Computer simulation of columnar phases in T and X shaped bolaamphiphiles

Martin A. Bates and Martin Walker

Department of Chemistry, University of York, YO10 4HU, UK.

Dissipative particle dynamics simulations are used to investigate the structure of the columnar phases in T and X shaped bolaamphiphiles. These amphiphilic molecules consist of a rod-like aromatic core, with a polar group at each end. A single lateral chain is present in the T shaped molecules and two lateral chains are present for X shaped molecules. The phase behaviour is examined as a function of the length of the lateral chain(s). The simulations indicate that both types of molecules exhibit columnar phases, in which the walls of the columns are formed by the aromatic core, the polar groups are located at the edges and the lateral chains fill the interiors of the columns. Square columnar phases are observed for short chains and hexagonal columnar phases are observed as the length of the chain is increased, due to the larger volume necessary for the chains. Lamellar phases are observed on increasing the length further. For the T shaped molecules, the columns are always double walled, the walls being twice as thick as a rod. In contrast, for X shaped molecules, the columnar phases are single walled, in agreement with X-ray diffraction studies. For the X shaped bolaamphiphiles, we also examine a model that corresponds to fluorinating one of the chains, leading to a larger repulsion between the two chains. For the square columnar phase, local demixing does not disrupt the structure of the columns. However, the hexagonal columnar phase cannot be 'coloured' with two different types of chain and so is frustrated. We will discuss the outcomes of this frustration, and how these outcomes relate to the molecular structure. We also discuss models in which the two arms are of different length. This can, in some cases, lead to non-frustrated structures of different symmetry to those observed for the more simple models.