

Supporting Information

First-Principles Computation on Electron Transfer and Reaction Rate at the Perovskite Cathode for Hydrogen Production

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Table S1 Electron transmitting path of H-cluster/MAPbI₂Br perovskite

Calculation method	Electron transmitting path
GGA/BLYP	HOMO->LUMO+6
Meta-GGA	HOMO->LUMO+2

Table S2 Electron transmitting path of H-cluster/MAPbI₂Cl perovskite

Calculation method	Electron transmitting path
GGA/BLYP	HOMO->LUMO+6
Meta-GGA	HOMO->LUMO

Table S3 One minimal cluster model of H-cluster/MAPbI₂Br

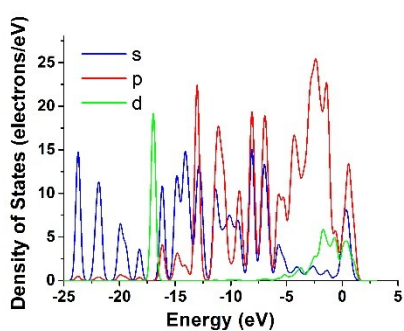
Energy level (GGA/BLYP)	Eigenvalue (eV)	Energy level (by B3LYP)	Eigenvalue (eV)	Energy level (by PBE0)	Eigenvalue (eV)
HOMO-10	-0.269	HOMO-10	-0.314	HOMO-10	-0.307
HOMO-9	-0.263	HOMO-9	-0.313	HOMO-9	-0.305
HOMO-8	-0.263	HOMO-8	-0.313	HOMO-8	-0.305
HOMO-7	-0.255	HOMO-7	-0.305	HOMO-7	-0.297
HOMO-6	-0.255	HOMO-6	-0.304	HOMO-6	-0.296
HOMO-5	-0.252	HOMO-5	-0.301	HOMO-5	-0.294
HOMO-4	-0.252	HOMO-4	-0.301	HOMO-4	-0.294
HOMO-3	-0.241	HOMO-3	-0.292	HOMO-3	-0.292
HOMO-2	-0.241	HOMO-2	-0.291	HOMO-2	-0.290
HOMO-1	-0.238	HOMO-1	-0.288	HOMO-1	-0.280
HOMO	-0.238	HOMO	-0.288	HOMO	-0.280
LUMO	-0.228	LUMO	-0.230	LUMO	-0.222
LUMO+1	-0.228	LUMO+1	-0.228	LUMO+1	-0.220
LUMO+2	-0.221	LUMO+2	-0.221	LUMO+2	-0.212
LUMO+3	-0.221	LUMO+3	-0.221	LUMO+3	-0.212
LUMO+4	-0.218	LUMO+4	-0.218	LUMO+4	-0.210

LUMO+5	-0.218	LUMO+5	-0.218	LUMO+5	-0.210
LUMO+6	-0.213	LUMO+6	-0.213	LUMO+6	-0.208
LUMO+7	-0.203	LUMO+7	-0.213	LUMO+7	-0.208
LUMO+8	-0.203	LUMO+8	-0.203	LUMO+8	-0.198
LUMO+9	-0.201	LUMO+9	-0.201	LUMO+9	-0.191
LUMO+10	-0.201	LUMO+10	-0.201	LUMO+10	-0.191

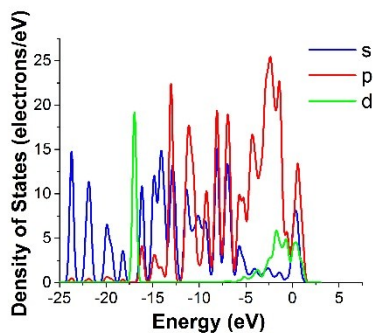
Table S4 One minimal cluster model of H-cluster/MAPbI₂Cl

Energy level (GGA/BLYP)	Eigenvalue (eV)	Energy level (by B3LYP)	Eigenvalue (eV)	Energy level (by PBE0)	Eigenvalue (eV)
HOMO-10	-0.269	HOMO-10	-0.329	HOMO-10	-0.329
HOMO-9	-0.263	HOMO-9	-0.323	HOMO-9	-0.323
HOMO-8	-0.263	HOMO-8	-0.323	HOMO-8	-0.323
HOMO-7	-0.255	HOMO-7	-0.315	HOMO-7	-0.315
HOMO-6	-0.255	HOMO-6	-0.315	HOMO-6	-0.315
HOMO-5	-0.252	HOMO-5	-0.312	HOMO-5	-0.312
HOMO-4	-0.252	HOMO-4	-0.312	HOMO-4	-0.312
HOMO-3	-0.241	HOMO-3	-0.301	HOMO-3	-0.301
HOMO-2	-0.241	HOMO-2	-0.301	HOMO-2	-0.301
HOMO-1	-0.238	HOMO-1	-0.298	HOMO-1	-0.298
HOMO	-0.238	HOMO	-0.298	HOMO	-0.298
LUMO	-0.231	LUMO	-0.241	LUMO	-0.241
LUMO+1	-0.231	LUMO+1	-0.231	LUMO+1	-0.220
LUMO+2	-0.224	LUMO+2	-0.230	LUMO+2	-0.220
LUMO+3	-0.224	LUMO+3	-0.228	LUMO+3	-0.199
LUMO+4	-0.221	LUMO+4	-0.226	LUMO+4	-0.199
LUMO+5	-0.221	LUMO+5	-0.226	LUMO+5	-0.196
LUMO+6	-0.213	LUMO+6	-0.203	LUMO+6	-0.196
LUMO+7	-0.205	LUMO+7	-0.201	LUMO+7	-0.192
LUMO+8	-0.205	LUMO+8	-0.201	LUMO+8	-0.192
LUMO+9	-0.201	LUMO+9	-0.192	LUMO+9	-0.189
LUMO+10	-0.201	LUMO+10	-0.192	LUMO+10	-0.189

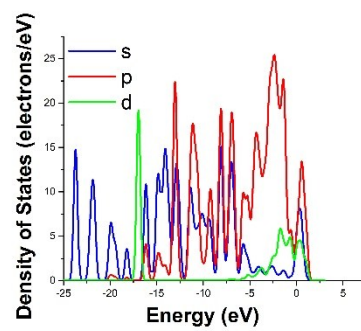
The PDOS comparison of the minimal cluster model of H-cluster/MAPbI₂Br



GGA/BLYP

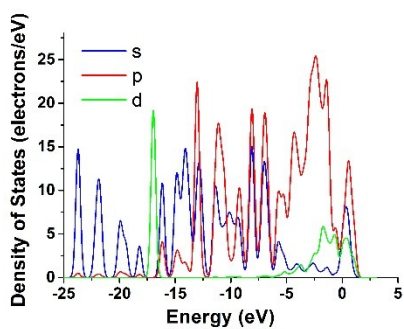


B3LYP

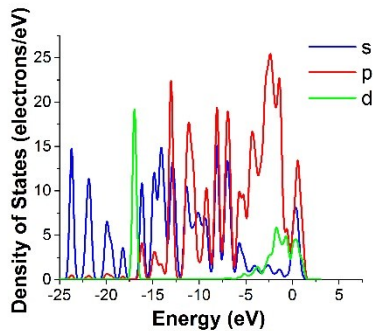


PBE0

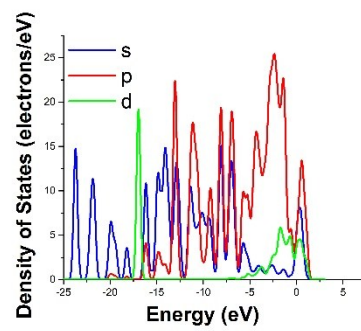
The PDOS comparison of the minimal cluster model of H-cluster/MAPbI₂Cl



GGA/BLYP



B3LYP



PBE0