Supporting Information

Design of Doped Cesium Lead Halide Perovskite as Photo-Catalytic CO$_2$ Reduction Catalyst

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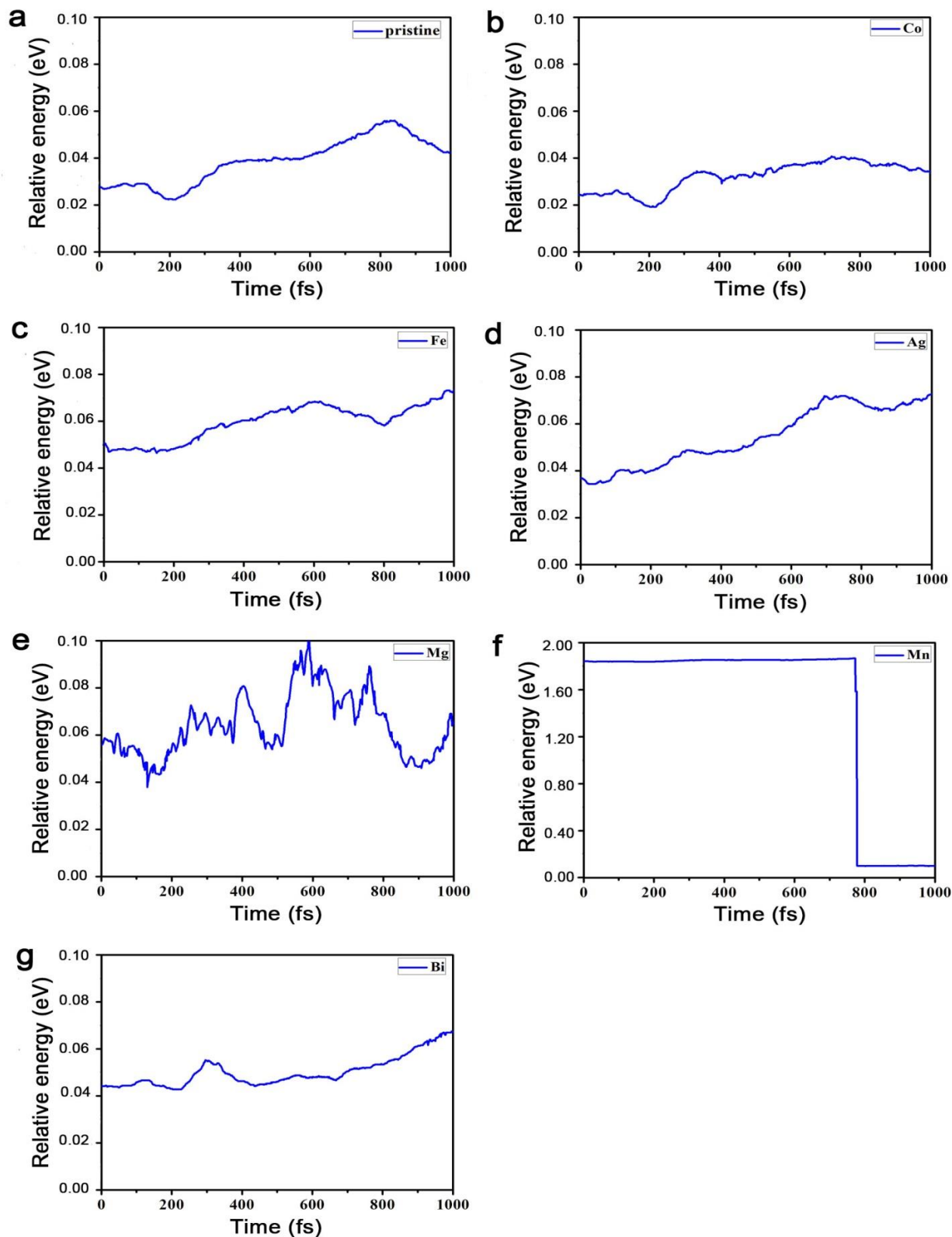
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Figure S1. The ab initio molecular dynamics (AIMD) calculations of structures corresponding to Fig. 1 at 300 K (NVT) for 1 ps, (a) is pristine, (b-i) represents the doping of Co, Fe, Ag, Mg, Mn and Bi respectively.

Table S1. Lattice parameters of pristine and doped perovskite with different metals corresponding to
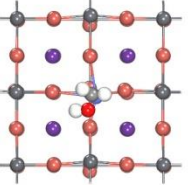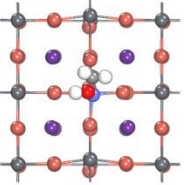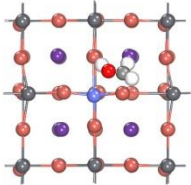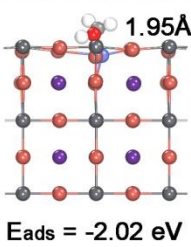
Figure 1.
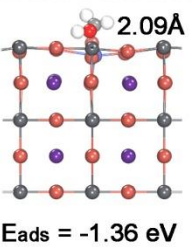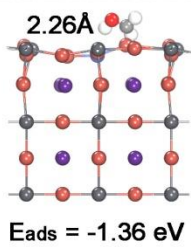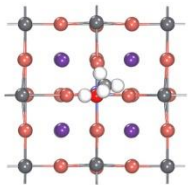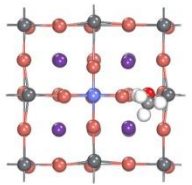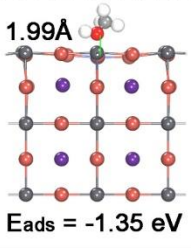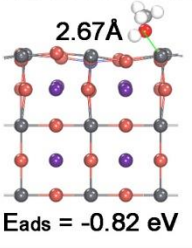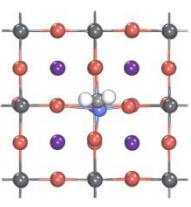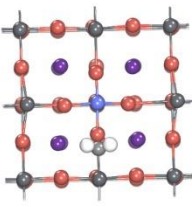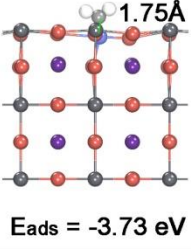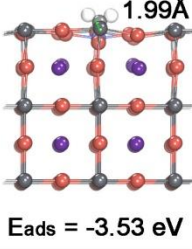
Name	a (Å)	b (Å)	c (Å)	α (º)	β (º)	γ (º)
pristine	11.92	11.92	11.92	84.54	84.54	89.48
Co-doped	12.06	11.95	11.93	86.41	87.97	91.55
Fe-doped	12.06	11.95	11.94	86.64	87.16	91.73
Ni-doped	12.09	11.99	11.93	86.48	85.59	92.09
Cu-doped	12.08	11.98	11.93	84.92	84.73	91.96
Ag-doped	11.92	11.92	11.93	87.17	87.39	89.96
Mg-doped	12.06	11.96	11.91	87.56	86.41	90.52
Mn-doped	12.07	11.96	11.94	87.08	87.25	89.37
Bi-doped	12.08	11.98	11.94	85.97	86.29	90.36

Table S2. Summary of adsorption energies and possible configurations on Co-doped CsPbBr$_3$ explored by this study.

CO$_2$*	Top View				
	Side View	2.23Å E_{ads} = -0.39 eV	2.24Å E_{ads} = -0.27 eV		
C*O	Top View				
	Side View	1.78Å E_{ads} = -2.89 eV	3.19Å E_{ads} = -0.68 eV	2.18Å E_{ads} = -1.91 eV	
C*OOH	Top View				
	Side View	1.90Å E_{ads} = -2.13 eV	1.99Å E_{ads} = -1.36 eV	1.97Å E_{ads} =-1.36 eV	2.74Å E_{ads} = -0.68 eV
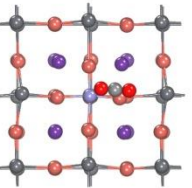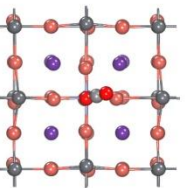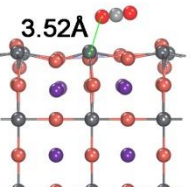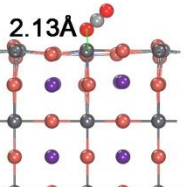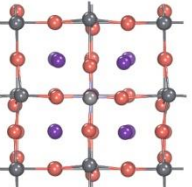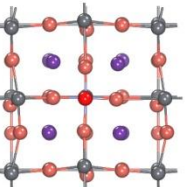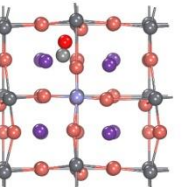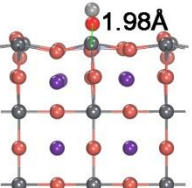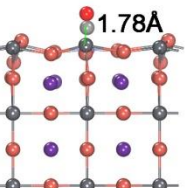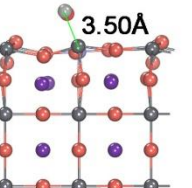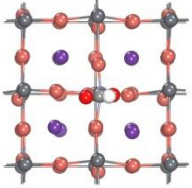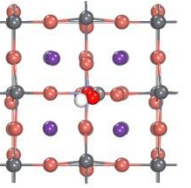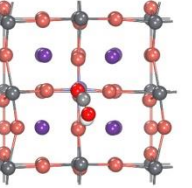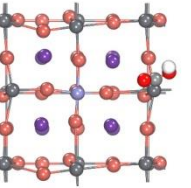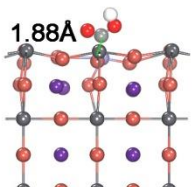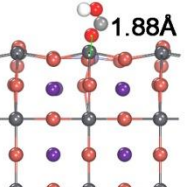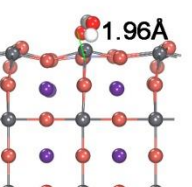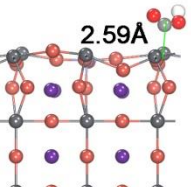
HCOO*	Top View				
	Side View	1.86Å E_{ads} = -2.37 eV	1.89Å E_{ads} = -2.32 eV	2.47Å E_{ads} = -2.31 eV	
HCO*OH	Top View				
	Side View	1.98Å E_{ads} = -1.23 eV	2.09Å E_{ads} = -0.82 eV	2.09Å E_{ads} = -0.89 eV	3.07Å E_{ads} = -0.81 eV	1.97Å E_{ads} = -1.16 eV
H₂CO*OH	Top View				
	Side View	1.79Å E_{ads} = -2.24 eV	2.45Å E_{ads} = -1.09 eV	2.29Å E_{ads} =-1.63 eV	

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HC*O	Top View				
	Side View	1.86Å	2.11Å	1.97Å	3.01Å
		E_{ads} = -2.57 eV	E_{ads} = -1.19 eV	E_{ads} = -1.09 eV	E_{ads} = -0.60 eV
H₂CO*	Top View				
	Side View	1.94Å	1.95Å	2.74Å	1.94Å
		E_{ads} = -1.29 eV	E_{ads} = -1.09 eV	E_{ads} = -0.81 eV	E_{ads} = -0.54 eV
H₃CO*	Top View				
	Side View	1.77Å	2.23Å		
		E_{ads} = -2.32 eV	E_{ads} = -1.89 eV		

C*H₂OH	Top View				
	Side View	1.95Å E_ads = -2.02 eV	2.09Å E_ads = -1.36 eV	2.26Å E_ads = -1.36 eV	
CH₃O*H	Top View				
	Side View	1.99Å E_ads = -1.35 eV	2.67Å E_ads = -0.82 eV		
C*H₂	Top View				
	Side View	1.75Å E_ads = -3.73 eV	1.99Å E_ads = -3.53 eV		

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C*H₃	Top View				
	Side View	1.94Å E$_{ads}$ = -1.86 eV	2.00Å E$_{ads}$ = -1.09 eV		
CH₄*	Top View				
	Side View	2.60Å E$_{ads}$ = -0.27 eV	3.17Å E$_{ads}$ = -0.26 eV		
HC*OH	Top View				
	Side View	1.80Å E$_{ads}$ = -3.47 eV			

Table S3. Summary of adsorption energies and possible configurations on Fe-doped $CsPbBr_3$ explored by this study.

CO_2*	Top View					
	Side View	3.52Å E_{ads} = -0.32 eV	2.13Å E_{ads} = -0.34 eV			
$C*O$	Top View					
	Side View	1.98Å E_{ads} = -0.56 eV	1.78Å E_{ads} = -1.83 eV	3.50Å E_{ads} = -0.31 eV		
$C*OOH$	Top View					
	Side View	1.88Å E_{ads} = -1.40 eV	1.88Å E_{ads} = -0.92 eV	1.96Å E_{ads} =-1.14 eV	2.59Å E_{ads} = -0.69 eV	

HCOO*	Top View				
	Side View	 1.88Å E_{ads} = -1.83 eV	 2.48Å E_{ads} = -0.92 eV		
HCO*OH	Top View					
	Side View	 1.99Å E_{ads} = -0.94 eV	 1.97Å E_{ads} = -0.81 eV	 2.05Å E_{ads} = -0.69 eV	 2.83Å E_{ads} = -0.23 eV	 2.82Å E_{ads} = -0.56 eV
H₂CO*OH	Top View				
	Side View	 1.77Å E_{ads} = -2.29 eV	 2.26Å E_{ads} = -1.19 eV		

(Row labels read vertically: HCOO*, HCO*OH, H₂CO*OH)

HC*O	Top View					
	Side View	1.89Å Eads = -1.83 eV	1.94Å Eads = -0.72 eV			
H₂CO*	Top View					
	Side View	1.92Å Eads = -1.01 eV	2.74Å Eads = -0.42 eV	2.68Å Eads = -0.33 eV		
H₃CO*	Top View					
	Side View	1.77Å Eads = -2.44 eV	2.25Å Eads = -1.27 eV			

C*H₂OH	Top View				
	Side View	1.93Å E_{ads} = -1.64 eV	2.03Å E_{ads} = -0.96 eV	1.96Å E_{ads} = -1.09 eV	
CH₃O*H	Top View				
	Side View	2.02Å E_{ads} = -0.99 eV	2.72Å E_{ads} = -0.79 eV		
C*H₂	Top View				
	Side View	1.75Å E_{ads} = -3.85 eV	1.99Å E_{ads} = -3.11 eV		

C*H₃	Top View				
	Side View	1.94Å E_ads = -1.62 eV	2.41Å E_ads = -0.86 eV		
CH₄*	Top View				
	Side View	1.91Å E_ads = -0.14 eV	3.00Å E_ads = -0.13 eV		
HC*OH	Top View				
	Side View	1.80Å E_ads = -2.62 eV			

Figure S2. Optimized geometries of stable intermediates on the catalyst active sites. a-o: CO_2^*, C^*O, C^*OOH, $HCOO^*$, HCO^*OH, H_2CO^*OH, HC^*O, H_2CO^*, H_3CO^*, C^*H_2OH, CH_3O^*H, C^*H_2, C^*H_3, CH_4^* and HC^*OH on the Co-doped $CsPbBr_3$.

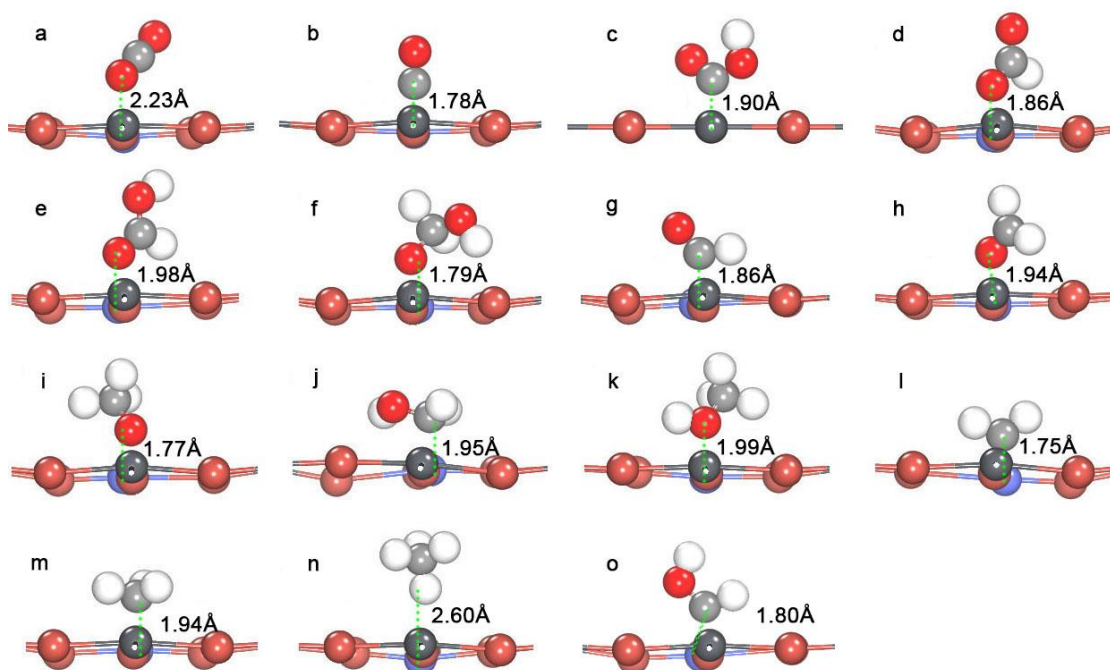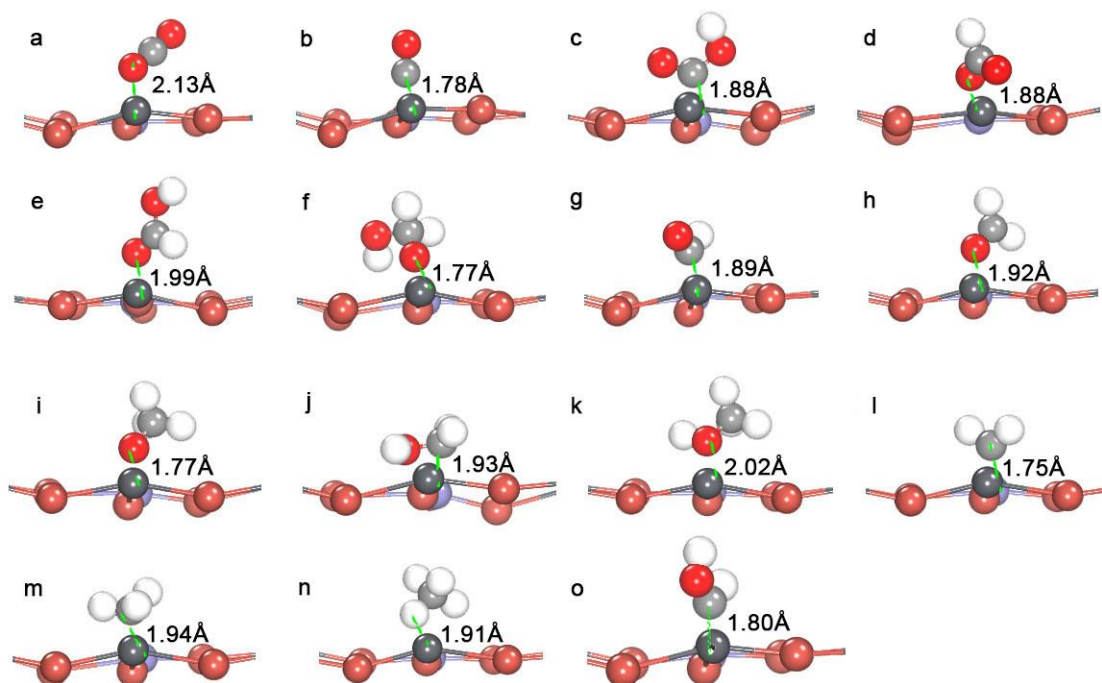**Figure S3.** Optimized geometries of stable intermediates on the catalyst active sites. a-o: CO_2^*, C^*O, C^*OOH, $HCOO^*$, HCO^*OH, H_2CO^*OH, HC^*O, H_2CO^*, H_3CO^*, C^*H_2OH, CH_3O^*H, C^*H_2, C^*H_3, CH_4^* and HC^*OH on the Fe-doped $CsPbBr_3$.

Table S4. Adsorption energies of the adsorbate molecules on (100) surfaces of pristine, Co-doped and Fe-doped $CsPbBr_3$ structures.

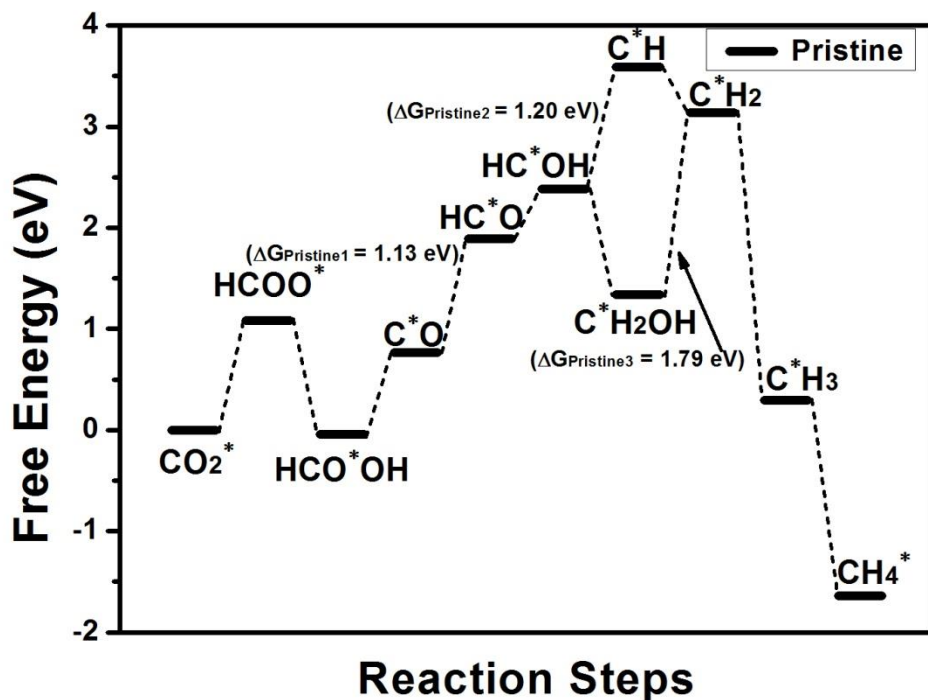| No.	Intermediate structure	$E_{ads}^{pristine}$ (eV)	$E_{ads}^{Co-doped}$ (eV)	$E_{ads}^{Fe-doped}$ (eV)
1	CO_2*	-0.25	-0.39	-0.34
2	C*O	-1.11	-2.89	-1.83
3	C*OOH	-0.22	-2.13	-1.40
4	HCOO*	-1.11	-2.37	-1.83
5	HC*O	-1.50	-2.57	-1.83
6	HCO*OH	-0.23	-1.23	-0.94
7	H_2CO*OH	-0.86	-2.24	-2.29
8	H_2CO*	-0.21	-1.29	-1.01
9	H_3CO*	-1.04	-2.32	-2.44
10	C*H_2OH	-1.66	-2.02	-1.64
11	CH_3O*H	-0.24	-1.35	-0.99
12	C*H_2	-1.21	-3.73	-3.85
13	C*H_3	-0.66	-1.86	-1.62
14	CH_4*	-0.26	-0.27	-0.14
15	HC*OH	-1.94	-3.47	-2.62

Figure S4. The free energy diagrams of possible paths of CO_2 reduction process on pristine $CsPbBr_3$, and the important ΔG of the reaction steps are listed.

Table S5. Hirshfeld charge of Pb, Co and Fe in the pristine, Co-doped and Fe-doped $CsPbBr_3$ respectively.

Steps	Pb@pristine	Co@Co-doped	Fe@Fe-doped
Free Standing	0.477	0.153	0.055
CO_2*	0.455	0.041	0.028
HCOO*	0.468	0.104	0.068
HCO*OH	0.455	0.058	0.044
HC*OH	0.361	0.013	0.006
C*H_2OH	0.447	0.034	0.024
C*H_2	0.353	0.048	0.047
C*H_3	0.400	0.075	0.077
CH_4*	0.461	0.044	0.063
C*O	0.442	0.003	0.001
HC*O	0.383	0.034	0.013

Table S6. Hirshfeld charge of O1, O2 and C in the Co-doped $CsPbBr_3$.

Steps	O1	O2	C
Free Standing	-0.151	-0.151	0.302
CO_2*	-0.092	-0.118	0.308
HCOO*	-0.192	-0.272	0.114
HCO*OH	-0.138	-0.113	0.185
HC*OH	-0.073	NA	0.047
C*H_2OH	-0.106	NA	0.051
C*H_2	NA	NA	-0.075
C*H_3	NA	NA	-0.191
CH_4*	NA	NA	-0.165
C*O	-0.071	NA	0.123
HC*O	-0.17	NA	0.04

Table S7. Hirshfeld charge of O1, O2 and C in the Fe-doped $CsPbBr_3$.

Steps	O1	O2	C
Free Standing	-0.151	-0.151	0.302
CO_2*	-0.082	-0.109	0.317
HCOO*	-0.179	-0.262	0.143
HCO*OH	-0.143	-0.117	0.183
HC*OH	-0.101	NA	0.012
C*H$_2$OH	-0.049	NA	0.033
C*H$_2$	NA	NA	-0.078
C*H$_3$	NA	NA	-0.205
CH$_4$*	NA	NA	-0.159
C*O	-0.093	NA	0.095
HC*O	-0.172	NA	0.025