Electronic Supplementary Information

Because accurate interatomic potentials for a-BC:H are not readily available, and the interatomic potentials we used in LAMMPS—a combined global interatomic pair potentials using the Lennard-Jones pair style and local interatomic pair potentials using the simple harmonic oscillator bond and angle styles—are not accurate and cannot produce a realistic atomic configuration as observed experimentally, we have limited the role of LAMMPS interatomic potentials in deciding which atom should be bonded to which. Instead, we took advantage of a program code (a so-called "fix") that has the ability to manage bond breaking/creation, those fixes were modified to include a "molecule" identifier for each atom along with explicit limitations on the number of bonds that each type of atom could have with other types. The applied fixes are shown below and the meaning of each command is tabulated in **Table ESI-1**.

Bond create input file syntax:

```
fix <fixID> <group> bond/create <nevery> <itype> <jtype> <Rmin> <bondtype> iparam<maxbond> <newtype> jparam <maxbond> <newtype> prob <fraction> <seed>
```

Bond break input file syntax:

```
fix <fixID> <group> bond/break <nevery> <bondtype> <Rmax> iparam <itype> <minbond> <newtype> jparam <jtype> <minbond> <newtype> prob <fraction> <seed>
```

Table ESI-1: Meaning of the different fix commands

Fix	Meaning
< >	substitute with desired numerical value
fixID	name to refer to the fix (our naming convention is: itype + u + jtype for bond/create and itype + n + jtype for bond/break)
group	the subset of atoms this applies to (e.g. all)

nevery	apply the fix every nevery timesteps
itype	first atom type in the bond
jtype	second atom type in the bond
Rmin	allow bond if distance between iatom and jatom is < Rmin
bondtype	type of new bond to be created
maxbond & newtype:	if a new bond is created, iatom and jatom each calculate how many bonds of type bondtype they now have. If maxbonds exist, their atom type is changed to newtype
fraction	create a bond with this probability
seed	random number seed for probability (positive integer)

Generally, the `bond create` fixes indicate that specific atoms from two different molecules can bond to each other through certain pairs (B-B, B-C, B-H, C-H), these pairs of atoms should be bonded when at a defined minimum distance from each other, the creation of these bonds occurs at certain probabilities. The `bond break` fixes are mainly for breaking H atoms from H saturated molecules leaving open bonding spots to create other bonds (specified by the `bond create` fixes), the bond breaking occurs at given probabilities as well. For instance: the atoms (in case of bonding an icosahedra B to a linker C) that may form a bond are already fully bound because of H saturation. Therefore, before a new bond can be formed between two molecules, the H bonds must first be broken. That is, the binding of an H saturated icosahedral B and an H saturated C atom from a hydrocarbon linker must follow the following sequence: (i) the two molecules approach; (ii) once the two H atoms on the separate molecules are within a defined range they each separate from their bonded atoms. (The harmonic oscillator potentials between the B and H, and between the C and H each are turned off and removed from the record of bonds in the LAMMPS registry); (iii) the B and C form a new bond in the LAMMPS registry. Managing the dynamic bond creation and bond breaking process is a complicated and delicate task (probably the most challenging part of this thesis). The parameters (R_{min}, maxbond, prob, *etc*.) that need to be given in the fixes had to be so carefully thought out, by carrying out a tremendous number of trial runs. The risks associated with giving wrong values maybe non-fully bonded molecules (not all

molecules will bond to form one giant chunk of a-BC:H) when the condensation reaches the specified cell size and number of iterations, or excess of certain bond types compared to others. Furthermore, these parameters are not transferable quantities among models with different densities (e.g. the R_{min} distance for creating a bond in a model with d=1.7g/cm^3 is not the same for a model with d=2.1g/cm^3). The above rules assure the following bonding patterns in the final models which correspond to observed patterns from the literature; the C in the orthocarborane molecules (icosahedron) will not bond with other icosahedra or hydrocarbon linkers, thus the C atom will have a static list of bound atoms that includes only its nearest neighbors in the icosahedron (five B atoms and one H). In contrast, the B atoms can be bonded —on top of its 5 C and B neighboring atoms in the same icosahedron—with B atoms of other icosahedra, C from the hydrocarbon cross-linkers, and H atoms.

Essentially, the LAMMPS condensation consists of positioning a collection of molecules (including hydrogenated icosahedral orthocarborane molecules ($B_{10}C_2H_{12}$) and hydrocarbon cross-linkers (CH_3CH_3, and CH_4) in specific ratios) within a large, periodic simulation cell such that the cell is mostly empty.

The number of each type of molecule was dictated by experimental data defining the elemental ratios observed (ref 25 of the manuscript). The simulation molecules were then set into motion with random velocities while the cell size was slowly reduced. As the molecules move about the cell they randomly encounter each other breaking and forming bonds according to the fixes specified above. The simulation had a target final density (from experimental feedback), which is achieved by controlling the final cell size (atomic masses of the different species are known). The stage of the simulation sequence that is most associated with LAMMPS is graphically illustrated in Figure ESI-1.

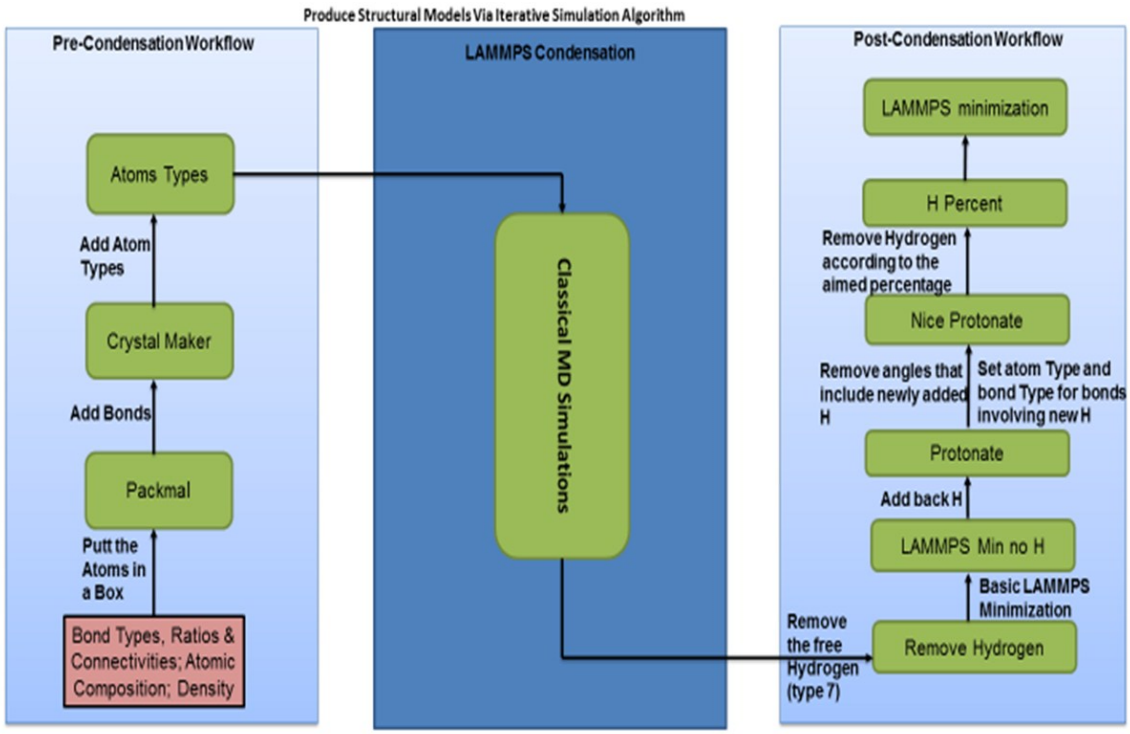

Figure ESI-1: Flow chart depicting the sequence of events that were used to model a-BC:H.