Supporting Information

DFT Study on the H_2 Storage Properties of Sc Decorated Covalent Organic Frameworks Based on Adamantane Units

Amol Deshmukh,[a,b,c‡] Thong Nguyen Minh Le, [a,b,c,‡] Cheng-chau Chiu,[a,*] Jer-Lai Kuo[a,*]

[a] Institute of Atomic and Molecular Sciences, Academia Sinica, Daan District, Taipei City 10617, Taiwan

[b] Molecular Science and Technology Program, Taiwan International Graduate Program, Academia Sinica, Nankang District, Taipei City 11529, Taiwan.

[c] Department of Physics, National Central University, Zhongli District, Taoyuan City 32001, Taiwan.

‡ Both authors contributed equally

* cheng.chau.chiu@gmail.com, jlkuo@pub.iams.sinica.edu.tw

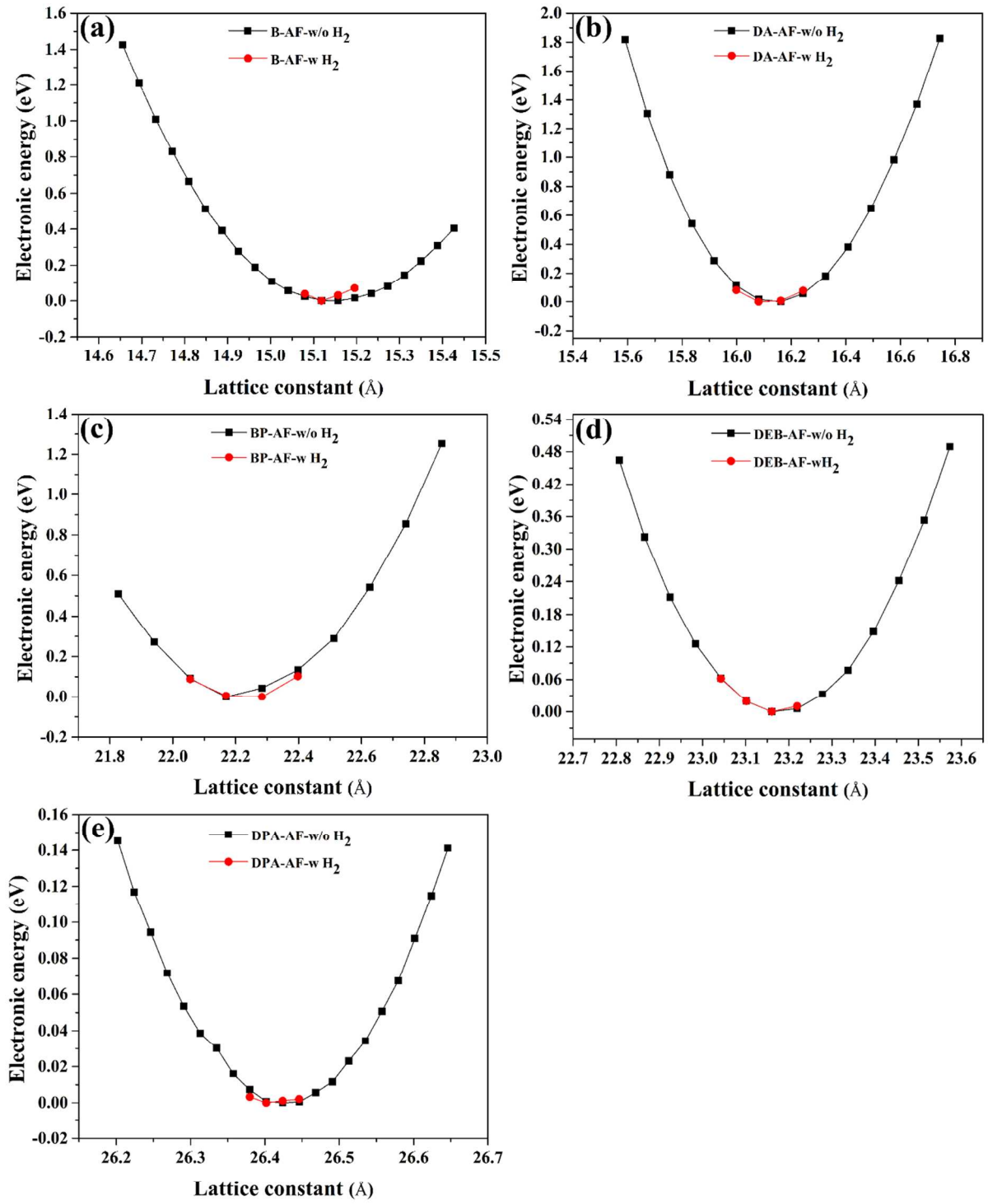

Fig. S1. Stability of the unit cells, as characterized by the electronic energy in eV, of (a) B-AF, (b) DA-AF, (c) BP-AF, (d) DEB-AF and (e) DPA-AF as a function of the lattice constant. The black squares denote a unit cell without any H_2 adsorbed, the red dots represent unit cells at full H_2 coverage. The electronic energies of the minima are arbitrarily set to zero.

Table S1: Selected geometric parameters as well as the masses of the AFs under study.

Framework	Volume ($Å^3$)	Unit cell vector *a* (Å)	Mass, full H_2 coverage (amu)	Mass, no H_2 (amu)
B-AF	2462	15.16	1352.87	1288.23
DA-AF	2985	16.16	1240.66	1176.02
BP-AF	7704	22.17	1657.26	1592.62
DEB-AF	8784	23.16	1545.05	1480.41
DPA-AF	13046	26.42	1753.35	1688.71

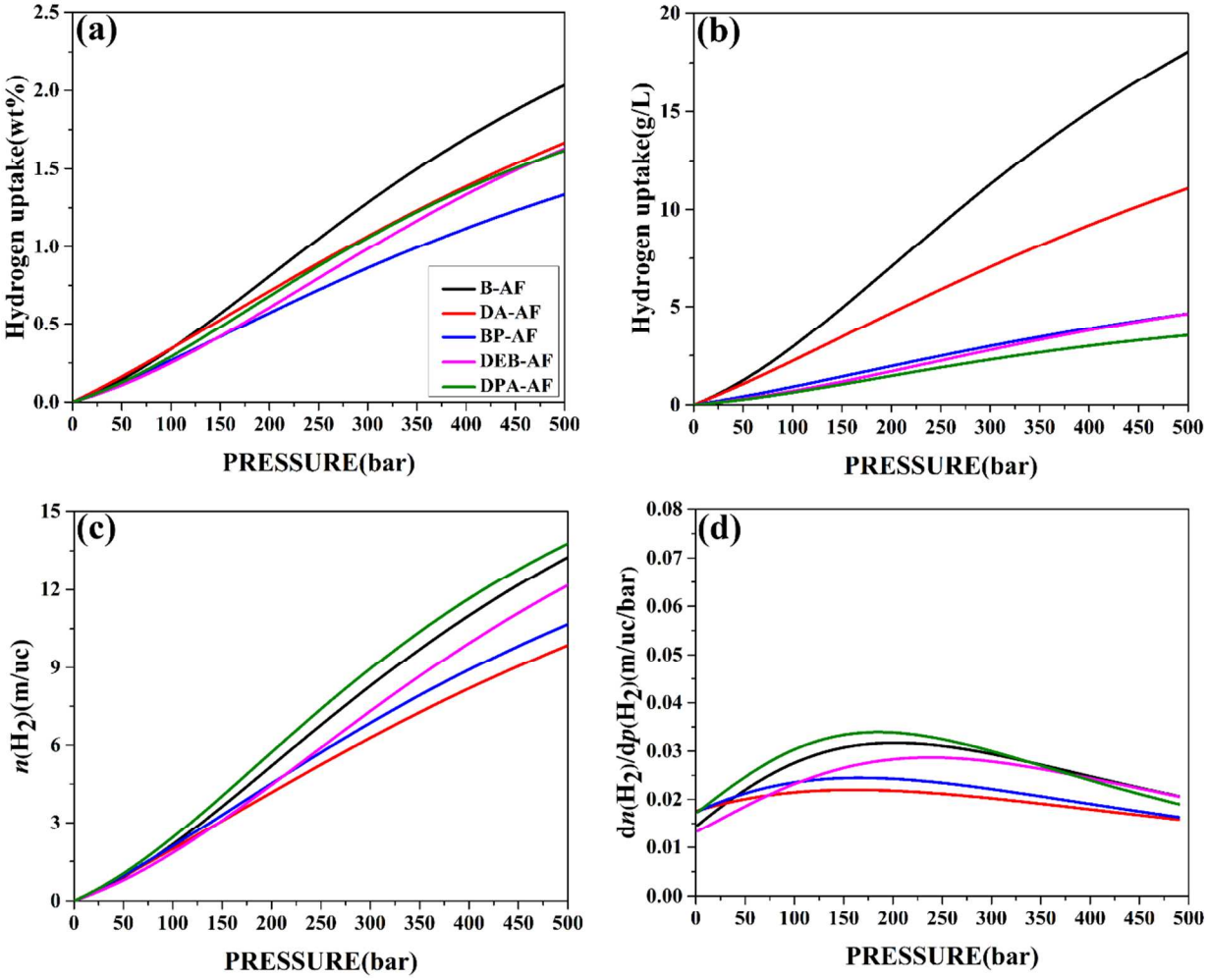

Fig S2. (a) Gravimetric, (b) volumetric hydrogen uptakes and (c) the number of adsorbed H_2 molecules per unit cell $n(H_2)$ (in molecules/unit cell, "m/uc") as a function of H_2 pressure at 358 K for the five AFs studied here. (d) shows the derivative of $n(H_2)$ with respect to the H_2 pressure (in molecules/unit cell/bar, "m/uc/bar")

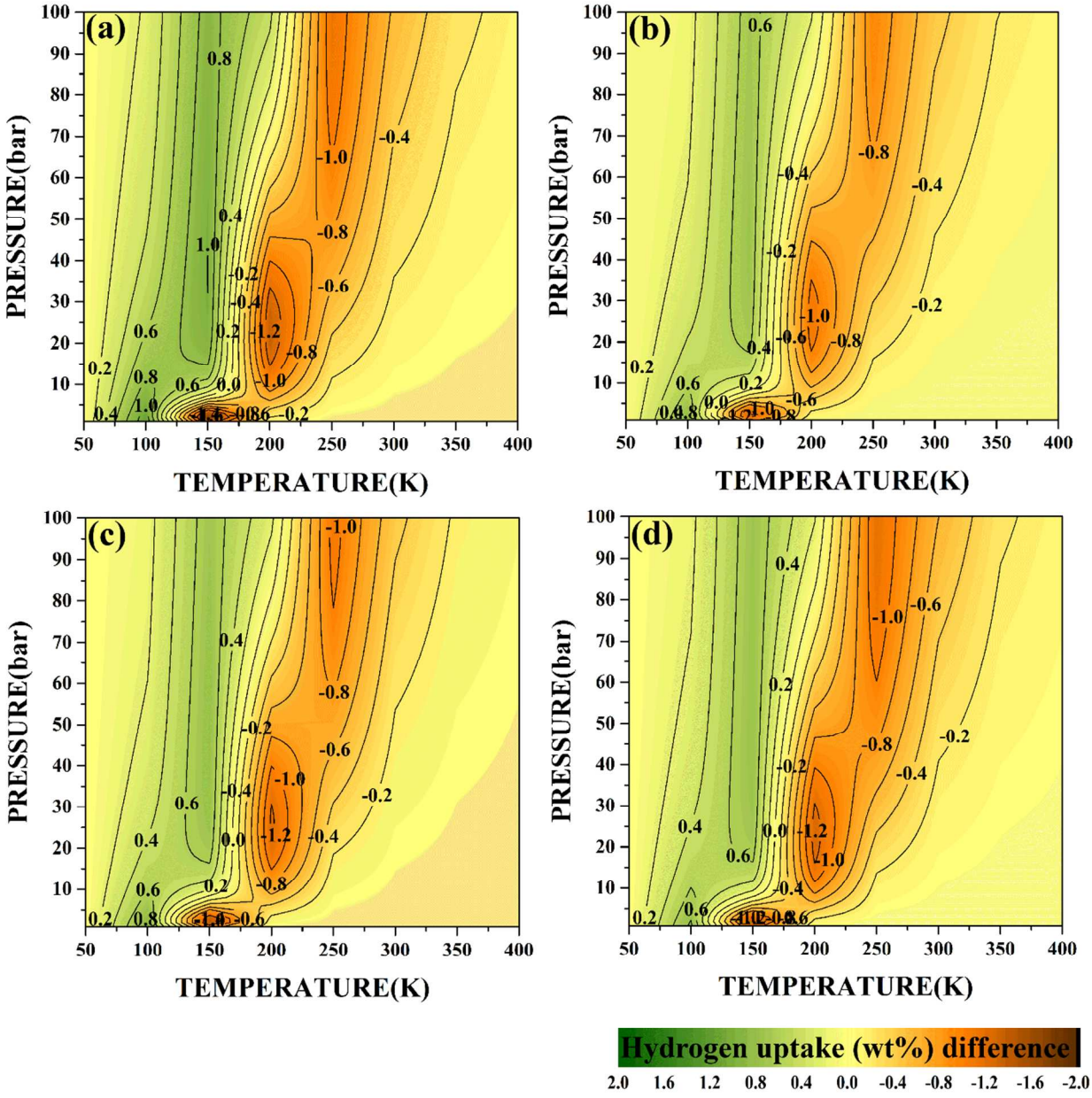

Fig. S3. Difference between the gravimetric H_2 uptake calculated with the average Gibbs free energy of adsorption ΔG^0_{av} and with explicitly calculated Gibbs free energy of adsorption for each adsorption step: (a) DA-AF, (b) BP-AF (c) DEB-AF and (d) DPA-AF. All values are calculated by subtracting the H_2 uptake obtained by explicitly considering each adsorption step from the values obtained with ΔG^0_{av}.

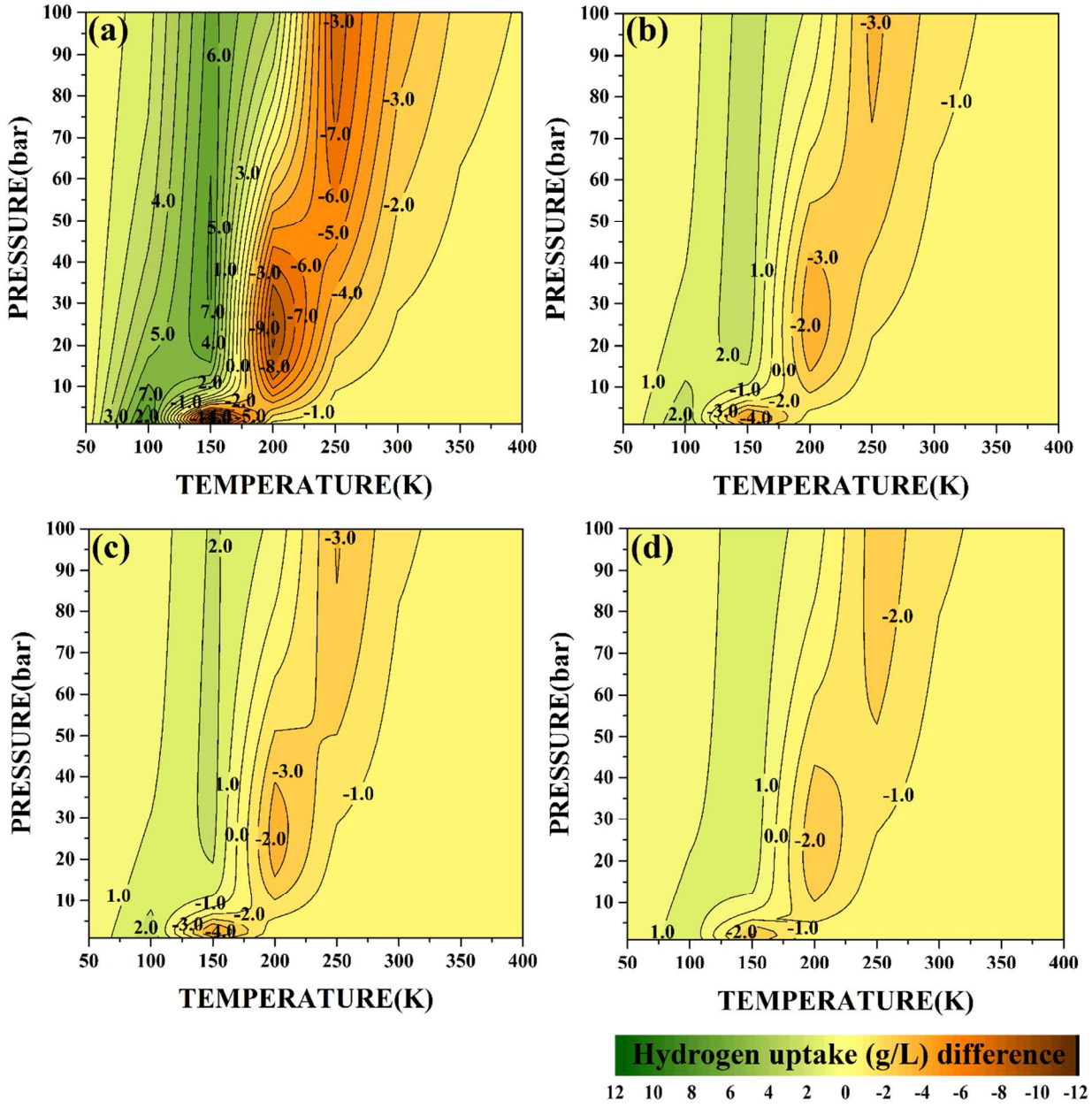

Fig. S4. Difference between the volumetric H_2 uptake calculated with the average Gibbs free energy of adsorption ΔG^0_{av} and with explicitly calculated Gibbs free energy of adsorption for each adsorption step: (a) DA-AF, (b) BP-AF (c) DEB-AF and (d) DPA-AF. All values are calculated by subtracting the H_2 uptake obtained by explicitly considering each adsorption step from the values obtained with ΔG^0_{av}.

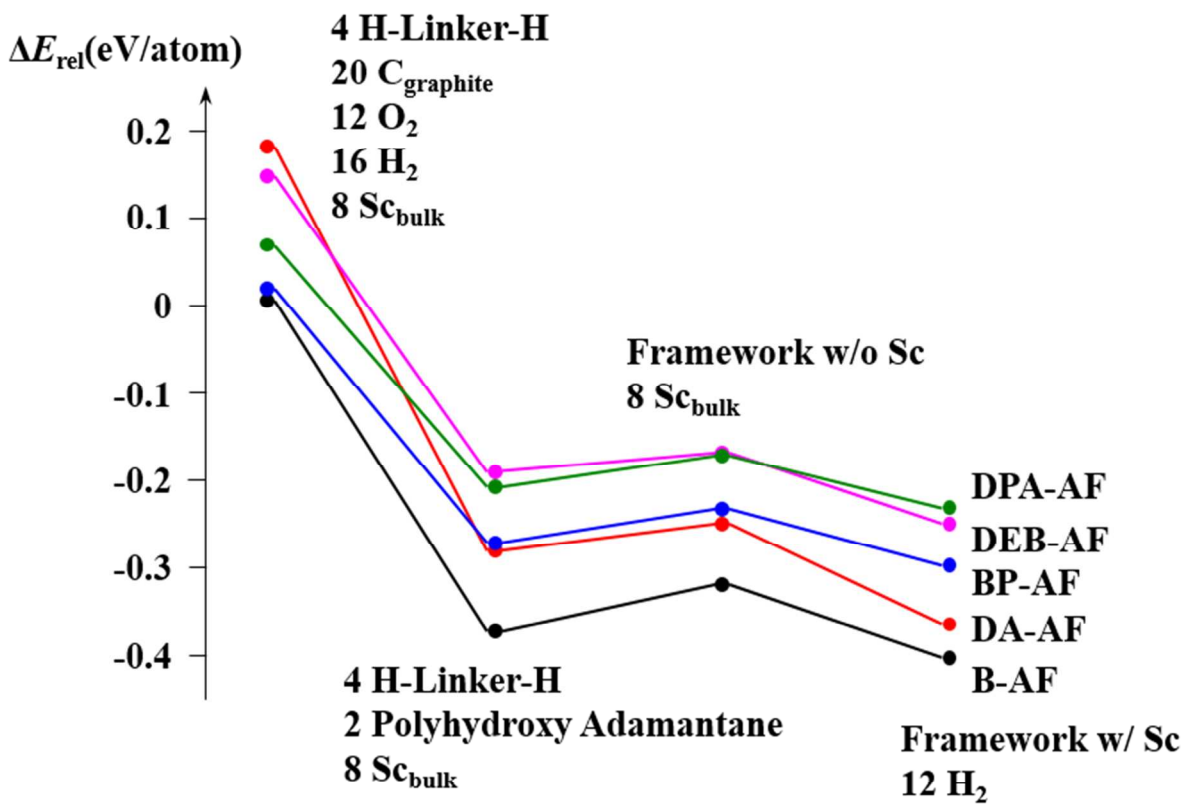

Fig. S5. Relative energy ΔE_{rel} of the AFs under study compared to the energies of the separeted building blocks as well as to pure elements in the most stable form. The energies shown are normalized by deviding by the number of atoms involved in building up a unit cell, i.e., atoms in a unit cell plus the 12 H_2 molecules (B-AF: 132, DA-AF: 108, BP-AF: 172, DEB-AF: 148, DPA-AF: 180). The energies of $C_{graphite}$, O_2, H_2, and Sc_{bulk} are set to zero.