Supplemental material for

Electrochemical potential of the metal-organic framework MIL-101(Fe) as cathode material in Li-ion batteries

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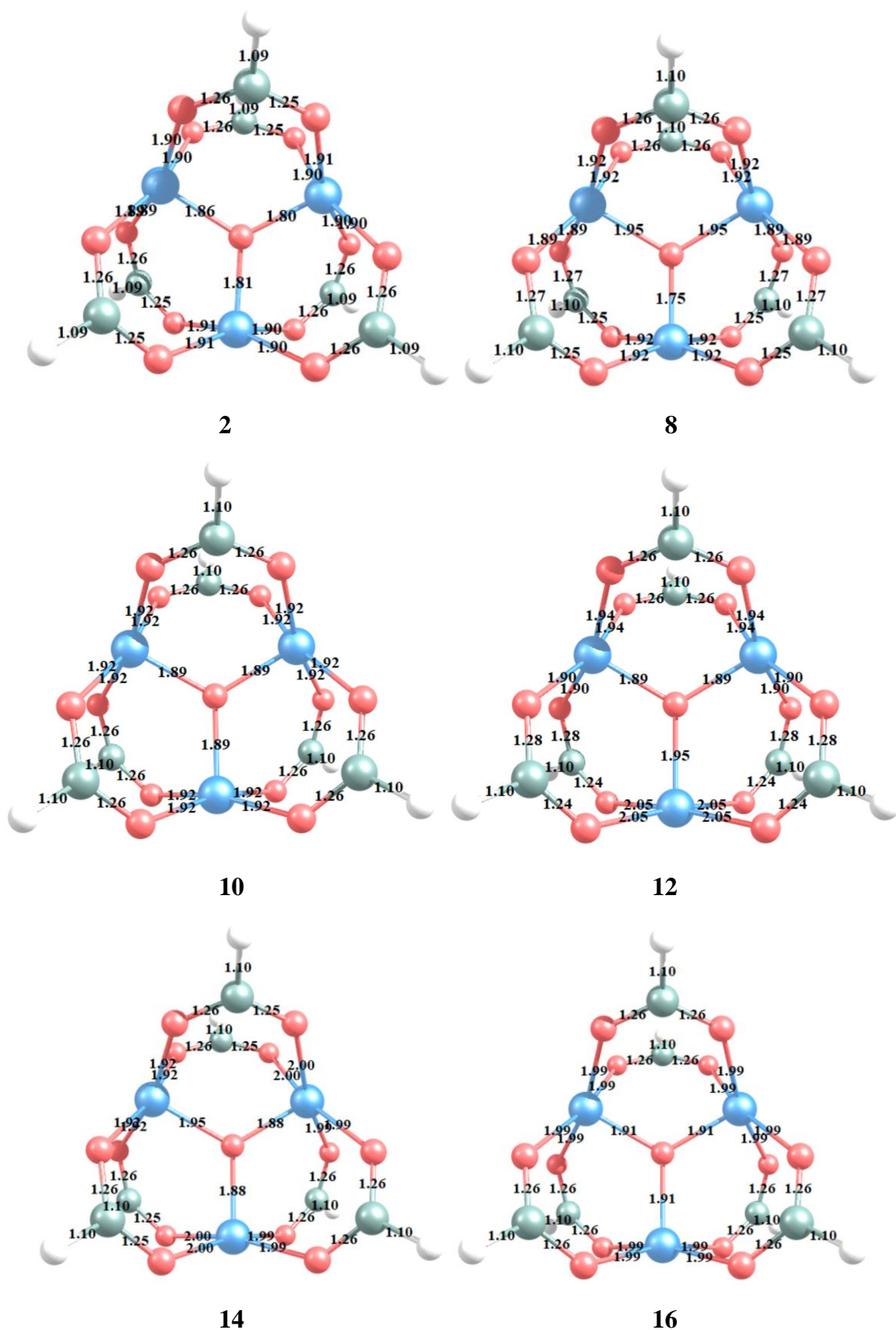Ar.Bansil@northeastern.edu

Figure S1. Geometries of the structures for various spin states at the B3LYP/def2-TZVP level of theory. The Fe, C, O and H atoms are shown as blue, grey, red and white balls, respectively. All bond lengths are in Å. The number written under each structure is the corresponding spin state.
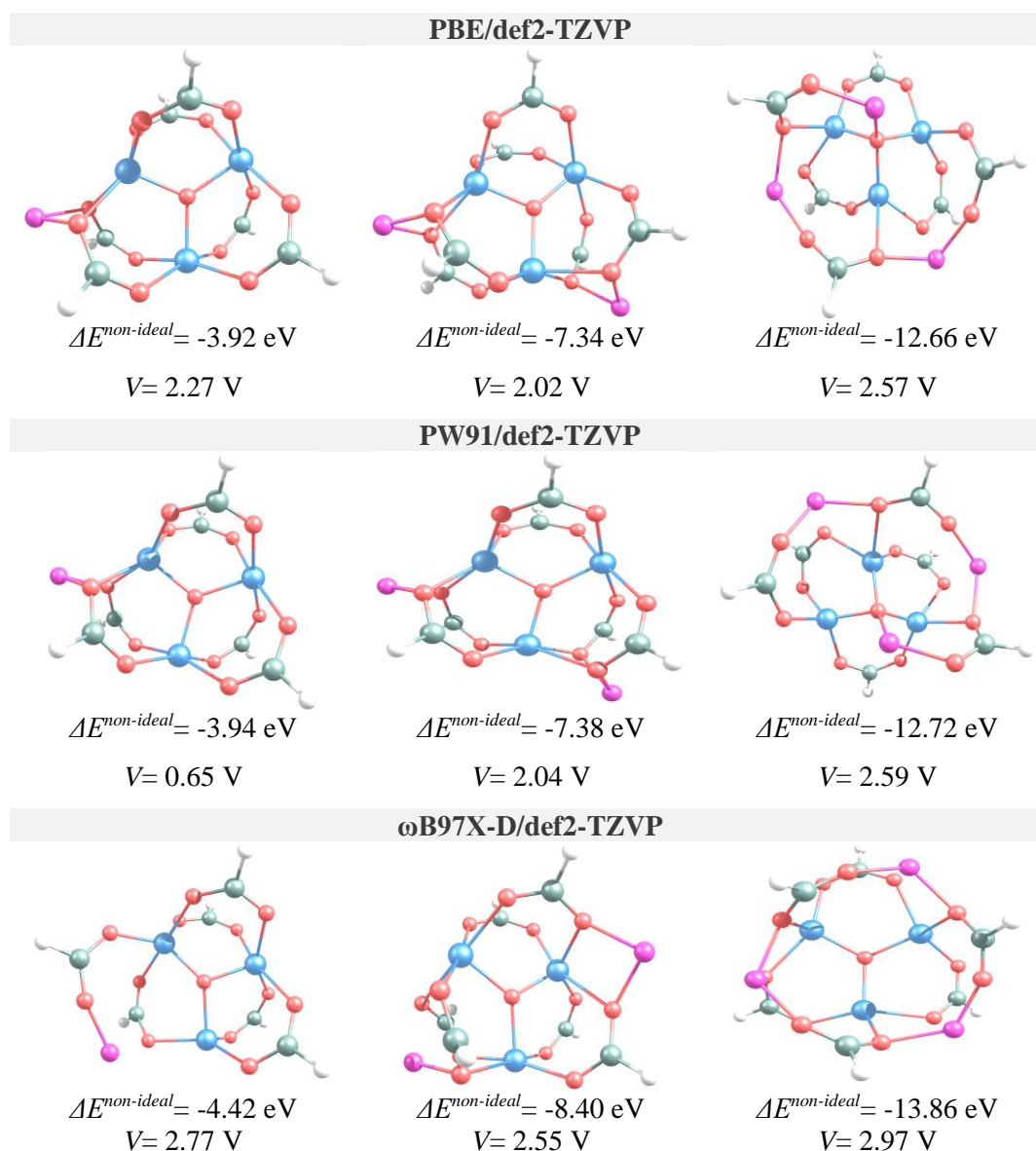
PBE/def2-TZVP

$\Delta E^{non\text{-}ideal}= -3.92$ eV

$V= 2.27$ V

$\Delta E^{non\text{-}ideal}= -7.34$ eV

$V= 2.02$ V

$\Delta E^{non\text{-}ideal}= -12.66$ eV

$V= 2.57$ V

PW91/def2-TZVP

$\Delta E^{non\text{-}ideal}= -3.94$ eV

$V= 0.65$ V

$\Delta E^{non\text{-}ideal}= -7.38$ eV

$V= 2.04$ V

$\Delta E^{non\text{-}ideal}= -12.72$ eV

$V= 2.59$ V

ωB97X-D/def2-TZVP

$\Delta E^{non\text{-}ideal}= -4.42$ eV

$V= 2.77$ V

$\Delta E^{non\text{-}ideal}= -8.40$ eV

$V= 2.55$ V

$\Delta E^{non\text{-}ideal}= -13.86$ eV

$V= 2.97$ V

Figure S2. Intercalation of one to three Li atoms (from left to right) into the MIL-101(Fe) model at different computational levels. The electrochemical potential (*V*) values are reported with reference to the Li anode electrode. The Li, Fe, C, O and H atoms are respectively shown as purple, blue, grey, red and white balls.

Table S1. Changes in energies (in eV) of the HOMO (E_{HOMO}), LUMO (E_{LUMO}), band gap (E_g) and Fermi level (E_F) and the natural atomic charges upon intercalation of m Li$^+$ ions.

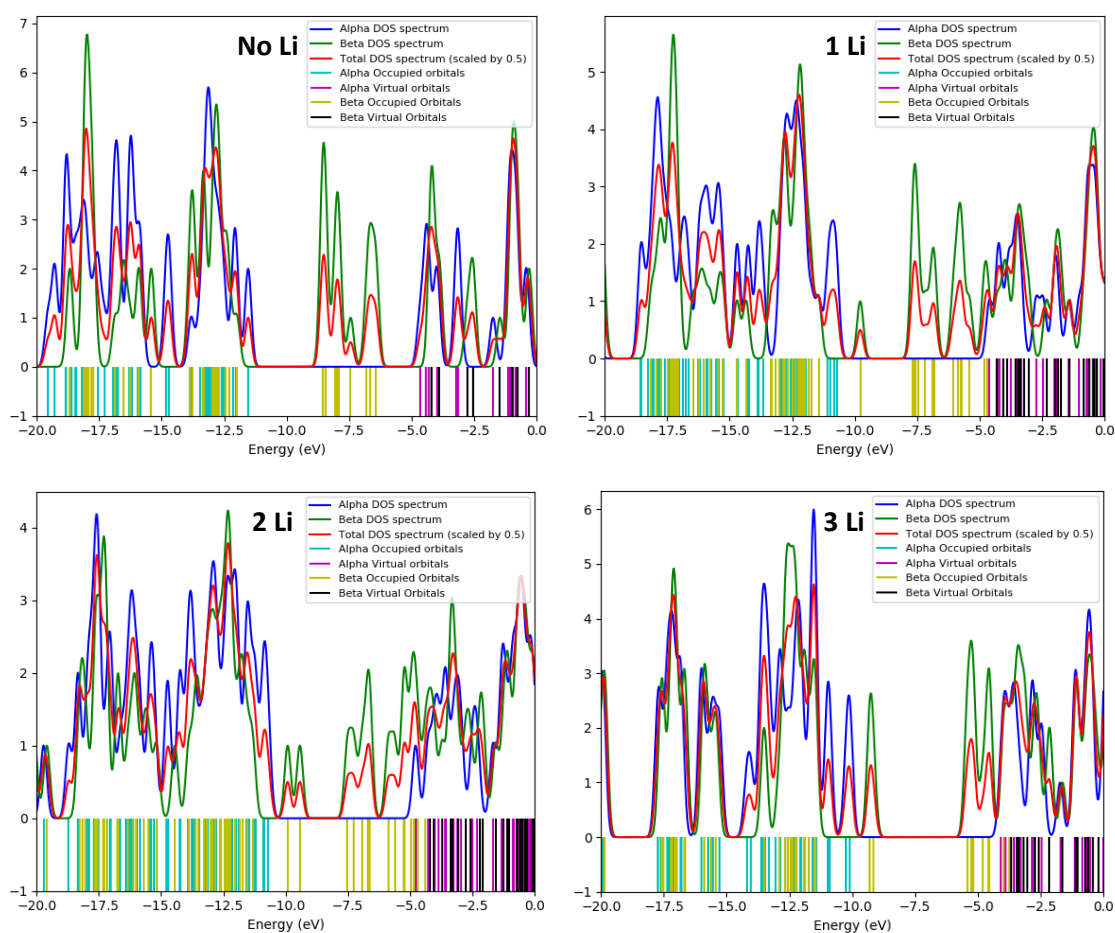| Computational level	m	E_{HOMO}	E_{LUMO}	E_g	E_F	Natural atomic charges						
						Fe1	Fe2	Fe3	Oμ	Li1	Li2	Li3
B3LYP/ def2-TZVP	0	-11.54	-4.66	6.88	-8.10	1.4897	1.4897	1.4897	-0.9325	-	-	-
	1	-11.04	-4.64	6.40	-7.84	1.2733	1.4113	1.4417	-0.9948	0.9602	-	-
	2	-10.69	-4.78	5.91	-7.74	1.4549	1.2957	1.2486	-1.0683	0.9193	0.9364	-
	3	-10.09	-4.07	6.02	-7.08	1.2459	1.2457	1.2458	-1.2209	0.9312	0.9312	0.9313
PBE/ def2-TZVP	0	-9.71	-5.54	4.16	-7.63	1.3083	1.3084	1.3084	-0.8309	-	-	-
	1	-8.89	-5.45	3.44	-7.17	1.1528	1.2908	1.2325	-0.8685	0.9667	-	-
	2	-8.11	-4.95	3.16	-6.53	1.0826	1.2199	1.0707	-0.9071	0.9592	0.9648	-
	3	-8.49	-5.01	3.48	-6.75	0.7541	0.9943	0.9993	-1.0510	0.9369	0.9370	0.9545
PW91/ def2-TZVP	0	-9.77	-5.61	4.16	-7.69	1.3023	1.3023	1.3023	-0.8281	-	-	-
	1	-8.96	-5.53	3.43	-7.24	1.1457	1.2847	1.2283	-0.8650	0.9661	-	-
	2	-8.16	-5.03	3.13	-6.60	1.0656	1.2151	1.0740	-0.9030	0.9640	0.9607	-
	3	-8.55	-5.07	3.48	-6.81	0.7547	0.9897	0.9827	-1.0497	0.9370	0.9363	0.9541
ωB97X-D/ def2-TZVP	0	-13.75	-2.46	11.29	-8.11	1.5394	1.5393	1.5393	-0.9700	-	-	-
	1	-13.19	-2.45	10.74	-7.82	1.2739	1.4852	1.4723	-1.0193	0.9671	-	-
	2	-11.92	-2.54	9.38	-7.23	1.2826	1.2929	1.3852	-1.0286	0.9423	0.9704	-
	3	-12.14	-1.81	10.33	-6.98	1.2613	1.2607	1.2613	-1.2506	0.9383	0.9386	0.9388

Figure S3. Changes in the density of states (DOS) of the system upon intercalation of one to three Li atoms, at the B3LYP/def2-TZVP level.
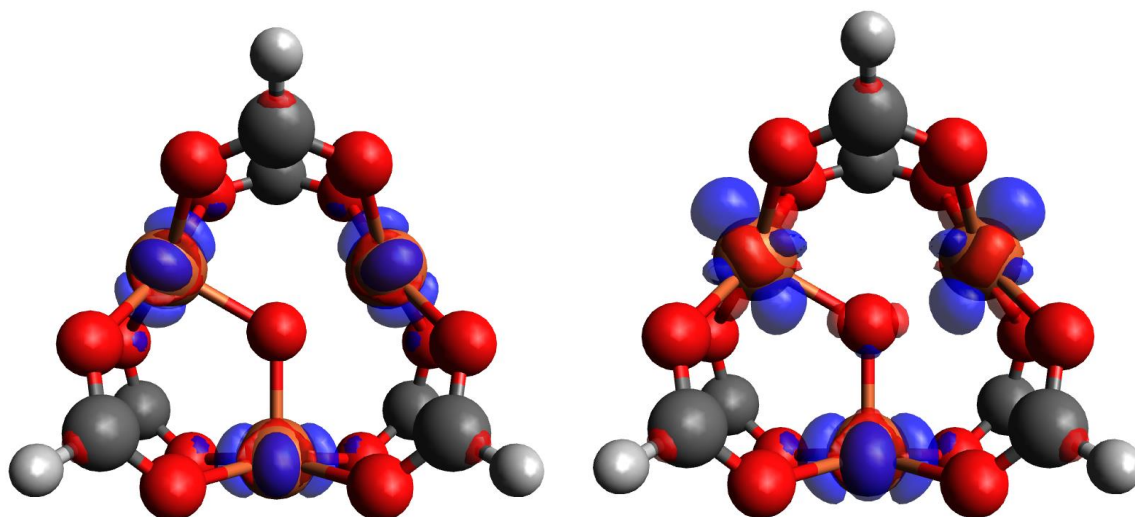
Figure S4. Fukui functions of the MIL-101(Fe) model with one (left) and two (right) additional electrons (iso value= 0.005). The structure is optimized at the B3LYP/def2-TZVP level and the ideal case is concerned, meaning no explicit Li atom is added. The blue and red bubbles respectively represent positive and red charges in the unit of Bohr^{-3}.