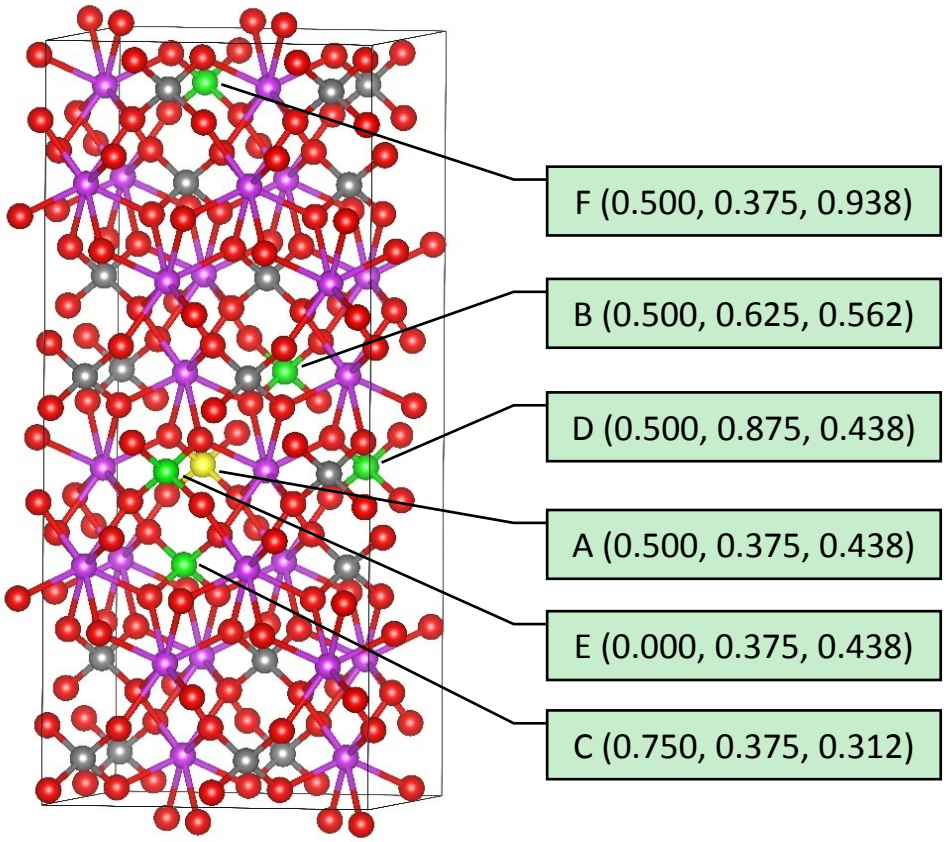

Figure S1. (2×2×2) $BiVO_4$ supercell; purple, silver and red balls represent Bi, V, and O atoms respectively. Initial and final sites of selected nearest neighbor V-V electron polaron transfer are shown in color. Site A, as marked in yellow, is considered the initial site for all depicted electron polaron transfer pathways. While nearest neighbor final sites are marked in green. The long distance transfer along [001] crystal direction is A to F.

Initial site	Final site	Bridge	dist (Å)
A	B	space	3.847
A	C	space	3.945
A	D	space	5.094
A	E	space	5.196
A	F	space	11.705

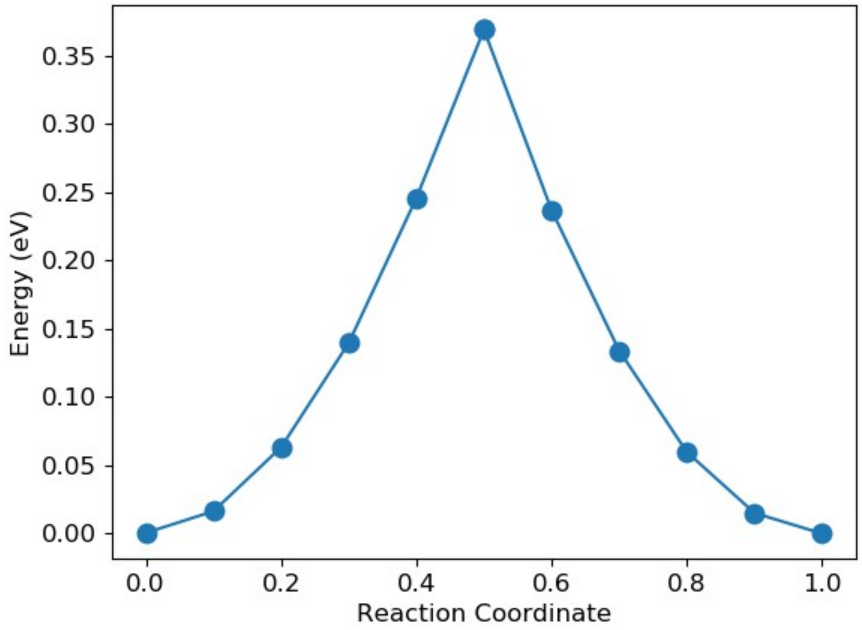

Figure S2a. Energy curve for electron hop A-to-B (e-hop # 1).

Table S2a. Site of electron localization and activation energy along e-hop # 1 (3.847 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	A	0.0000
0.1	A	0.0159
0.2	A	0.0628
0.3	A	0.1393
0.4	A	0.2456
0.5	B	0.3692
0.6	B	0.2367
0.7	B	0.1336
0.8	B	0.0593
0.9	B	0.0146
1.0	B	-0.0005

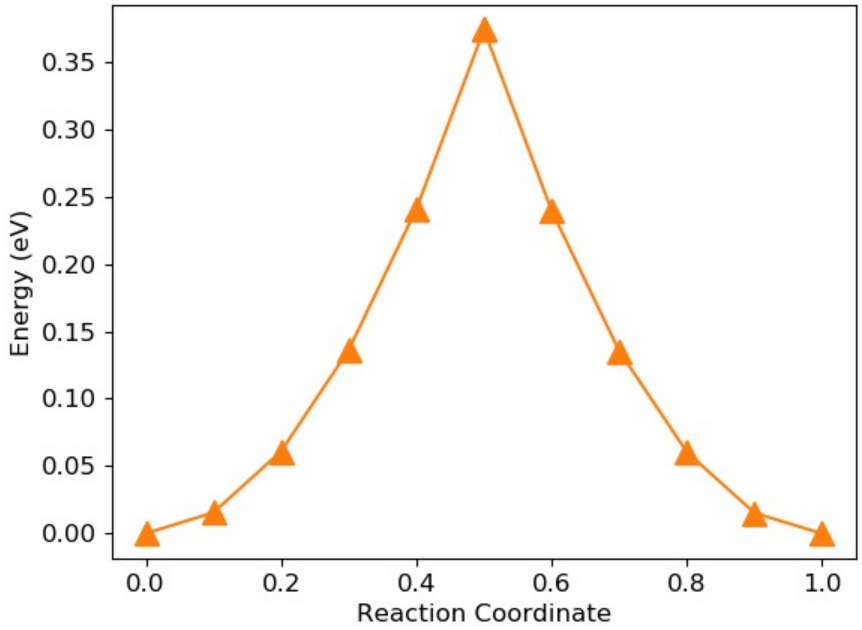

Figure S2b. Energy curve for electron hop A-to-C (e-hop # 2).

Table S2b. Site of electron localization and activation energy along e-hop # 2 (3.945 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	A	0.0000
0.1	A	0.0155
0.2	A	0.0610
0.3	A	0.1362
0.4	A	0.2408
0.5	A	0.3740
0.6	C	0.2396
0.7	C	0.1354
0.8	C	0.0604
0.9	C	0.0152
1.0	C	-0.0001

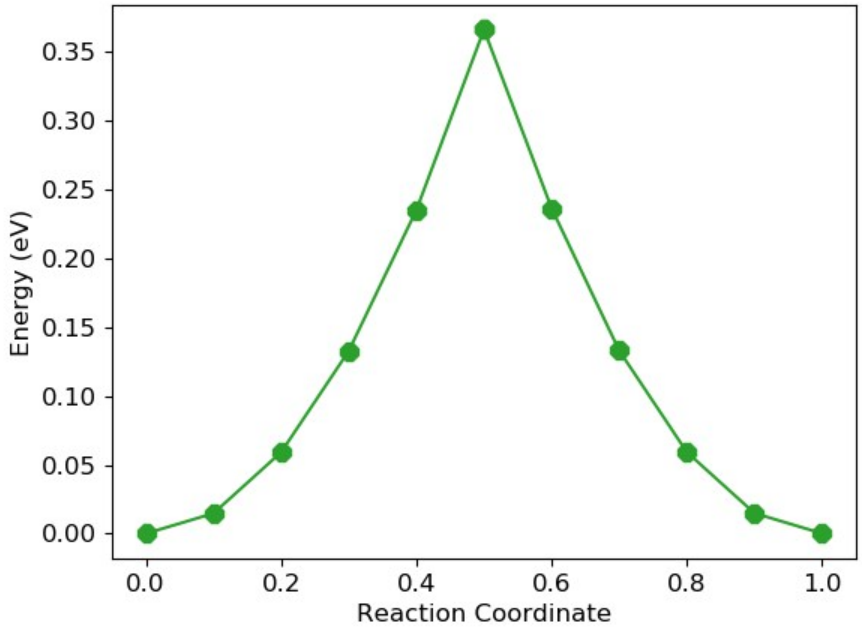

Figure S2c. Energy curve for electron hop A-to-D (e-hop # 3).

Table S2c. Site of electron localization and activation energy along e-hop # 3 (5.094 Å in [010] crystal direction).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	A	0.0000
0.1	A	0.0147
0.2	A	0.0591
0.3	A	0.1327
0.4	A	0.2351
0.5	A	0.3663
0.6	D	0.2364
0.7	D	0.1329
0.8	D	0.0592
0.9	D	0.0148
1.0	D	0.0001

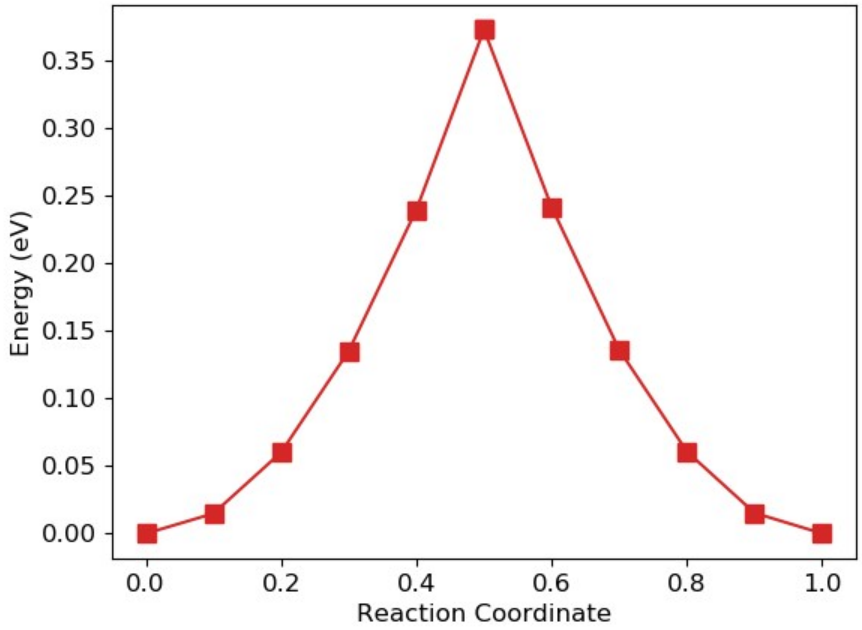

Figure S2d. Energy curve for electron hop A-to-E (e-hop # 4).

Table S2d. Site of electron localization and activation energy along e-hop # 4 (5.196 Å in [100] crystal direction).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	A	0.0000
0.1	A	0.0149
0.2	A	0.0602
0.3	A	0.1353
0.4	A	0.2399
0.5	A	0.3734
0.6	E	0.2419
0.7	E	0.1361
0.8	E	0.0608
0.9	E	0.0153
1.0	E	0.0001

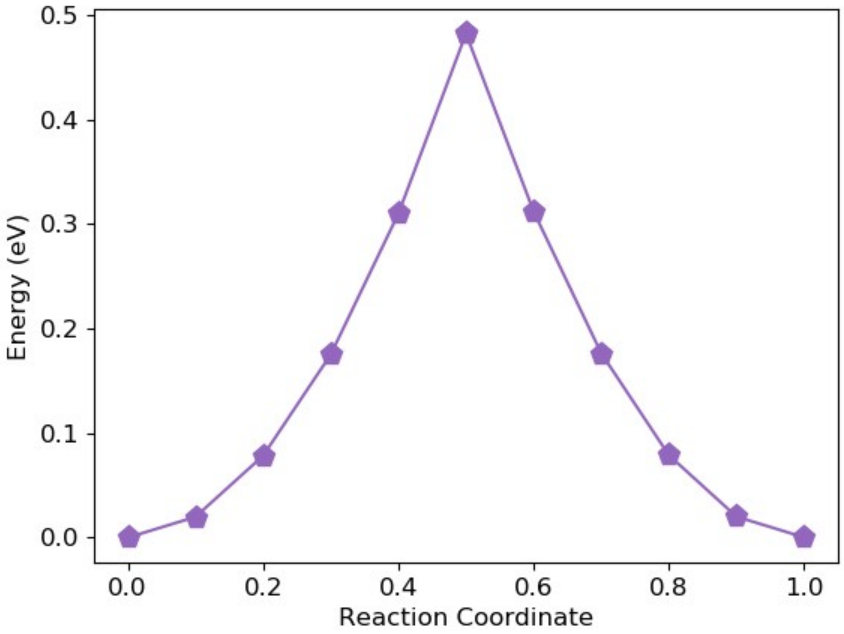

Figure S2e. Energy curve for electron hop A-to-F (e-hop # 5).

Table S2e. Site of electron localization and activation energy along e-hop # 4 (11.705 Å in [001] crystal direction).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	A	0.0000
0.1	A	0.0198
0.2	A	0.0783
0.3	A	0.1751
0.4	A	0.3098
0.5	A	0.4821
0.6	F	0.3120
0.7	F	0.1763
0.8	F	0.0788
0.9	F	0.0200
1.0	F	0.0002

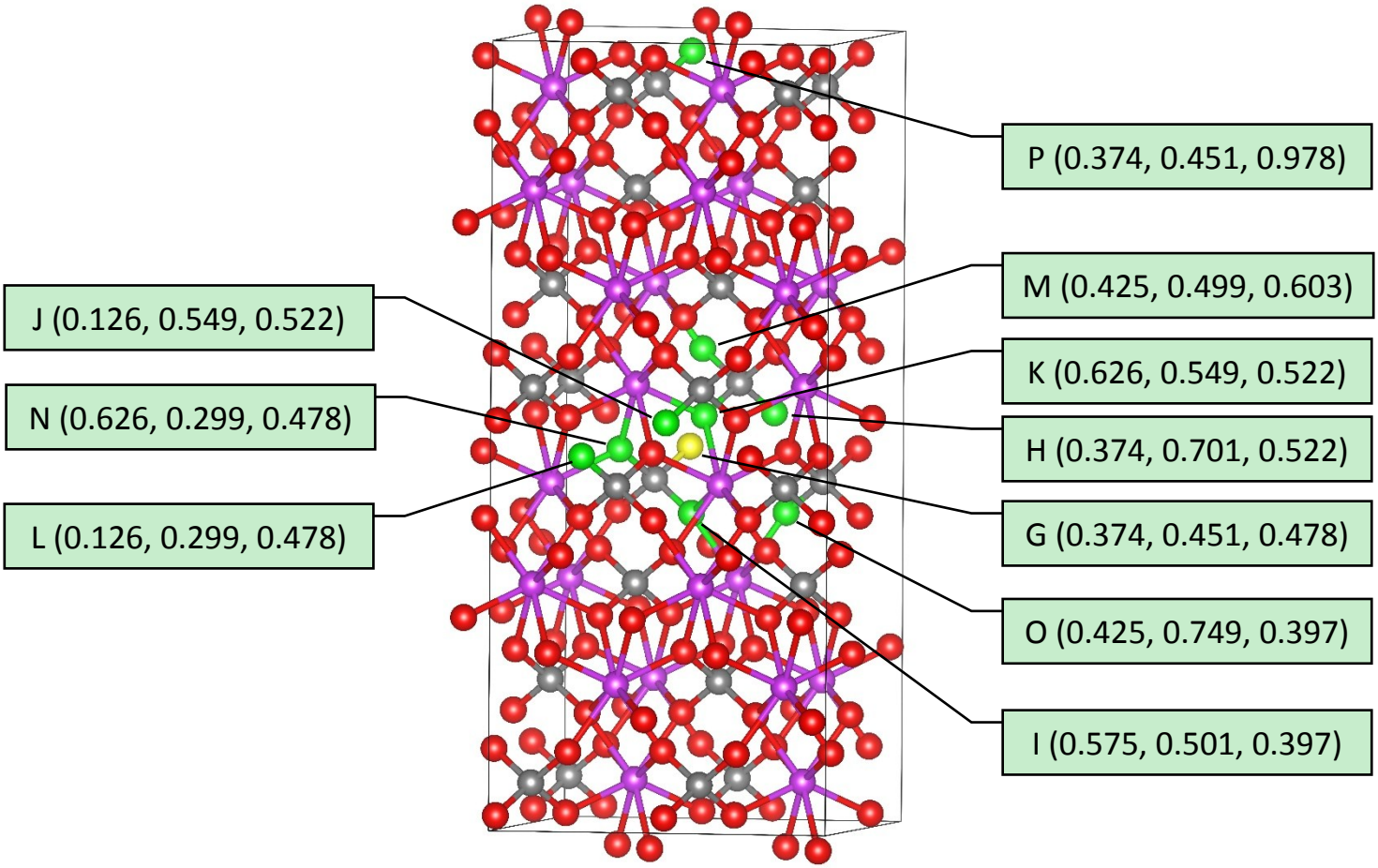

Figure S3. (2×2×2) $BiVO_4$ supercell; Site G, as marked in yellow, is considered the initial site for all depicted hole polaron transfer pathways. While nearest neighbor final sites are marked in green. The long distance transfer along [001] crystal direction is G to P.

Initial site	Final site	Bridge	dist (Å)
G	H	Bi	2.745
		Bi	2.745
G	I	V	2.854
		V	2.860
G	J	Bi, Bi	2.957
G	K	space	2.972
G	L	Bi	3.003
G	M	Bi	3.008
		Bi	3.021
G	N	V	3.047
G	O	Bi	3.612
		Bi	3.685
G	P	space	11.705

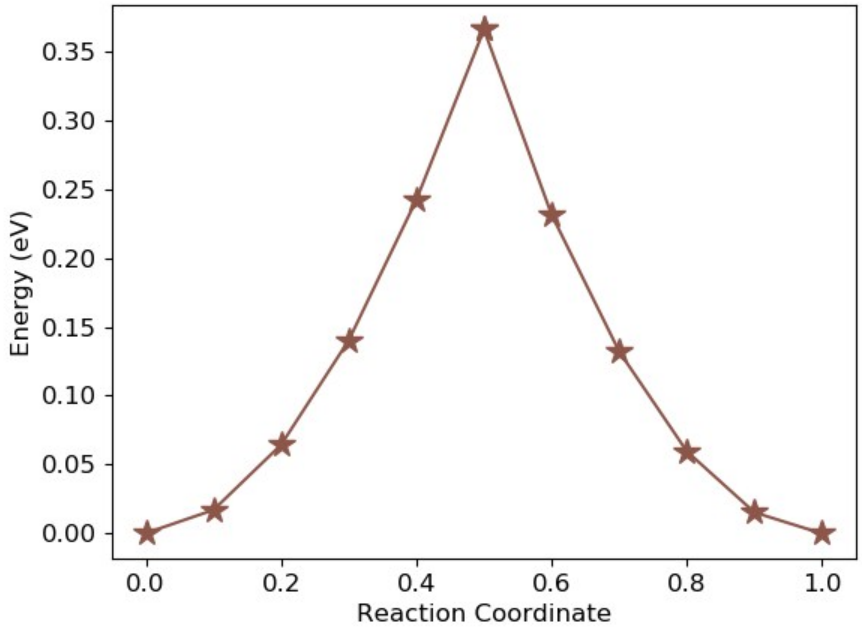

Figure S4a. Energy curve for hole hop G-to-H (h-hop # 1).

Table S4a. Site of hole localization and activation energy along h-hop # 1 (2.745 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0169
0.2	G	0.0643
0.3	G	0.1403
0.4	G	0.2425
0.5	G:0.158, H:0.699	0.3664
0.6	H	0.2317
0.7	H	0.1321
0.8	H	0.0595
0.9	H	0.0151
1.0	H	-0.0003

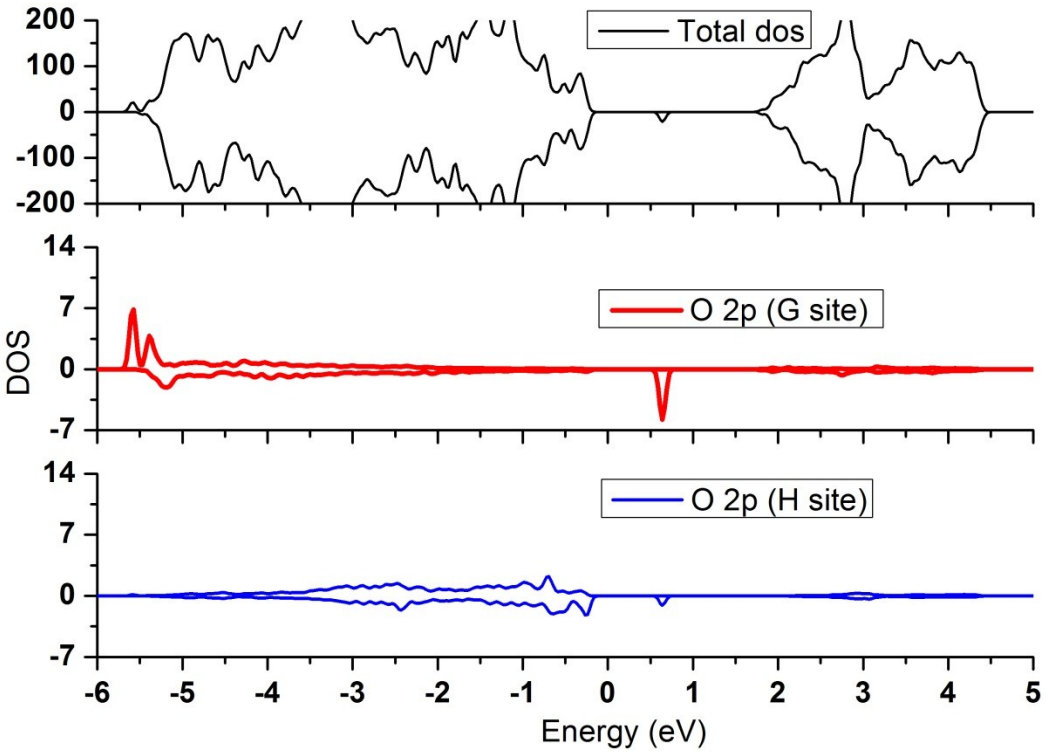

Figure S5a. Total and projected Density of states (oxygen 2p, marked as O 2p) at the midpoint of hole hop from G site to H site (h-hop # 1).

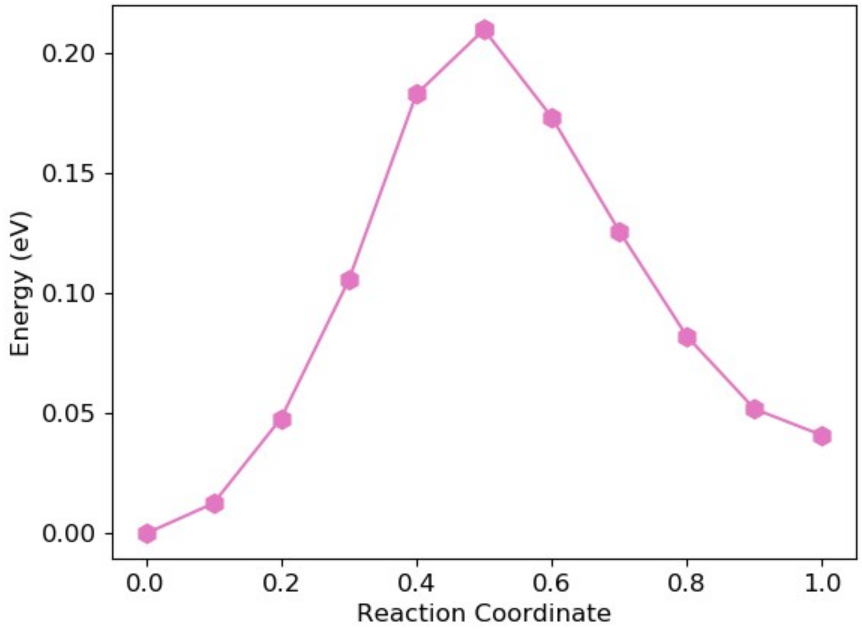

Figure S4b. Energy curve for hole hop G-to-I (h-hop # 2).

Table S4b. Site of hole localization and activation energy along h-hop # 2 (2.860 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0126
0.2	G	0.0480
0.3	G	0.1055
0.4	G:0.728, I:0.140	0.1829
0.5	G:0.558, I:0.596	0.2098
0.6	G:0.140, I:0.728	0.1734
0.7	I	0.1259
0.8	I	0.0821
0.9	I	0.0519
1.0	I	0.0409

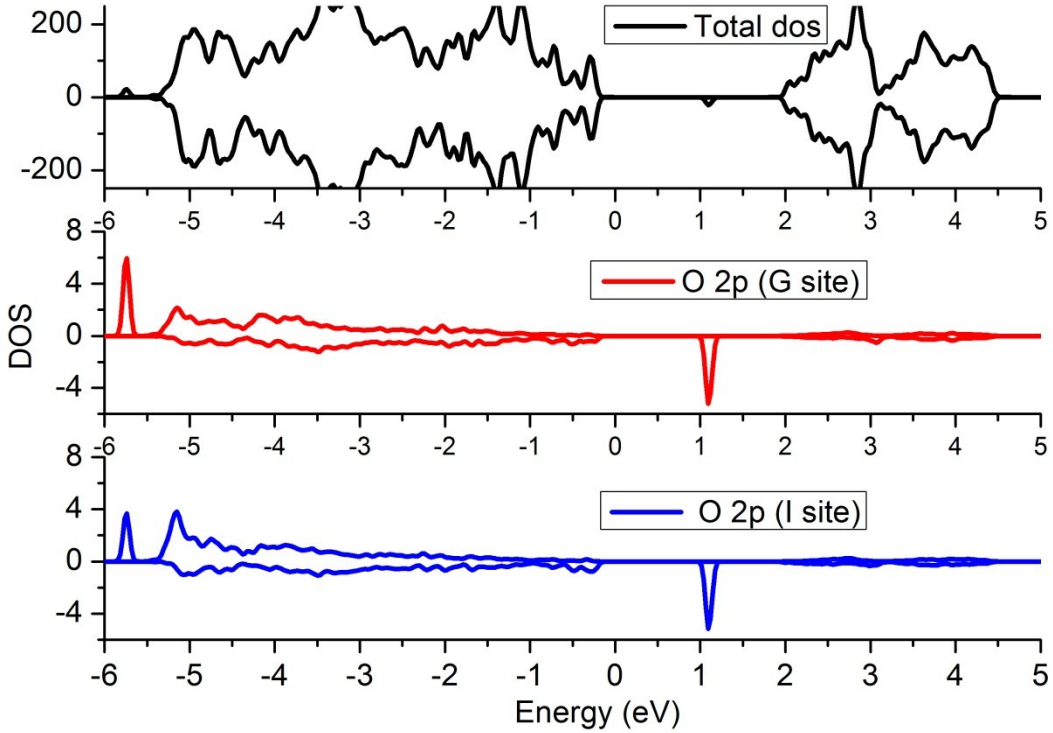

Figure S5b. Total and projected density of states at the midpoint of hole hop from G site to I site (h-hop # 2).

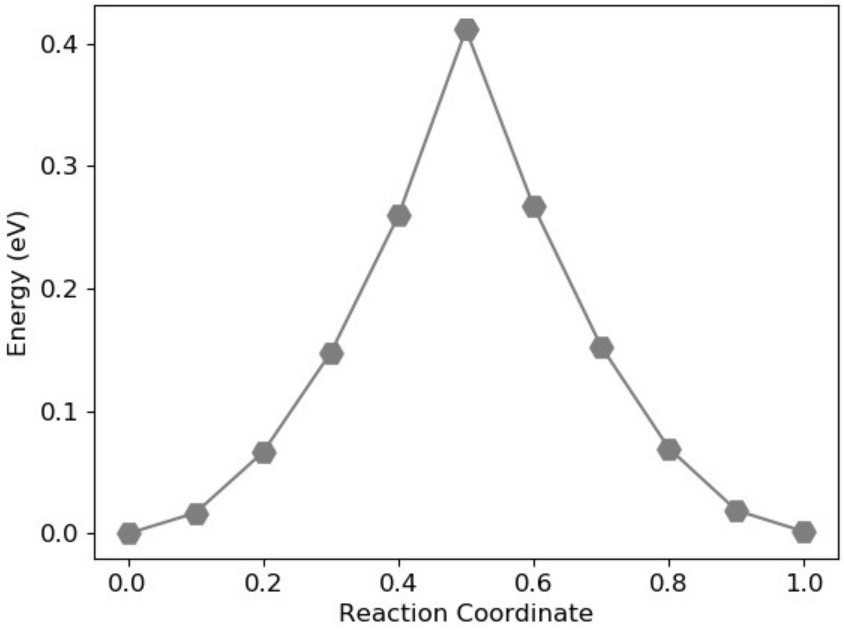

Figure S4c. Energy curve for hole hop G-to-J (h-hop # 3).

Table S4c. Site of hole localization and activation energy along h-hop # 3 (2.957 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0169
0.2	G	0.0665
0.3	G	0.1476
0.4	G	0.2594
0.5	J	0.4113
0.6	J	0.2669
0.7	J	0.1526
0.8	J	0.0696
0.9	J	0.0189
1.0	J	0.0016

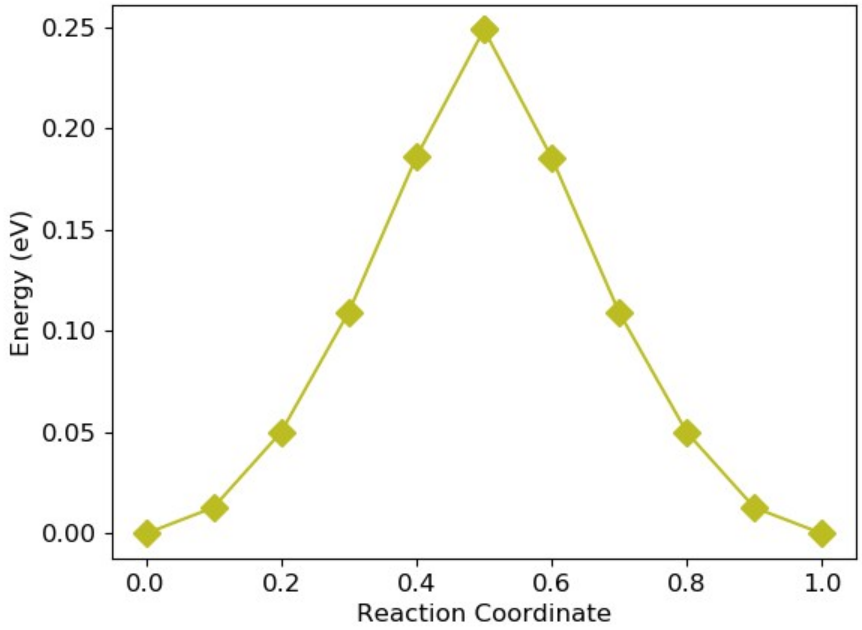

Figure S4d. Energy curve for hole hop G-to-K (h-hop # 4).

Table S4d. Site of hole localization and activation energy along h-hop # 4 (2.972 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0129
0.2	G	0.0501
0.3	G:0.736, K:0.135	0.1094
0.4	G:0.712, K:0.211	0.1859
0.5	G:0.536, K:0.535	0.2488
0.6	G:0.212, K:0.712	0.1856
0.7	G:0.136, K:0.736	0.1091
0.8	K	0.0499
0.9	K	0.0128
1.0	K	0.0000

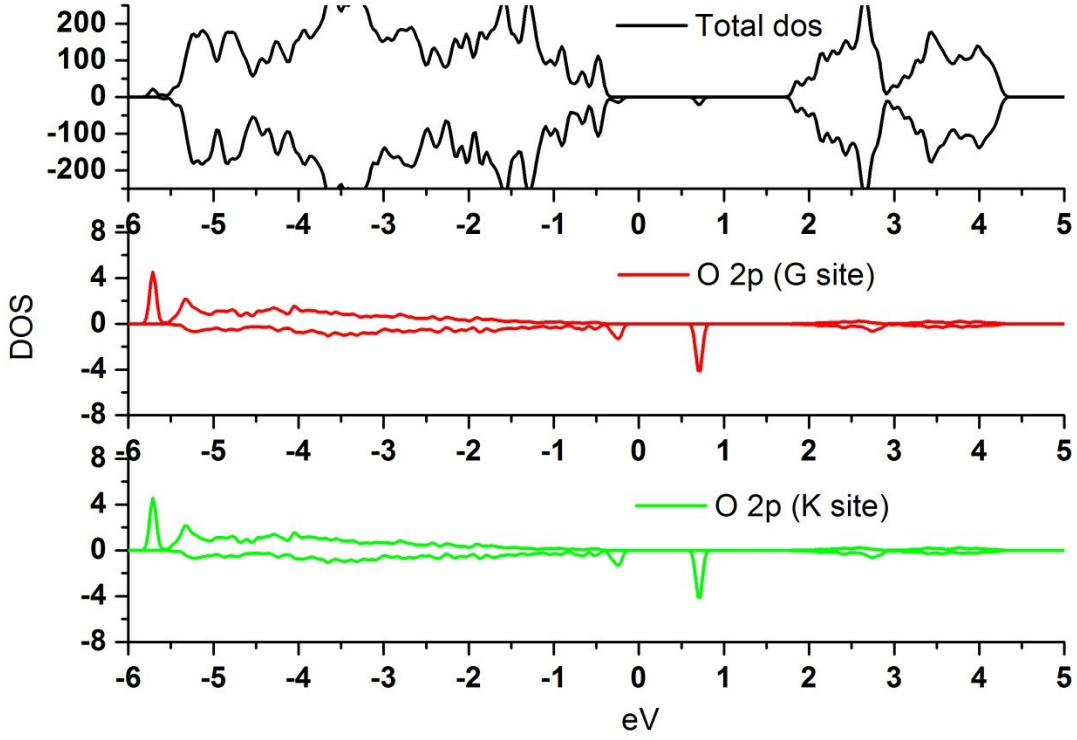

Figure S5d. Total and projected density of states at the midpoint of hole hop from G site to K site (h-hop # 4).

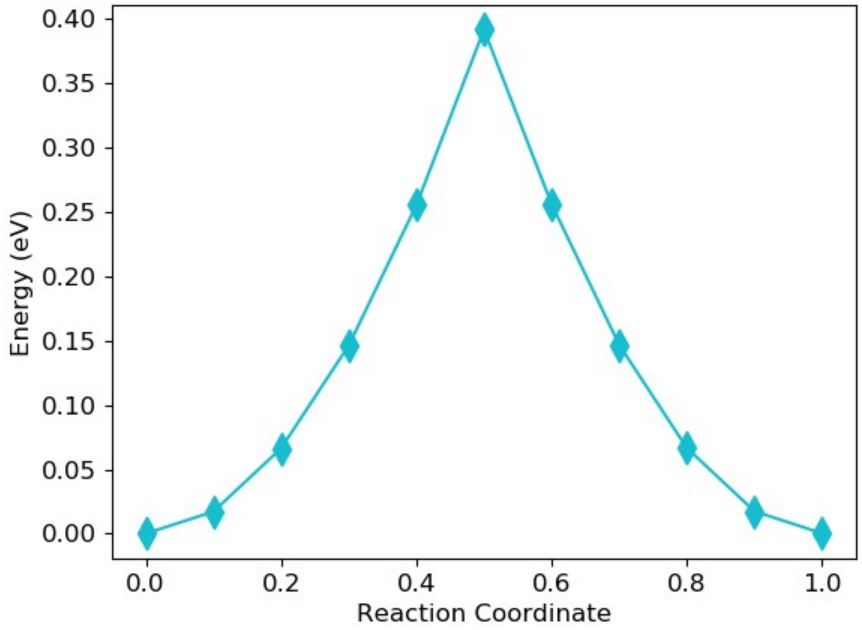

Figure S4e. Energy curve for hole hop G-to-L (h-hop # 5).

Table S4e. Site of hole localization and activation energy along h-hop # 5 (3.003 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0171
0.2	G	0.0663
0.3	G	0.1462
0.4	G	0.2553
0.5	G	0.3918
0.6	L	0.2561
0.7	L	0.1466
0.8	L	0.0665
0.9	L	0.0173
1.0	L	0.0002

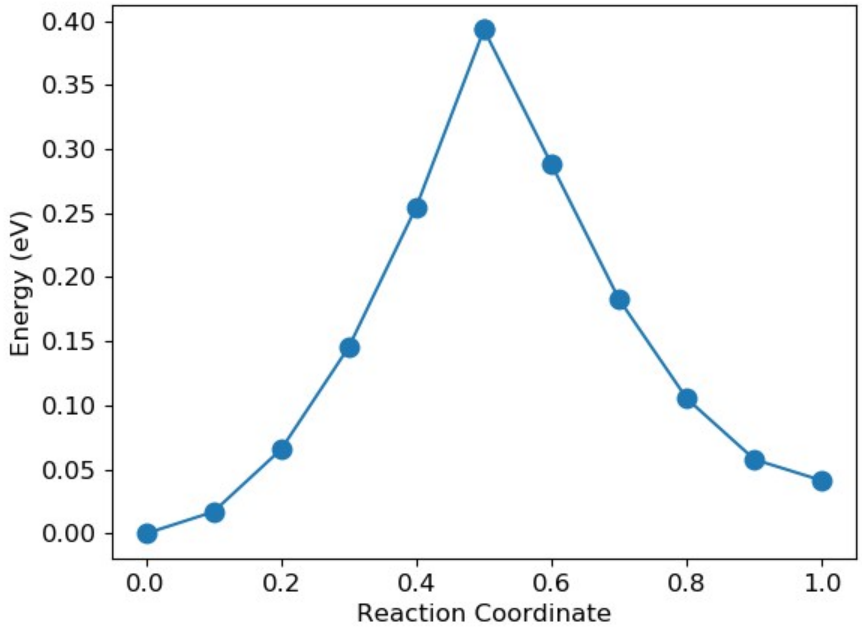

Figure S4f. Energy curve for hole hop G-to-M (h-hop # 6).

Table S4f. Site of hole localization and activation energy along h-hop # 6 (3.008 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0170
0.2	G	0.0657
0.3	G	0.1454
0.4	G	0.2549
0.5	G	0.3931
0.6	M	0.2877
0.7	M	0.1824
0.8	M	0.1052
0.9	M	0.0578
1.0	M	0.0413

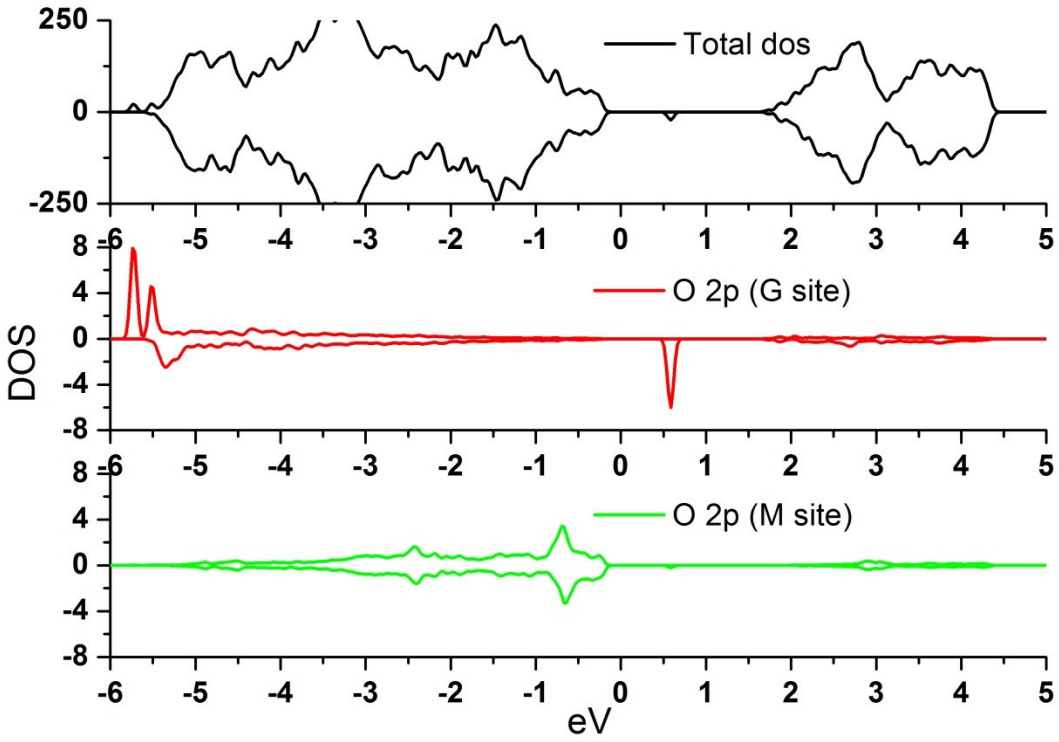

Figure S5f. Total and projected density of states at the midpoint of hole hop from G site to M site (h-hop # 6).

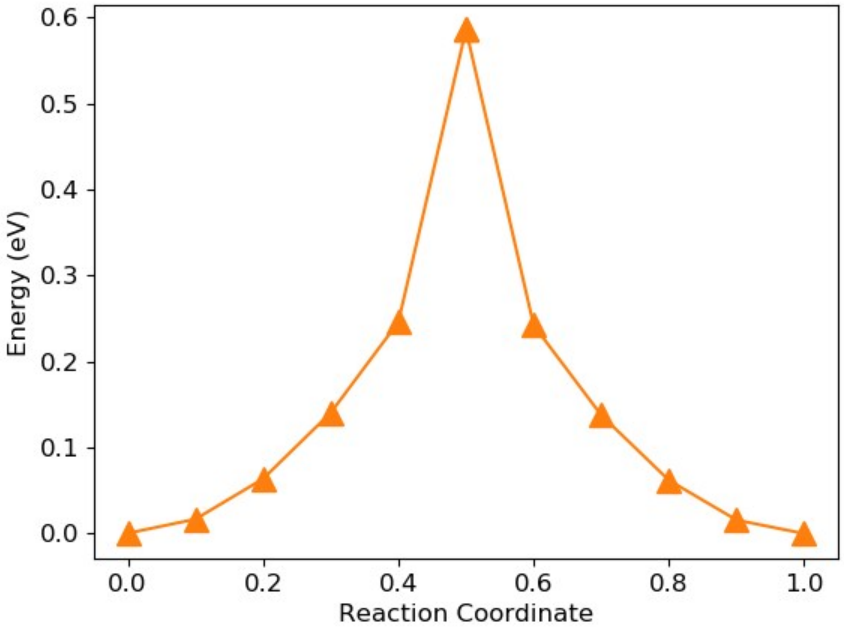

Figure S4g. Energy curve for hole hop G-to-N (h-hop # 7).

Table S4g. Site of hole localization and activation energy along h-hop # 7 (3.047 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0164
0.2	G	0.0634
0.3	G	0.1402
0.4	G	0.2458
0.5	G:0.610, N:0.124	0.5862
0.6	N	0.2421
0.7	N	0.1375
0.8	N	0.0617
0.9	N	0.0154
1.0	N	-0.0004

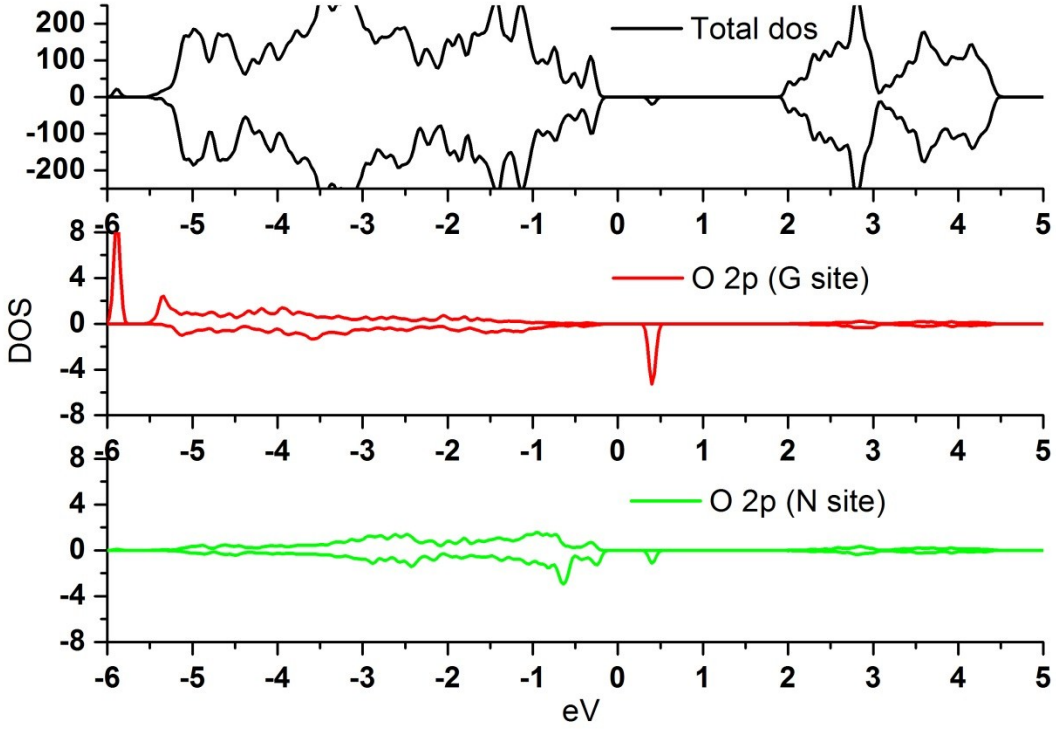

Figure S5g. Total and projected density of states at the midpoint of hole hop from G site to N site (h-hop # 7).

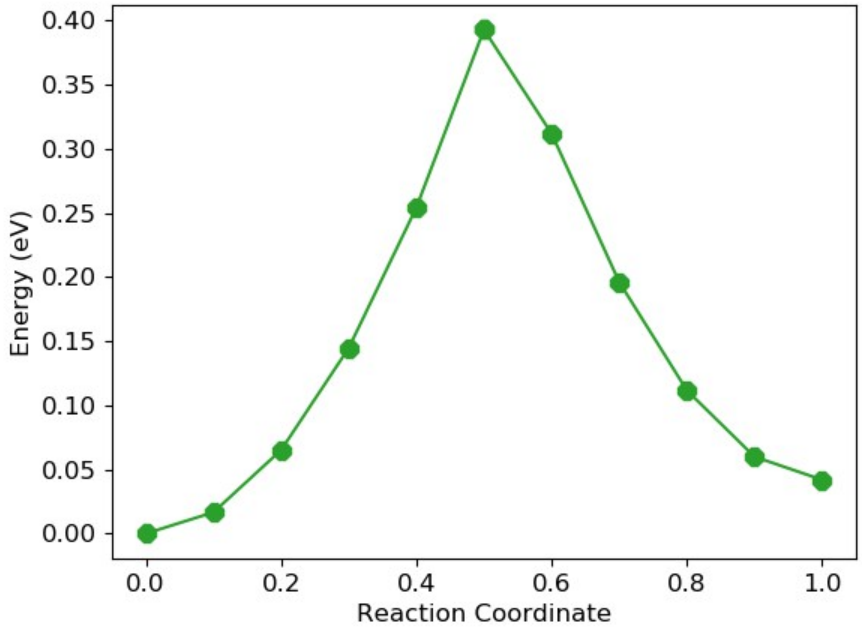

Figure S4h. Energy curve for hole hop G-to-O (h-hop # 8).

Table S4h. Site of hole localization and activation energy along h-hop # 8 (3.612 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0166
0.2	G	0.0651
0.3	G	0.1446
0.4	G	0.2541
0.5	G	0.3928
0.6	O	0.3117
0.7	O	0.1960
0.8	O	0.1116
0.9	O	0.0599
1.0	O	0.0419

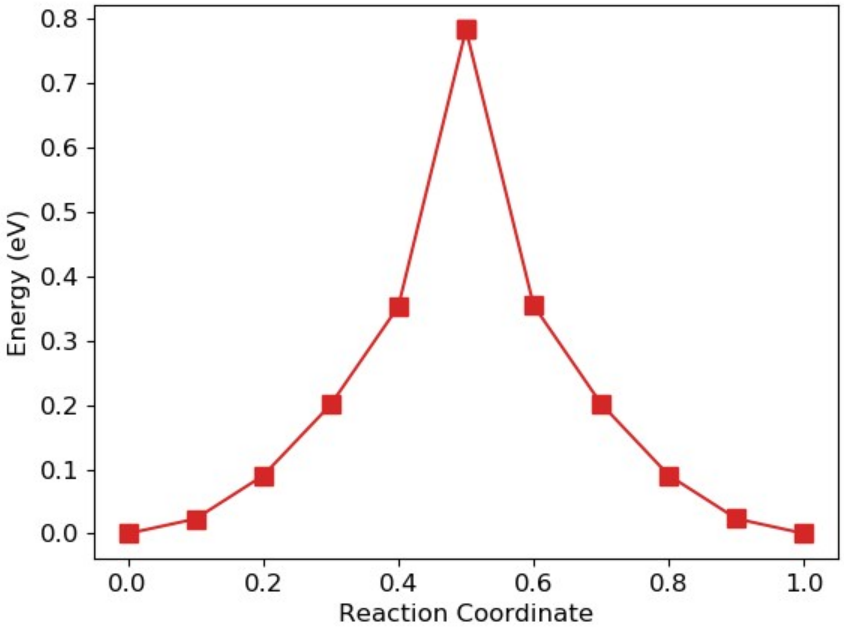

Figure S4i. Energy curve for hole hop G-to-P (h-hop # 9).

Table S4i. Site of hole localization and activation energy along h-hop # 9 (11.705 Å).

Reaction coordinate	Localization site	Activation energy (eV)
0.0	G	0.0000
0.1	G	0.0229
0.2	G	0.0900
0.3	G	0.2005
0.4	G	0.3531
0.5	G:0.222, P:0.413	0.7833
0.6	P	0.3545
0.7	P	0.2014
0.8	P	0.0904
0.9	P	0.0231
1.0	P	0.0001

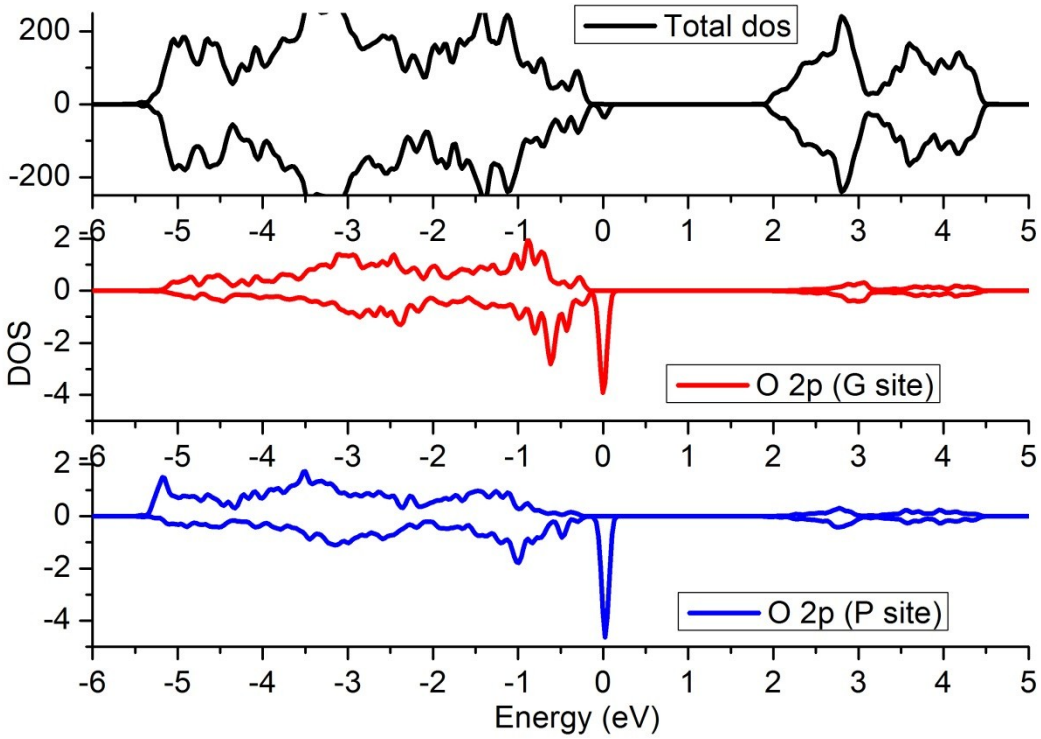

Figure S5i. Total and projected density of states at the midpoint of hole hop from G site to P site (h-hop # 9).