Modelling Analysis of the Structure and Porosity of Covalent Triazine-Based Frameworks

C. Reece, D.J. Willock and Abbie Trewin*

Electronic Supporting Information

1. Structure Files

CIF files containing the node-strut and cluster structure for each CTF system are to be found as ESI. Please note that periodic boundary conditions are redundant and are present only for the CIF format.

2. Computational Detail 1

Models were generated using the *Material Studio Modelling 5.0* package (Accelrys Inc. San Diego, CA, 2009) and the geometry optimised using the *Forcite* module and PCFF forcefield. The geometry of node-strut models consisting of two nodes and the respective linking strut were further optimised using NWChem 6.1 with the 6-311G basis set and B3LYP functional and incorporating the Grimme dispersion correction.[15]

3. Topological analysis

Node-to-node: Node-to-node measured from a centroid positioned at the centre of each nodal triazine/phenyl ring or N.

In-plane angle: The in-plane angle is defined as the average of the four angles available between the terminating linker, the node, through the linker to the adjacent node.

Out-of-plane angle: The out of plane angle is defined as the angle made between a nodal centroid to linking node centroid to a centroid placed between the two remaining linkers.

Nodal dimensionality: The nodal dimensionality is defined as a measure of how close the structure is to being 2-dimensional (all connection points of the node lie within a two dimensional plane) or 3-dimensional (the connection points do not lie within a two dimensional plane but, at its extreme, extend to 3-dimensional space). The dimensionality is the average of the two torsional angles between two linking nodes. The ideal 2-dimensionality is 0° and 3-dimensionality is 90°.

3. Computational detail 2

The clusters were built sequentially by adding the DFT-optimised node-strut model units to a DTF-optimised node-strut core pair, saturating all attachment points at each layer addition. A total of three layers were added to form the cluster. Each node-strut model pair is added as part of a motion group, fixing its internal structure but allowing bonds between motion groups to be optimised. After each layer addition the geometry of the cluster is optimised using the *Forcite* module and PCFF force field.[1] Finally, the motion groups are removed and the structure is fully optimised.

4. Cluster Dimension Analysis

Polymer	Cluster diameter (Å)				Cluster height (Å)			
	1	2	3	Average	1	2	3	Average
P1	79	85	94	86	16	36	10	21
P2	117	98	118	111	84	79	69	77
P3	101	90	87	93	96	91	85	91
P4	83	82	75	80	68	55	63	62
P5	65	62	58	62	61	54	62	59

Table.ESI.1. The diameter and height of clusters generated for a series of CTF polymers. Three clusters for each polymer were constructed and the cluster diameter and height for each is presented. Figure.ESI.1 shows an example how these measurements are obtained for P1.

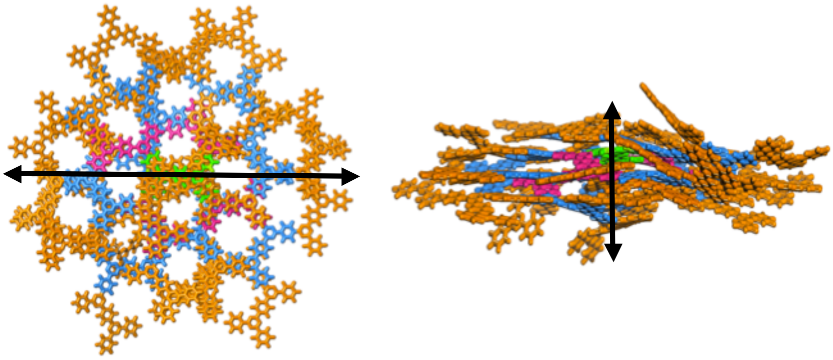
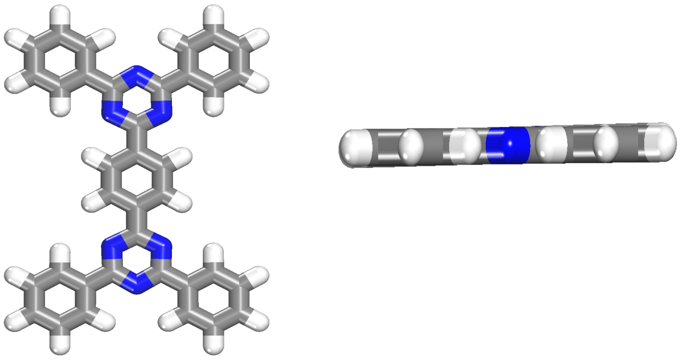


Figure.ESI.1. The cluster diameter (left) and cluster height (right). The clusters were generated by step-wise addition of building units to a central building unit based on the respective DFT optimised node-strut pairs. The cluster diameter was measured along the molecular axis of the starting building unit (green) from furthest atom-to-atom. The cluster height was measured orthogonally to the molecular axis of the starting building unit from furthest atom-to-atom. Both measurements were made to transect the centre of the starting building unit as closely as possible.

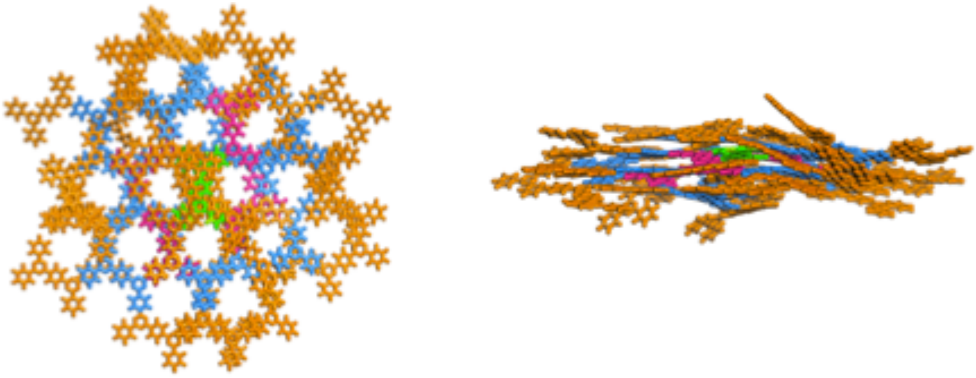
5. Cluster Structure Figures

P1

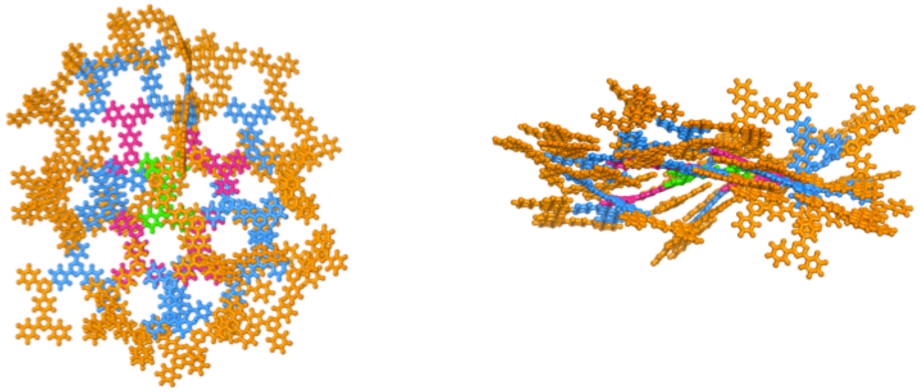
Node-strut:



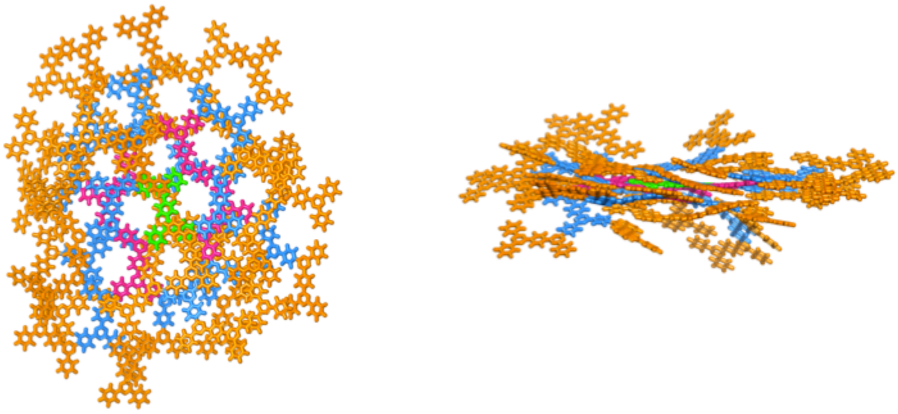
Cluster 1:



Cluster 2:

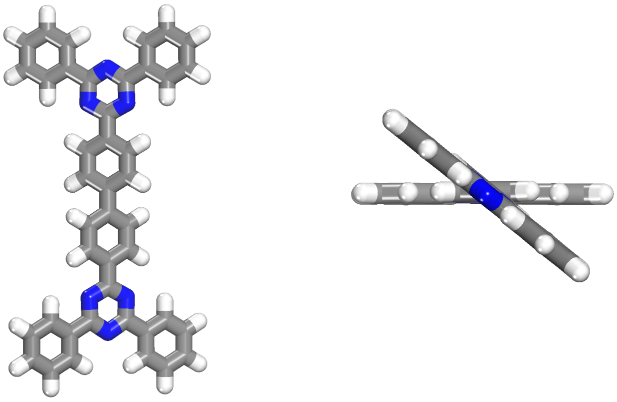


Cluster 3:

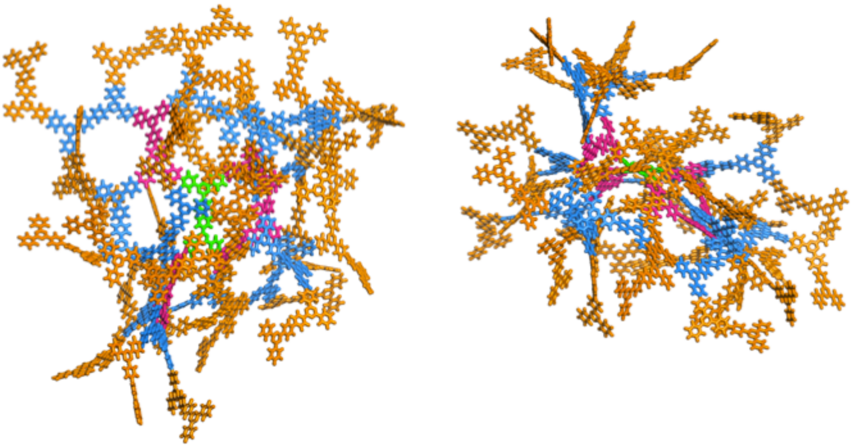


P2

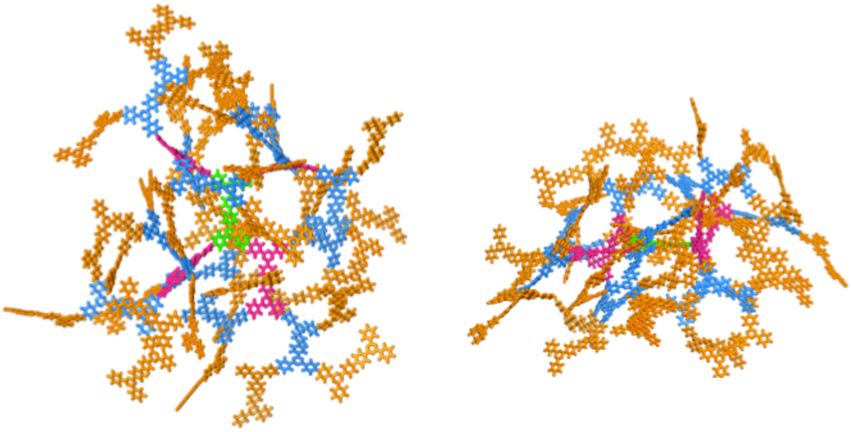
Node-strut:



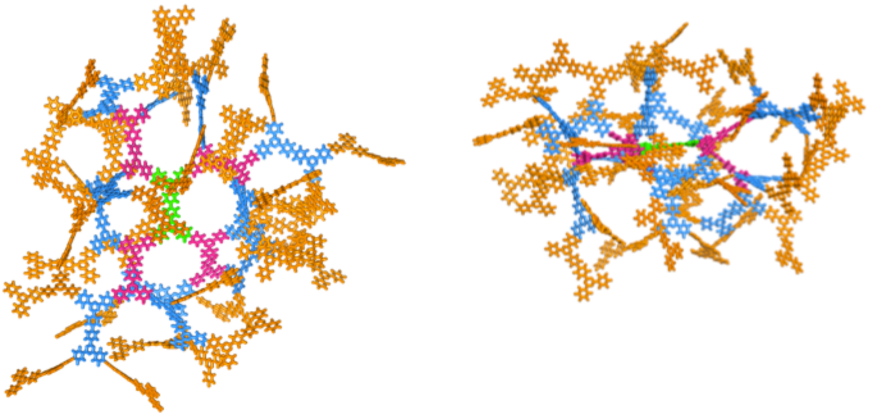
Cluster 1:



Cluster 2:

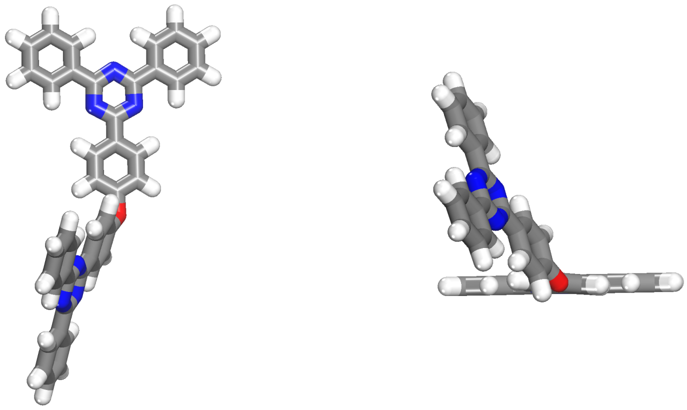


Cluster 3:

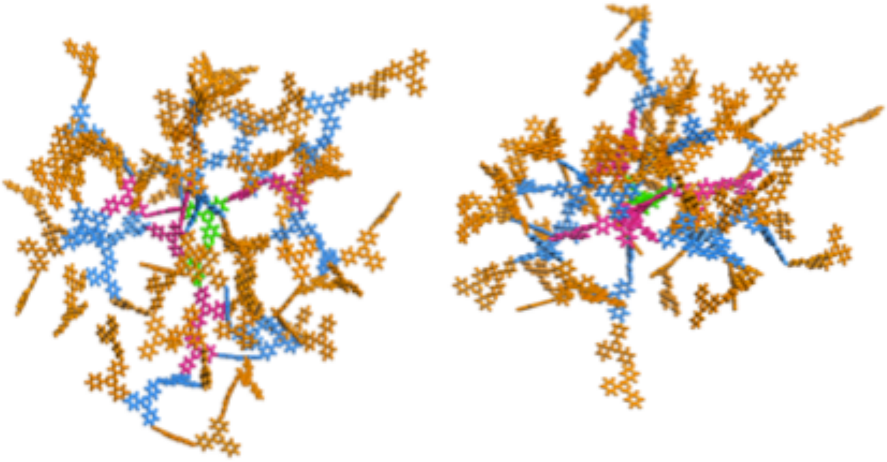


P3

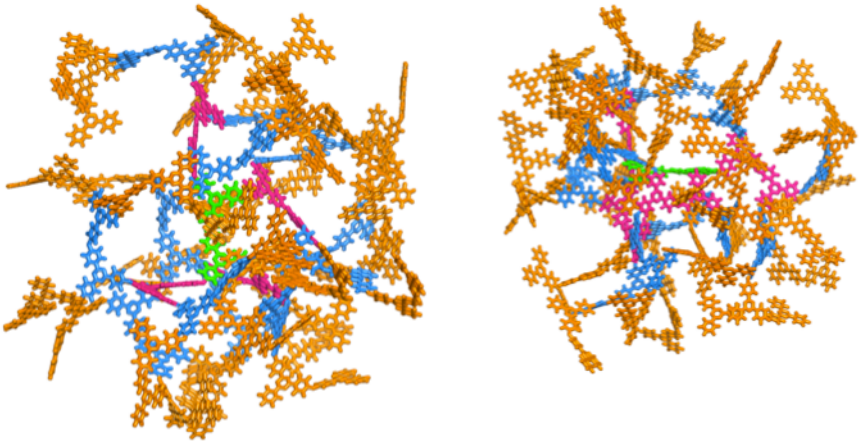
Node-strut:



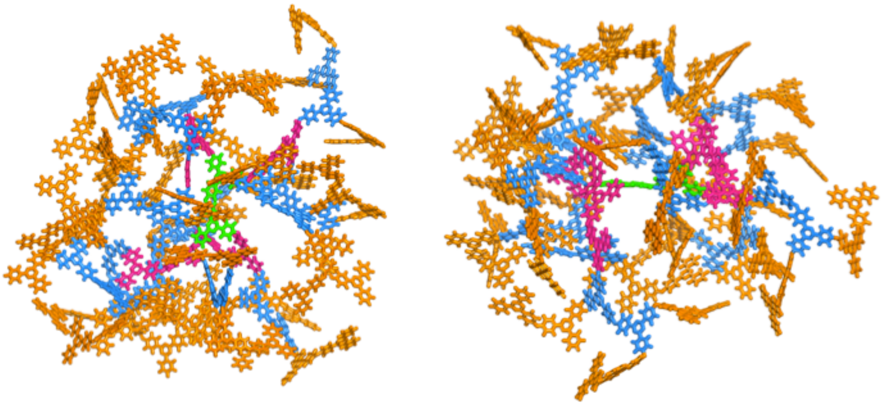
Cluster 1:



Cluster 2:

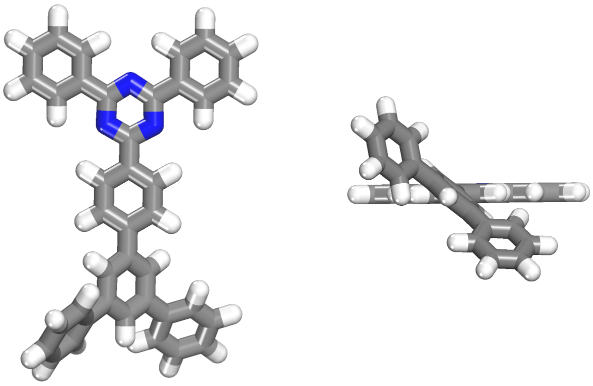


Cluster 3:

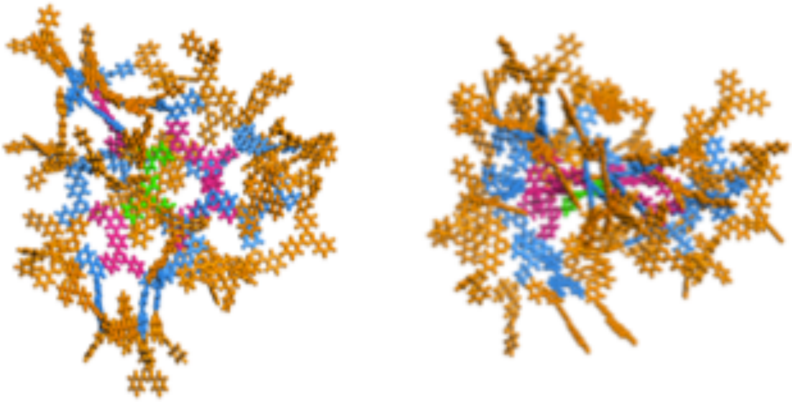


P4

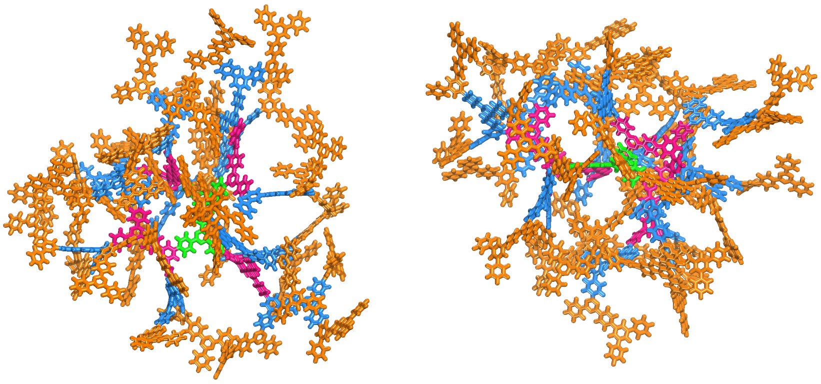
Node-strut:



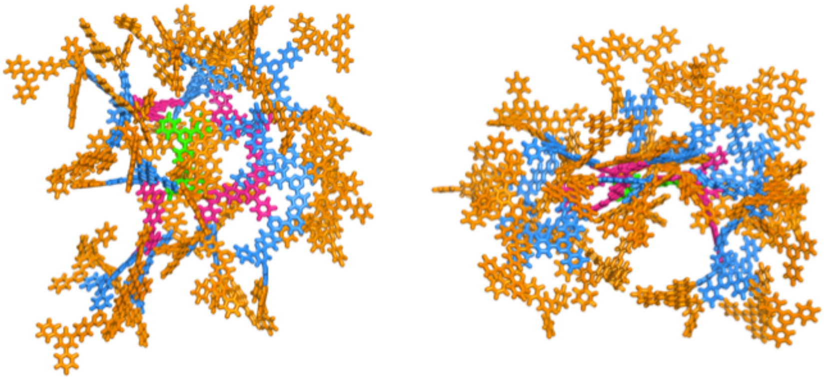
Cluster 1:



Cluster 2:

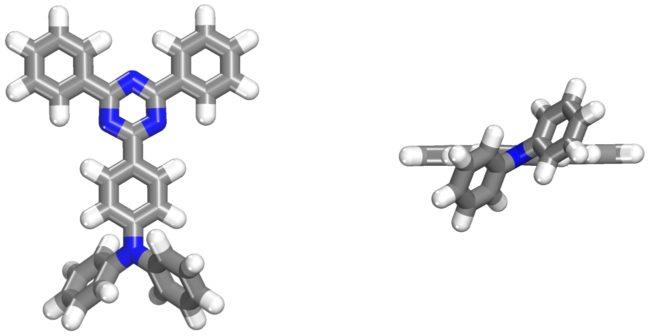


Cluster 3:

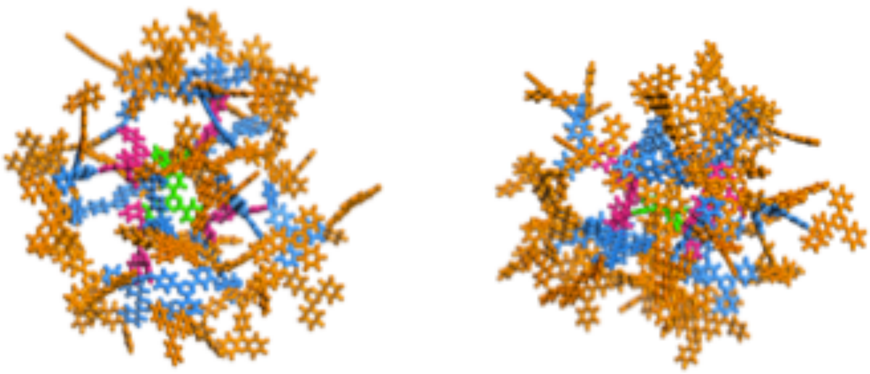


P5

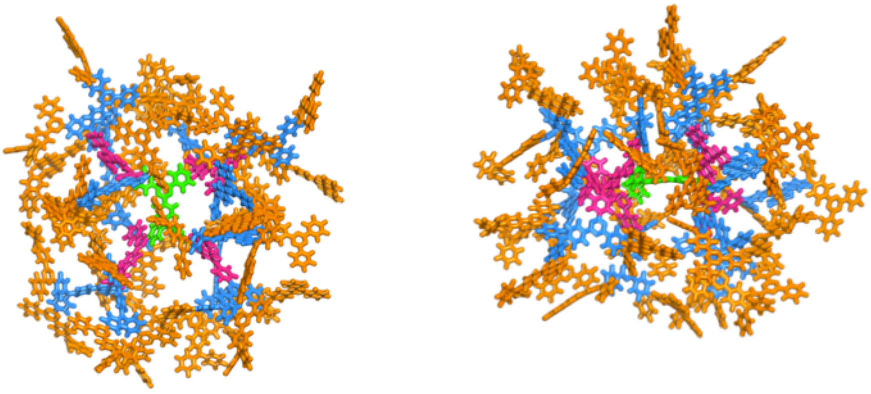
Node-Strut:



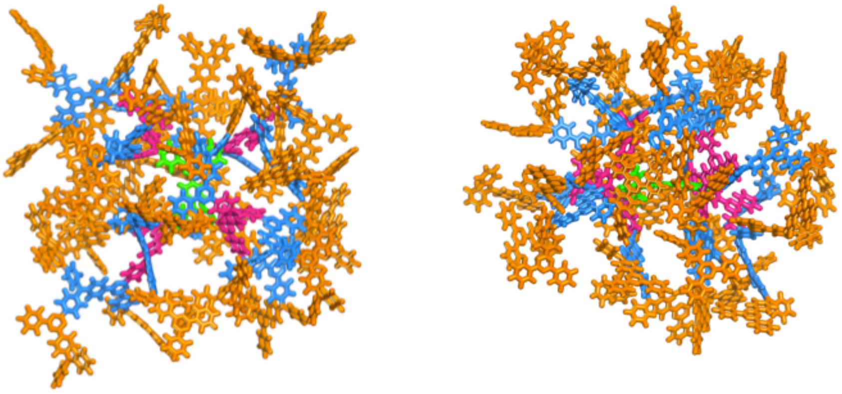
Cluster 1:



Cluster 2:



Cluster 3:



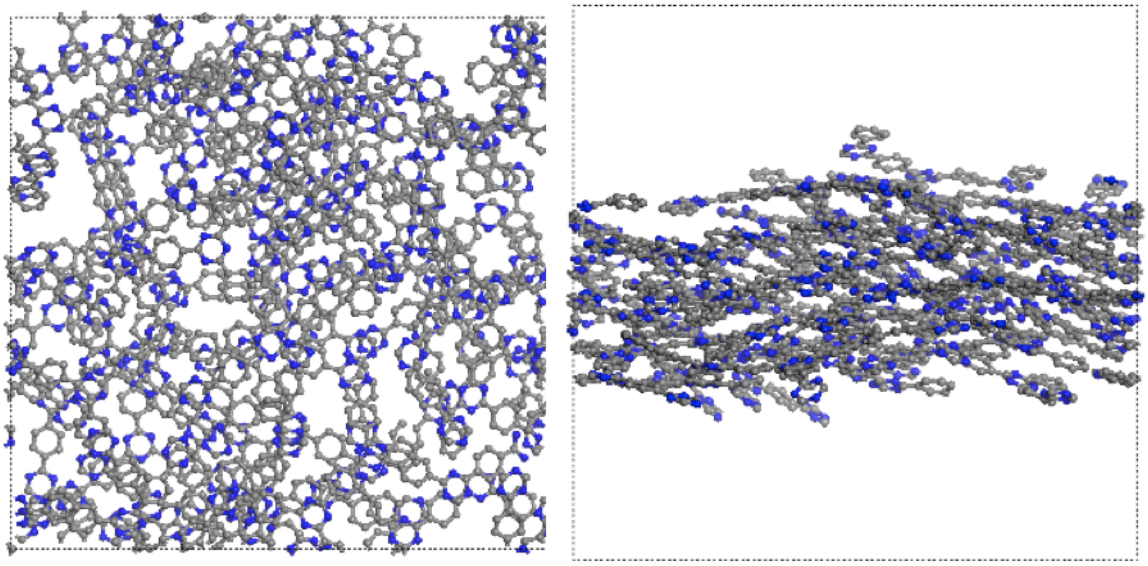
6. Zebedde Construction process: Computational Details

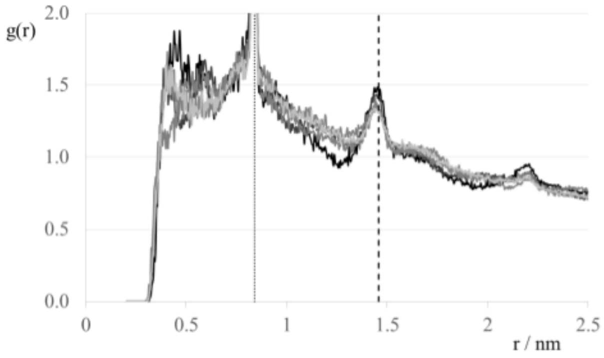
For each system three triazine molecules were placed in a cubic periodic repeat unit 50 Å on a side as seeds for polymer growth. The H atoms of the triazine were denoted "HA" and H atoms at the polymer forming positions on each of the PX (X=1,5) monomers were labeled "HB". For each building run one of the PX and the triazine molecule were included in a fragment library and additions made to the growing polymer by picking these at random with equal probability. Additions to the current structure followed the rule that new bonds could only form by elimination of one HA and one HB each chosen at random from either the current structure or the seed molecule. During the growth process additional Monte Carlo (MC) moves involving random bond twists and whole molecule translations/rotations were included. After an addition to the growing structure the probability of testing was set to 0.5% so that a significant number of MC moves were attempted after each new build action. The total build sequence consisted of 5×10^6 build/MC move attempts at a simulation temperature of 350 K. The system energy was calculated using the PCFF forcefield.

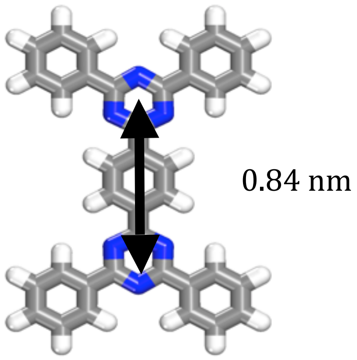
The growth procedure produced large cluster models of each CTF material consisting of 100-150 monomer units connected to form three inter-penetrating networks. These structures were then used as inputs to microcanonical (NVE) Molecular dynamics (MD) simulations at a temperature of 300 K using the DLPOLY code.[2] After 50 ps equilibration the MD runs were used to produce 1 ns simulations with the trajectory sampled every 2.5 ps. The degree of order in each system was then analysed use the radial distribution function (g(r)) based on the triazine ring centroids.

6. Zebedde structure images

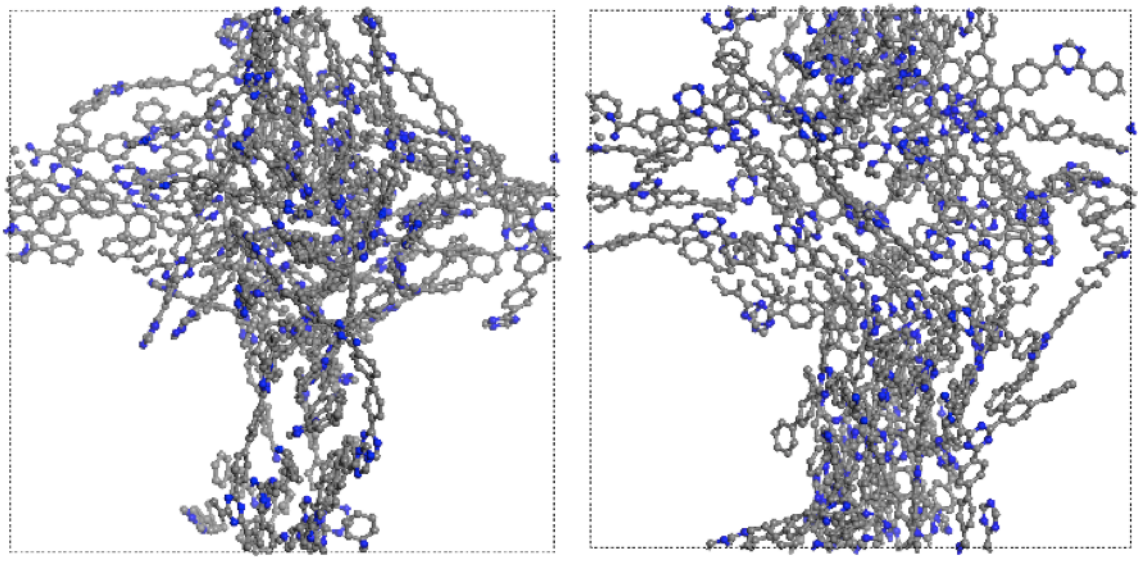
P1

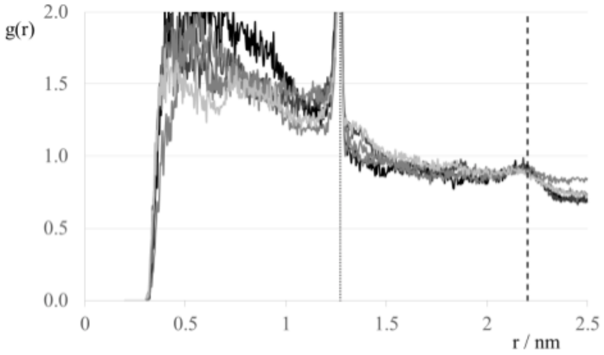


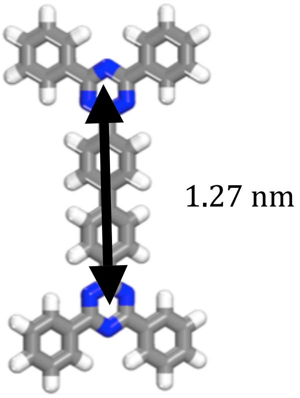




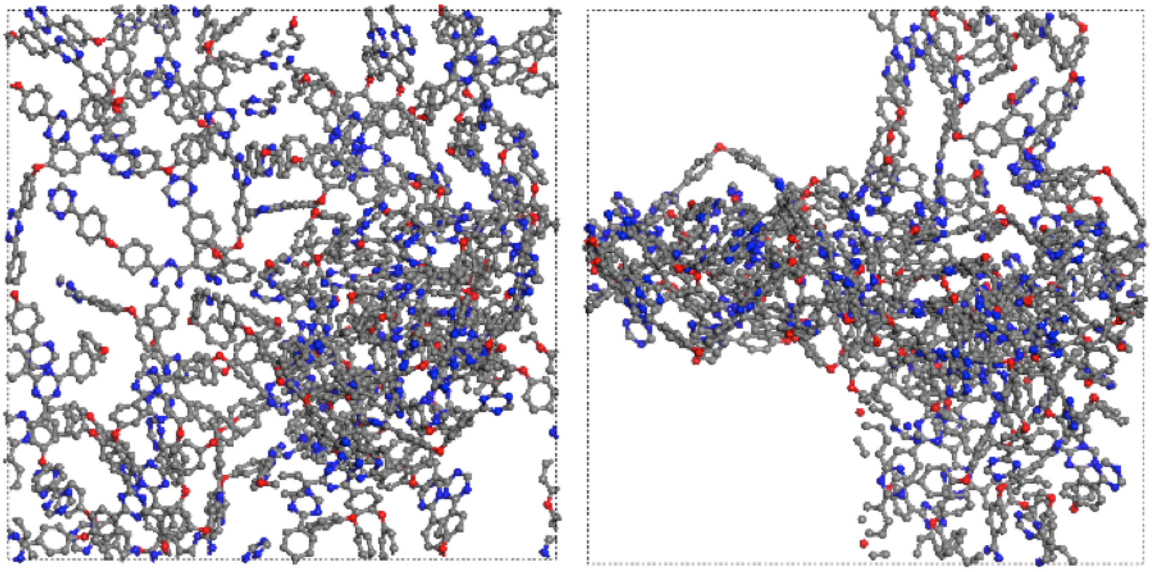
P2

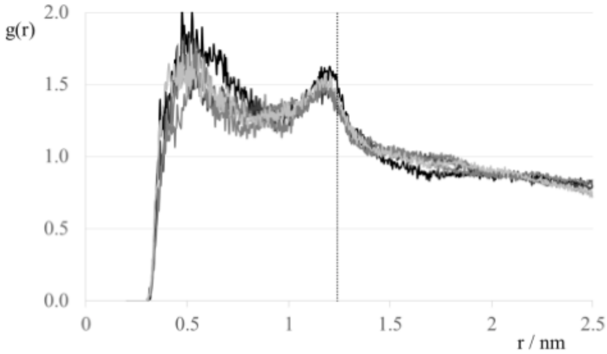


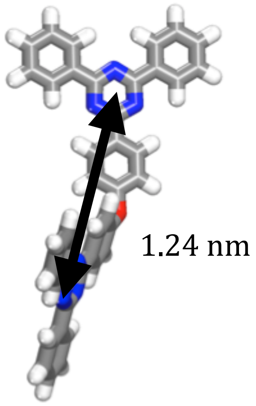




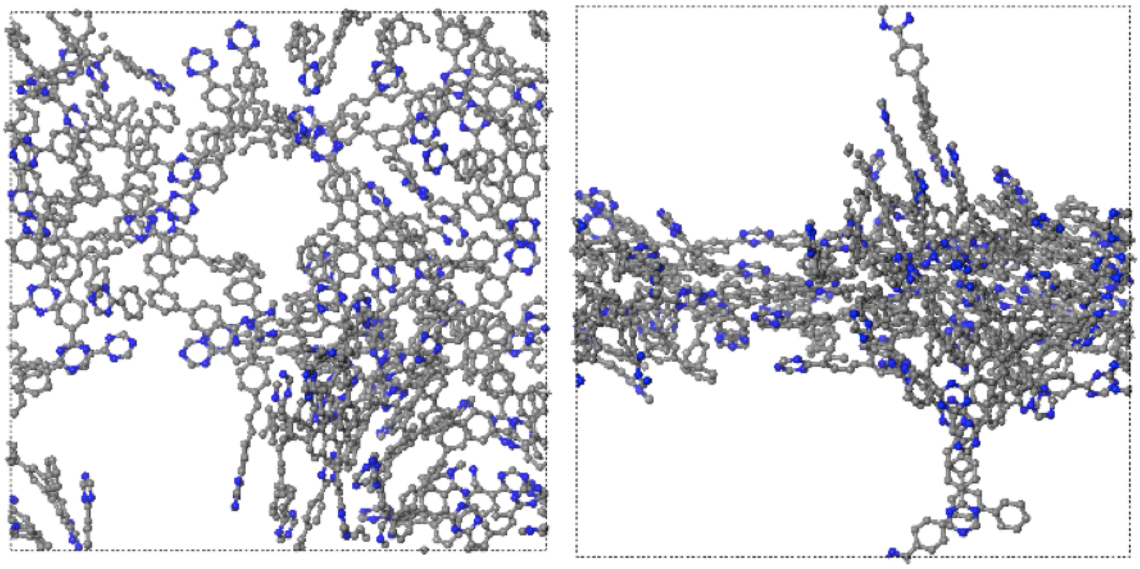
P3

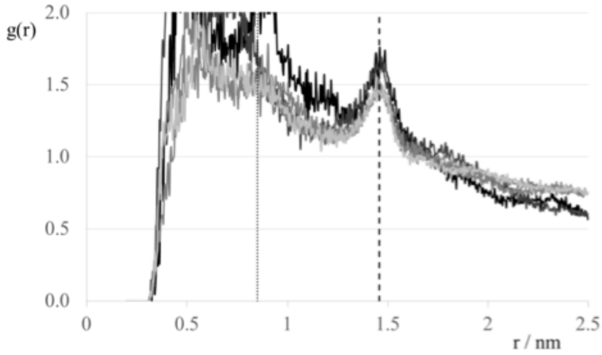


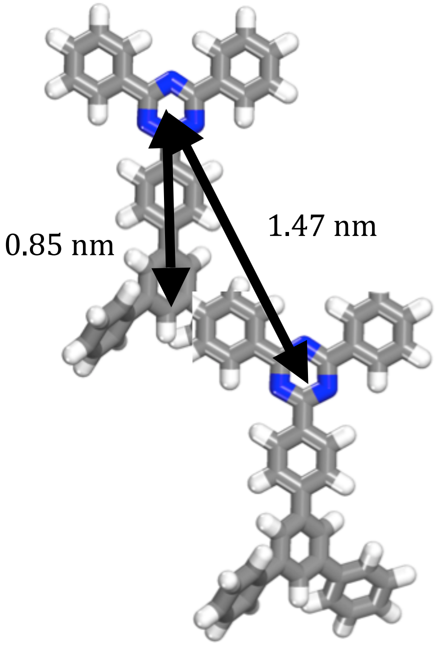




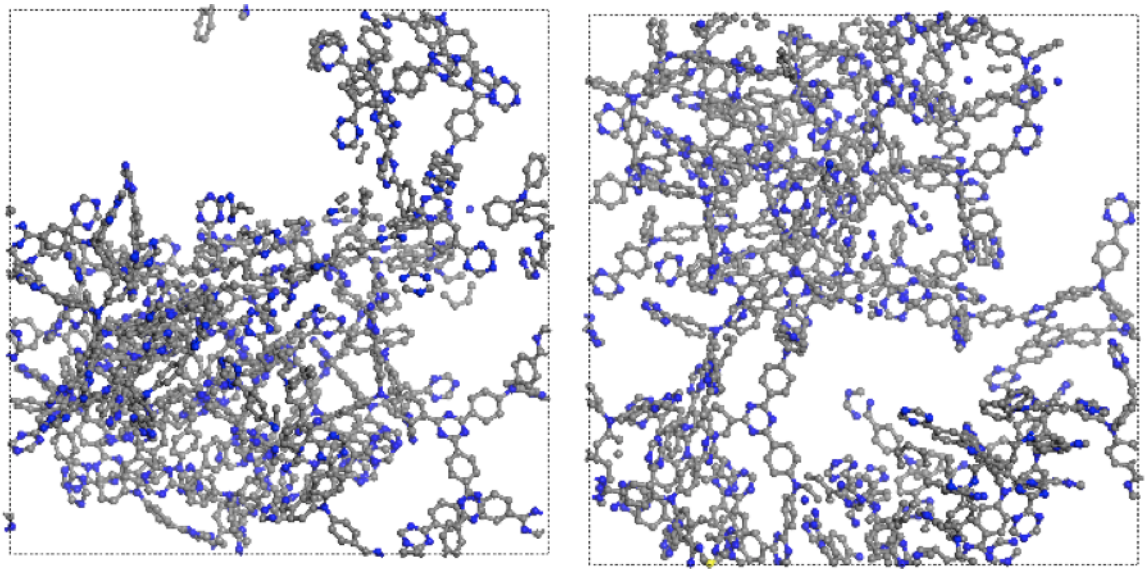
P4

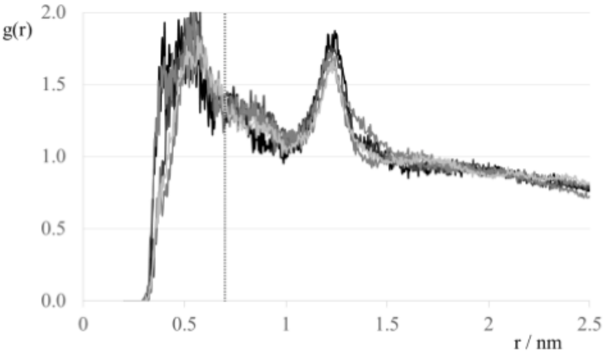


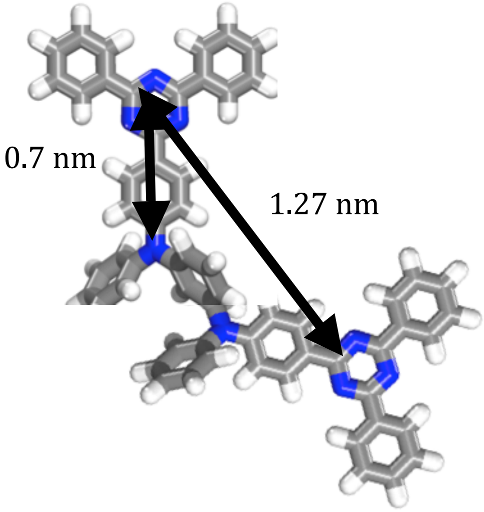


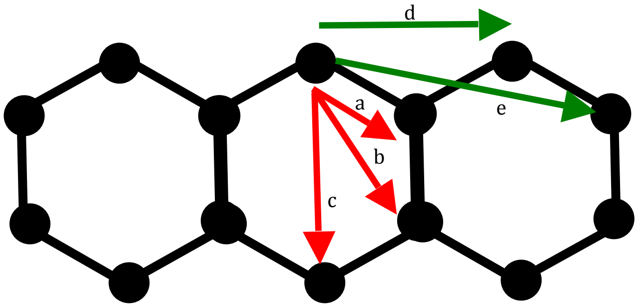


P5









a. 1st neighbour within a hexagon = 0.84

b. 2nd neighbour within a hexagon = 1.45 nm

c. 3rd neighbour within a hexagon = 1.68 nm

d. 2nd neighbour in adjacent hexagon = 1.45 nm

e. 3rd neighbour in adjacent hexagon = 2.20 nm

ESI. Figure 2. Neighbour distances correlating to peaks in g(r) for P1.

1 H. Sun, *Macromolecules*, 1995, **28**, 701.
2 I. Todorov, W. Smith, K. Trachenko and M. T. Dove, *J. Mater. Chem.*, 2006, **16**, 1611.