Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Electronic Supplementary Information (ESI) for "Designing Molecular Building Blocks for the Self-assembly of Complex Porous Networks"

T. Ann Maula,[1] Harold W. Hatch,[2] Vincent K. Shen,[2]
Srinivas R. Rangarajan,[1,*] and Jeetain Mittal[1,†]

[1] *Department of Chemical and Biomolecular Engineering, Lehigh University, 111 Research Dr., Bethlehem, Pennsylvania 18015-4791, USA.*

[2] *Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8320, USA.*

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[*] srr516@lehigh.edu

[†] jem309@lehigh.edu

I. SUPPLEMENTARY FIGURES AND TABLES

A. Supplementary figures

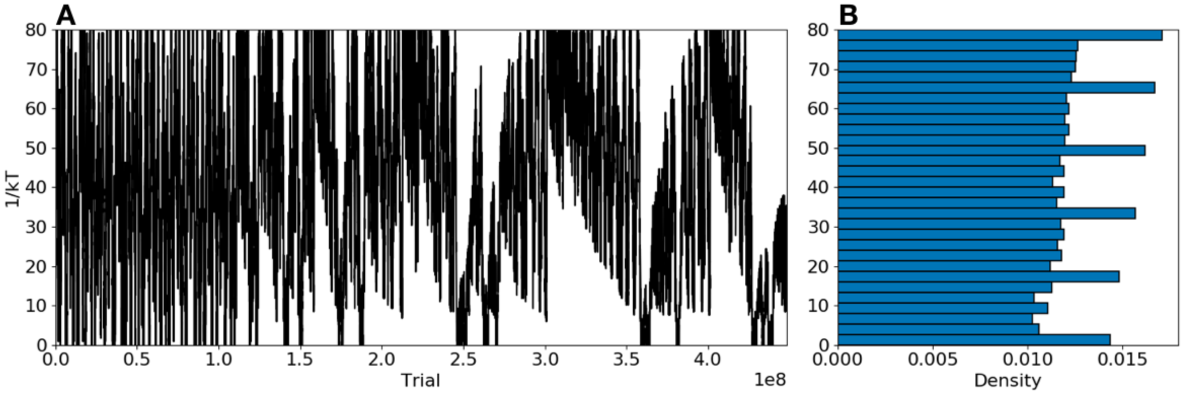

FIG. S1. (A) shows the temperature evolution in a Temperature Expanded Ensemble (TEE) simulation, and (B) shows a histogram of the temperatures sampled.

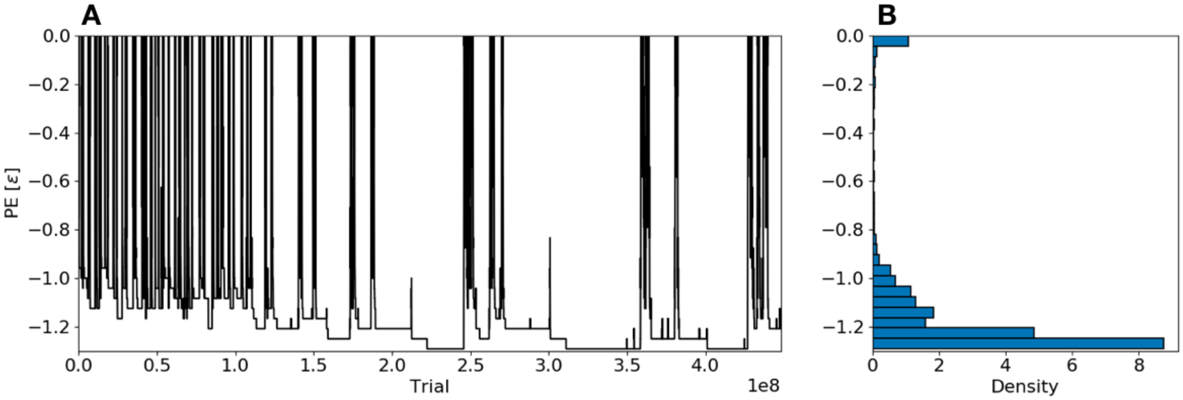

FIG. S2. (A) shows the evolution of potential energy in a Temperature Expanded Ensemble (TEE) simulation, and (B) shows a histogram of the potential energies sampled.

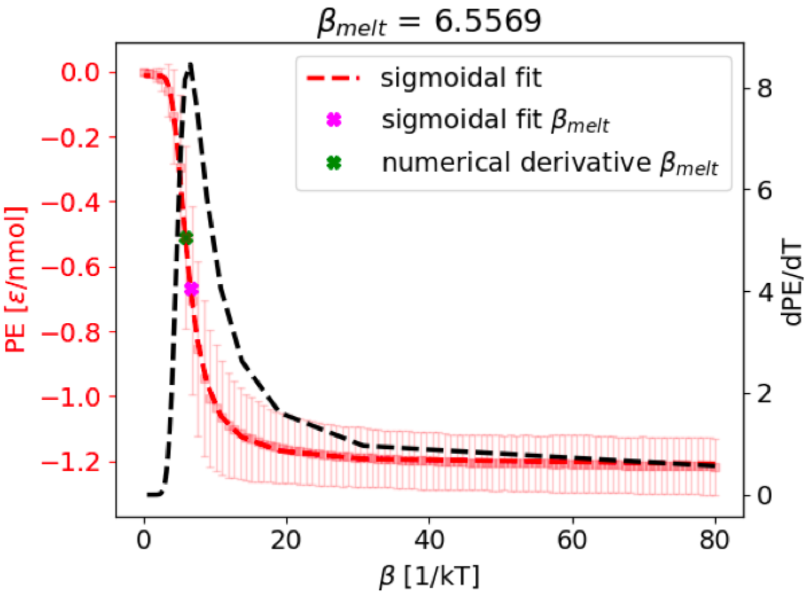

FIG. S3. Temperature Expanded Ensemble (TEE) simulations were used to generate a putative melting curve in order to find an appropriate temperature region (around β_{melt}) at which to conduct NVT simulations of a given model.

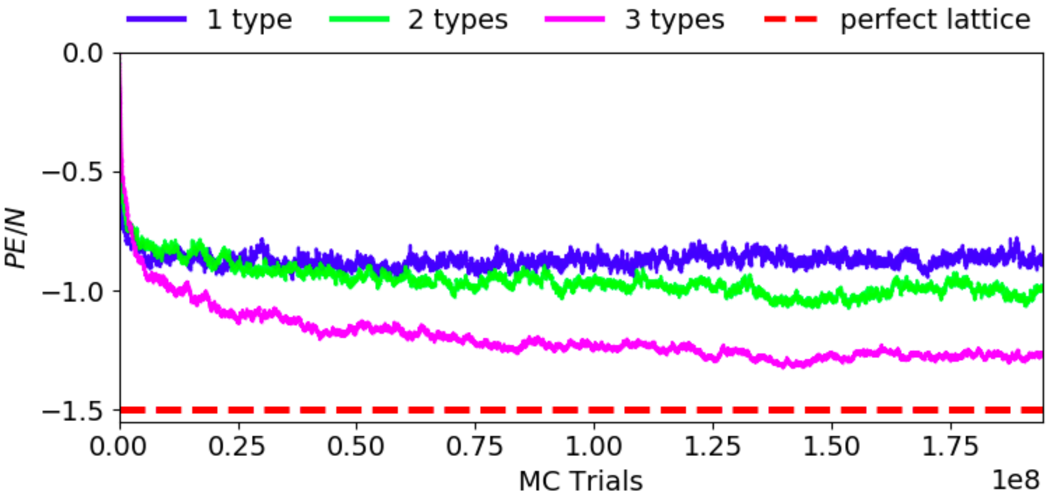

FIG. S4. Time evolution of the potential energy in production NVT simulations of fes building blocks at different interaction schemes.

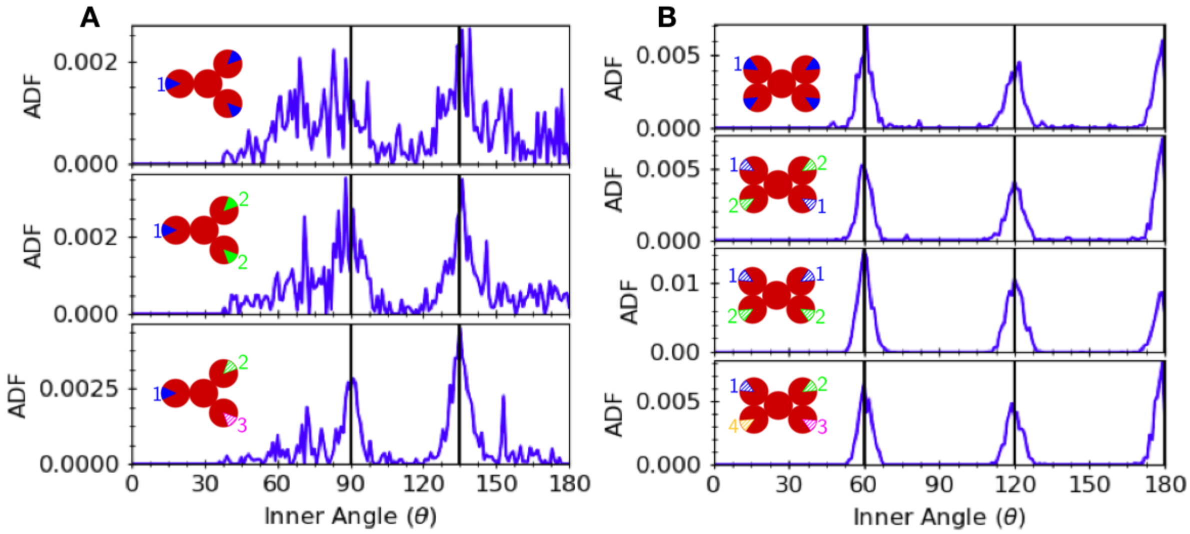

FIG. S5. The angular distribution functions (ADFs) with respect to the central particles of the minimum energy structures of (A) fes building blocks and (B) kgm building blocks. Black lines are location of the peaks for the perfect lattices. Only inner angle ADFs are shown.

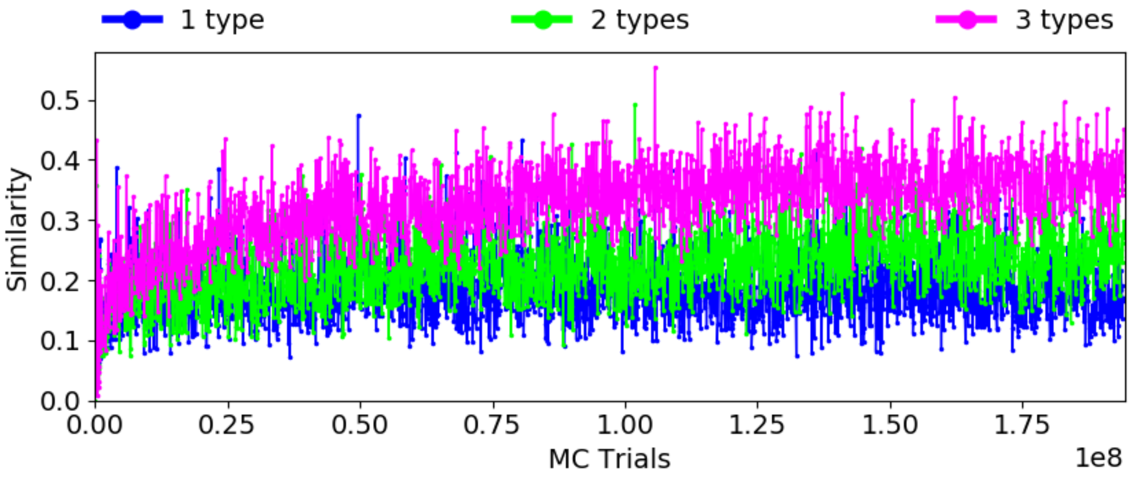

FIG. S6. Time evolution of the similarity between the angular distribution functions (ADFs) of the perfect lattice and the structures formed by fes building blocks with different interaction schemes in simulation. The similarity between ADFs were computed with respect to inner angle ADFs.

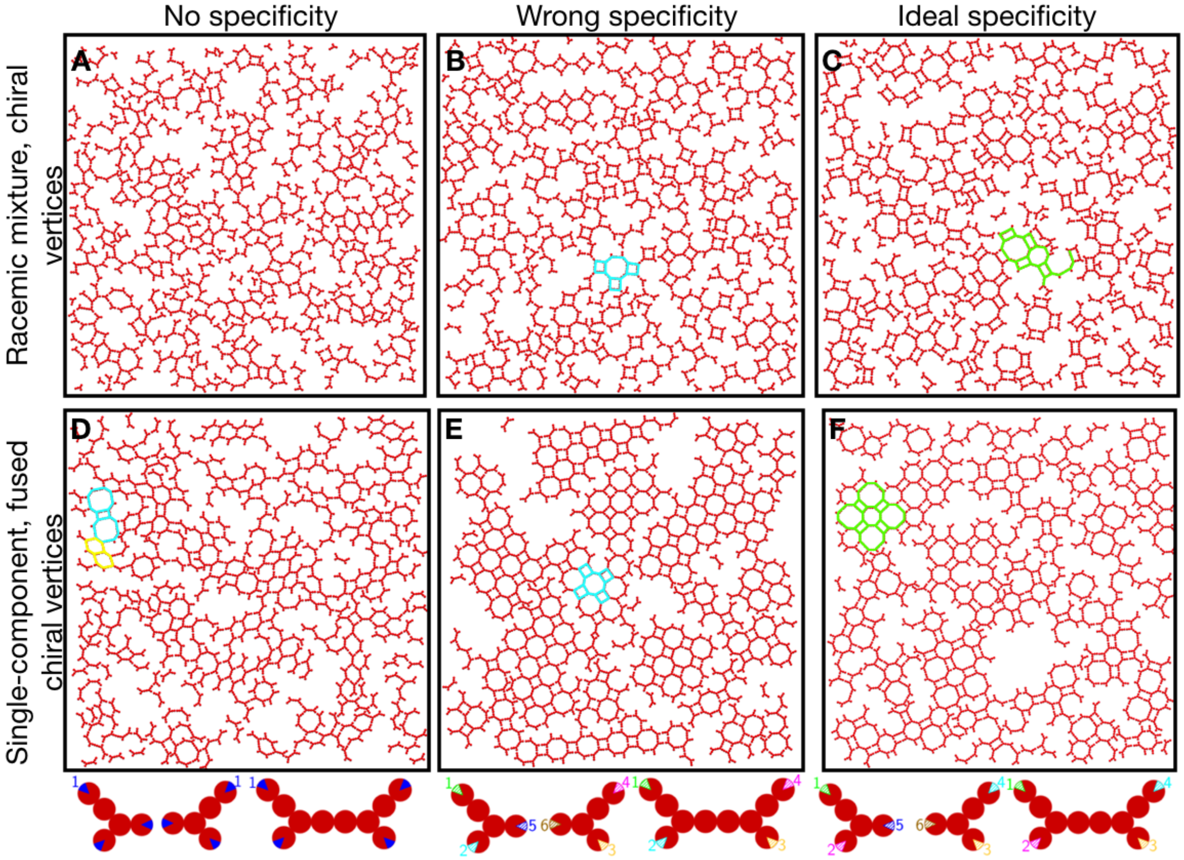

FIG. S7. Effect of chemical specificity and the use of ”secondary vertices” on the assembled structure of a desymmetrized fes building block. Using secondary vertices improves the extent of crystallinity. The tendency of building blocks to assemble into a polymorphous, biporous or triporous structure depends on the intermolecular interaction scheme used. The interaction schemes for (A) and (D) is 1-1; for (B) and (E) they are 1-2, 3-4, 5-6; and for (C) and (F) they are 1-4, 2-3, 5-6.

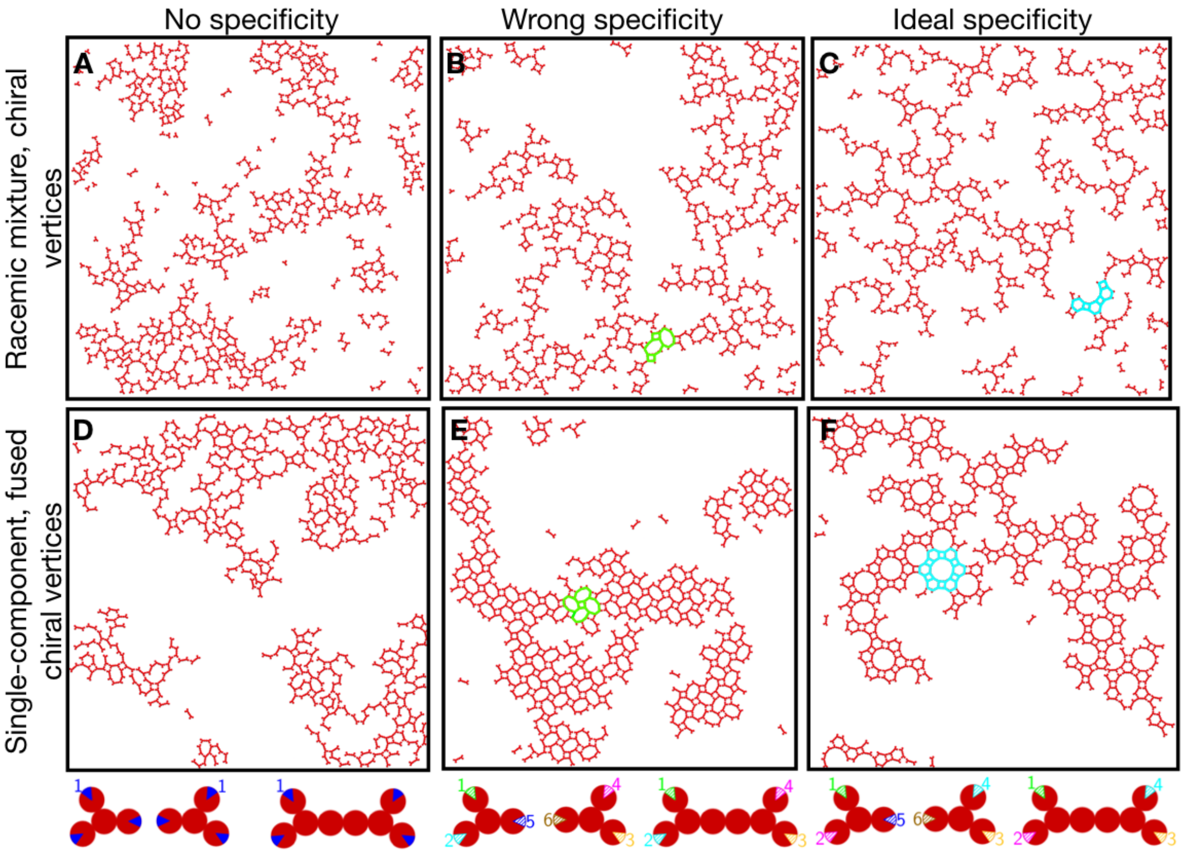

FIG. S8. Effect of chemical specificity and the use of ”secondary vertices” on the assembled structure of a desymmetrized fxt building block. Using secondary vertices improves the extent of crystallinity. The tendency of building blocks to assemble into a polymorphous, biporous or triporous structure depends on the intermolecular interaction scheme used. The interaction schemes (A) and (D) are 1-1; for (B) and (E) they are 1-2, 3-4, 5-6; and for (C) and (F) they are 1-4, 2-3, 5-6.

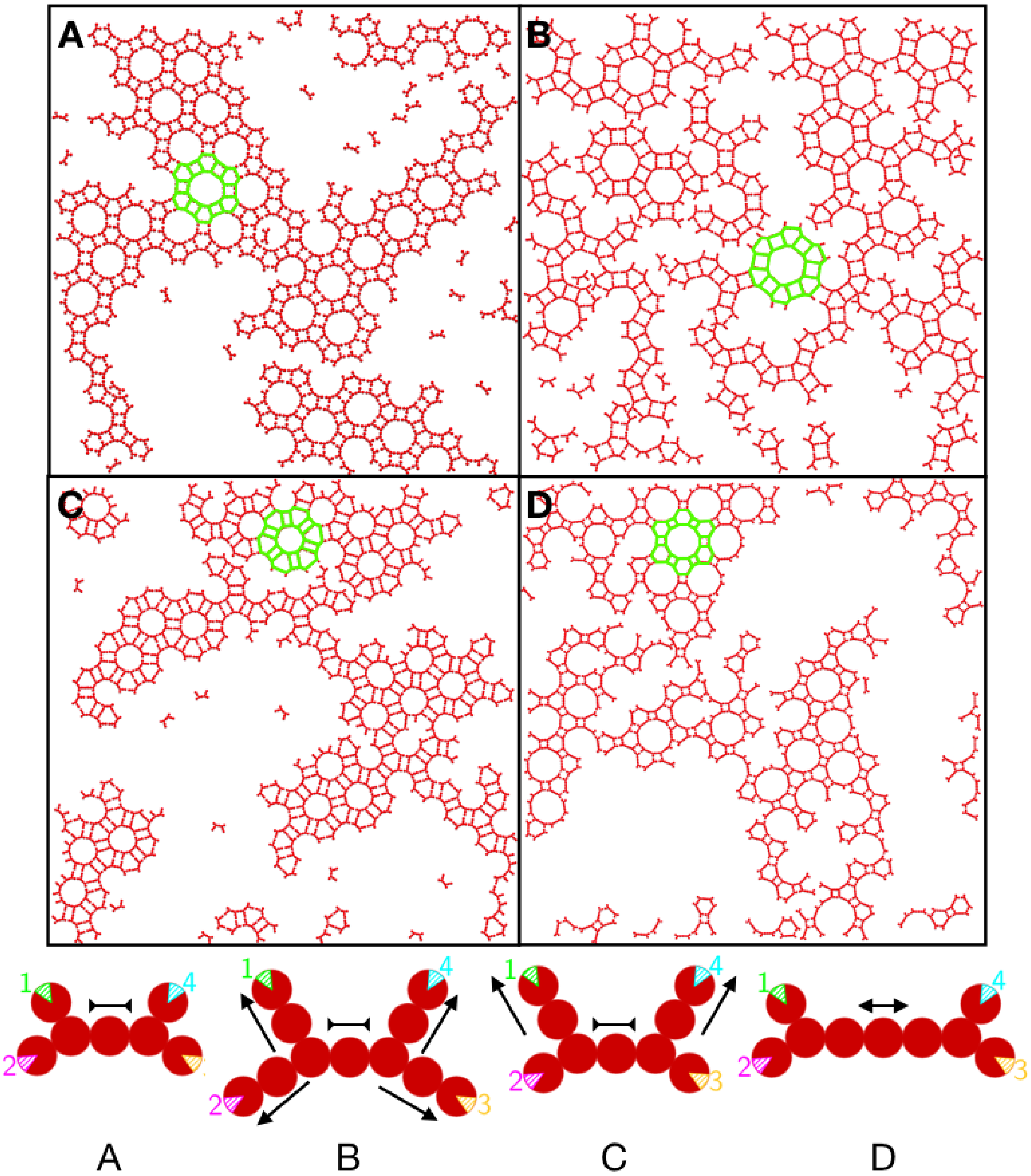

FIG. S9. Controlling the relative pore sizes in a fxt net or 4-6-12 tiling. In (A), we enlarge 8-gons and 6-gons relative to 4-gons; while in (B) and (C), we enlarge 4-gons relative to 6-gons and 8-gons; and in (D), we turn the previously square 4-gons to rectagular 4-gons and we reduce the pore size of the 8-gons with respect to the other polygons. The principle of relative pore size control is easily as applicable to tetratopic secondary vertices as it is for tritopic vertices. The interaction scheme for all molecules is 1-4, 2-3.

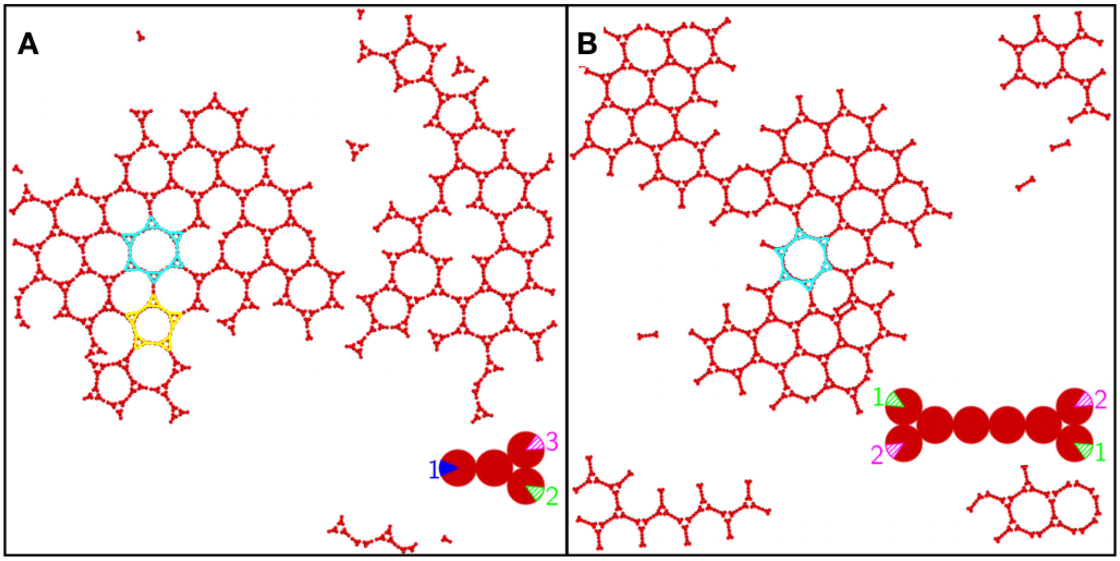

FIG. S10. Tetratopic vs tritopic building blocks for creating a hca net or 3-12-12 tiling. The interaction scheme for (A) is 1-1, 2-3; and for (B) it is 1-2.

B. Supplementary tables

TABLE I. Attractive pair interactions for all simulation snapshots of chemically specific building blocks used in the main body of the paper.

Figure	Attractive Pair Interactions
2B	1-1, 2-2
2C	1-1, 2-3
3B	1-2
3C	1-2
3D	1-3, 2-4
4A	1-1, 2-3
4B	1-1, 2-3
5C	1-1, 2-2
5D	1-1, 2-3
6A	1-4, 2-3, 5-6
6B	1-4, 2-3
7D	1-1, 2-3
7E	1-2
7F	1-2
7G	1-1, 2-3, 4-5
7H	1-1, 2-5, 3-3, 4-4
7I	1-1, 2-3, 4-5
7J	1-2, 3-4
7K	1-2, 3-4