Supplementary Information

Charge carrier transport dynamics in W/Mo-doped $BiVO_4$: first principles-based mesoscale characterization.

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The supporting information includes:

1. free energy data of electron polaron localized on the sites involved in the doping region
2. corresponding spin density contours
3. Interpolation energy curves for electron hop between sites involved in doping region.
4. Comparison of electron mobility curves between 2-shell, 3-shell models
5. Bar plot showing shell-wise residence frequency

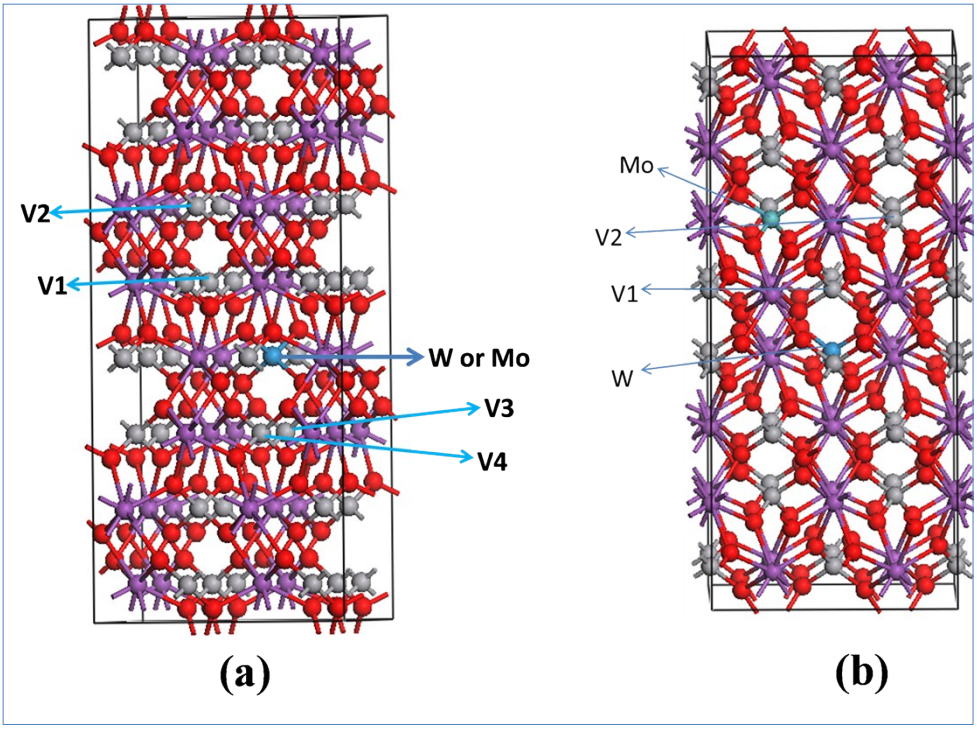

Figure S1. (a) Mo or W single doping in the supercell: V1~V4 are the selected sites for electron localization; (b) Mo and W co-doping: V1 and V2 are the sites for electron localization

Table S1. The free energy of electron polarons at different sites for W/Mo doping and co-doping, based on DFT calculations for a (2x2x2) supercell. (The data is slightly different from but qualitatively similar to those for a 3x3x1 supercell mentioned in the main text).

Polaron site	Free energy for Mo doping	Polaron site	Free energy for W doping	Polaron site	Free energy for Mo / W co-doping
V2	-0.034	V1	-0.022	V1-V2	0.00
V3	-0.005	V2	-0.058	V1-Mo	0.09
V4	-0.005	V3	-0.058	V1-V1	0.12
V1	-0.010	V4	-0.025	V1-W	0.68
Mo	0.087	W	0.661	Mo-W	0.83

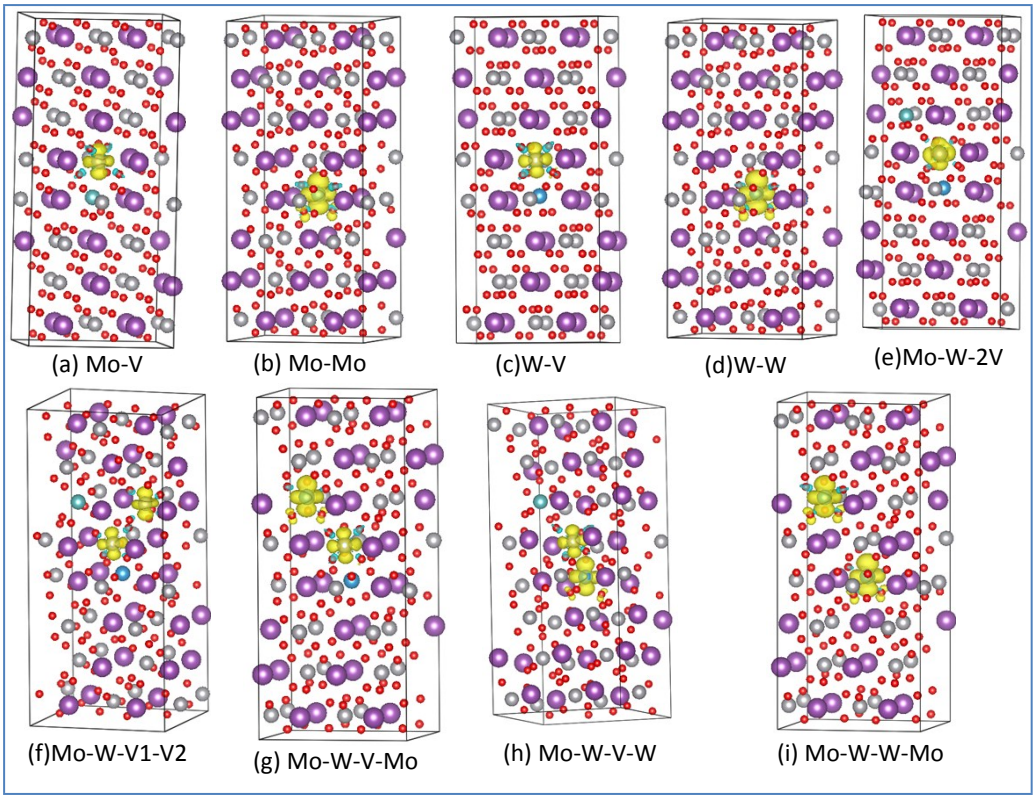

Figure S2. Spin density contours of electron polarons for Mo or W single doping and W/Mo co-doping, (a-d) are for single doping cases, and (e-i) are for co-doping cases. In (a) Mo-V corresponds to single Mo doping with the electron localized on a V atom. In (e) Mo-W-2V corresponds to W/Mo co-doping, with the two electrons localized on one single V atom forming a bi-polaron.

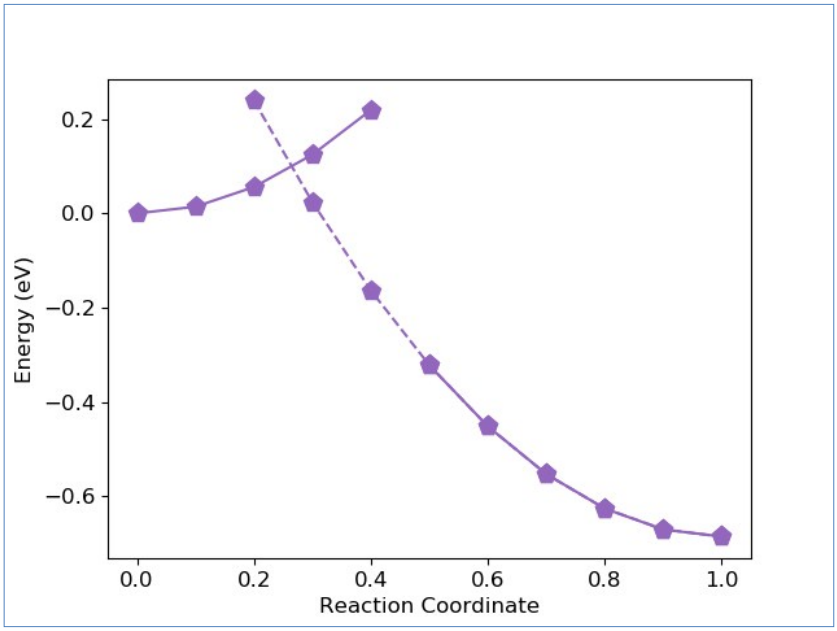

Figure S3. Energy curves for electron hopping between W and V1 site in the W single doping calculated for a 2x2x2 supercell.

Table S3. Energy and localization condition between W and V1 site in the W single doping (Atom labeling W/V1 is given in Figure S1 in the SI) calculated for a 2x2x2 supercell.

Reaction coordinate	Reaction energy (eV)	Localization site
0.0	0.00	W
0.1	0.01	W
0.2	0.06	W
0.3	0.12	W
0.4	0.22	W
0.5	-0.32	V1
0.6	-0.45	V1
0.7	-0.55	V1
0.8	-0.63	V1
0.9	-0.67	V1
1.0	-0.69	V1

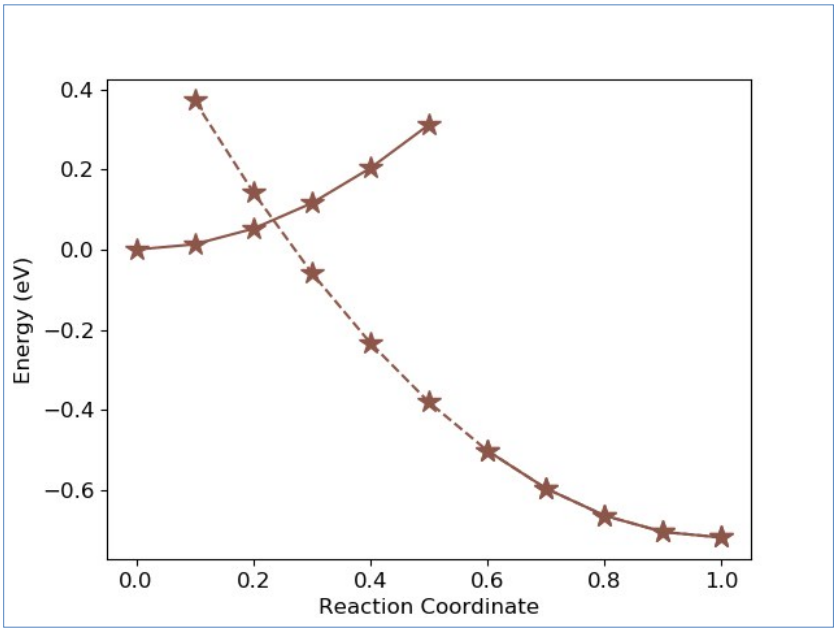

Figure S4. Energy curves for electron hopping between W and V3 site in the W single doping.

Table S4. Energy and localization condition between W and V3 site in the W single doping. (Atom labeling W/V3 is given in Figure S1 in the SI)

Reaction coordinate	Reaction energy (eV)	Localization site
0.0	0.00	W
0.1	0.01	W
0.2	0.05	W
0.3	0.12	W
0.4	0.20	W
0.5	0.31	W
0.6	-0.50	V2
0.7	-0.60	V2
0.8	-0.66	V2
0.9	-0.70	V2
1.0	-0.72	V2

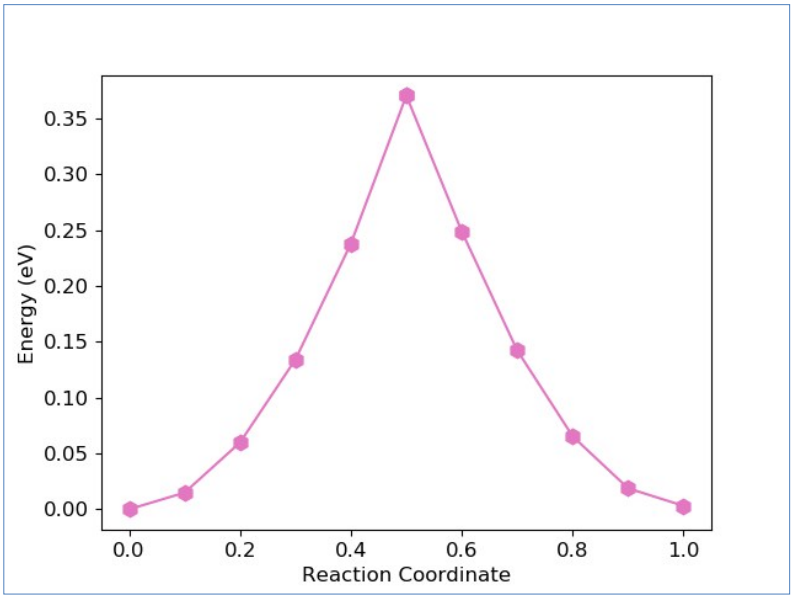

Figure S5. Energy curves for electron hopping between V1 and V2 sites in W single doping calculated for a 2x2x2 supercell.

Table S5. Energy and localization site for hopping between V1 and V2 sites in W single doping (Atom labeling V1/V2 is given in Figure S1) calculated for a 2x2x2 supercell.

Reaction coordinate	Reaction energy (eV)	Localization site
0.0	0.00	V1
0.1	0.01	V1
0.2	0.06	V1
0.3	0.13	V1
0.4	0.24	V1
0.5	0.37	V1
0.6	0.25	V2
0.7	0.14	V2
0.8	0.07	V2
0.9	0.02	V2
1.0	0.00	V2

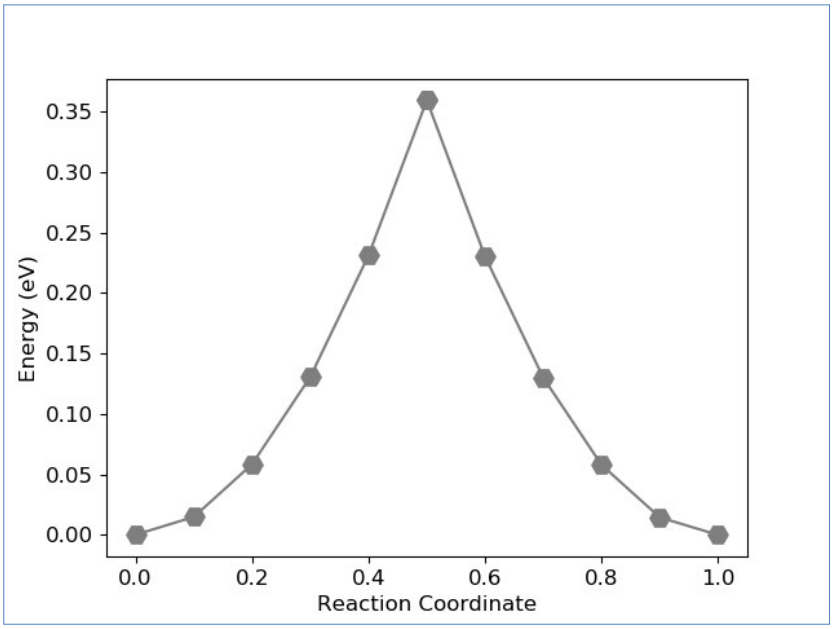

Figure S6. Energy curves for electron hopping between V3 and V4 site in W single doping calculated for a 2x2x2 supercell.

Table S6. Energy and localization sites for hopping between V3 and V4 sites in W single doping (Atom labeling V3/V4 is given in Figure S1) calculated for a 2x2x2 supercell.

Reaction coordinate	Reaction energy (eV)	Localization site
0.0	0.00	V3
0.1	0.01	V3
0.2	0.06	V3
0.3	0.13	V3
0.4	0.23	V3
0.5	0.36	V3
0.6	0.23	V4
0.7	0.13	V4
0.8	0.06	V4
0.9	0.01	V4
1.0	0.00	V4

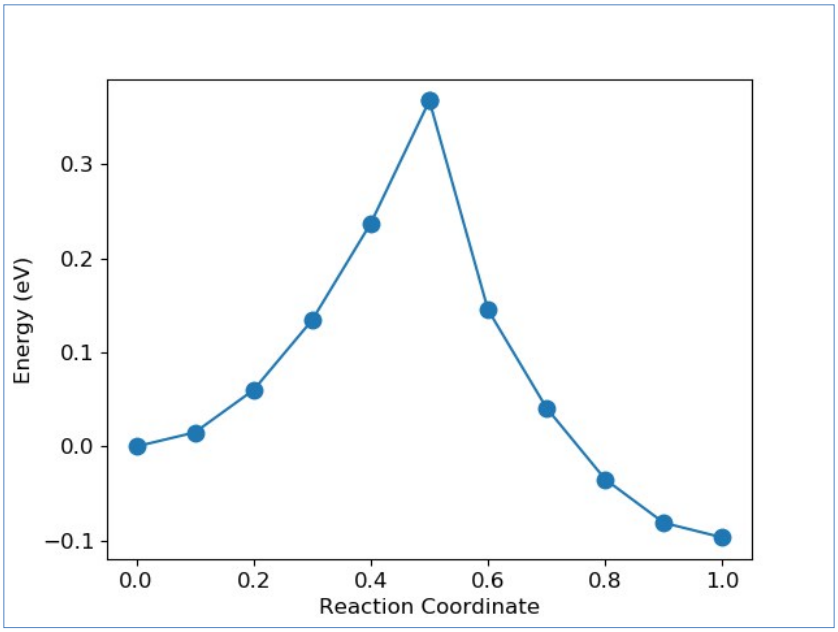

Figure S7. Energy curves for electron hopping between Mo and V1 site in Mo single doping calculated for a 2x2x2 supercell.

Table S7. Energy and localization site for hopping between Mo and V1 sites in Mo single doping (Atom labeling Mo/V1 is given in Figure S1) calculated for a 2x2x2 supercell.

Reaction coordinate	Reaction energy (eV)	Localization site
0.0	0.00	Mo
0.1	0.01	Mo
0.2	0.06	Mo
0.3	0.13	Mo
0.4	0.24	Mo
0.5	0.37	Mo
0.6	0.15	V1
0.7	0.04	V1
0.8	-0.03	V1
0.9	-0.08	V1
1.0	-0.10	V1

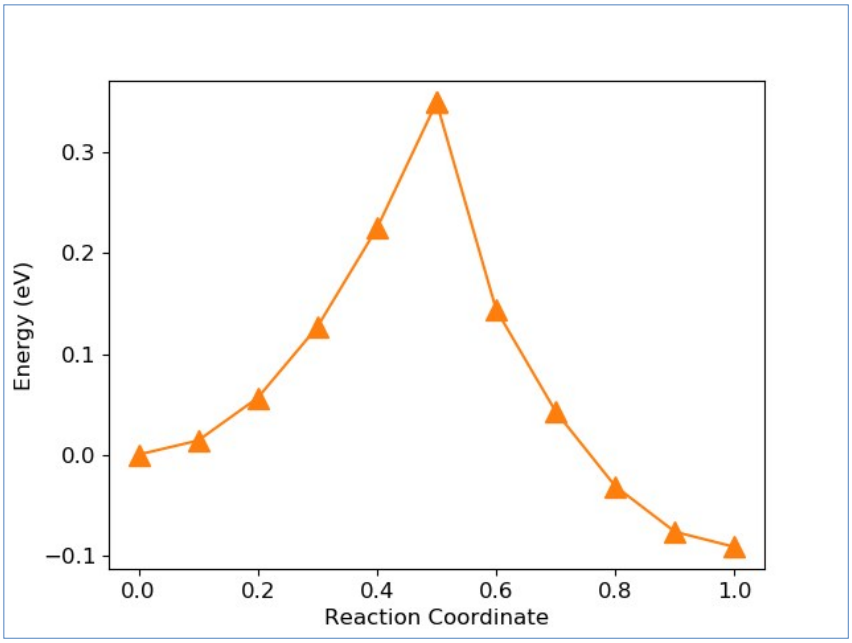

Figure S8. Energy curves for electron hopping between Mo and V3 site in Mo single doping calculated for a 2x2x2 supercell.

Table S8. Energy and localization site for hopping between Mo and V3 sites in Mo single doping (Atom labeling Mo/V3 is given in Figure S1) calculated for a 2x2x2 supercell.

Reaction coordinate	Reaction energy (eV)	Localization site
0.0	0.00	Mo
0.1	0.01	Mo
0.2	0.06	Mo
0.3	0.13	Mo
0.4	0.22	Mo
0.5	0.35	Mo
0.6	0.14	V3
0.7	0.04	V3
0.8	-0.03	V3
0.9	-0.08	V3
1.0	-0.09	V3

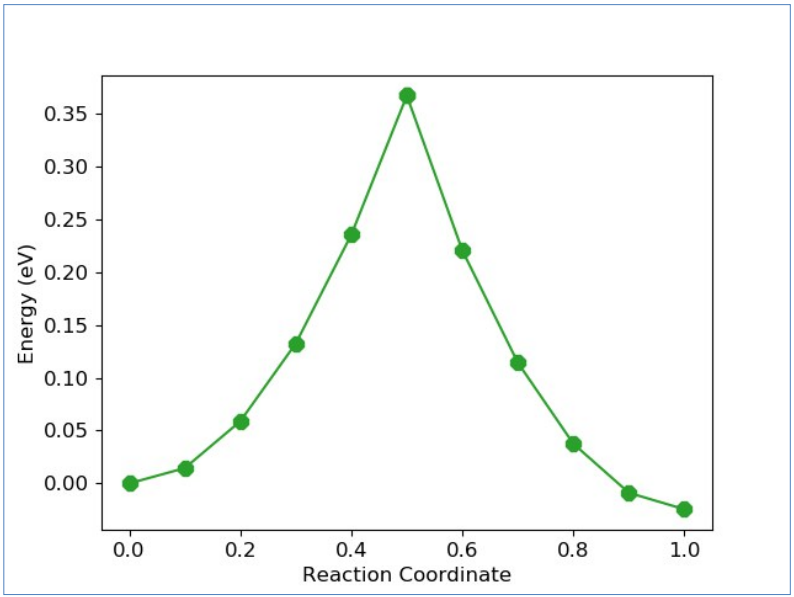

Figure S9. Energy curves for electron hopping between V1 and V2 site in Mo single doping calculated for a 2x2x2 supercell.

Table S9. Energy and localization site for hopping between V1 and V2 sites in Mo single doping (Atom labeling V1/V2 is given in Figure S1) calculated for a 2x2x2 supercell.

Reaction coordinate	Reaction energy (eV)	Localization site
0.0	0.00	V1
0.1	0.01	V1
0.2	0.06	V1
0.3	0.13	V1
0.4	0.24	V1
0.5	0.37	V1
0.6	0.22	V2
0.7	0.11	V2
0.8	0.04	V2
0.9	-0.01	V2
1.0	-0.02	V2

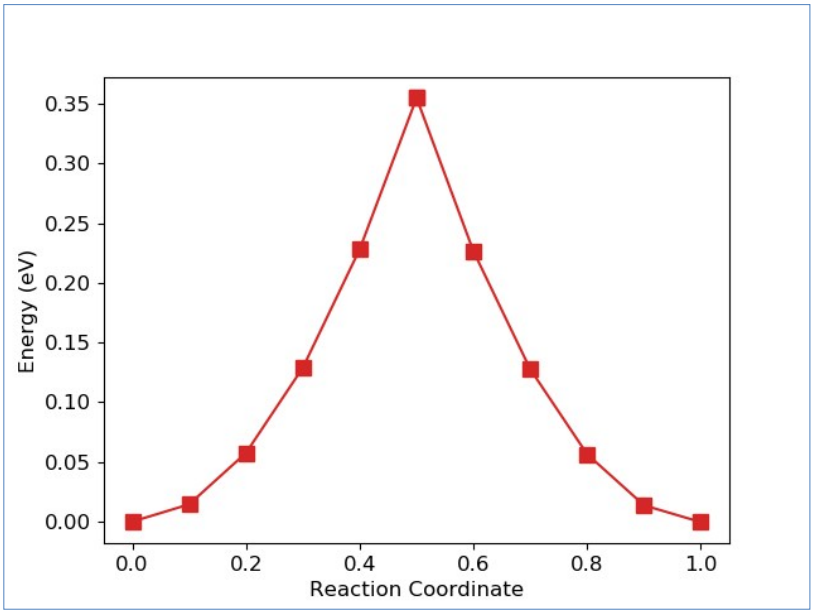

Figure S10. Energy curves for electron hopping between V3 and V4 site in Mo single doping calculated for a 2x2x2 supercell.

Table S10. Energy and localization site for hopping between V3 and V4 sites in Mo single doping (Atom labeling V3/V4 is given in Figure S1) calculated for a 2x2x2 supercell.

Reaction coordinate	Reaction energy (eV)	Localization site
0.0	0.00	V3
0.1	0.01	V3
0.2	0.06	V3
0.3	0.13	V3
0.4	0.23	V3
0.5	0.35	V3
0.6	0.23	V4
0.7	0.13	V4
0.8	0.06	V4
0.9	0.01	V4
1.0	0.00	V4

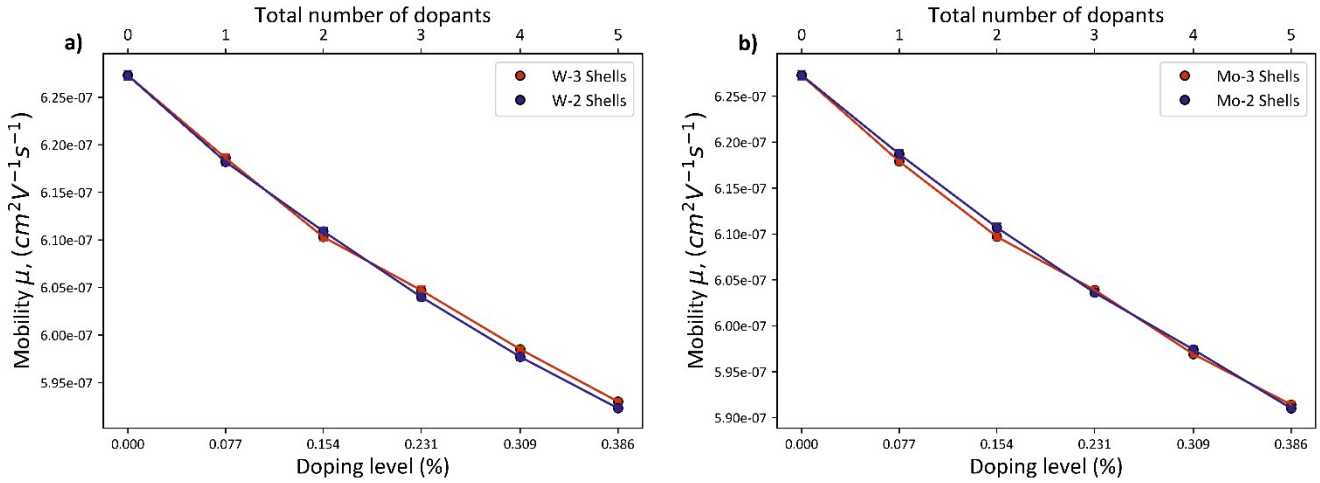

Figure S11. Comparison of electron polaron mobility between using '2Shells' and '3Shells' models of interaction regions around W/Mo dopant atoms.

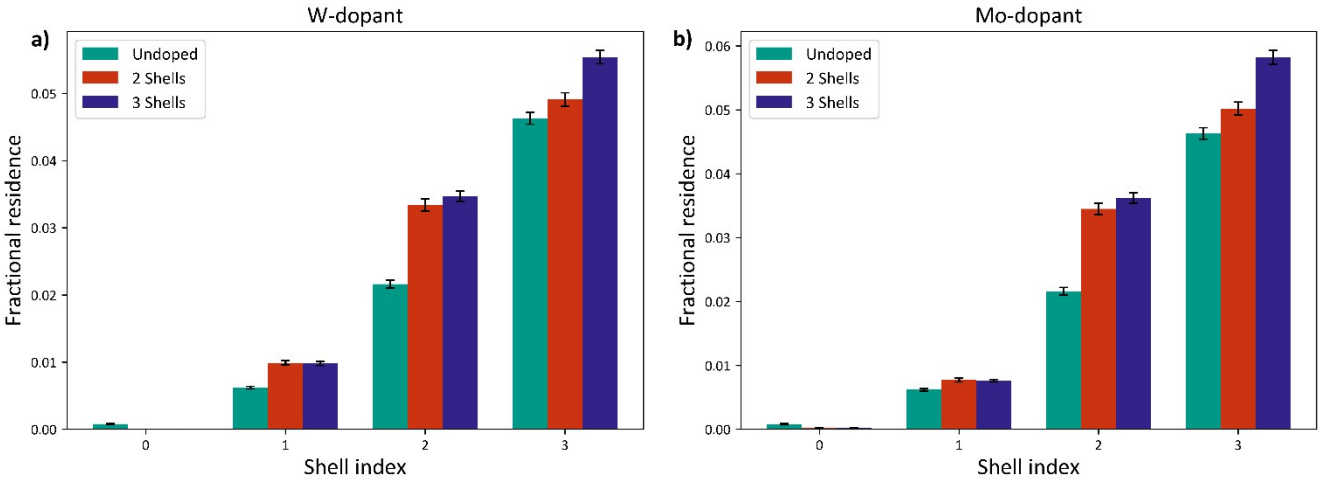

Figure S12. Shell-wise residence frequency as a fraction of trajectory length for system with W/Mo dopants for 2shells and 3shells models of interaction region.