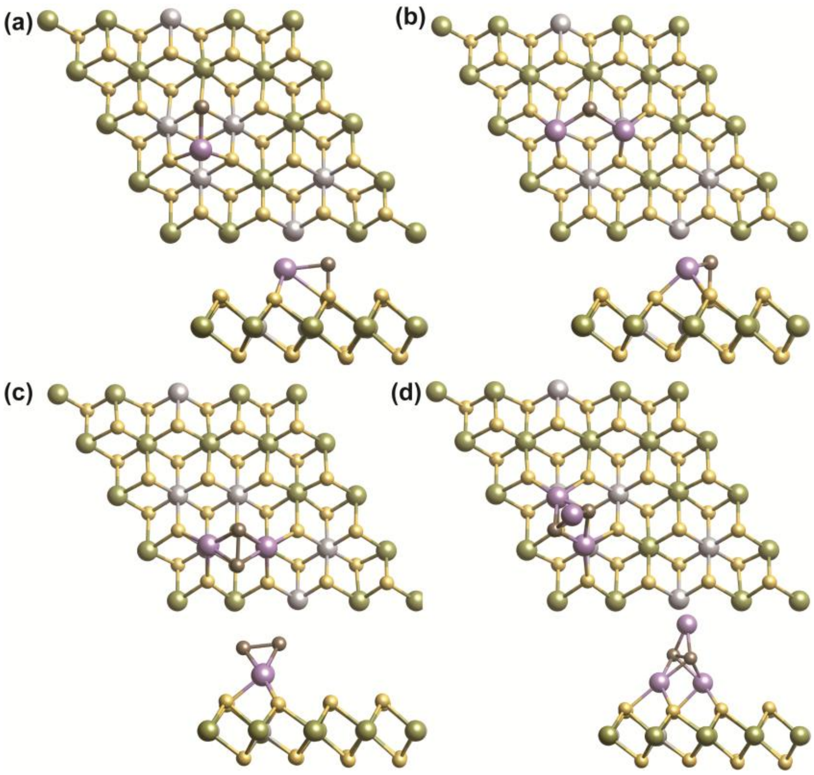


Figure S12. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.69}Ti_{0.31}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.69}Ti_{0.31}S_2}$, S_{LiPSs}, and Li respectively.

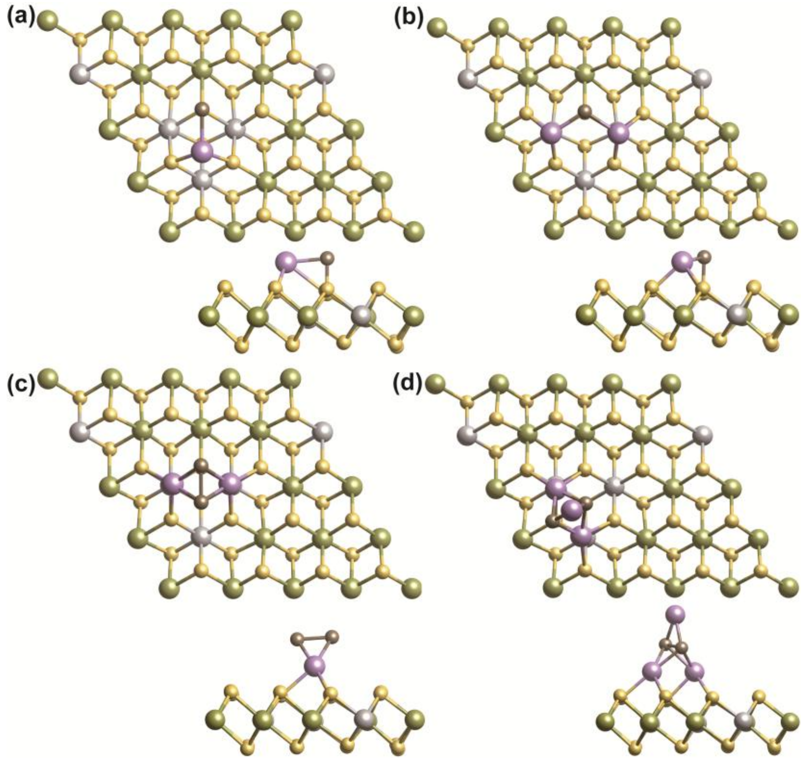


Figure S13. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.75}Ti_{0.25}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.75}Ti_{0.25}S_2}$, S_{LiPSs}, and Li respectively.

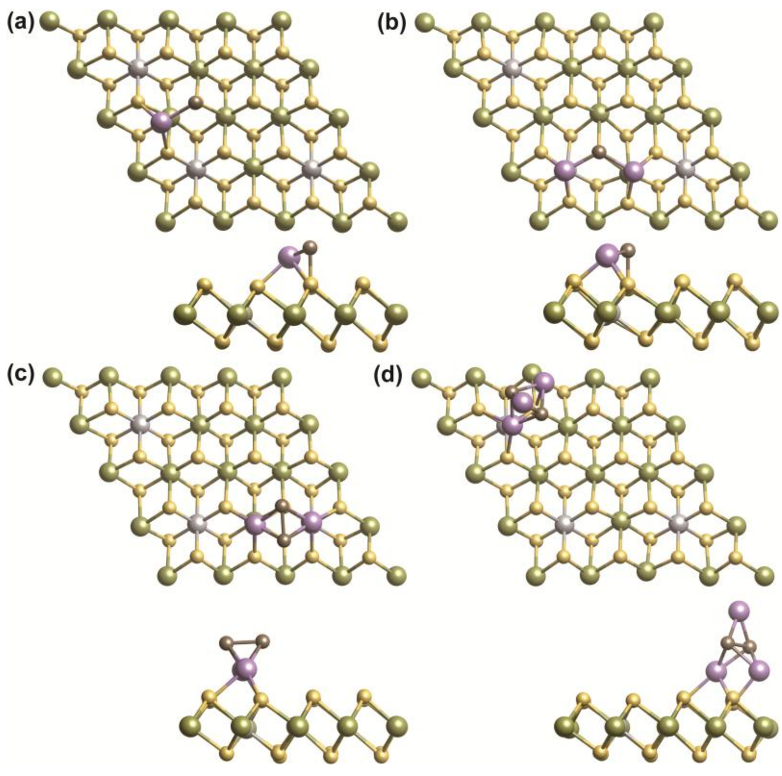


Figure S14. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.82}Ti_{0.18}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.82}Ti_{0.18}S_2}$, S_{LiPSs}, and Li respectively.

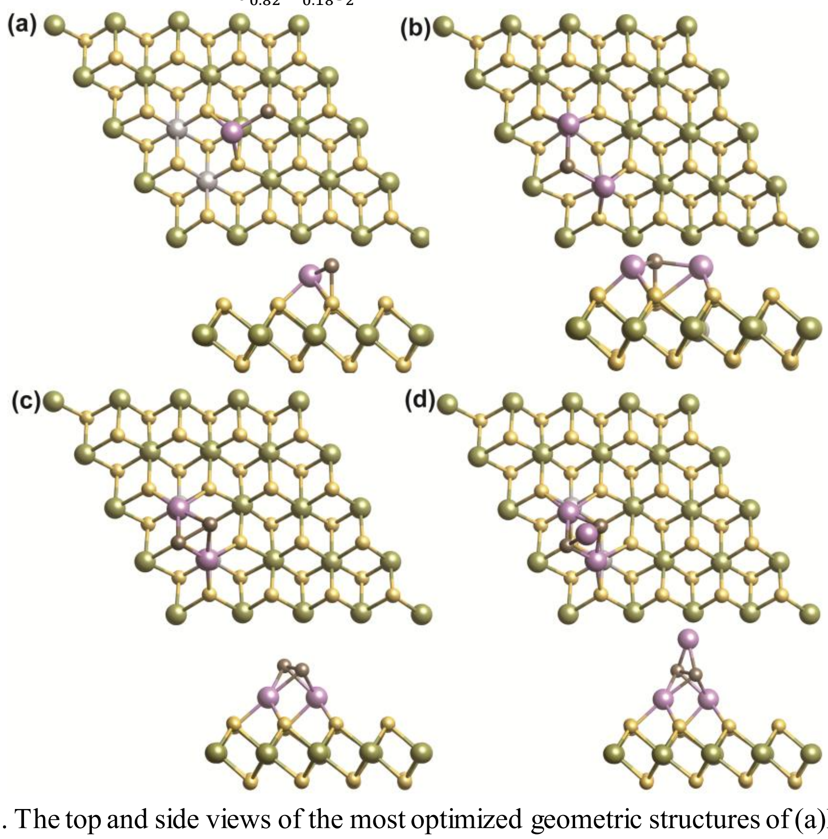


Figure S15. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.88}Ti_{0.12}S_2$ .The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.88}Ti_{0.12}S_2}$, S_{LiPSs}, and Li respectively.

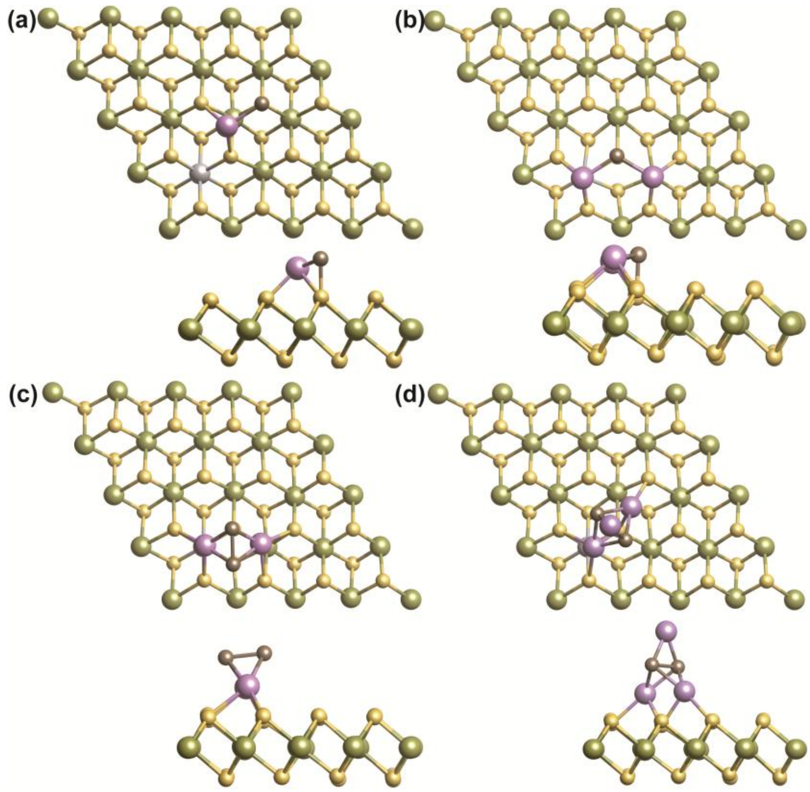


Figure S16. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on $Ta_{0.94}Ti_{0.06}S_2$.The grey, green, yellow brown and purple atom is Ti, Ta,$S_{Ta_{0.94}Ti_{0.06}S_2}$, S_{LiPSs}, and Li respectively.

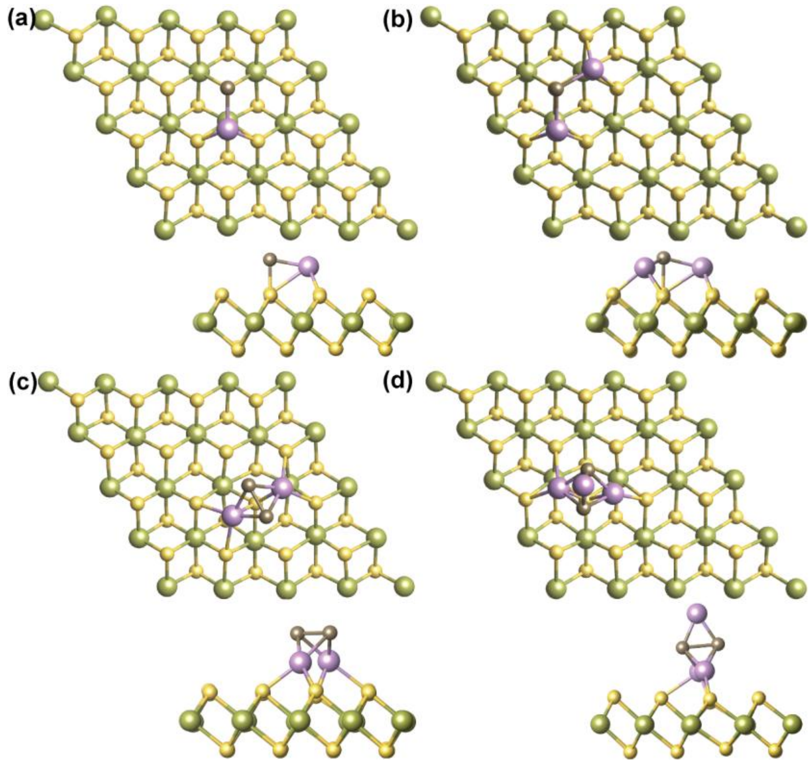


Figure S17. The top and side views of the most optimized geometric structures of (a)LiS (b)Li_2S (c)Li_2S_2 (d)Li_3S_2 on TaS_2.The green, yellow brown and purple atom is Ta,S_{TaS_2}, S_{LiPSs}, and Li respectively.

Table S1. The calculated adsorption energy (E_a) of LiS, Li_2S, Li_2S_2 and Li_3S_2 on $Ta_XTi_{(1-X)}S_2$($0 \leq X \leq 1$).

E_a(eV)	LiS	Li_2S	Li_2S_2	Li_3S_2
TiS_2	-2.51	-3.36	-2.03	-2.75
$Ta_{0.06}Ti_{0.94}S_2$	-2.41	-3.25	-1.92	-2.69
$Ta_{0.13}Ti_{0.87}S_2$	-2.41	3.12	-1.94	-2.64
$Ta_{0.19}Ti_{0.81}S_2$	-2.37	-3.05	-1.90	-2.59
$Ta_{0.25}Ti_{0.75}S_2$	-2.29	-3.04	-1.87	-2.56
$Ta_{0.31}Ti_{0.69}S_2$	-2.29	-2.99	-1.82	-2.53
$Ta_{0.38}Ti_{0.62}S_2$	-2.40	-3.14	-1.87	-2.58
$Ta_{0.44}Ti_{0.56}S_2$	-2.31	-3.00	-1.86	-2.51
$Ta_{0.5}Ti_{0.5}S_2$	-2.25	-2.94	-1.77	-2.57
$Ta_{0.56}Ti_{0.44}S_2$	-2.32	-3.01	-1.98	-2.85
$Ta_{0.63}Ti_{0.37}S_2$	-2.32	-3.05	-1.95	-2.60
$Ta_{0.69}Ti_{0.31}S_2$	-2.34	-3.04	-1.88	-2.53
$Ta_{0.75}Ti_{0.25}S_2$	-2.38	-3.17	-1.89	-2.59
$Ta_{0.82}Ti_{0.18}S_2$	-2.31	-2.93	-1.79	-2.48
$Ta_{0.88}Ti_{0.12}S_2$	-2.38	-3.07	-1.90	-2.55
$Ta_{0.94}Ti_{0.06}S_2$	-2.32	-2.99	-1.82	-2.48
TaS_2	-2.42	-2.96	-1.83	-2.48

Table S2. The closest distance of the Li atom to $S_{Ta_XTi_{(1-X)}S_2}$ when LiS, Li_2S, Li_2S_2 and Li_3S_2 on $Ta_XTi_{(1-X)}S_2$ ($0 \le X \le 1$).

The closest distance(Å)	d_{LiS}	d_{Li_2S}	$d_{Li_2S_2}$	$d_{Li_3S_2}$
TiS_2	2.46	2.42	2.57	2.53
$Ta_{0.06}Ti_{0.94}S_2$	2.45	2.46	2.58	2.54
$Ta_{0.13}Ti_{0.87}S_2$	2.44	2.45	2.57	2.54
$Ta_{0.19}Ti_{0.81}S_2$	2.45	2.42	2.56	2.53
$Ta_{0.25}Ti_{0.75}S_2$	2.44	2.45	2.57	2.54
$Ta_{0.31}Ti_{0.69}S_2$	2.44	2.41	2.58	2.53
$Ta_{0.38}Ti_{0.62}S_2$	2.45	2.41	2.56	2.53
$Ta_{0.44}Ti_{0.56}S_2$	2.45	2.45	2.55	2.53
$Ta_{0.5}Ti_{0.5}S_2$	2.46	2.42	2.56	2.54
$Ta_{0.56}Ti_{0.44}S_2$	2.45	2.44	2.56	2.48
$Ta_{0.63}Ti_{0.37}S_2$	2.46	2.43	2.59	2.53
$Ta_{0.69}Ti_{0.31}S_2$	2.45	2.41	2.55	2.52
$Ta_{0.75}Ti_{0.25}S_2$	2.46	2.41	2.57	2.53
$Ta_{0.82}Ti_{0.18}S_2$	2.46	2.41	2.55	2.52
$Ta_{0.88}Ti_{0.12}S_2$	2.46	2.41	2.54	2.52
$Ta_{0.94}Ti_{0.06}S_2$	2.43	2.41	2.53	2.49
TaS_2	2.45	2.42	2.47	2.49

Table S3. Bader charge numbers indicate the number of electrons transferred from LiS, Li_2S, Li_2S_2 and Li_3S_2 to $Ta_XTi_{(1-X)}S_2$ ($0 \leq X \leq 1$). Here, Bader charge difference means the difference of charge value between adsorbed case and free-standing case.

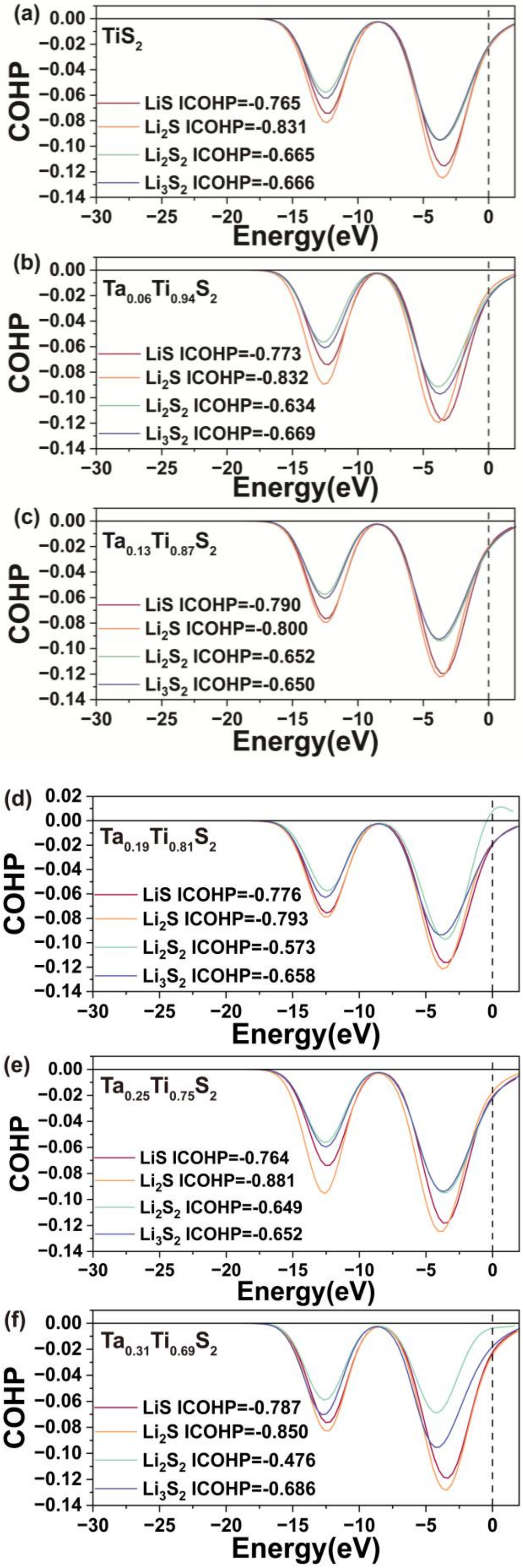
$\Delta e_{Ta_XTi_{(1-X)}S_2} = -\Delta e_{LiPSs}$	Q_{LiS}	Q_{Li_2S}	$Q_{Li_2S_2}$	$Q_{Li_3S_2}$
TiS_2	-0.54	-1.12	-1.01	-1.09
$Ta_{0.06}Ti_{0.94}S_2$	-0.48	-1.21	-0.98	-1.09
$Ta_{0.13}Ti_{0.87}S_2$	-0.53	-1.15	-0.98	-1.08
$Ta_{0.19}Ti_{0.81}S_2$	-0.53	-1.12	-1.03	-1.07
$Ta_{0.25}Ti_{0.75}S_2$	-0.50	-1.18	-0.95	-1.04
$Ta_{0.31}Ti_{0.69}S_2$	-0.54	-1.21	-0.92	-1.04
$Ta_{0.38}Ti_{0.62}S_2$	-0.46	-1.09	-0.97	-1.06
$Ta_{0.44}Ti_{0.56}S_2$	-0.50	-1.17	-0.94	-1.03
$Ta_{0.5}Ti_{0.5}S_2$	-0.50	-1.15	-0.93	-1.02
$Ta_{0.56}Ti_{0.44}S_2$	-0.52	-1.12	-0.92	-1.45
$Ta_{0.63}Ti_{0.37}S_2$	-0.48	-1.15	-0.90	-1.02
$Ta_{0.69}Ti_{0.31}S_2$	-0.51	-1.14	-0.93	-1.02
$Ta_{0.75}Ti_{0.25}S_2$	-0.46	-1.10	-0.92	-1.01
$Ta_{0.82}Ti_{0.18}S_2$	-0.47	-1.16	-0.87	-0.99
$Ta_{0.88}Ti_{0.12}S_2$	-0.50	-1.15	-0.90	-1.00
$Ta_{0.94}Ti_{0.06}S_2$	-0.50	-1.13	-0.87	-0.98
TaS_2	-0.47	-1.11	-0.83	-0.99

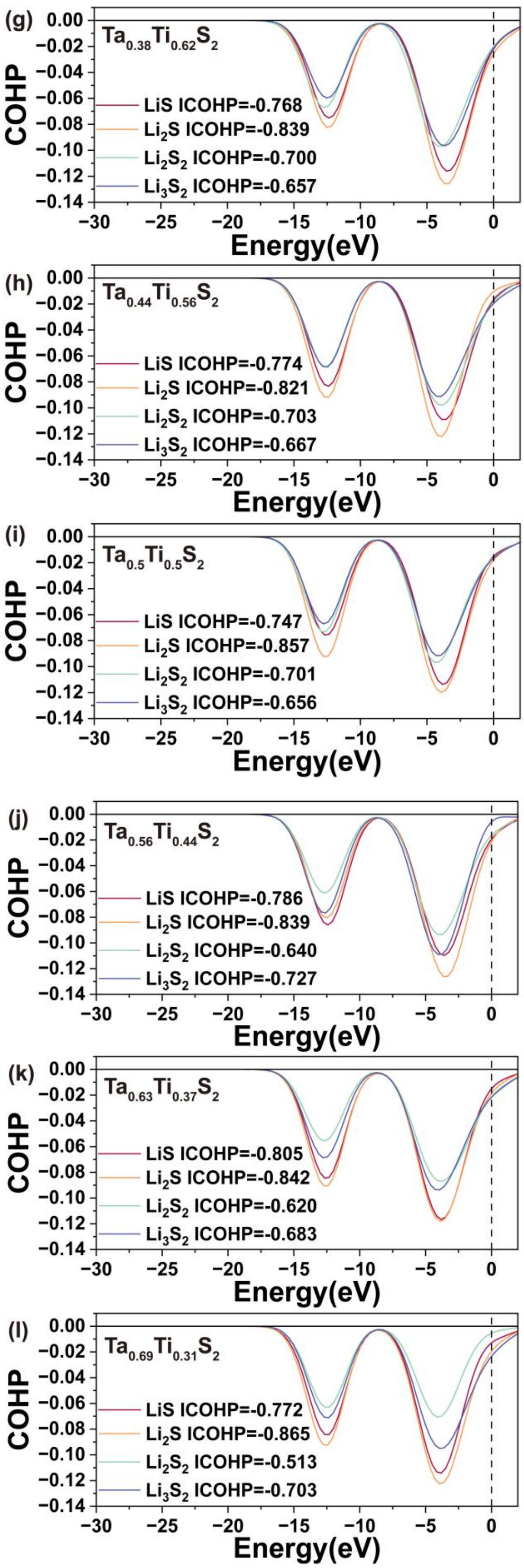
Table S4. Bader charge numbers indicate the number of electrons transferred from Li and S of LiS, Li_2S, Li_2S_2 and Li_3S_2 to $Ta_XTi_{(1-X)}S_2$($0 \leq X \leq 1$). Here, Bader charge difference means the difference of charge value between adsorbed case and free-standing case.

$\Delta e_{Ta_XTi_{(1-X)}S_2}$	**LiS**		**Li_2S**		**Li_2S_2**		**Li_3S_2**	
$= -\Delta e_{LiPSs}$	Δe_{Li}	Δe_S	Δe_{Li}	Δe_S	Δe_{Li}	Δe_S	Δe_{Li}	Δe_S
TiS_2	-0.87	0.33	-1.72	0.60	-1.73	0.72	-2.62	1.53
$Ta_{0.06}Ti_{0.94}S_2$	-0.87	0.39	-1.74	0.53	-1.74	0.76	-2.63	1.54
$Ta_{0.13}Ti_{0.87}S_2$	-0.87	0.34	-1.75	0.60	-1.74	0.76	-2.63	1.55
$Ta_{0.19}Ti_{0.81}S_2$	-0.87	0.34	-1.74	0.62	-1.76	0.73	-2.62	1.55
$Ta_{0.25}Ti_{0.75}S_2$	-0.88	0.38	-1.74	0.56	-1.74	0.79	-2.62	1.58
$Ta_{0.31}Ti_{0.69}S_2$	-0.87	0.33	-1.74	0.53	-1.74	0.82	-2.63	1.59
$Ta_{0.38}Ti_{0.62}S_2$	-0.87	0.41	-1.74	0.65	-1.74	0.77	-2.63	1.57
$Ta_{0.44}Ti_{0.56}S_2$	-0.87	0.37	-1.74	0.57	-1.74	0.80	-2.62	1.59
$Ta_{0.5}Ti_{0.5}S_2$	-0.88	0.38	-1.74	0.60	-1.74	0.81	-2.62	1.60
$Ta_{0.56}Ti_{0.44}S_2$	-0.87	0.35	-1.74	0.62	-1.75	0.83	-2.61	1.16
$Ta_{0.63}Ti_{0.37}S_2$	-0.87	0.39	-1.73	0.58	-1.74	0.84	-2.62	1.60
$Ta_{0.69}Ti_{0.31}S_2$	-0.87	0.36	-1.74	0.60	-1.74	0.81	-2.62	1.60
$Ta_{0.75}Ti_{0.25}S_2$	-0.87	0.41	-1.73	0.63	-1.74	0.82	-2.62	1.61
$Ta_{0.82}Ti_{0.18}S_2$	-0.87	0.40	-1.74	0.57	-1.74	0.87	-2.62	1.63
$Ta_{0.88}Ti_{0.12}S_2$	-0.87	0.37	-1.74	0.59	-1.74	0.84	-2.62	1.62
$Ta_{0.94}Ti_{0.06}S_2$	-0.87	0.37	-1.73	0.60	-1.74	0.87	-2.62	1.64
TaS_2	-0.87	0.40	-1.74	0.63	-1.74	0.91	-2.62	1.63

Table S5. The difference of Work function(ΔWF), when LiS, Li_2S, Li_2S_2 and Li_3S_2 absorb on $Ta_XTi_{(1-X)}S_2$($0 \leq X \leq 1$).

ΔWF(eV)	**ΔWF_{LiS}**	**ΔWF_{Li_2S}**	**$\Delta WF_{Li_2S_2}$**	**$\Delta WF_{Li_3S_2}$**
TiS_2	-0.27	-0.60	-0.19	-0.84
$Ta_{0.06}Ti_{0.94}S_2$	-0.30	-0.57	-0.19	-0.84
$Ta_{0.13}Ti_{0.87}S_2$	-0.27	-0.54	-0.19	-0.84
$Ta_{0.19}Ti_{0.81}S_2$	-0.27	-0.54	-0.16	-0.82
$Ta_{0.25}Ti_{0.75}S_2$	-0.27	-0.54	-0.16	-0.82
$Ta_{0.31}Ti_{0.69}S_2$	-0.24	-0.49	-0.14	-0.82
$Ta_{0.38}Ti_{0.62}S_2$	-0.14	-0.38	-0.08	-0.71
$Ta_{0.44}Ti_{0.56}S_2$	-0.19	-0.41	-0.11	-0.79
$Ta_{0.5}Ti_{0.5}S_2$	-0.22	-0.46	-0.11	-0.79
$Ta_{0.56}Ti_{0.44}S_2$	-0.22	-0.41	-0.14	-0.19
$Ta_{0.63}Ti_{0.37}S_2$	-0.14	-0.44	-0.11	-0.79
$Ta_{0.69}Ti_{0.31}S_2$	-0.22	-0.47	-0.11	-0.76
$Ta_{0.75}Ti_{0.25}S_2$	-0.19	-0.44	-0.08	-0.73
$Ta_{0.82}Ti_{0.18}S_2$	-0.16	-0.46	-0.08	-0.73
$Ta_{0.88}Ti_{0.12}S_2$	-0.14	-0.44	-0.05	-0.73
$Ta_{0.94}Ti_{0.06}S_2$	-0.14	-0.41	-0.05	-0.73
TaS_2	-0.16	-0.90	0	-0.68


(a)
TiS2
LiS ICOHP=-0.765
Li2S ICOHP=-0.831
Li2S2 ICOHP=-0.665
Li3S2 ICOHP=-0.666
COHP
Energy(eV)
(b)
Ta0.06Ti0.94S2
LiS ICOHP=-0.773
Li2S ICOHP=-0.832
Li2S2 ICOHP=-0.634
Li3S2 ICOHP=-0.669
COHP
Energy(eV)
(c)
Ta0.13Ti0.87S2
LiS ICOHP=-0.790
Li2S ICOHP=-0.800
Li2S2 ICOHP=-0.652
Li3S2 ICOHP=-0.650
COHP
Energy(eV)
(d)
Ta0.19Ti0.81S2
LiS ICOHP=-0.776
Li2S ICOHP=-0.793
Li2S2 ICOHP=-0.573
Li3S2 ICOHP=-0.658
COHP
Energy(eV)
(e)
Ta0.25Ti0.75S2
LiS ICOHP=-0.764
Li2S ICOHP=-0.881
Li2S2 ICOHP=-0.649
Li3S2 ICOHP=-0.652
COHP
Energy(eV)
(f)
Ta0.31Ti0.69S2
LiS ICOHP=-0.787
Li2S ICOHP=-0.850
Li2S2 ICOHP=-0.476
Li3S2 ICOHP=-0.686
COHP
Energy(eV)



(g)
Ta0.38Ti0.62S2
LiS ICOHP=-0.768
Li2S ICOHP=-0.839
Li2S2 ICOHP=-0.700
Li3S2 ICOHP=-0.657
(h)
Ta0.44Ti0.56S2
LiS ICOHP=-0.774
Li2S ICOHP=-0.821
Li2S2 ICOHP=-0.703
Li3S2 ICOHP=-0.667
(i)
Ta0.5Ti0.5S2
LiS ICOHP=-0.747
Li2S ICOHP=-0.857
Li2S2 ICOHP=-0.701
Li3S2 ICOHP=-0.656
(j)
Ta0.56Ti0.44S2
LiS ICOHP=-0.786
Li2S ICOHP=-0.839
Li2S2 ICOHP=-0.640
Li3S2 ICOHP=-0.727
(k)
Ta0.63Ti0.37S2
LiS ICOHP=-0.805
Li2S ICOHP=-0.842
Li2S2 ICOHP=-0.620
Li3S2 ICOHP=-0.683
(l)
Ta0.69Ti0.31S2
LiS ICOHP=-0.772
Li2S ICOHP=-0.865
Li2S2 ICOHP=-0.513
Li3S2 ICOHP=-0.703
COHP
Energy(eV)

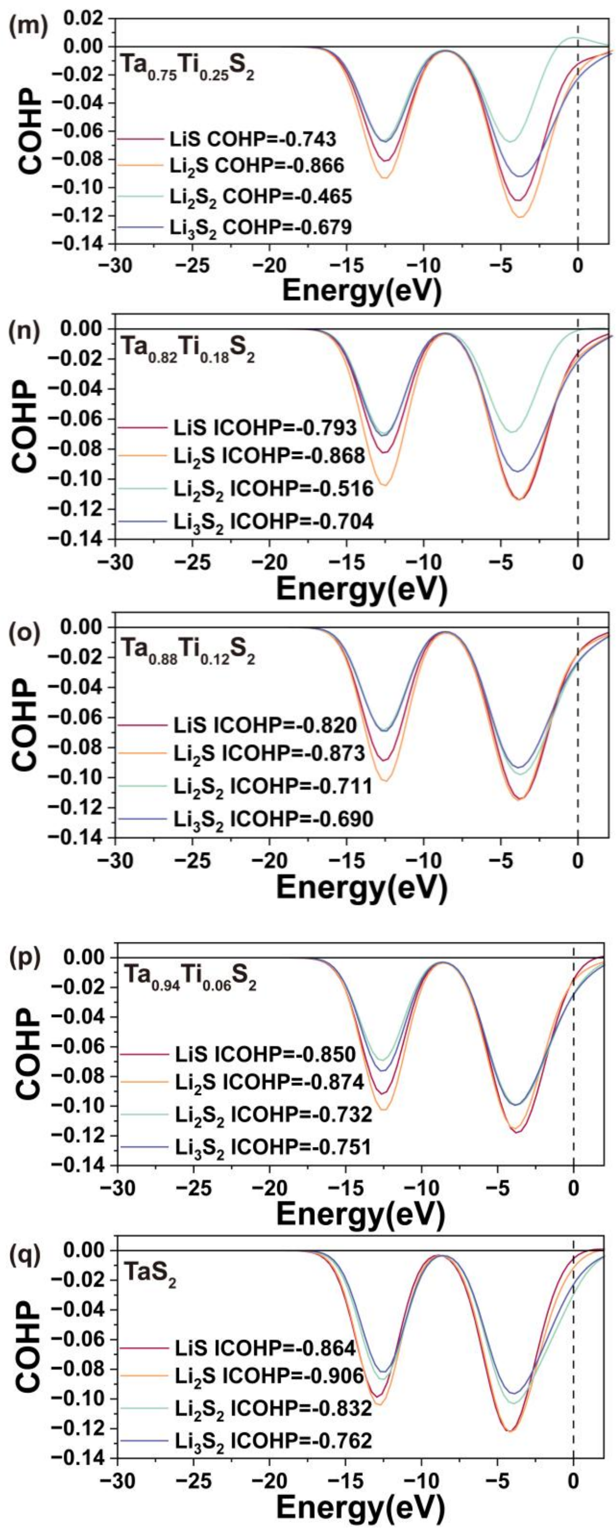


Figure S18. COHP diagram of the Li–$S_{Ta_XTi_{(1-X)}S_2}$ ($0 \leq X \leq 1$) bond in(a)TiS_2, (b)$Ta_{0.06}Ti_{0.94}S_2$, (c)$Ta_{0.13}Ti_{0.87}S_2$, (d)$Ta_{0.19}Ti_{0.81}S_2$, (e)$Ta_{0.25}Ti_{0.75}S_2$, (f)$Ta_{0.31}Ti_{0.69}S_2$, (g)$Ta_{0.38}Ti_{0.62}S_2$, (h)$Ta_{0.44}Ti_{0.56}S_2$, (i)$Ta_{0.5}Ti_{0.5}S_2$, (j)$Ta_{0.56}Ti_{0.44}S_2$, (k)$Ta_{0.63}Ti_{0.37}S_2$, (l)$Ta_{0.69}Ti_{0.31}S_2$, (m)$Ta_{0.75}Ti_{0.25}S_2$, (n)$Ta_{0.82}Ti_{0.18}S_2$, (o)$Ta_{0.88}Ti_{0.12}S_2$, (p)$Ta_{0.94}Ti_{0.06}S_2$, and (q)TaS_2, respectively.

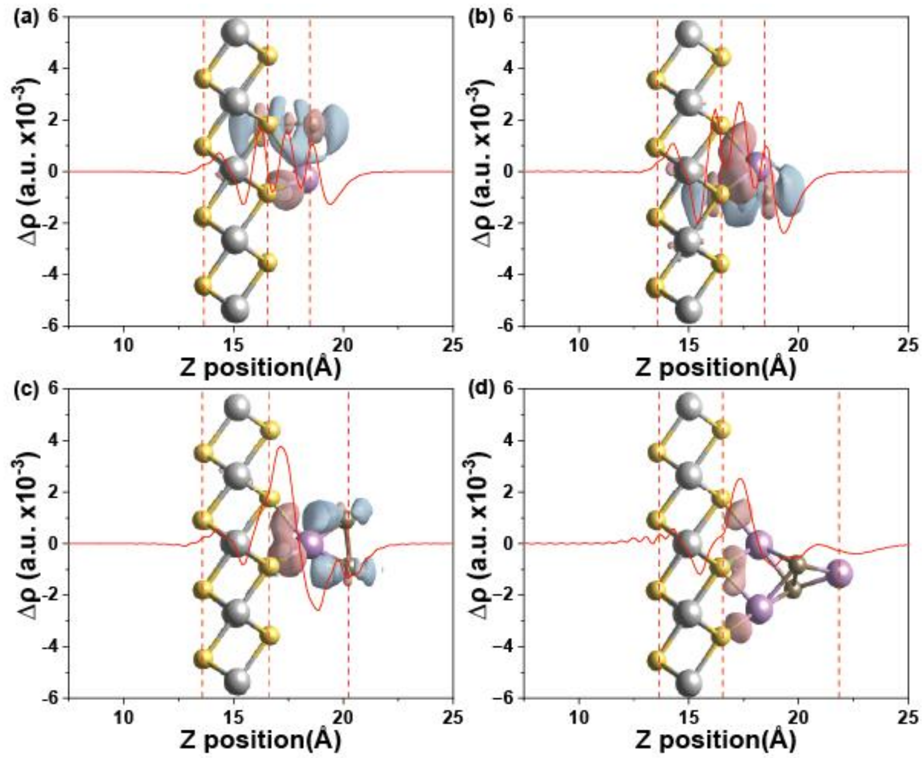


Figure S19. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on TiS_2. blue and pink represent charge depletion and gain, respectively.

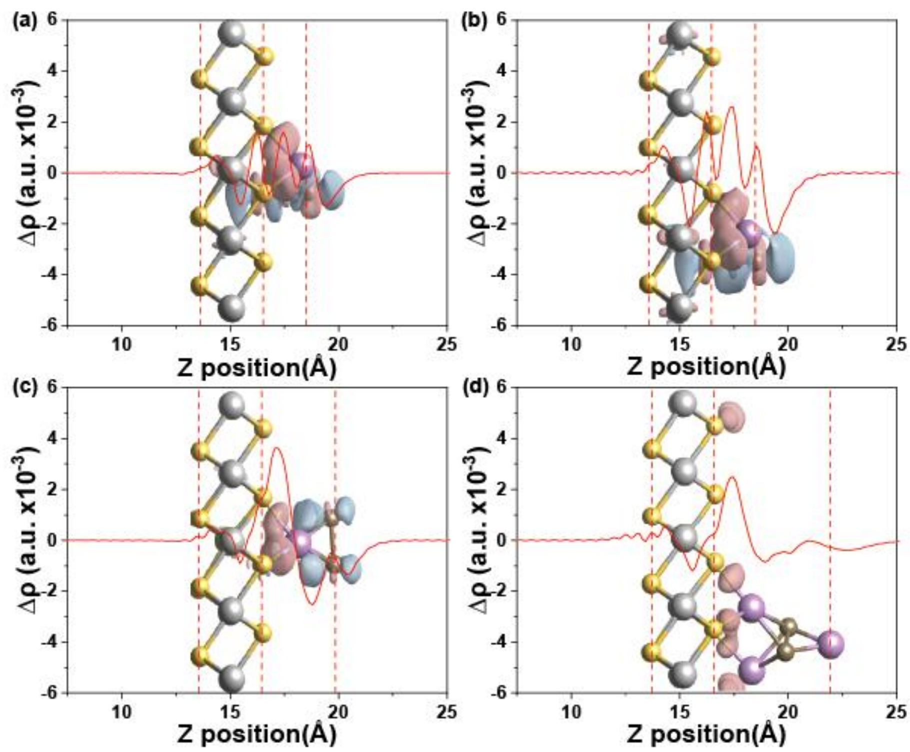


Figure S20. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.06}Ti_{0.94}S_2$. blue and pink represent charge depletion and gain, respectively.

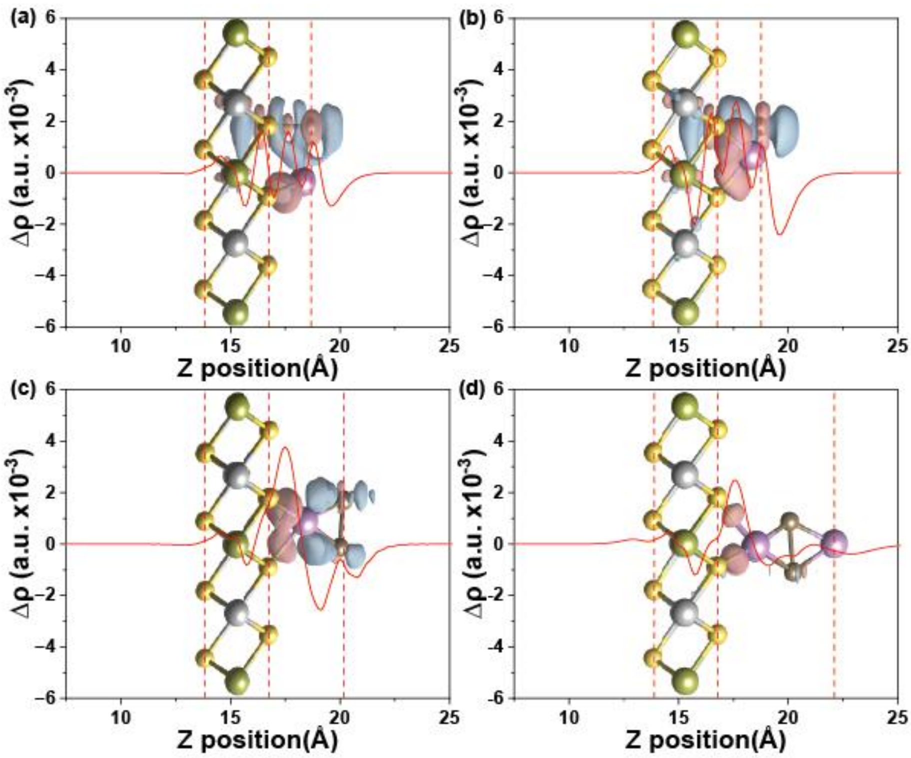


Figure S21. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.13}Ti_{0.87}S_2$. blue and pink represent charge depletion and gain, respectively.

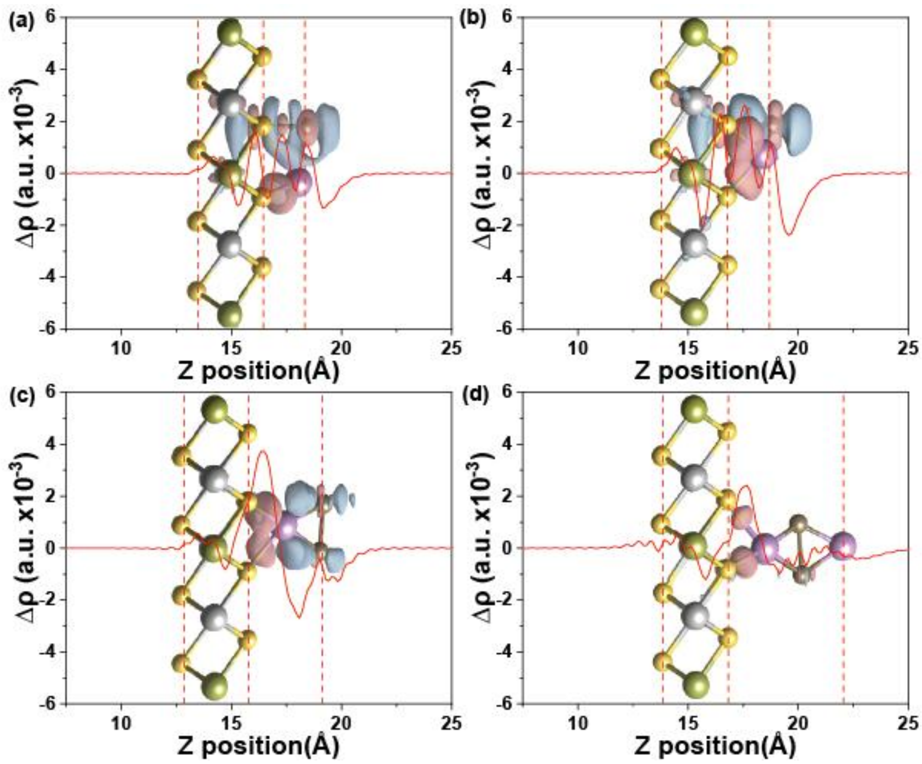


Figure S22. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.19}Ti_{0.81}S_2$. blue and pink represent charge depletion and gain, respectively.

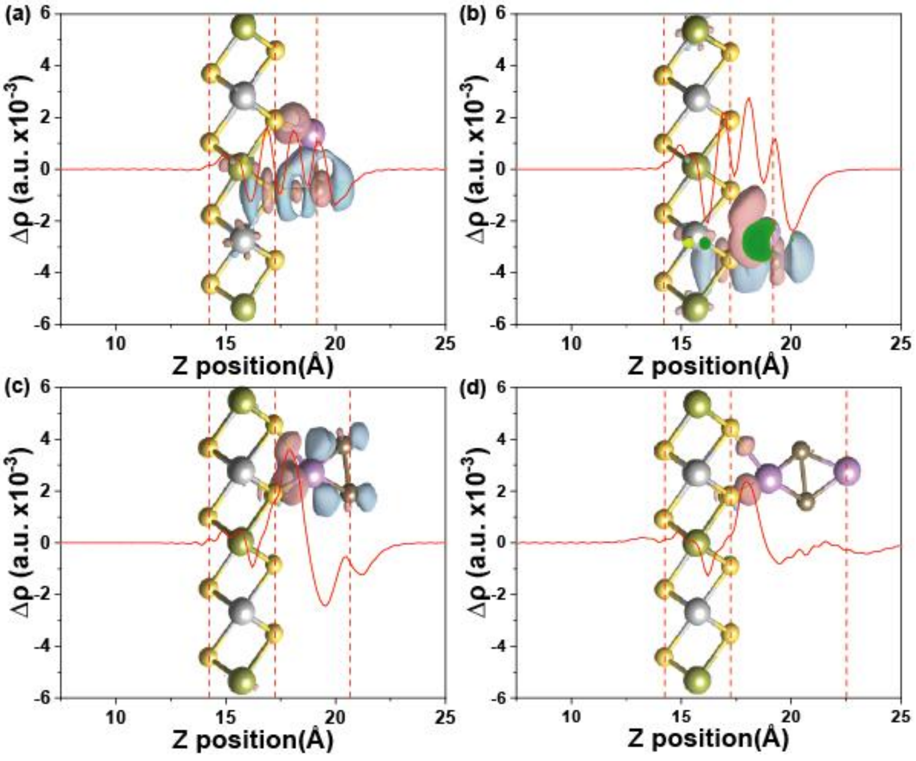


Figure S23. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.25}Ti_{0.75}S_2$. blue and pink represent charge depletion and gain, respectively.

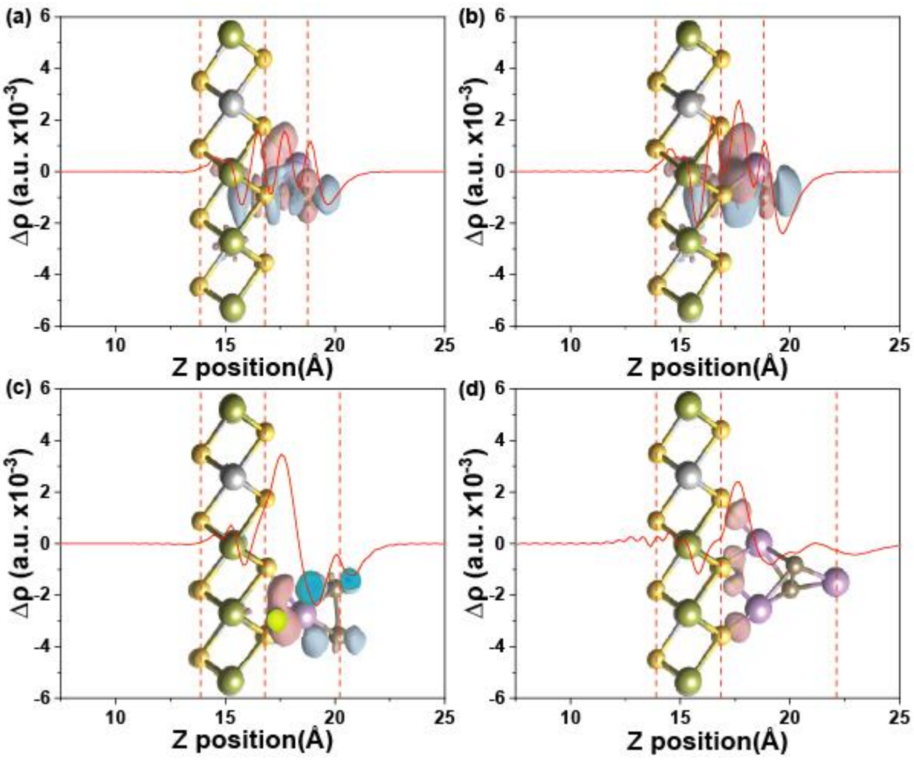


Figure S24. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.31}Ti_{0.69}S_2$. blue and pink represent charge depletion and gain, respectively.

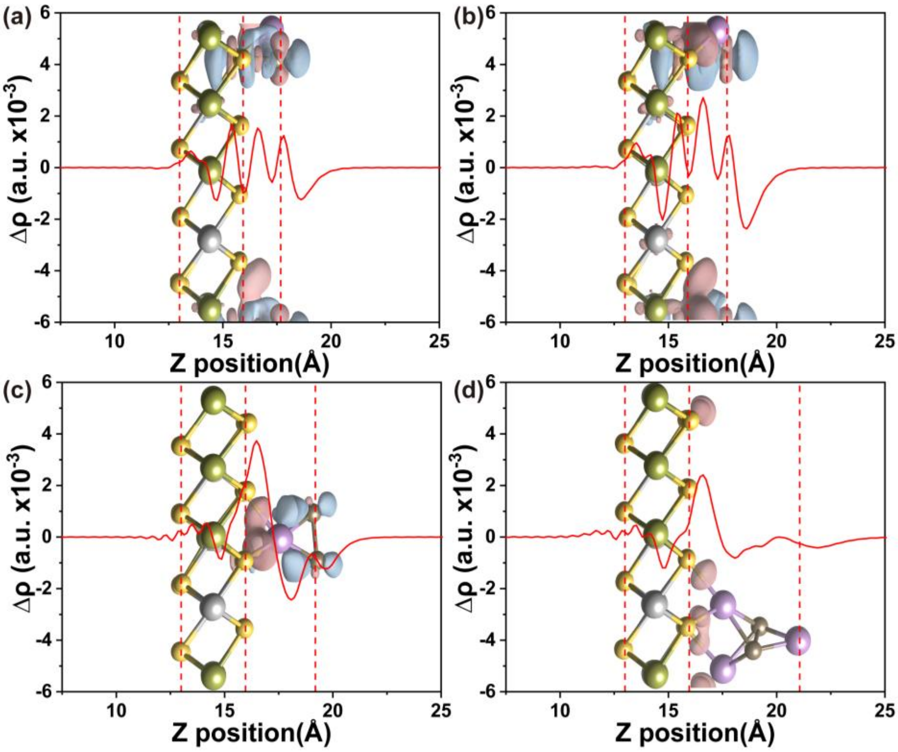


Figure S25. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.38}Ti_{0.62}S_2$. blue and pink represent charge depletion and gain, respectively.

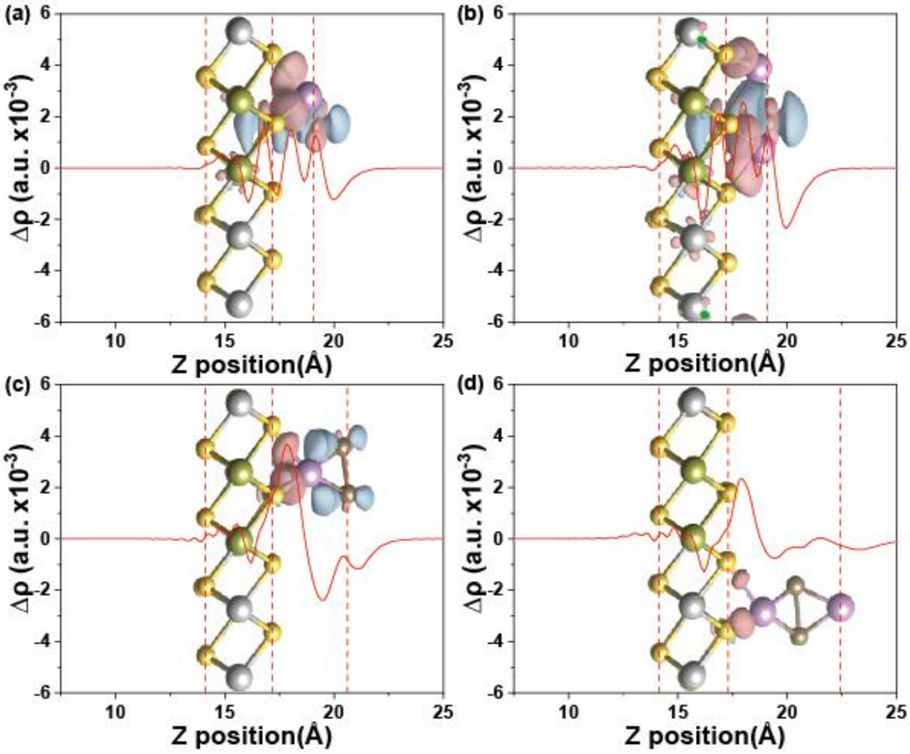


Figure S26. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.44}Ti_{0.56}S_2$. blue and pink represent charge depletion and gain, respectively.

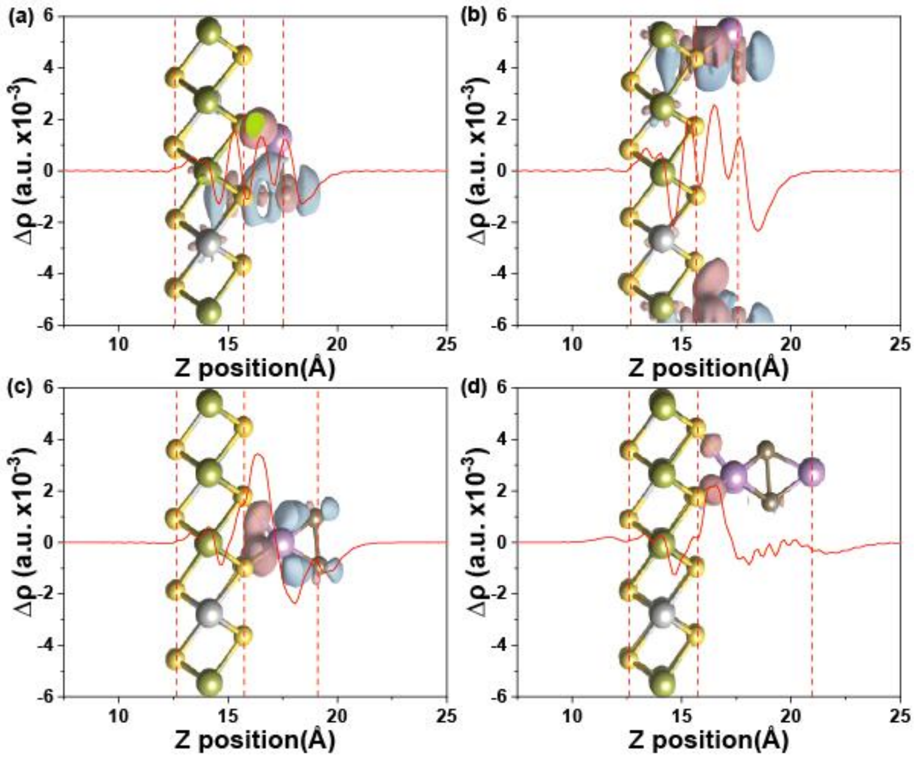


Figure S27. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.5}Ti_{0.5}S_2$. blue and pink represent charge depletion and gain, respectively.

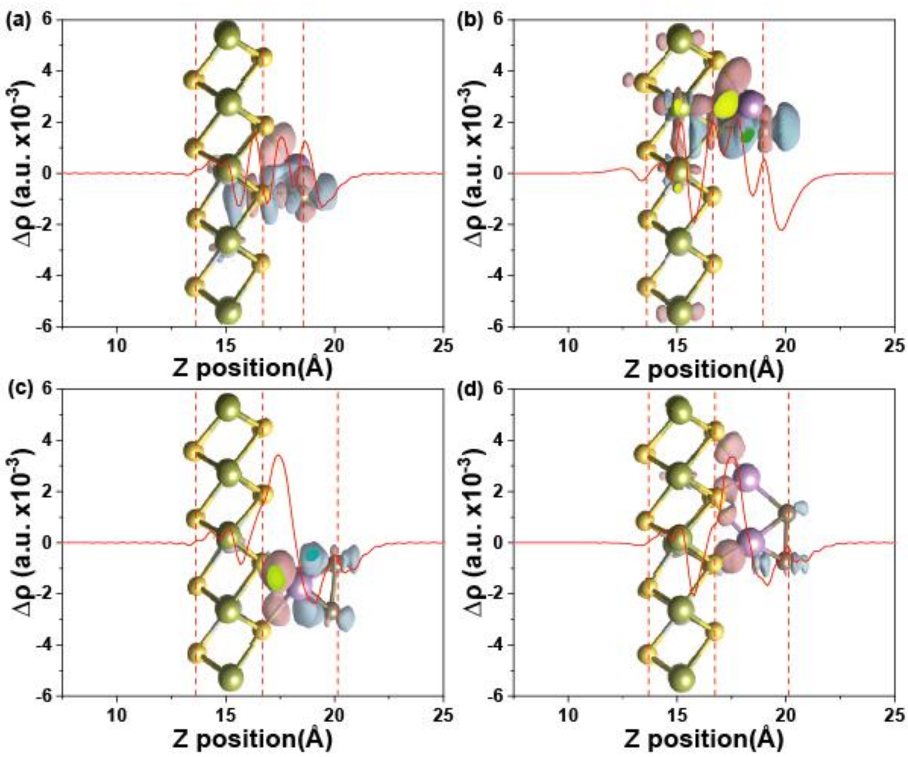


Figure S28. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.56}Ti_{0.44}S_2$. blue and pink represent charge depletion and gain, respectively.

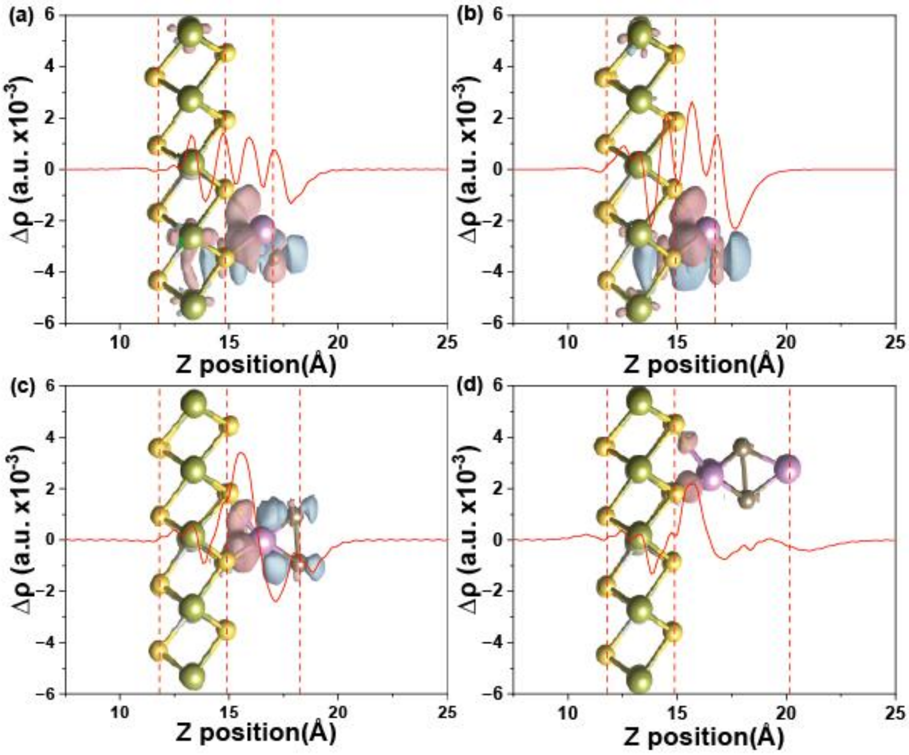


Figure S29. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.63}Ti_{0.37}S_2$. blue and pink represent charge depletion and gain, respectively.

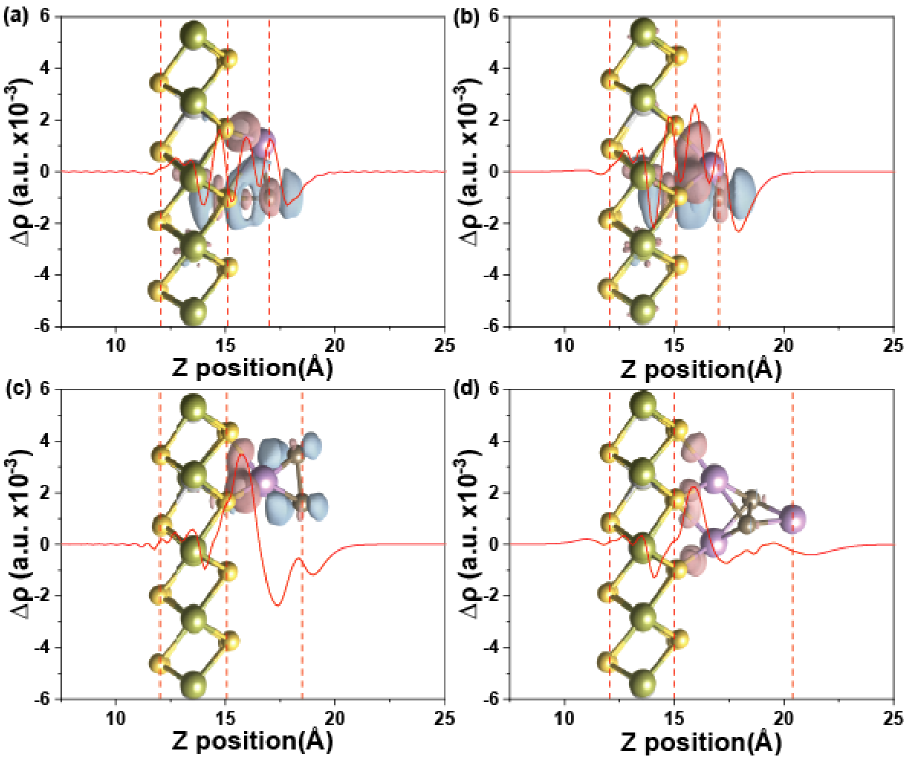


Figure S30. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.69}Ti_{0.31}S_2$. blue and pink represent charge depletion and gain, respectively.

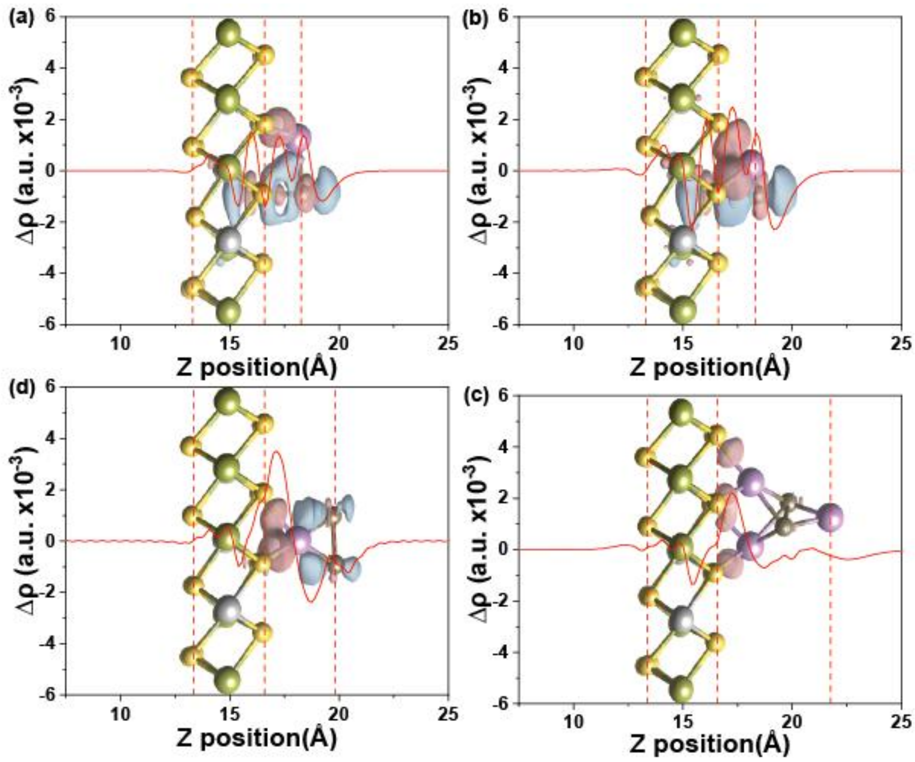


Figure S31. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.75}Ti_{0.25}S_2$. blue and pink represent charge depletion and gain, respectively.

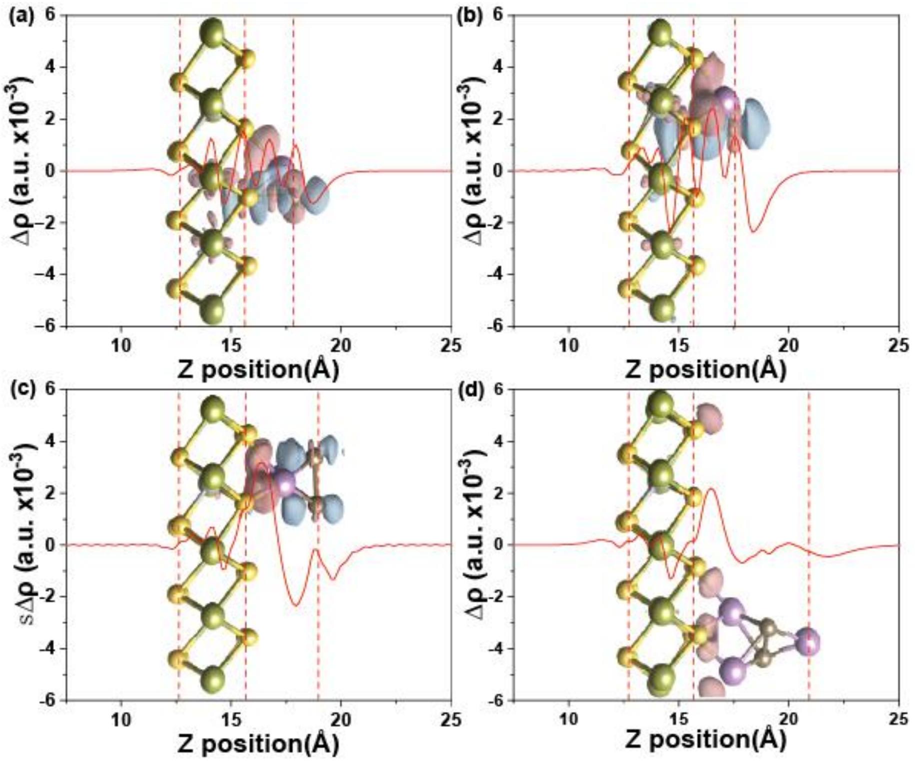


Figure S32. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.82}Ti_{0.18}S_2$. blue and pink represent charge depletion and gain, respectively.

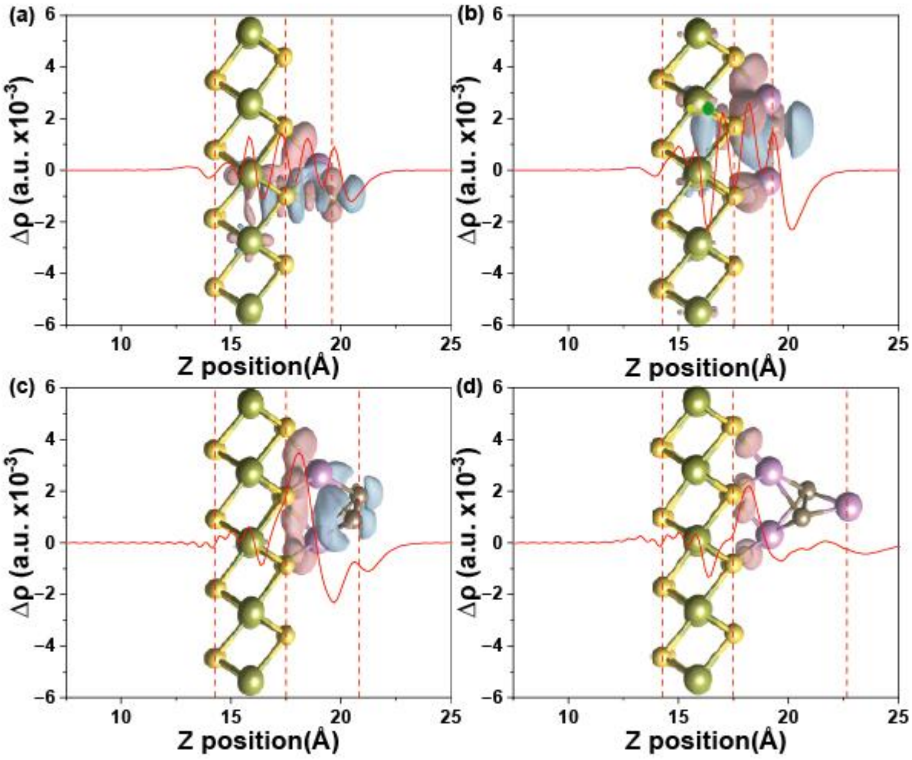


Figure S33. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.88}Ti_{0.12}S_2$. blue and pink represent charge depletion and gain, respectively.

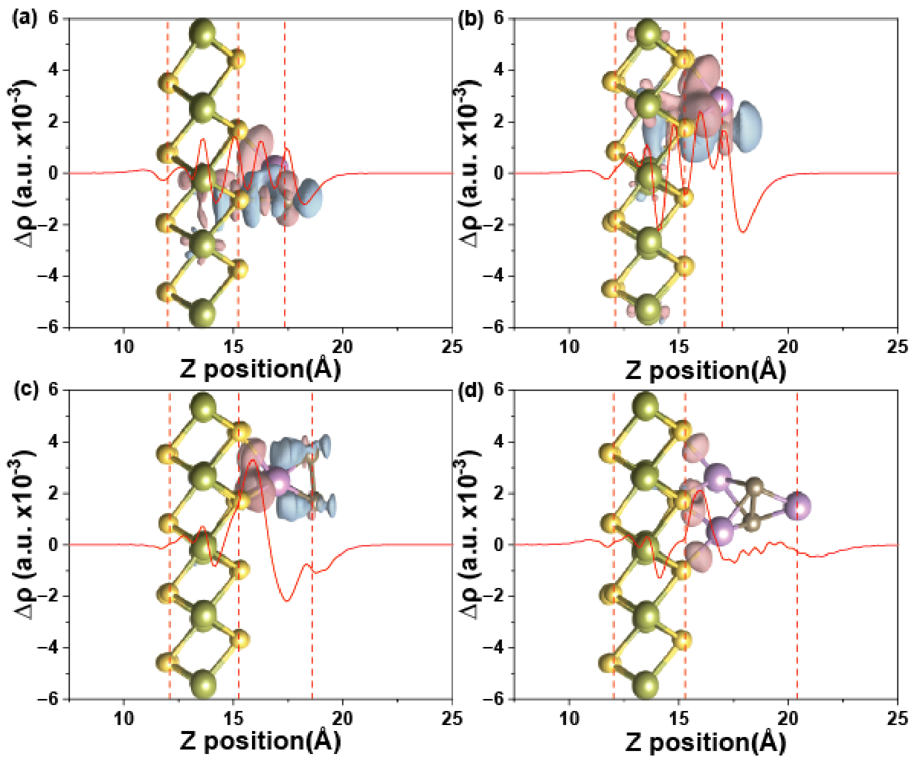


Figure S34. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on $Ta_{0.94}Ti_{0.06}S_2$. blue and pink represent charge depletion and gain, respectively.

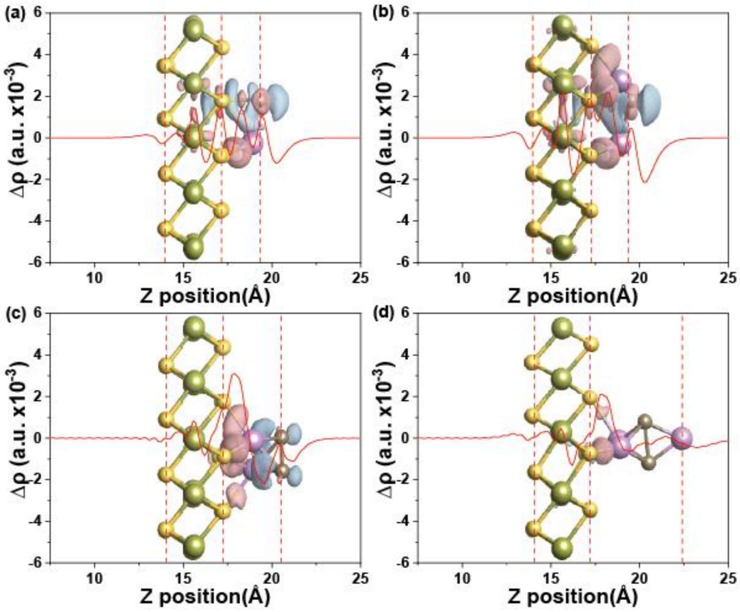


Figure S35. Side views of the Plane-averaged charge density difference between (a) LiS, (b) Li_2S, (c) Li_2S_2, (d) Li_3S_2 on TaS_2. blue and pink represent charge depletion and gain, respectively.

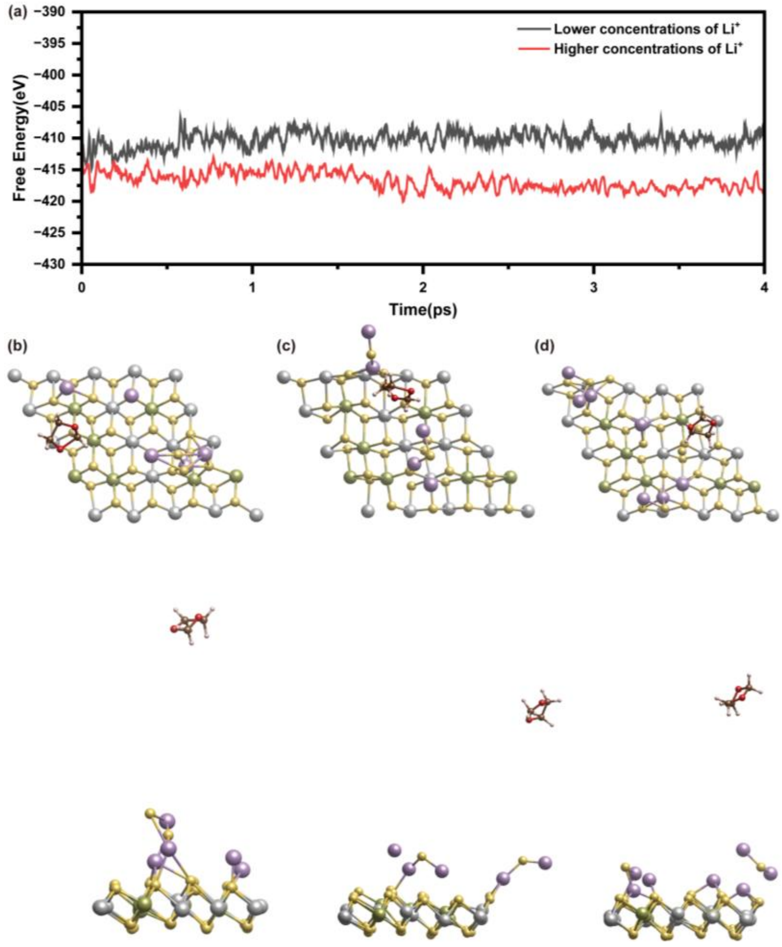


Figure S36. (a) Total energy change of $Ta_{0.38}Ti_{0.62}S_2$ in AIMD simulations at lower and higher concentration Li^+, (b) top and side views of $Ta_{0.38}Ti_{0.62}S_2$ forming Li_3S_2 at 0.8 ps in lower concentration of Li^+. Top and side views of the final structure in (c) lower and (d) higher concentration Li^+.

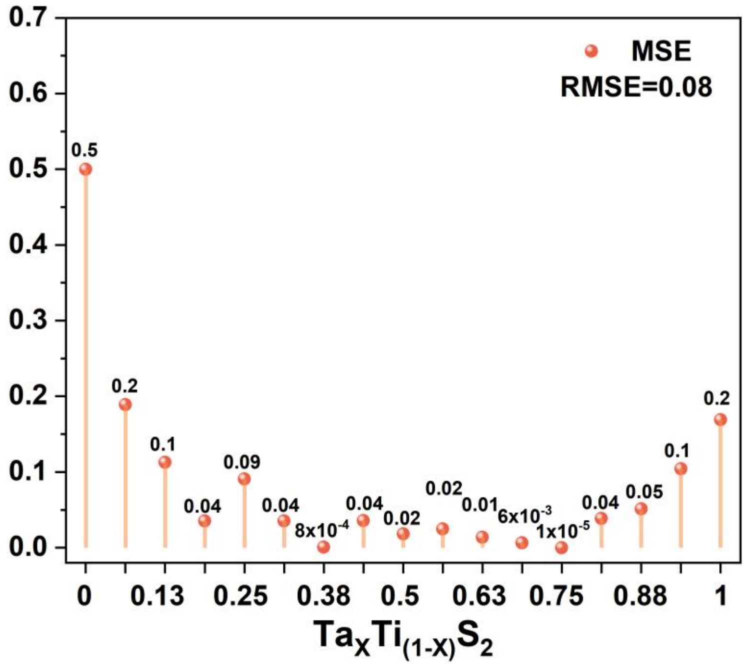


Figure S37. The leave-one-out cross-validation of $Ta_XTi_{(1-X)}S_2$ MSE and RMSE.

Table S6. The correlation (Pearson correlation coefficient) between a single parameter and the Gibbs free energy of Pathways 1.

Pearson correlation coefficient	WF	ΔWF_{Li_2S}	$\Delta WF_{Li_2S_2}$	Δd-p	ΔX	Ea_{Li_2S}	$Ea_{Li_2S_2}$
ΔG1-P1	-0.57	-0.21	0.42	0.32	-0.57	0.81	0.42

Pearson correlation coefficient	Q_{Li_2S}	$Q_{Li_2S_2}$	d_{Li_2S}	$d_{Li_2S_2}$	$ICOHP_{Li_2S}$	$ICOHP_{Li_2S_2}$
ΔG1-P1	-0.09	0.65	0.09	-0.46	-0.45	-0.06