Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Li-decorated carbyne for hydrogen storage: charge induced polarization and van't Hoff hydrogen desorption temperature

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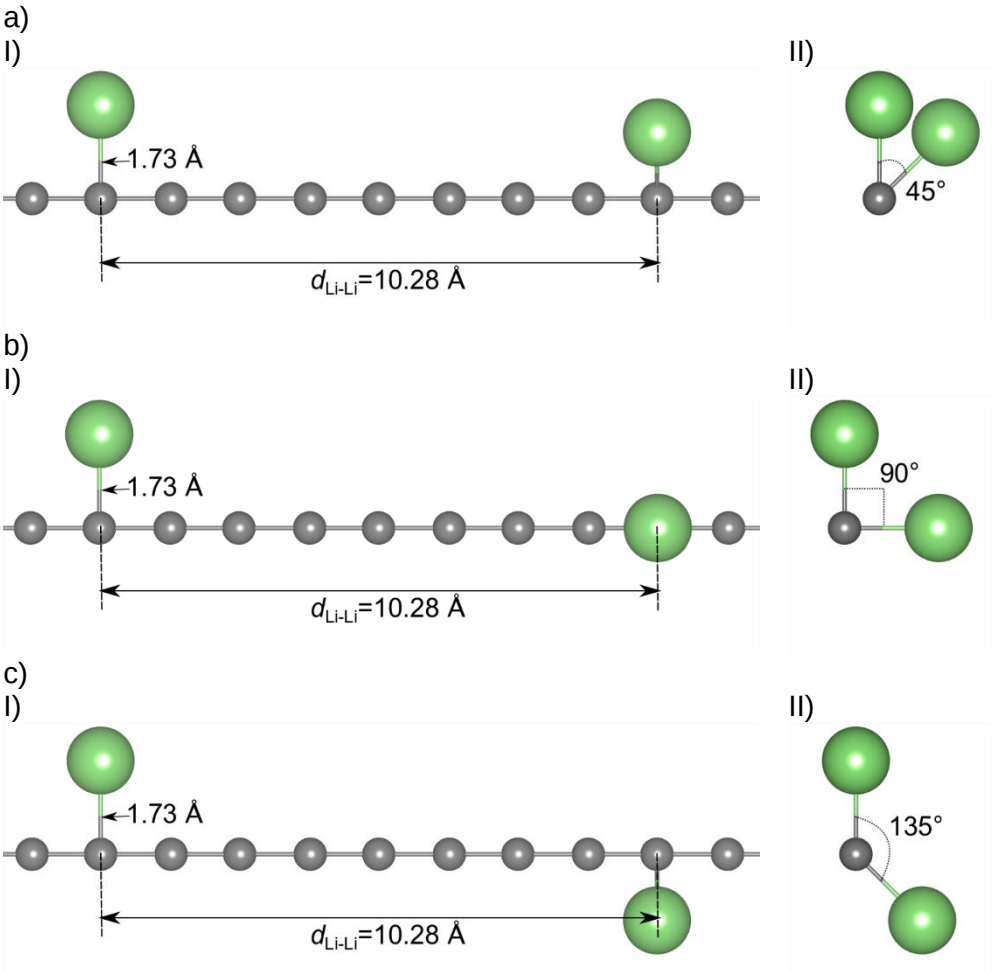

Figure S1. Different from s- and o-Li carbyne starting configurations of two Li atoms. C and Li atoms are gray and green, respectively. The position of the second Li atom is translated by d_{Li-Li} along the carbon chain and rotated by a) 45º; b) 90º; and c) 135º. I) and II) denote views along the chain and perpendicular to it, respectively. Calculations were made using SIESTA code for the carbyne supercell with forty C atoms

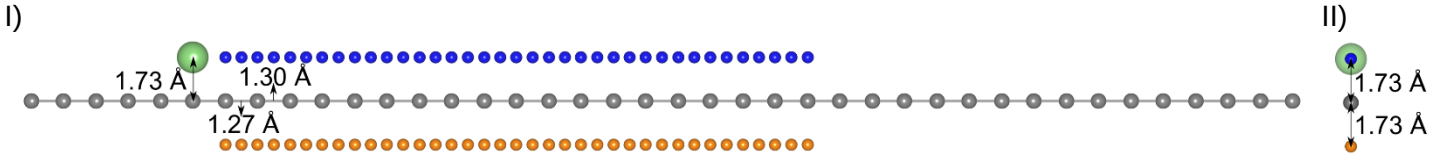

Figure S2. Starting positions of the second Li atom in the case of s-Li carbyne (blue balls) and o-Li carbyne (orange balls): I) view along the chain; II) side view. Carbon atoms are gray; the first Li atom is green. Supercell contains forty carbon atoms. Li atoms were located either above C atom, C-C, or C≡C bond, which correspond to axial distances $d_{\mathrm{Li-Li}}$ from 1.30 to 24.45 Å. Subsequent geometry optimization was performed in SIESTA, using generalized gradient approximation for exchange-correlation functional

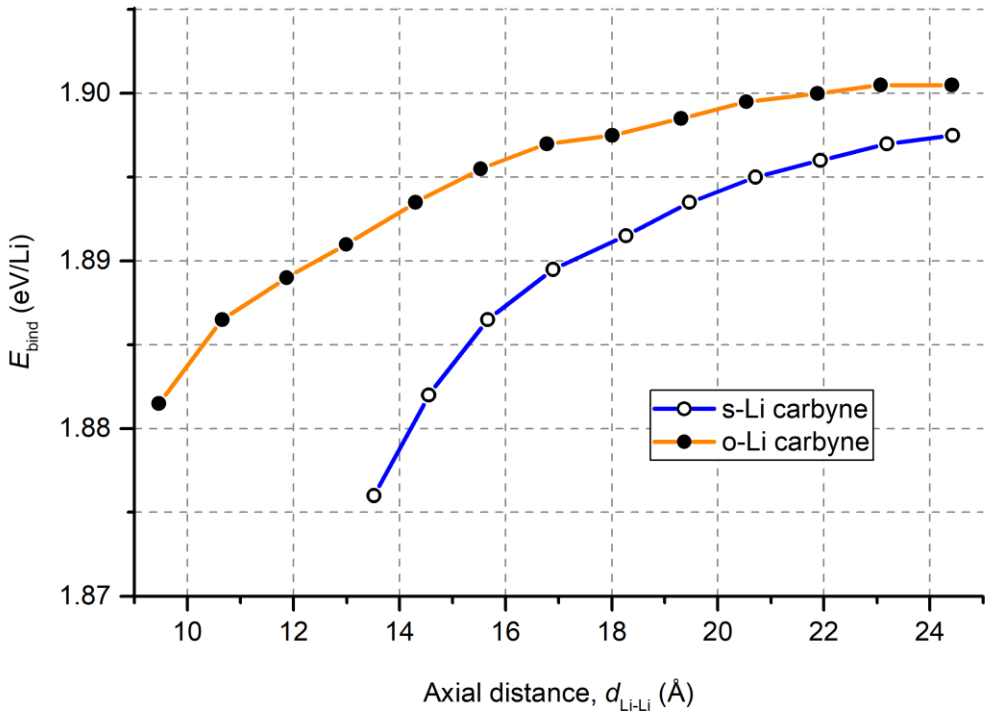

Figure S3. Dependence of Li binding energy E_{bind} on the axial distances $d_{\mathrm{Li-Li}}$ between neighboring Li atoms on the o-Li carbyne (filled circles) and the s-Li carbyne (empty circles). Calculations were made in GGA (SIESTA package) for two Li atoms on the chain of forty carbon atoms in the supercell

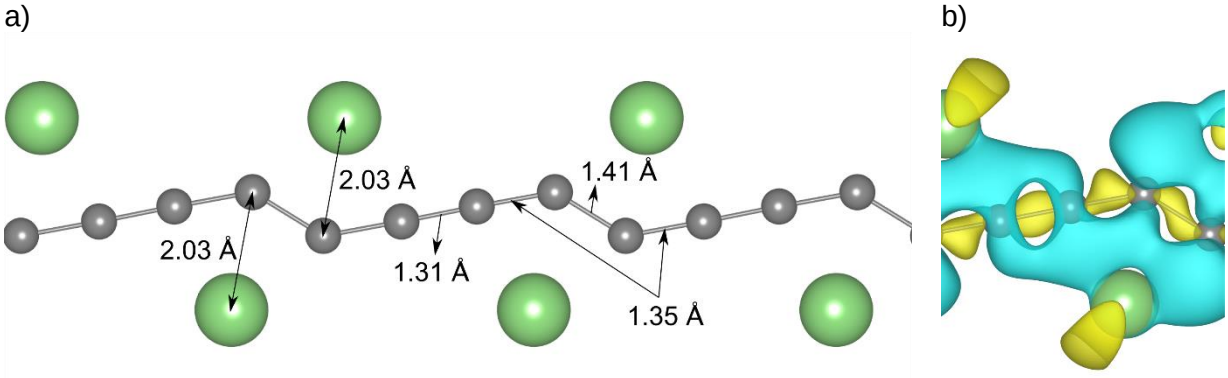

Figure S4. Relaxed structure of o-Li carbyne C_2Li: a) three unit cells; b) charge density distribution of a single unit cell. Carbon atoms are gray, lithium is green. Yellow and cyan isosurfaces (0.0025*e*) show charge depletion and accumulation, respectively

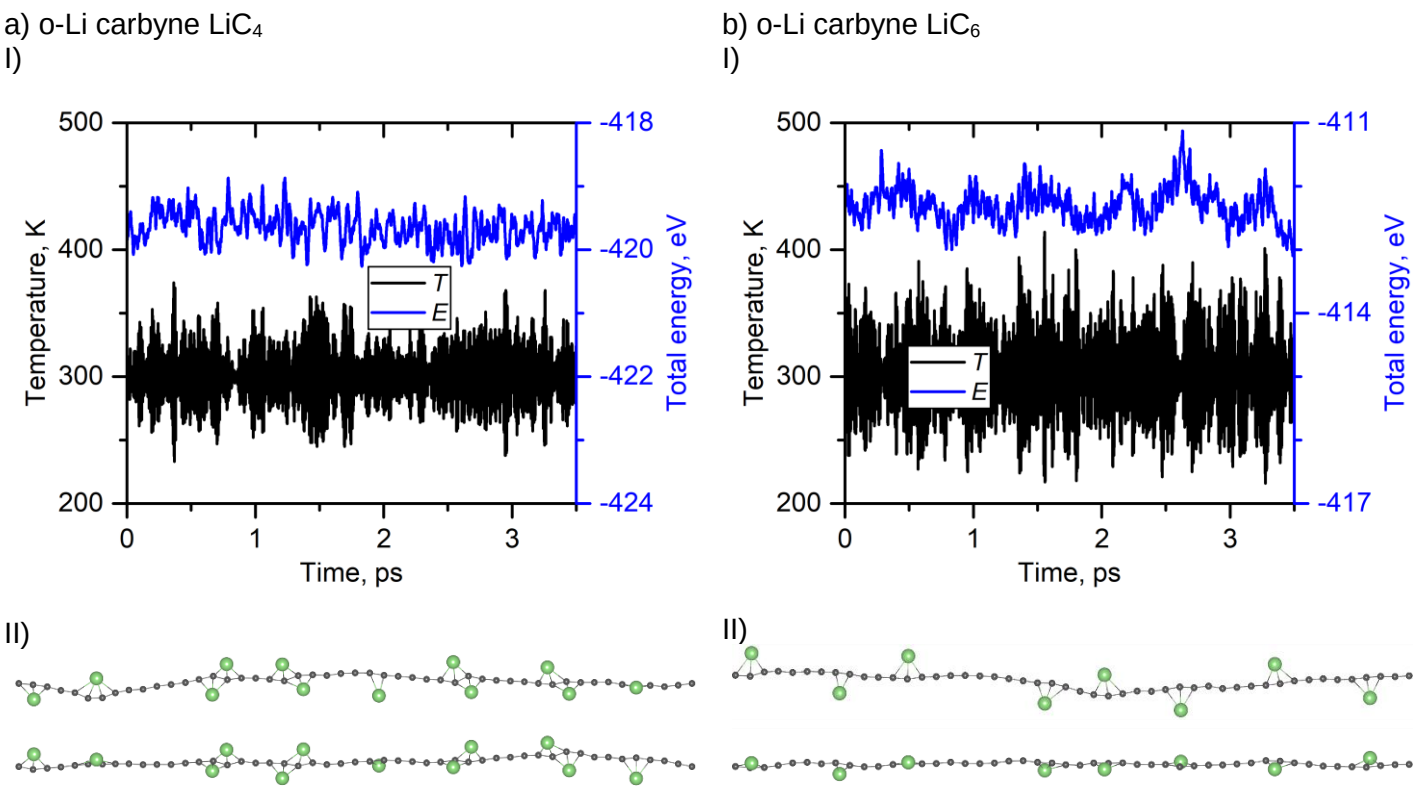

Figure S5. Production AIMD run at 300 K (NVT ensemble) of o-Li carbyne a) LiC_4 (60 atoms in the supercell; b) LiC_6 (56 atoms in the supercell). I) Dependence of temperature and total energy of carbyne@Li on the simulation time. II) Snapshots of structures (side and top views) after 3.5 ps: Carbon atoms are gray, Li - green

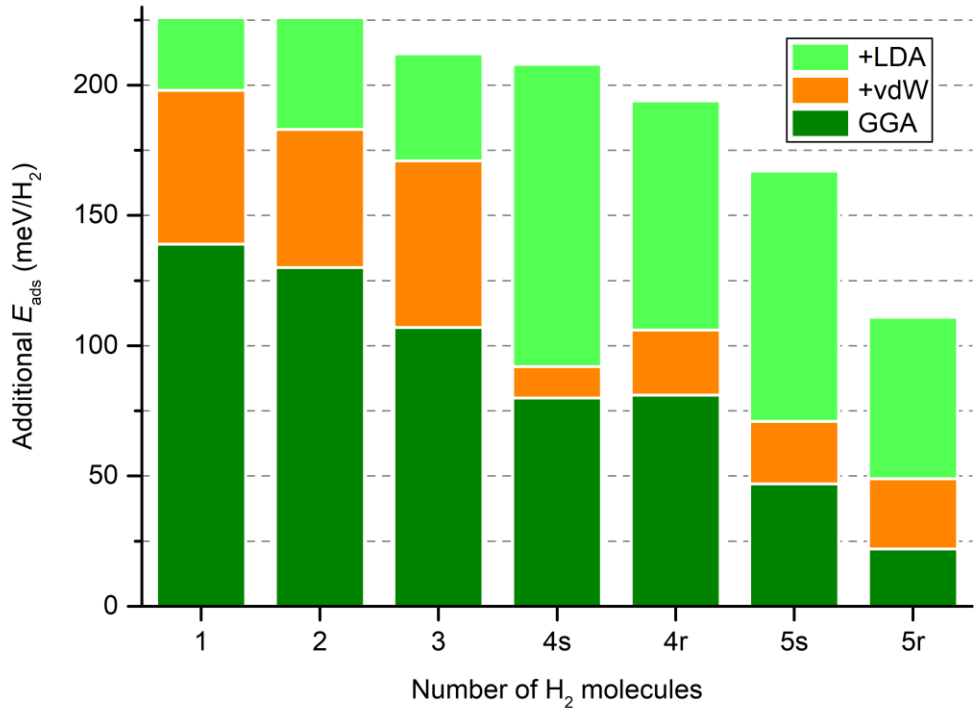

Figure S6. Additional hydrogen adsorption energies on s-Li carbyne (fourteen carbon atoms). For $k = 4, 5$ we considered two configurations of H_2 molecules ("*r*" and "*s*"). GGA and LDA results were obtained using SIESTA package

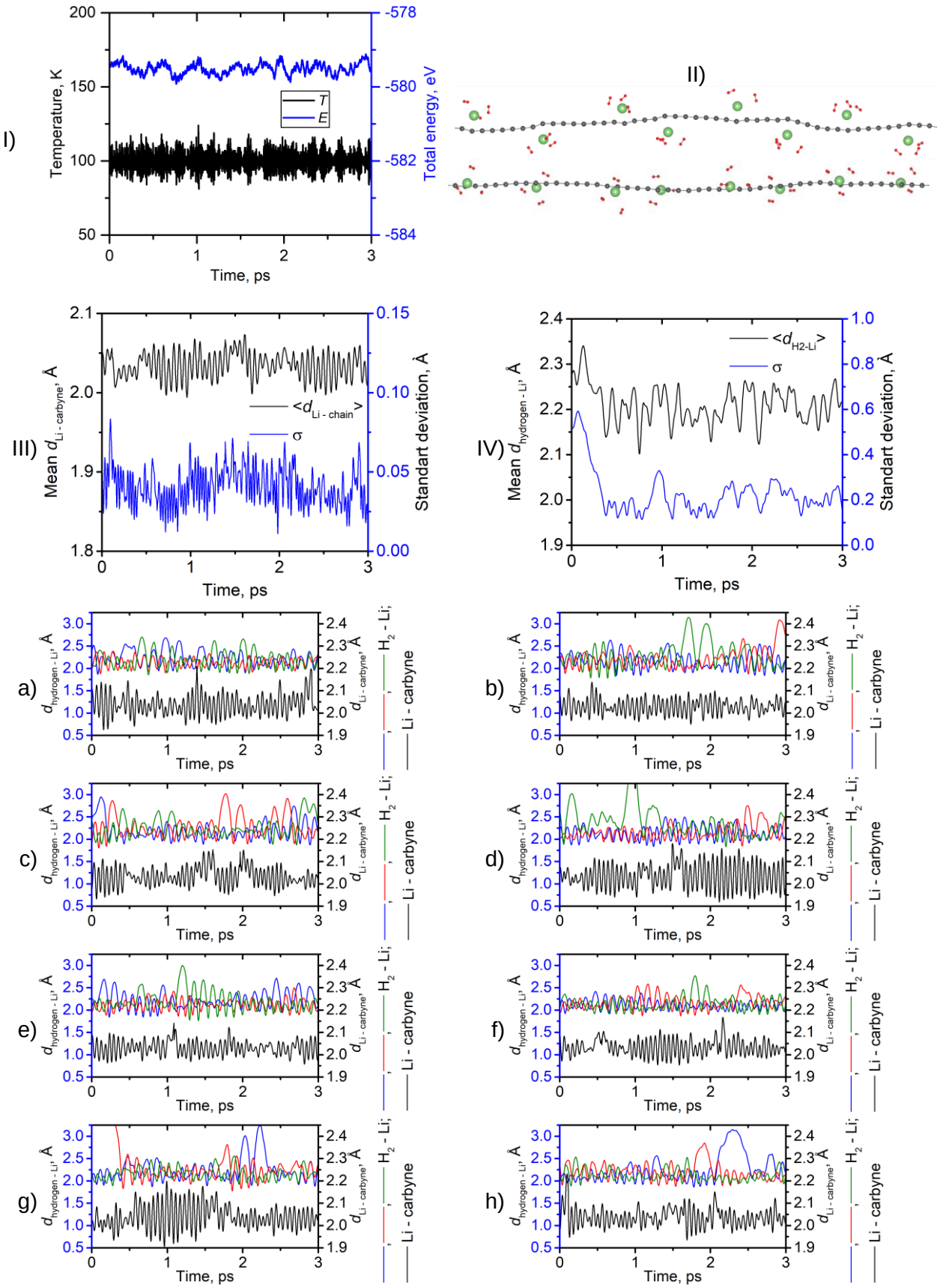

Figure S7. AIMD run of hydrogenated o-Li carbyne C_6Li at 100 K. I) Dependence of temperature and total energy of the system on the simulation time. II) Snapshots of the structure (side and top views) after 3 ps: C, Li, and H atoms are gray, green, and red, respectively. Dependence of III) mean $d_{\mathrm{Li-carbyne}}$ and its standard deviation; IV) mean $d_{\mathrm{H_2-Li}}$ and its standard deviation; a)-h) $d_{\mathrm{Li-carbyne}}$ and corresponding $d_{\mathrm{H_2-Li}}$ for each Li adatom in the supercell on the simulation time

Table S1

"Additional" hydrogen adsorption energies ($\mathrm{ad}E_{\mathrm{ads}}$, meV) calculated with Grimme corrections in complexes carbyne(*n*)@Li+*k*H_2, where *n* is the number of carbon atoms per Li in the considered computational cell

k	*n*				
	4	6	8	10	14
3	165	166	169	172	171
2	168	178	180	180	183
1	178	190	194	195	198