Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Ab initio identification of the Li-rich phase in $LiFePO_4$

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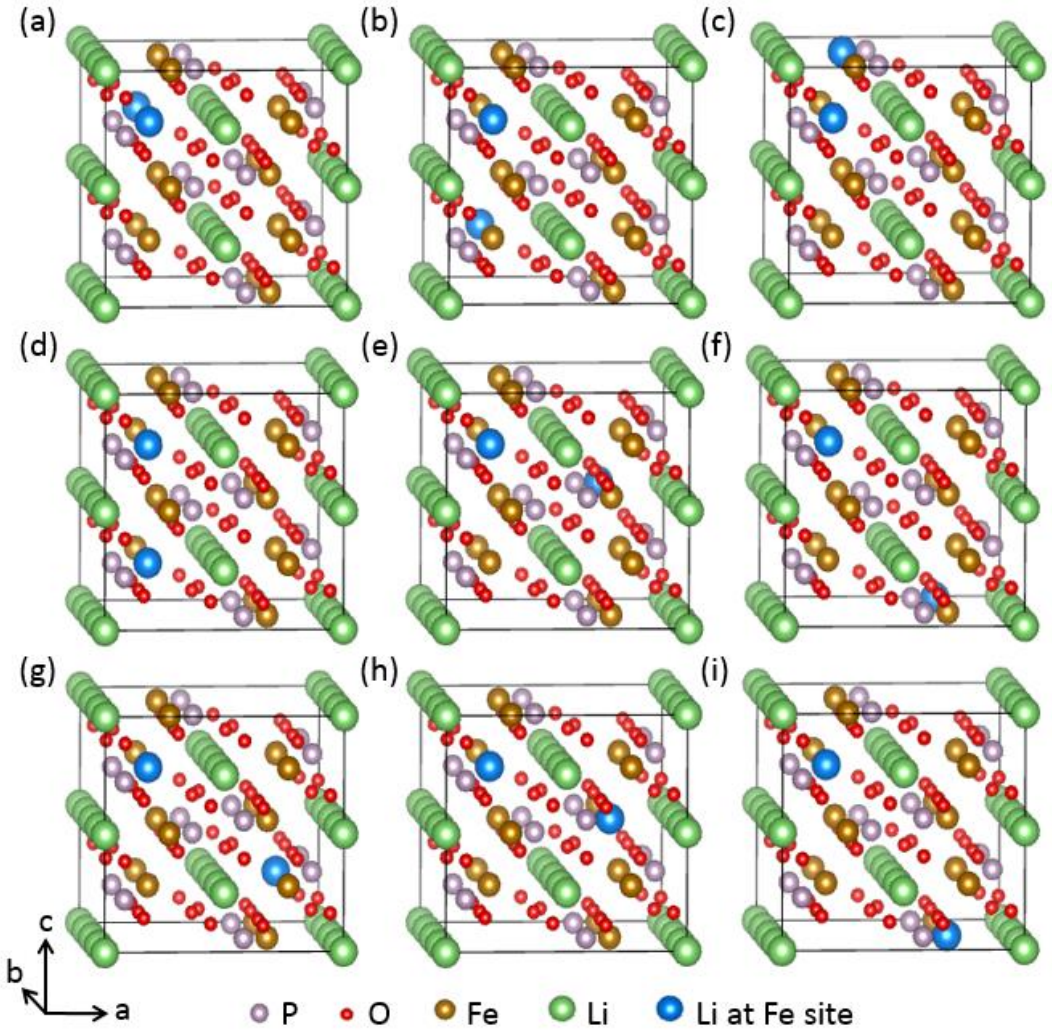

Fig. S1 (a-i) Schematics for different structures of $Li_{1+x}Fe_{1-x}PO_4$ (x = 12.5%). The total energies of them are -759.036, -758.512, -758.964, -758.441, -758.399, -758.384, -758.961, -758.894 and -758.284 eV, respectively.

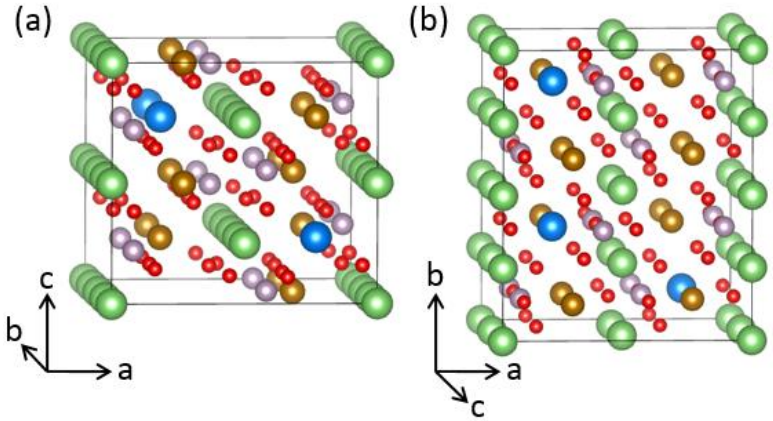

Fig. S2 Schematic for the structure of $Li_{1+x}Fe_{1-x}PO_4$ (x = 18.75%). (a) in *ac* plane; (b) in *ab* plane.

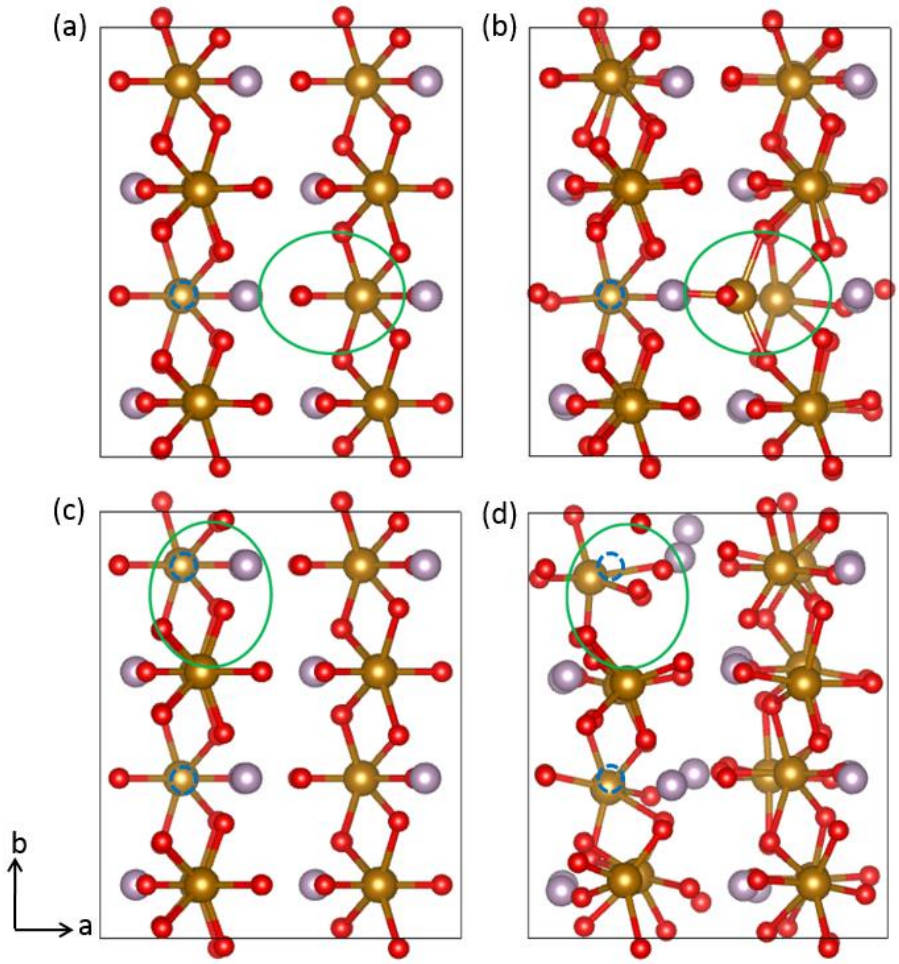

Fig. S3 The molecular dynamics simulation on $Fe_{1-x}PO_4$ (x = 6.25% and 12.5%) was performed under room temperature condition (300 K) with the Nose-Hoover thermostat. A 3 ps NVT (fixed number of atoms, constant volume and constant temperature) was carried out. (a) and (b) are the initial and final atomic configurations obtained at the time of 0 and 3 ps for x = 6.25%. (c) and (d) are the initial and final atomic configurations obtained at the time of 0 and 3 ps for x = 12.5%.

Table S1 The average Fe-O bond length for different Fe-ions in $LiFePO_4$ and around the excess Li-ion at Fe site in $Li_{1+x}Fe_{1-x}PO_4$ (x = 6.25% and 12.5%).

x	Fe_1-O [Å]	Fe_2-O [Å]	Fe_3-O [Å]	Fe_4-O [Å]
0	2.184	2.184	2.184	2.184
6.25%	2.179	2.179	2.127	2.127
12.5%	2.175	2.175	2.077	2.077

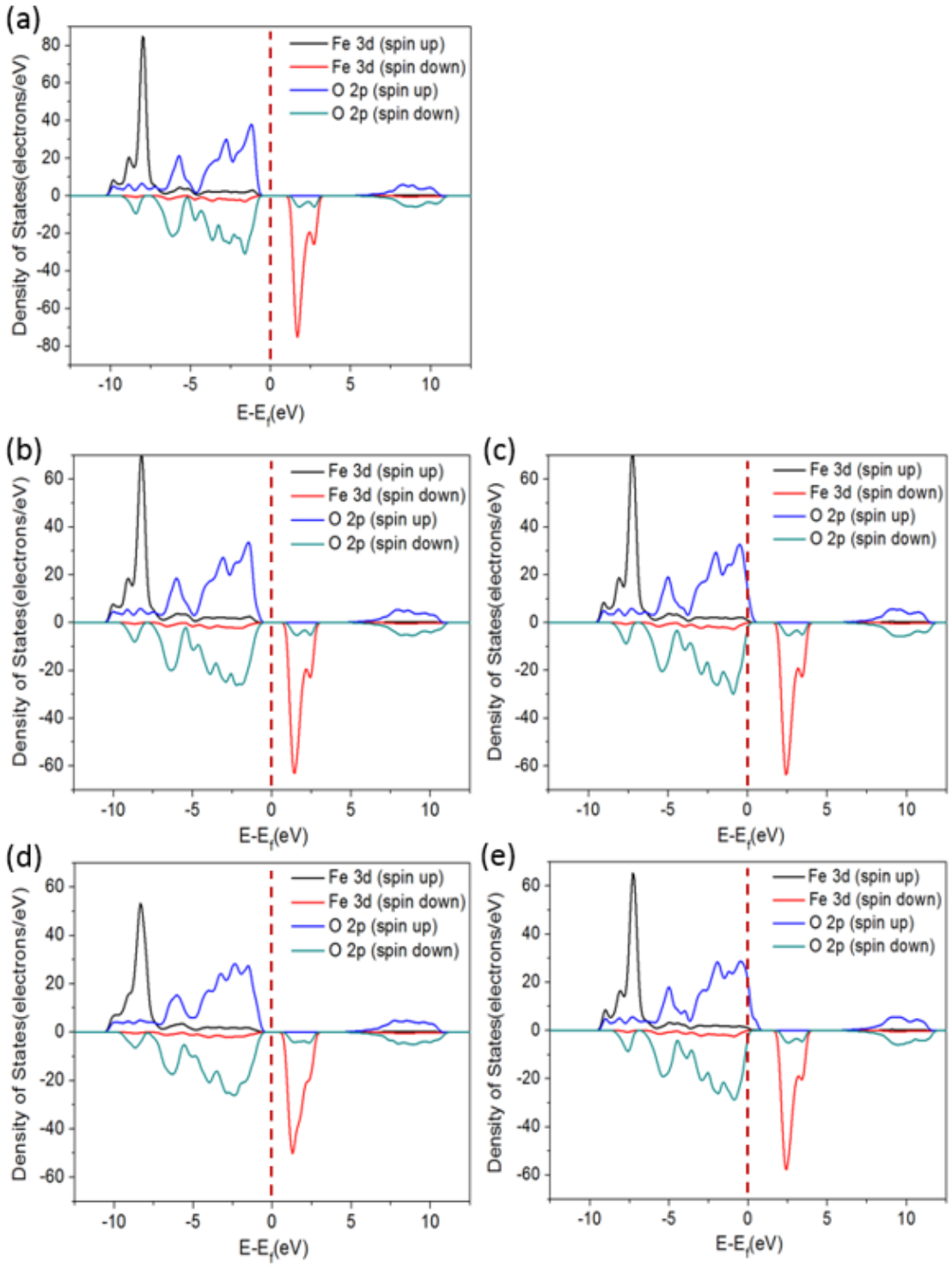

Fig. S4 The PDOS of $Li_{1+x-y}Fe_{1-x}PO_4$. (a) $x = 0$, $y = 1+x$; (b) $x = 6.25\%$, $y = 1-2x$; (c) $x = 6.25\%$, $y = 1+x$; (d) $x = 12.5\%$, $y = 1-2x$; (e) $x = 12.5\%$, $y = 1+x$. The Fermi level (the vertical red dashed line) is set to zero energy.

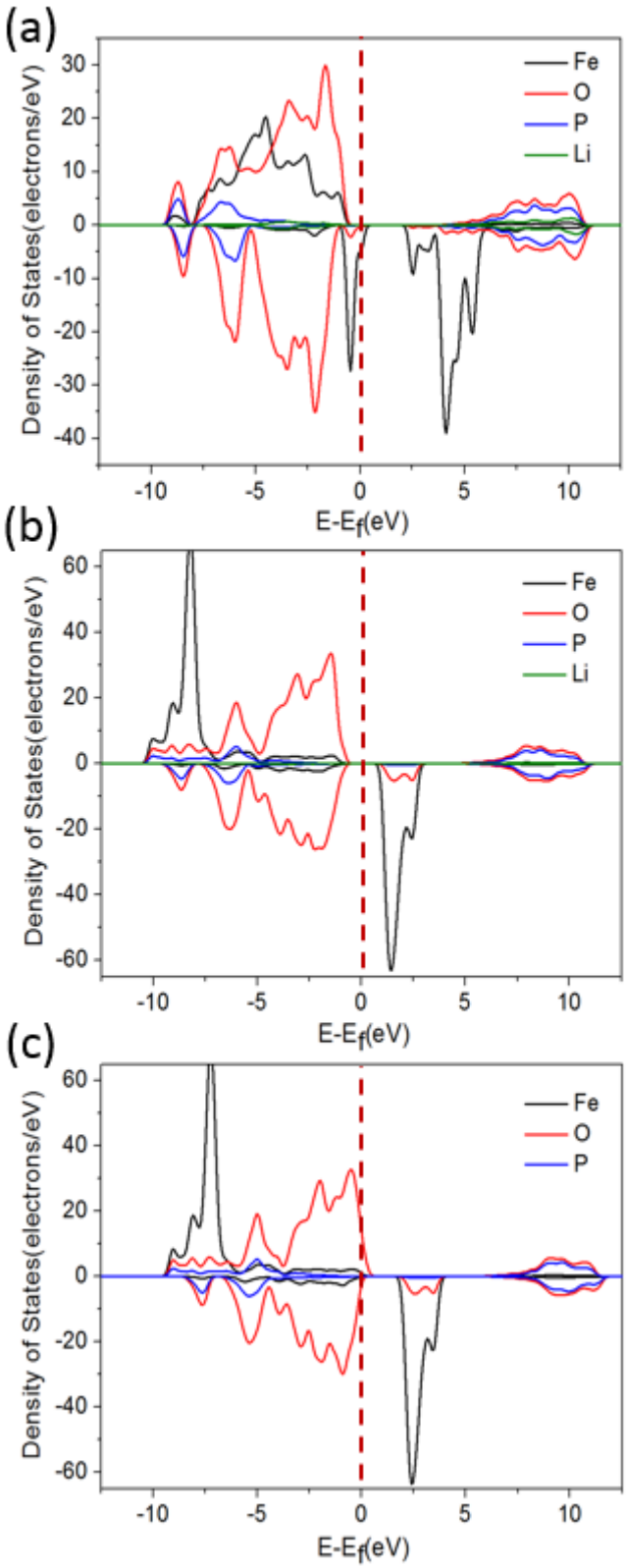

Fig. S5 The PDOS of $Li_{1+x-y}Fe_{1-x}PO_4$ (x = 6.25%). (a) y = 0; (b) y = 1-2x; (c) y = 1+x. The Fermi level (the vertical red dashed line) is set to zero energy.

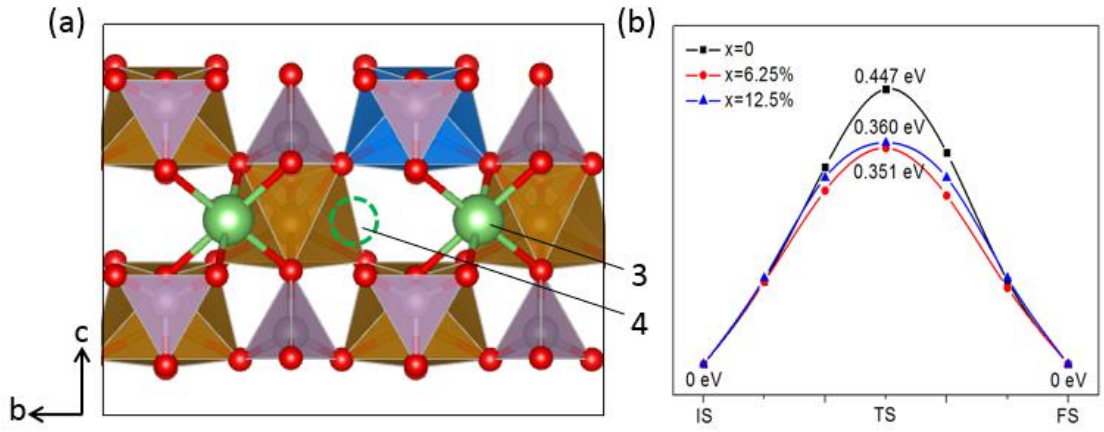

Fig. S6 (a) Schematic for the structure of $Li_{1+x}Fe_{1-x}PO_4$. 3 stands for a Li-ion, and 4 stands for a Li-vacancy in the [010] channel. (b) The energy barriers for a Li-ion to hop from the 3 site to the 4 site in the bulk $Li_{1+x}Fe_{1-x}PO_4$ (x = 0, 6.25% and 12.5%).

Table S2 The distance between two adjacent Li sites along the [010] channel in $Li_{1+x}Fe_{1-x}PO_4$.

x	1-2 [Å]	3-4 [Å]
0	3.042	3.042
6.25%	2.940	2.914
12.5%	2.941	2.892