Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information:

Enhancement of Band Gap and Birefringence Induced from π-Conjugated Chromophore with "Tail Effect"

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Table S1 ICSD code, space group, cell volume and group density of template compounds.

Compounds	ICSD code	Space group	Cell Volume	Density of $[CO_3]^{2-}$/$[HCO_3]^-$
Na_2CO_3	95549	$C2/m$	276.43	0.01447
$NaHCO_3$	18183	$P2_1/c$	254.65	0.01571
K_2CO_3	10191	$P2_1/c$	375.79	0.01064
$KHCO_3$	2076	$P2_1/a$	300.93	0.01329
Rb_2CO_3	14155	$P2_1/c$	431.56	0.00927
$RbHCO_3$	243962	$C\bar{1}$	334.58	0.01196
Cs_2CO_3	14156	$P2_1/c$	508.95	0.00786
$CsHCO_3$	300259	$P2_1/n$	364.36	0.01098
K_3CO_3F	660288	$R\bar{3}c$	781.16	0.00768
$K_2HCO_3F·H_2O$	188659	$P2_1/m$	279.28	0.00716
Na_3BO_3	1351	$P2_1/c$	341.09	0.01173
Na_2HBO_3	27211	$Pnma$	298.83	0.01339
$Ca_3(C_3N_3O_3)_2$	428357	$R3c$	1399.03	0.00858
$Rb_2(HC_3N_3O_3)$	131051	$Cmcm$	652.63	0.00613

Table S2 Static polarization components, polarizability anisotropy $\Delta\alpha$ and HOMO-LUMO energy gap of the $[CO_3]^{2-}$, $[BO_3]^{3-}$, $[C_3N_3O_3]^{3-}$, $[HCO_3]^-$, $[HBO_3]^{2-}$ and $[HC_3N_3O_3]^{2-}$.

Units	Static polarization						$\Delta\alpha$	HOMO-LUMO energy gap
	xx	*xy*	*yy*	*xz*	*yz*	*zz*		
$[HCO_3]^-$	25.92	-3.59	22.53	0.00	0.00	8.56	17.12	7.04
$[CO_3]^{2-}$	21.73	0.00	21.72	0.00	0.00	8.94	12.79	7.34
$[HBO_3]^{2-}$	26.48	-4.23	26.48	0.00	0.00	12.81	15.51	6.62
$[BO_3]^{3-}$	23.54	0.00	23.53	0.00	0.00	14.09	9.44	7.84
$[HC_3N_3O_3]^{2-}$	22.12	0.00	67.80	0.00	0.00	82.49	54.53	6.37
$[C_3N_3O_3]^{3-}$	74.40	0.00	74.39	0.00	0.00	22.48	51.91	6.58

Table S3 The contribution of $[CO_3]^{2-}$ or $[HCO_3]^{-}$ groups and A-site cationic polyhedra to birefringence by REDA analysis method.

Compounds	$[CO_3]^{2-}$/$[HCO_3]^{-}$ groups and A-site cationic polyhedra	$\Delta\rho$	Contribution
Na_2CO_3	$[CO_3]^{2-}$	0.03139	98.24 %
	$Na(1)O_6$ and $Na(2)O_6$ and $Na(3)O_9$	0.00056	1.76 %
K_2CO_3	$[CO_3]^{2-}$	0.01913	92.28 %
	$K(1)O_9$ and $K(2)O_6$	0.00160	7.72 %
Rb_2CO_3	$[CO_3]^{2-}$	0.00733	104.12 %
	$Rb(1)O_9$ and $Rb(2)O_6$	-0.00029	-4.12 %
Cs_2CO_3	$[CO_3]^{2-}$	0.01212	87.77 %
	CsO_9	0.00169	12.23 %
K_3CO_3F	$[CO_3]^{2-}$	0.01389	95.66 %
	KO_5F_2	0.00063	4.34 %
$NaHCO_3$	$[HCO_3]^{-}$	0.03912	101.33 %
	NaO_6	-0.00052	-1.33 %
$KHCO_3$	$[HCO_3]^{-}$	0.03391	102.82 %
	KO_8	-0.00093	-2.82 %
$RbHCO_3$	$[HCO_3]^{-}$	0.03140	98.91 %
	RbO_8	0.00035	1.09 %
$CsHCO_3$	$[HCO_3]^{-}$	0.02622	97.63 %
	CsO_9	0.00064	2.37 %
$K_2HCO_3F{\cdot}H_2O$	$[HCO_3]^{-}$	0.02584	77.19 %
	KO_5F_2	-0.00049	-1.46 %
	H_2O	0.00813	24.27 %

Table S4 The band gaps, birefringence and $\Delta\rho$ of Na_3BO_3, Na_2HBO_3, $Ca_3(C_3N_3O_3)_2$ and $Rb_2(HC_3N_3O_3)$.

Compounds	Band gap (GGA /eV)	Band gap (HSE06 /eV)	Birefringence @ 1064 nm	A-site cationic polyhedral and anion groups	$\Delta\rho$
Na_3BO_3	2.83	4.65	0.023	$Na(1)O_5$, $Na(2)O_5$, $Na(3)O_4$	-0.00026
				$[BO_3]^{3-}$	0.01130
Na_2HBO_3	3.75	5.49	0.084	$Na(1)O_5$, $Na(2)O_6$	0.00273
				$[HBO_3]^{2-}$	0.02537
$Ca_3(C_3N_3O_3)_2$	3.97	5.32	0.368	CaO_4N_2	0.00321
				$[C_3N_3O_3]^{3-}$	0.03137
$Rb_2(HC_3N_3O_3)$	4.54	6.05	0.381	RbO_6N_2	0.00042
				$[HC_3N_3O_3]^{2-}$	0.04341

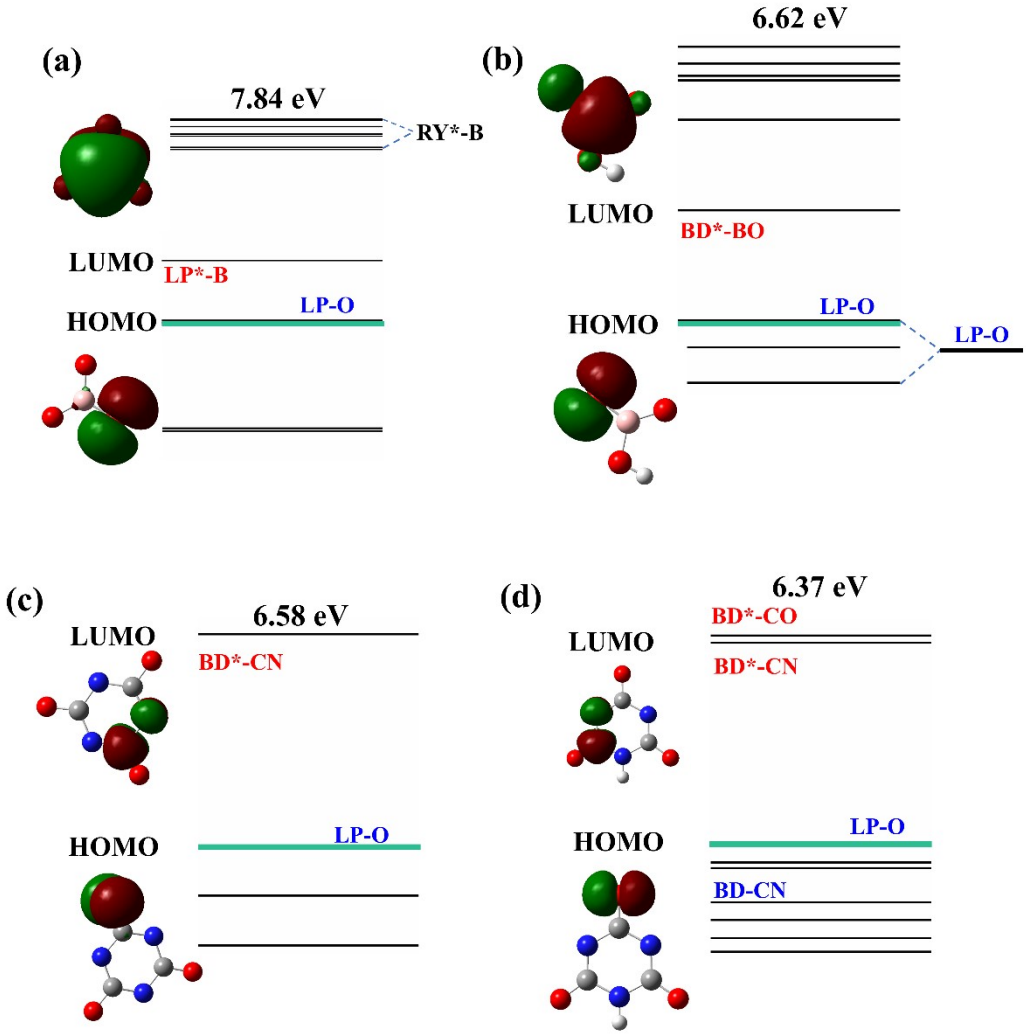
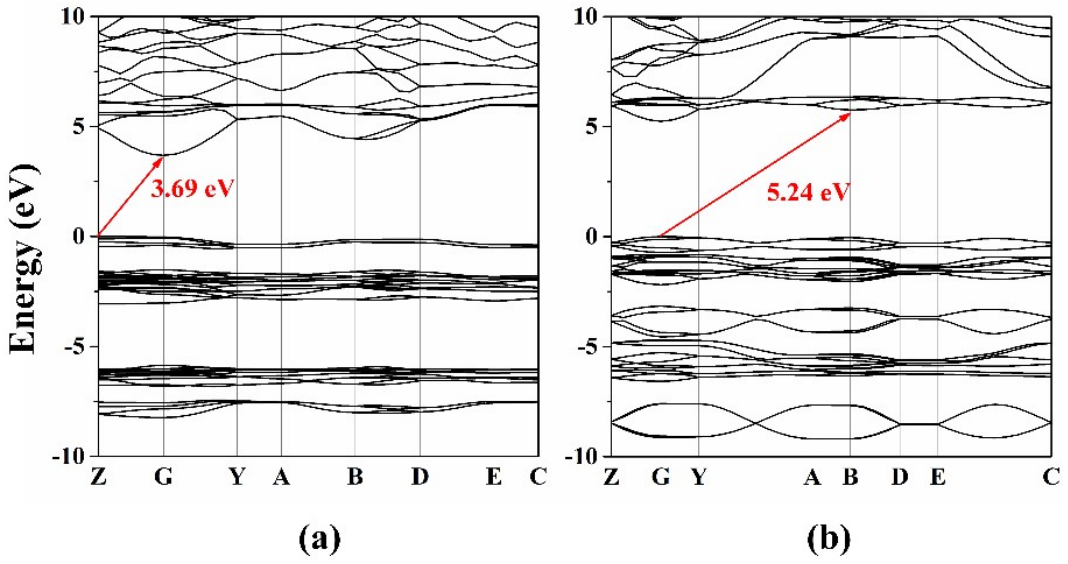
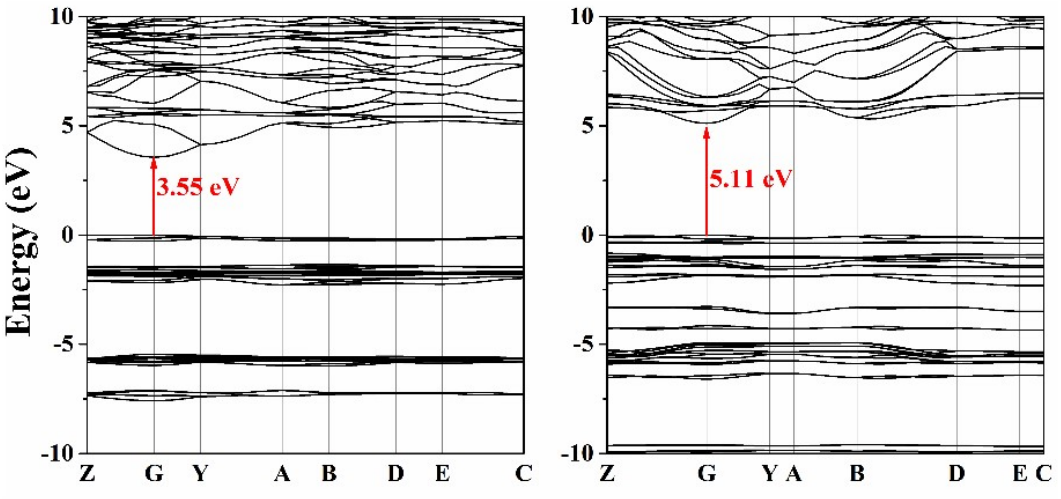
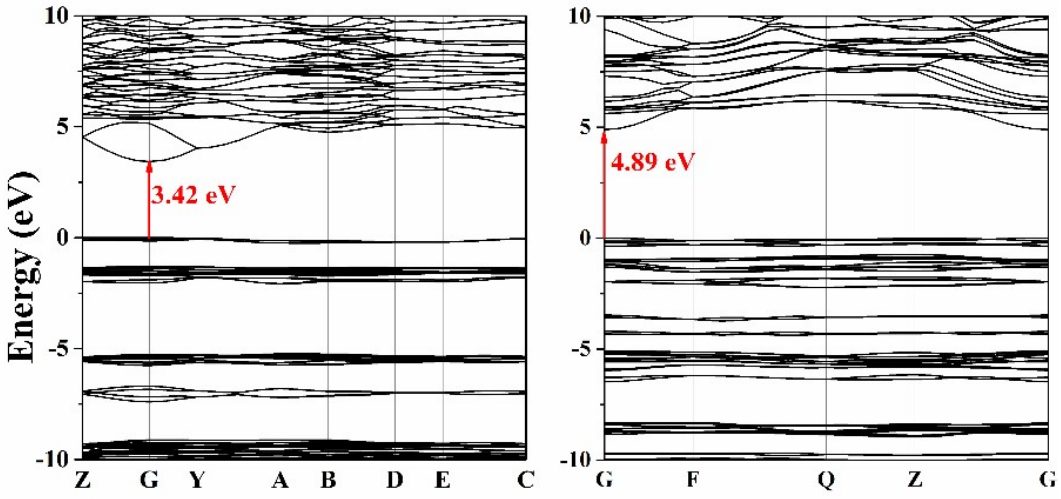
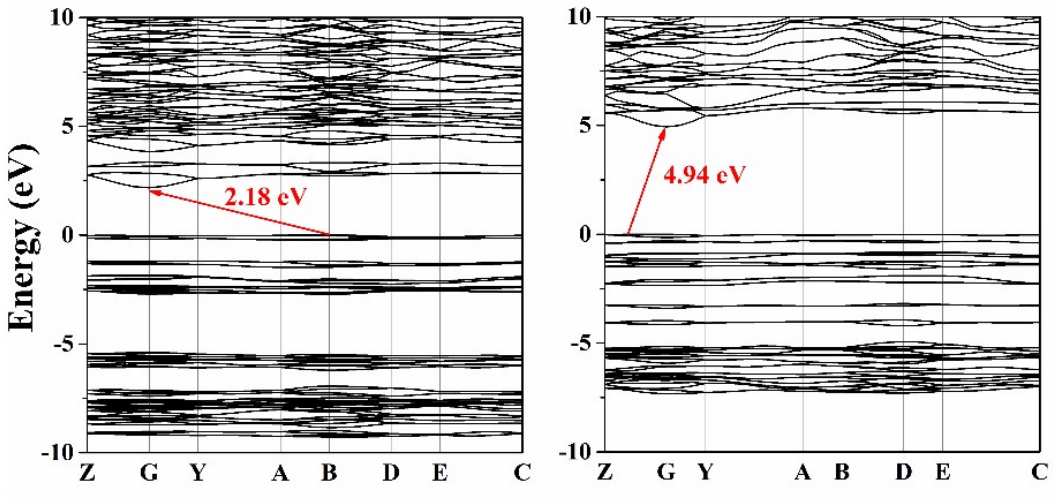


Figure S1 The HOMO-LUMO energy gaps, frontier molecule orbitals and energy levels of $[BO_3]^{3-}$, $[HBO_3]^{2-}$, $[C_3N_3O_3]^{3-}$ and $[HC_3N_3O_3]^{2-}$.




Energy (eV)
10
5
0
-5
-10
3.55 eV
Z G Y A B D E C
(c)
5.11 eV
Z G Y A B D E C
(d)


Energy (eV)
3.42 eV
Z G Y A B D E C
(e)
4.89 eV
G F Q Z G
(f)


Energy (eV)
2.18 eV
Z G Y A B D E C
(g)
4.94 eV
Z G Y A B D E C
(h)

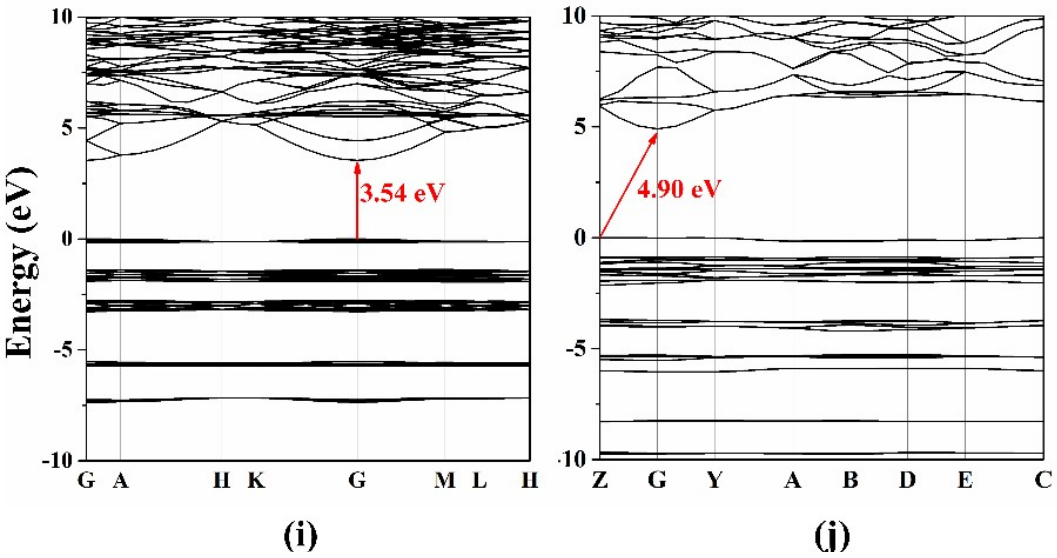


Figure S2. The GGA electronic band structures of Na_2CO_3 (a), $NaHCO_3$ (b), K_2CO_3 (c), $KHCO_3$ (d), Rb_2CO_3 (e), $RbHCO_3$ (f), Cs_2CO_3 (g), $CsHCO_3$ (h), K_3CO_3F (i), and $K_2HCO_3F·H_2O$ (j).

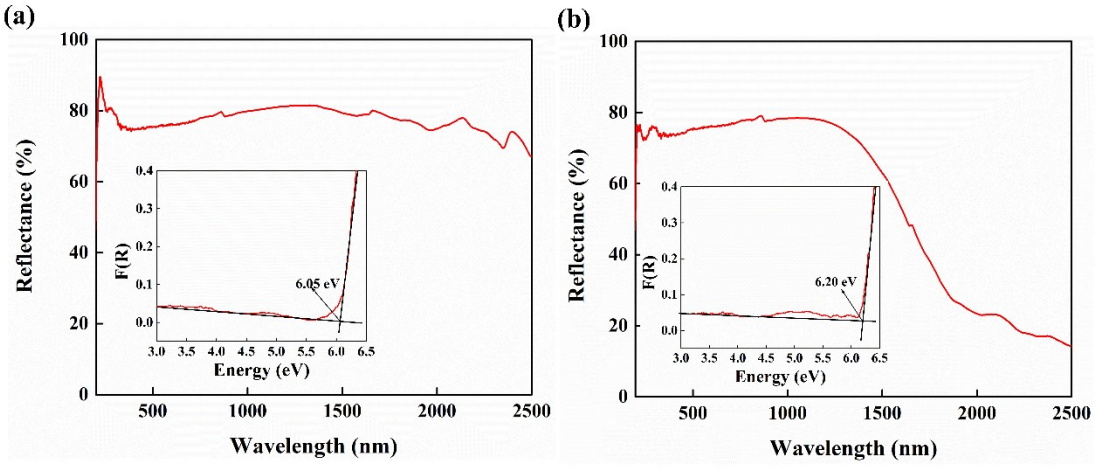
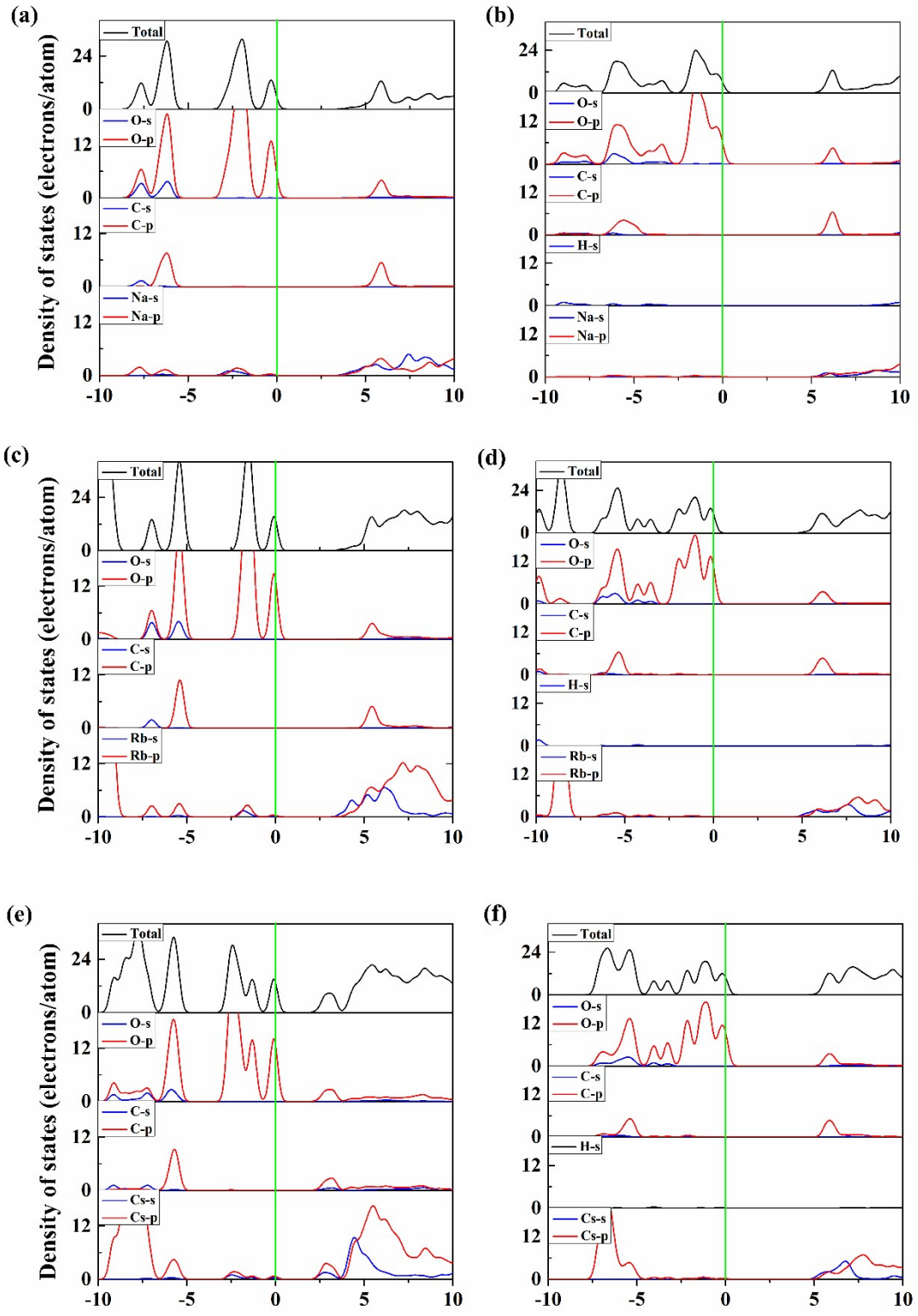


Figure S3 The UV-Vis-NIR diffuse reflectance spectra of Na_2CO_3 (a) and $NaHCO_3$ (b).


(a)
(b)
(c)
(d)
(e)
(f)
Density of states (electrons/atom)
Total
O-s
O-p
C-s
C-p
Na-s
Na-p
H-s
Rb-s
Rb-p
Cs-s
Cs-p
24
12
0
-10
-5
5
10

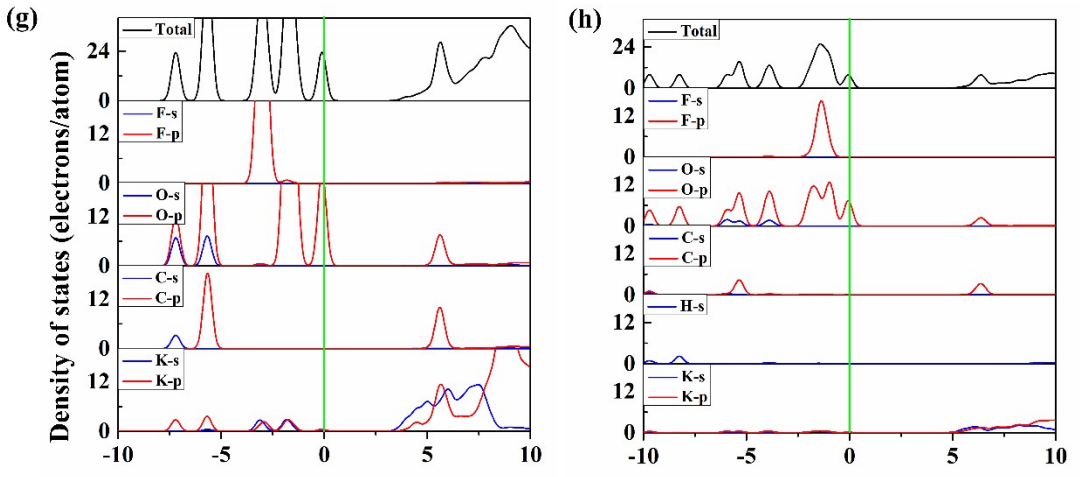


Figure S4. The partial density of states (PDOS) of Na_2CO_3 (a), $NaHCO_3$ (b), Rb_2CO_3 (c), $RbHCO_3$ (d), Cs_2CO_3 (e), $CsHCO_3$ (f), K_3CO_3F (g), and $K_2HCO_3F{\cdot}H_2O$ (h).