Skeletal bicontinuous mesophases of bundled axial rod-like molecules

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There are 3 types of molecules forming bicontinuous mesophases (BM) in thermotropic liquid crystals: (a) end-chain-bearing rod-like and (b) fan-shaped molecules that lie in the network segments perpendicular to the segment axis, and (c) side-chain-bearing rod-like molecules which assemble in bundles that lie along segment axis. The fans (a) form exclusively double gyroid (DG), while rods (b) form DG and two other BMs not found in either lyotropics or block polymers: a triple-network cubic *I*23

and a double network tetragonal "Smectic-Q", both chiral. Because of packing problems, these compounds cannot form tetrahedral or octahedral junctions. However the axial bundle forming compounds (c) suffer no such restriction and have so far been found to form single diamond (SD), single primitive (SP), double network DG and DD, as well as alternating gyroid. Figure 1 explains how the size of the side-chains determines the type of phase. The schematic molecules in the figure are to scale with real molecules published in the numbered references: 28 [1], 30 [2], 31 [3], 32 [4]. SG and DP have not been found so far, as the required side-chains are, respectively, too long and too short. However we just found a way around the latter problem and obtained the first thermotropic DP, or "Plumber's nightmare" phase [5]. This will be described in the presentation.



volume in the unit cell that is closest to a given network segment and at a distance r from it. Inset is a view down the bundle. The time-averaged shape of the side-chain should closely match the space bounded by dV/dr and -dv/dr for a given phase.

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