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Supporting Information

Prediction of Al_4C_4 superatom organic framework (SOF) material based on superatom network model

By

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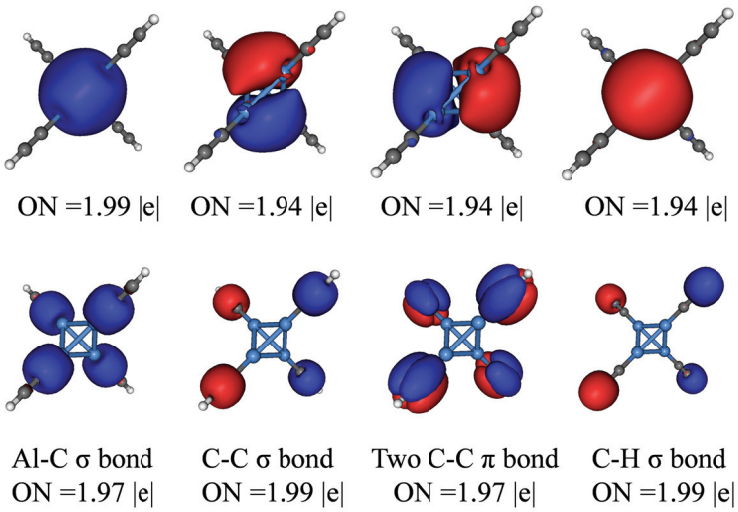

Fig. S1. Full AdNDP localized natural bonding orbitals of the $Al_4(C{\equiv}CH)_4$ cluster. Al, blue; C, grey; and H, white.

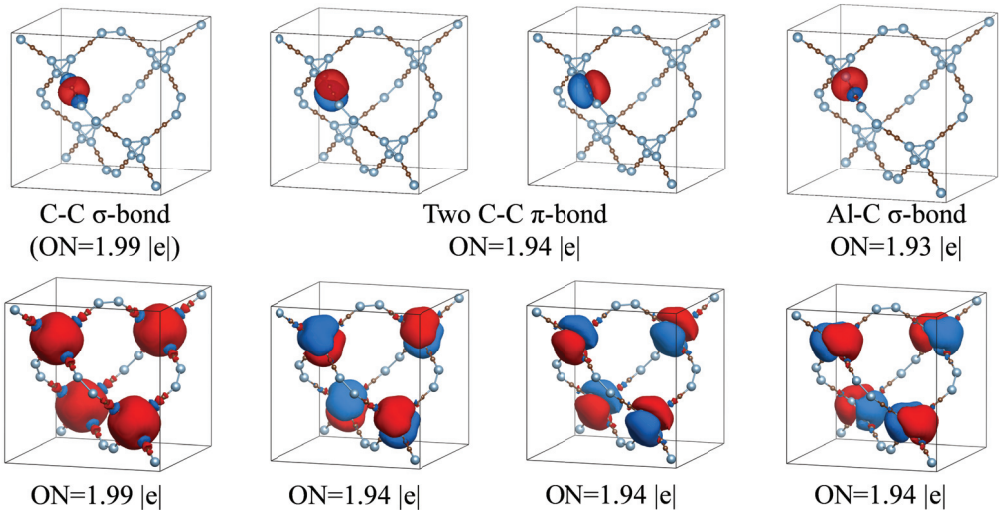

Fig. S2. Full SSAdNDP chemical bonding pattern of the Al_4C_4 crystal. Al, blue; and C, grey.

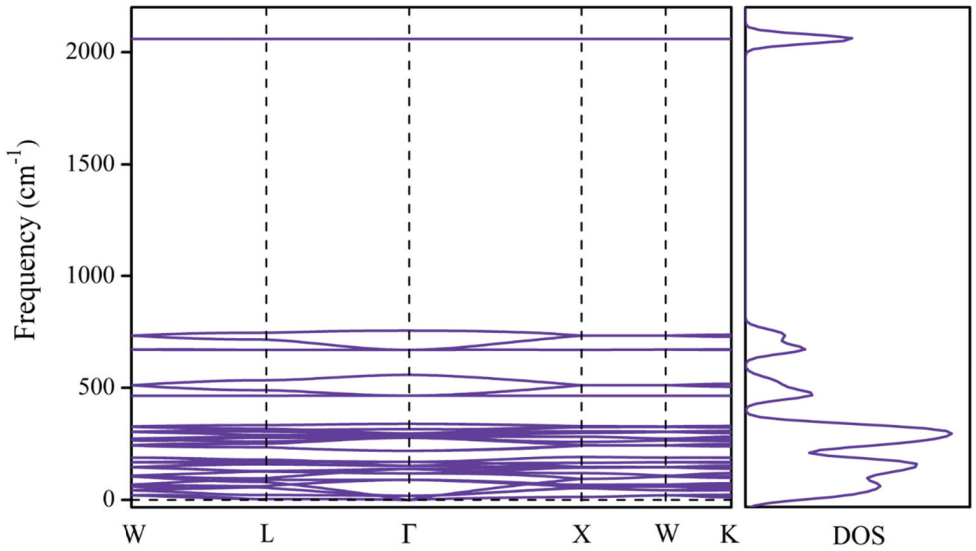

Fig. S3. Calculated phonon dispersion curves and phonon density of states for Al_4C_4 crystal.

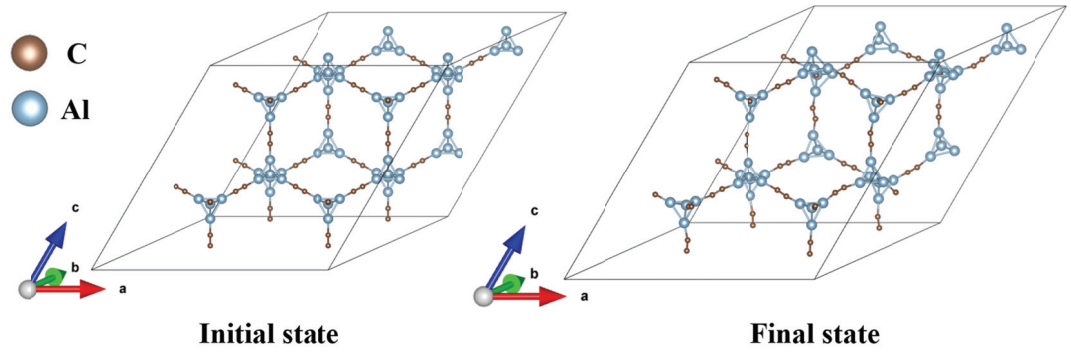

Fig. S4. The snapshot of the Al_4C_4 supercell before and after the AIMD simulation at 700 K.

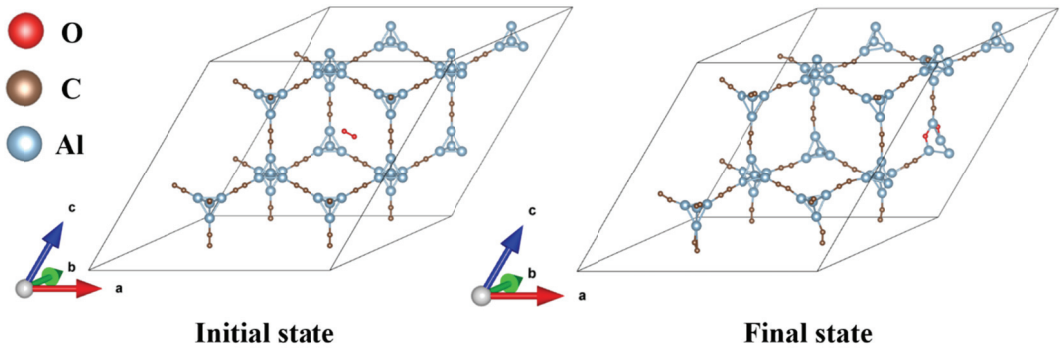

Fig. S5. The snapshot of the Al_4C_4 supercell with one O_2 molecule before and after the AIMD simulation at 300 K.

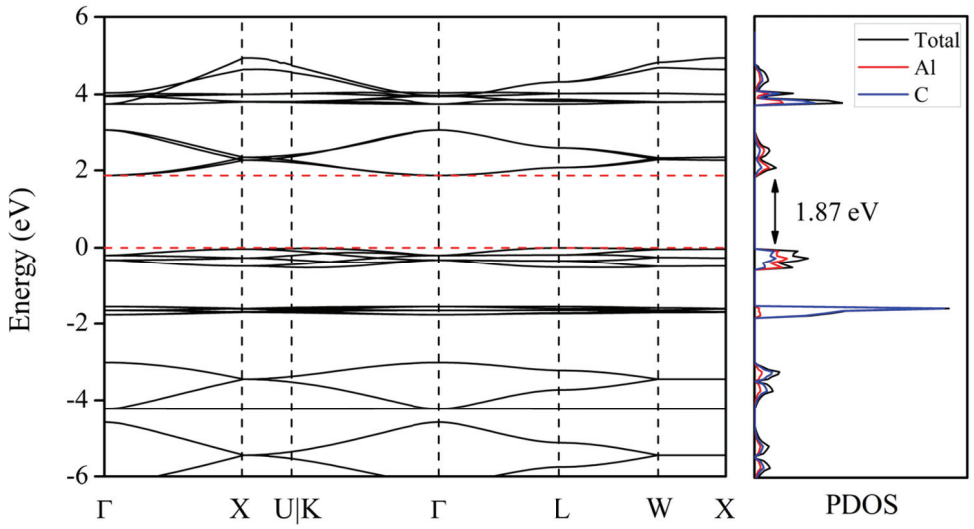

Fig. S6. Electronic band structure and projected density of states of the Al_4C_4 crystal at the PBE level. The Fermi level is set at zero.

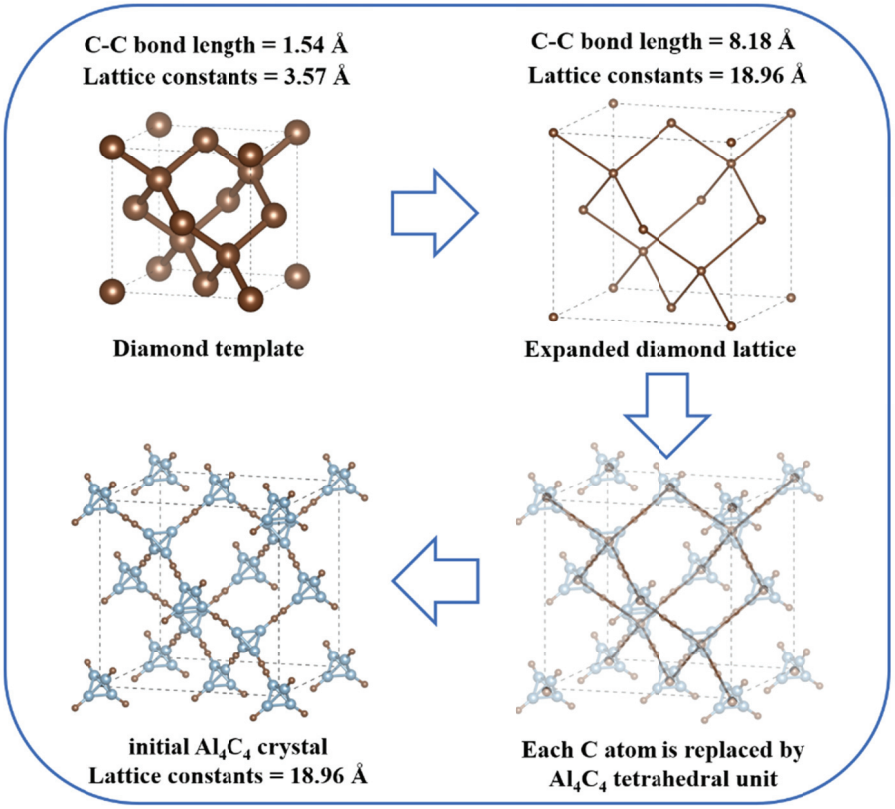

Fig. S7. Schematic diagram of the procedure used to generate the initial Al_4C_4 crystal structure.

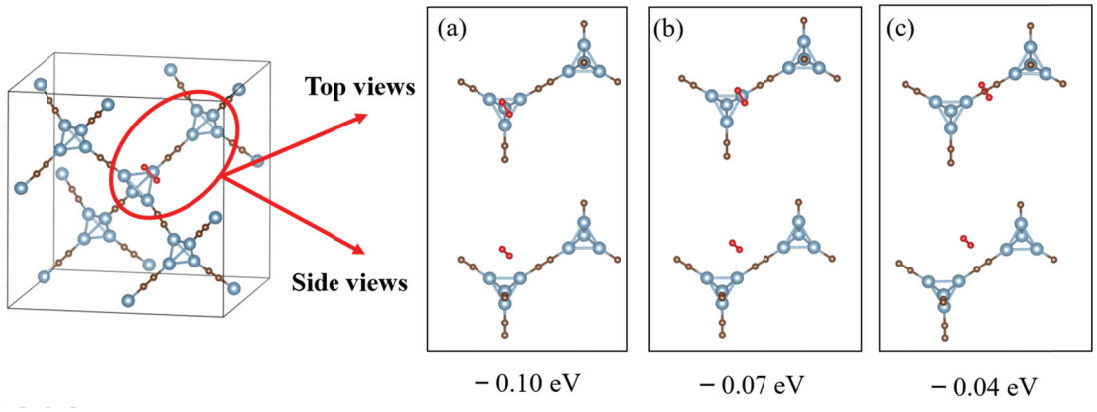

Fig. S8. Top and side views of local geometries for O_2 on different adsorption sites of Al_4C_4 (a)-(c). The binding energy of physisorbed O_2 on Al_4C_4 are labeled below. Al, blue; C, brown; and O, red.

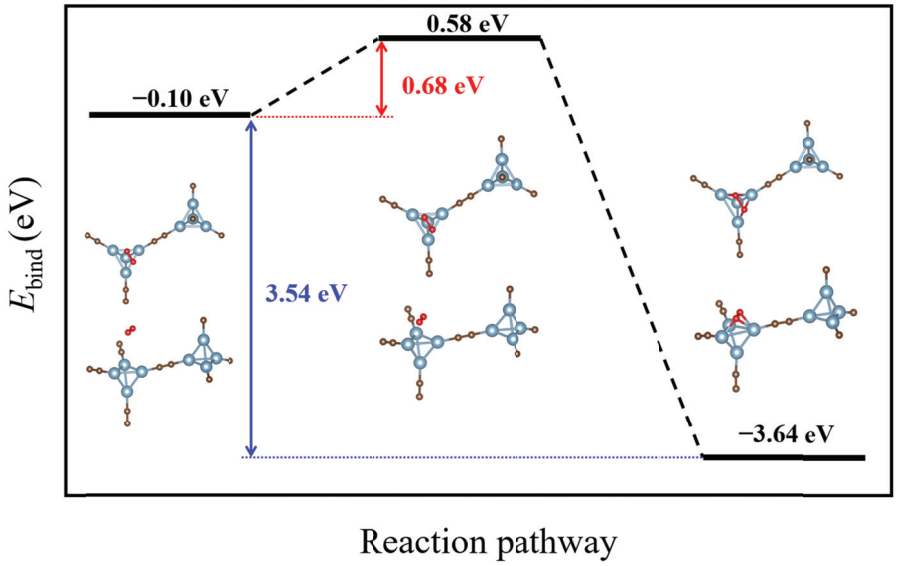

Fig. S9. The reaction pathway for an O_2 molecule from physisorption to chemisorption on Al_4C_4. Top and side views of local geometries for three different states are shown. The black line segments indicate the energy levels of the initial, transition, and final states, respectively. The binding energies (E_{bind}) of these states (in black), the heat of reaction (in blue), and the activation energy (E_a, in red) are labeled. Al, blue; C, brown; and O, red.

Table S1 The xyz coordinates (in Å) of Al4(C≡CH)4 cluster optimized at PBE/def2tzvp level.

Al	0.917811	0.917811	0.917811
Al	-0.917811	-0.917811	0.917811
Al	0.917811	-0.917811	-0.917811
Al	-0.917811	0.917811	-0.917811
C	-2.024570	2.024570	-2.024570
C	2.024570	2.024570	2.024570
C	-2.024570	-2.024570	2.024570
C	2.024570	-2.024570	-2.024570
C	2.730842	-2.730842	-2.730842
C	-2.730842	-2.730842	2.730842
C	-2.730842	2.730842	-2.730842
C	2.730842	2.730842	2.730842
H	3.350344	3.350344	3.350344
H	-3.350344	3.350344	-3.350344
H	3.350344	-3.350344	-3.350344
H	-3.350344	-3.350344	3.350344

Table S2. Single point energies of the initial state (IS), transition state (TS), and final state (FS) structures of the absorption of O_2 molecule on Al_4C_4 (Fig. S9) with specified singlet and triplet multiplicities and spin polarization.

Spin multiplicities	IS	TS	FS
Singlet	-364.59382968 eV (+0.39)	-364.49889990 eV (+0.42)	**-369.08675670 eV (+0.00)**
Triplet	**-364.98934649 eV (+0.00)**	**-364.92125043 eV (+0.00)**	-367.63211523 eV (+0.55)
Spin polarization	**-364.98934649 eV**	**-364.92125043 eV**	**-369.08675670 eV**