Electronic Supplementary Information (ESI) for

Roles of spin-state dangling bonds and strain on the electronic structure of polytetrafluoroethylene for charge transfer from first-principles

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Supplement figure captions

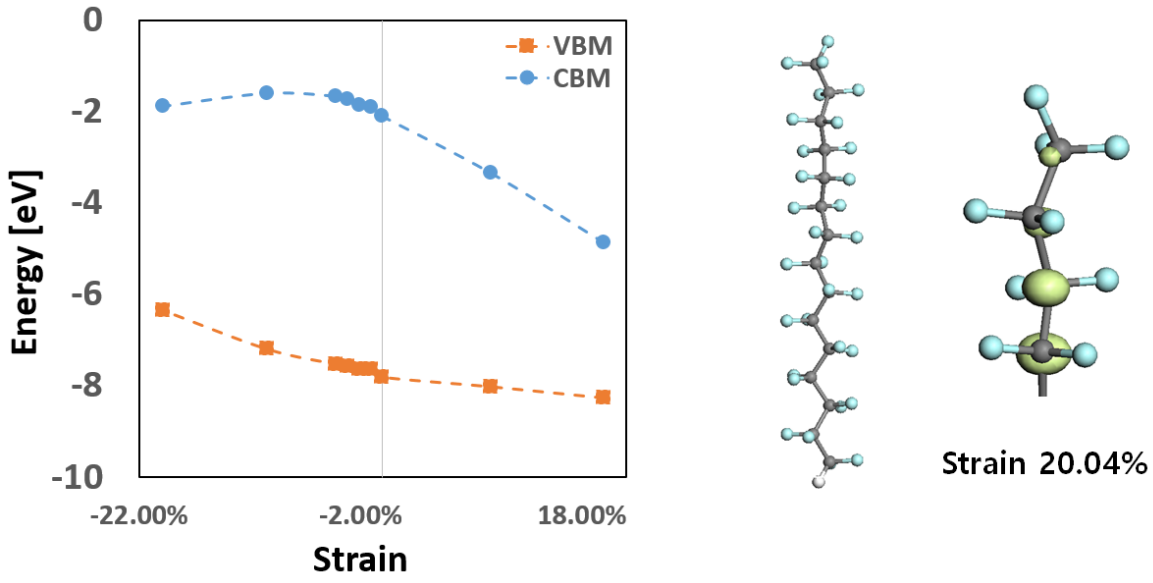


Figure S1. A plot of CBM/VBM for reference PTFE slab as a function of strain (-20% ~ 20%). Note that the orbital was shown for the PTFE under a strain of 20.04%.

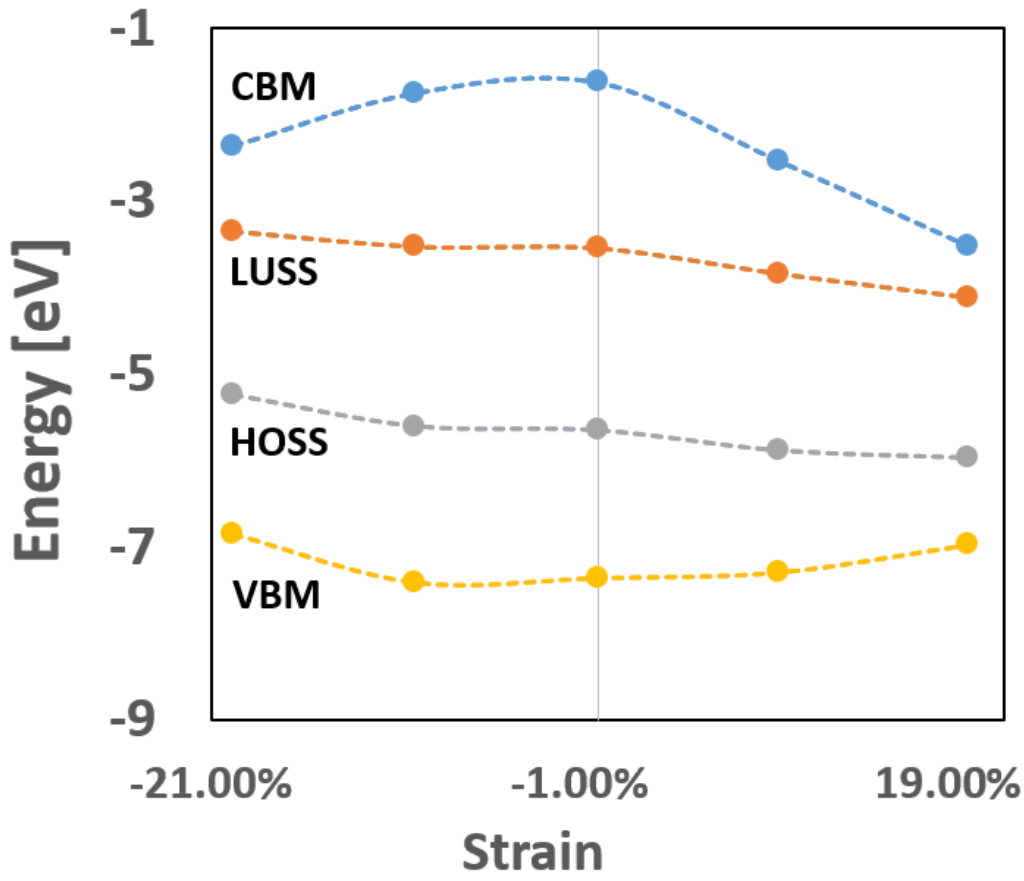


Figure S2. A plot of CBM, LUSS, HOSS, and VBM for the 1DB PTFE slab as a function of strain (-20% ~ 20%).

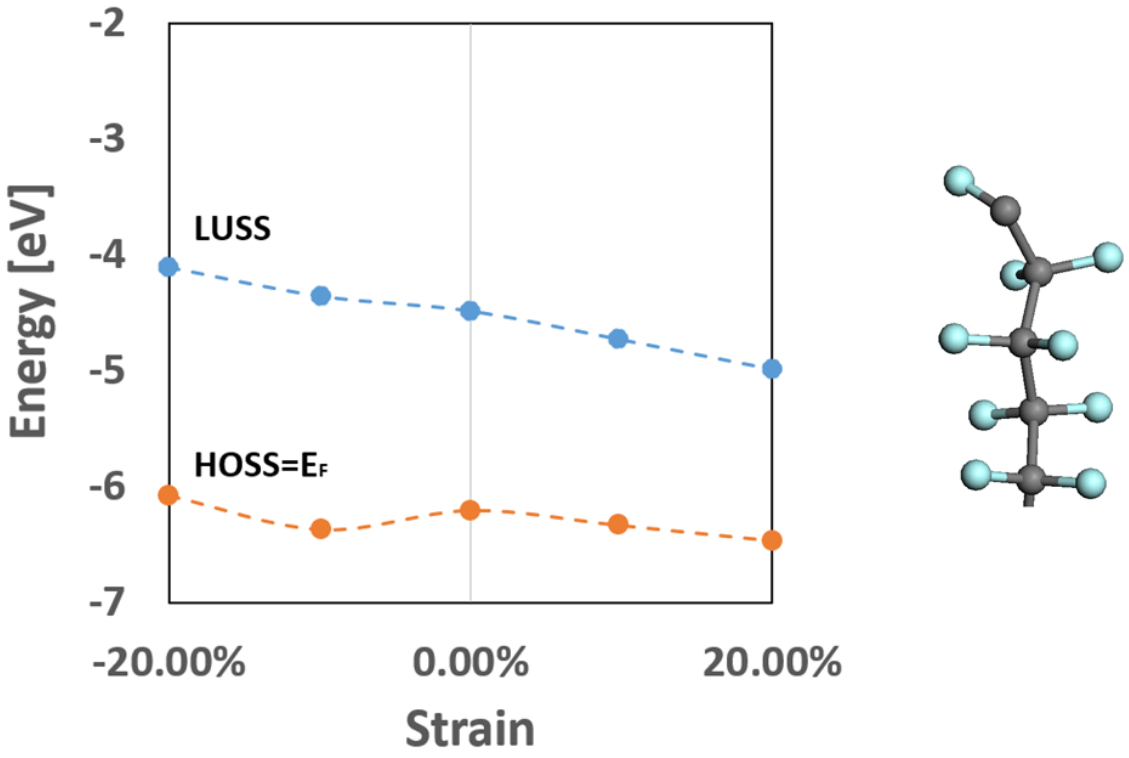
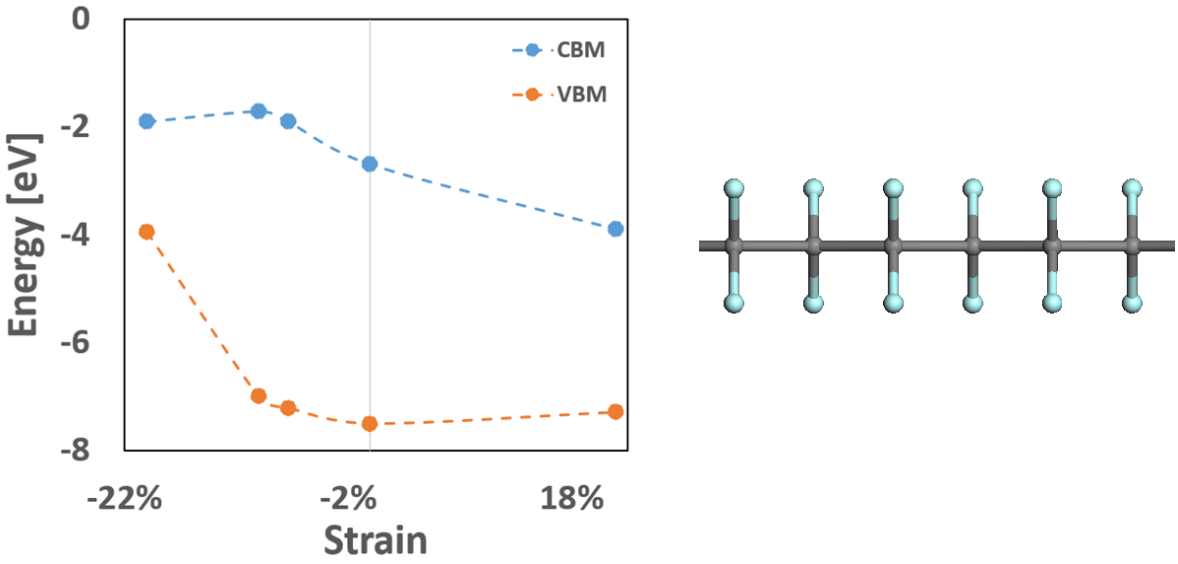


Figure S3. A plot of LUSS and HOSS for the 2DB PTFE slab as a function of strain (-20% ~ 20%).



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75 **Figure S4.** A plot of CBM and VBM for the 2_1 1-dimensional PTFE as a function of strain (-

76 20% ~ 20%).

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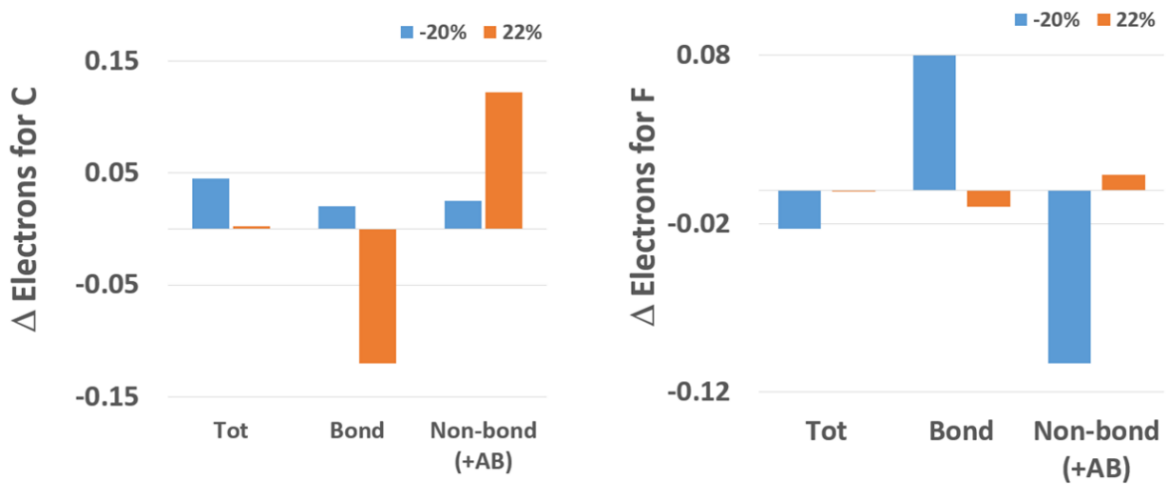

Figure S5. A plot of the change in the number of electrons for C and F in 2_1 1D PTFE. Note that for compression (-20%), electrons are transferred from F to C, and for elongation (20%), non-bonding electrons increase for C.

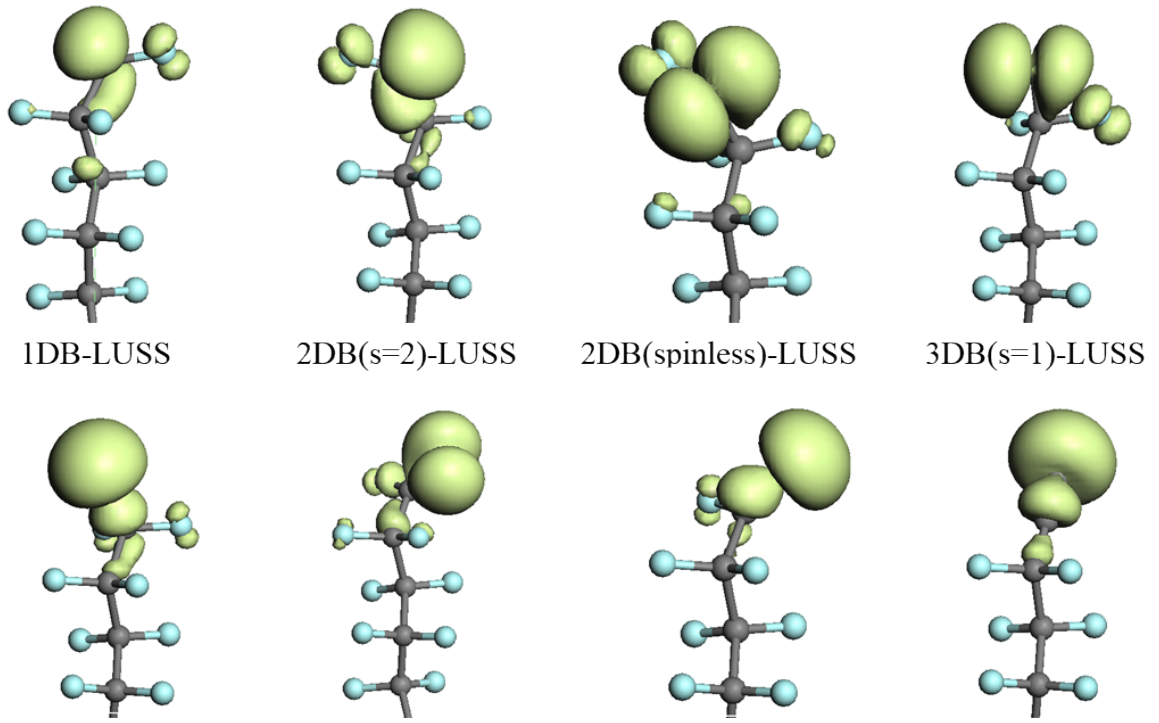

Figure S6. Shape of the acceptor orbitals.

Note. 1. Methodology of DFT

DFT calculations were performed using the CASTEP code, with the method detailed below. A 2D slab and contact model were used, incorporating a vacuum region exceeding 15 Å to avoid interactions between periodic images, along with a dipole correction to minimize spurious interactions. A TS semi-empirical dispersion correction was applied to account for long-range energy, and when the band gap was underestimated by GGA, meta-GGA (RSCAN) and hybrid XC functionals, such as HSE06 and PBE0, were used to correct for self-interaction errors in GGA. The on-the-fly-generation (OTFG) ultrasoft pseudopotential, implemented in Materials Studio, was used to calculate electron-ion interactions by treating the pseudovalence electrons of atoms. Structural optimization for the 1D PTFE polymer model was performed with the PBE functional under the BFGS line-search algorithm, using Monkhorst-Pack special k-points for Brillouin zone integration. A cutoff energy of 440 eV was applied for the plane wave basis set during electronic minimization, and a vacuum region of more than 20 Å was employed to prevent interactions between neighboring cells. The geometric optimization was performed with convergence criteria for energy, force, and displacement set to 1x10-5 eV/atom, 0.03 eV/ Å, and 0.001 Å, respectively. Density of states (DOS) and band structure calculations were carried out with k-spacing values of 0.04 and 0.015 Å-1. To correct band gap underestimation, hybrid exchange-correlation functionals were used with the GGA-derived wavefunctions and densities. Collinear spin polarization was applied for surface state (SS) modelling, optimizing spin states for unpaired electrons in various configurations. The combination of these advanced computational techniques provided accurate predictions of electronic properties and surface states, contributing to a deeper understanding of the material's behavior in various environments.

Defect type	Defect formation energy (eV)	Comparable chemical bond energy (eV)	Notes
Removal of 1F atom	4.2	C-H bond (~4.3 eV) / Si-Si bond (~3.6 eV)	Similar to the dissociation energy of a single bond
Removal of 2F atoms	8.3	C=C double bond (~6.3 eV) / C-O bond (~7.6 eV)	Higher than most double bonds
Removal of 3F atoms	12.8	C≡C triple bond (~12.6 eV) / Hydrogen ionization energy (~13.6 eV)	Comparable to ionizing hydrogen
Strain Formation (20% axial strain)	7-8	-	Comparable to defect formation of 2F atoms

111 **Table 1.** Defect formation energy and comparison with chemical bond energies

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System	Slab length (Å)	Length increase (Å)	Strain formation energy (eV)	Axial strain (%)
Ref.	20.437	4.087	8.15	20
1DB	19.333	3.87	7.60	20
2DB	19.223	3.845	7.43	20

Table. 2. Strain formation energy and slab length changes with axial strain of 20%