Self-Assembled Chiral Superstructures Composed of Rigid Achiral Molecules and Molecular Scale Chiral Induction by Dopants

Phys. Rev. Lett. **101** (2008) 157801

Authors: Fangyong Yan, Christopher Adam Hixson, and David J. Earl

Recommended and a commentary by Randall D. Kamien, University of Pennsylvania

The statesman Harry S Truman lamented, "Give me a one-handed economist! All my economists say, 'On the one hand on the other...'" Since Pasteur's time and the birth of stereochemistry [1], stereochemists likely have had similar wishes about chiral chemistry where molecules only form with one handedness. In Pasteur's seminal work, he identified paratartaric acid as the conglomerate of the two enantiomers of tartaric acid. Conglomerates are self-segregated crystallites of a single-handedness that arise in solutions of a racemate, that is, mixtures of both the left- and right-handed stereoisomers of molecules of the same composition. However, conglomerates can also occur in completely achiral systems: quartz, for instance, can adopt two equivalent, mirror-image crystal habits even though the constituent silica is achiral in solution. In the past ten years, with the flood of synthesis, experiment, and theory devoted to highly polar, smectic-forming, bent-core (banana) molecules, liquid conglomerates have been discovered [2]. Sometimes these phases also form "macroscopic racemates" in which the chiral separation is layer by layer and not in large domains.

Why do achiral molecules form chiral structures? Packing is one answer, presumably the answer for quartz. But what about in these softer liquid crystalline systems? We can get a hint from the existence of the rare and beautiful liquid crystalline blue phases [3,4]. These phases replace the usual chiral nematic, or cholesteric phases, with complex, three-dimensional orientational order. The key to their formation is their geometry; these phases are not only chiral, but the structure of the director field is intrinsically curved in the form of "double-twist tubes". Indeed, they are best understood as projections from positively curved, three-dimensional space into our relatively boring flat, Euclidean space [4]. Their existence begs the question: can chiral phases form just because of geometry? Is that the key to the liquid crystalline conglomerates and macroscopic racemates?

The authors simulated simple, rigid, bent molecules and, in addition to the standard phases, found columnar phases built out of spontaneously assembled chiral columns, recapitulating the prediction of these phases by Horsch, Zhang, and Glotzer [5]. Unlike that numerical experiment, the experiment by Yan, *et al.*, did not involve molecules with internal degrees of freedom; rods with tethers can themselves adopt chiral conformations, while rigid bent bananas remain achiral individually. Not surprisingly, they find equal numbers of left- and right-handed ribbons – a macroscopic racemate. More interestingly, Yan, *et al.* found a new phase made of chiral micelles, small twisted bundles of simple banana molecules. These bundles have precisely the core geometry necessary to generate blue phases (double-twist tubes). When a small amount of chiral dopant is added (no more than 4%), the authors find that the micelles all adopt the same handedness. This and subsequent studies should shed light on the organization and ordering mechanisms in bent-core mesogens.

[1] L. Pasteur, Ann. Chim. Phys., Series 3, **24** (1848) 442.

[2] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Körblova, D.M. Walba, Science **278** (1997) 1924; D.M. Walba, E. Körblova, R. Shao, J.E. Maclennan, D.R. Link, M.A. Glaser, and N.A. Clark, Science **288** (2000) 2181.

[3] D.C. Wright and N.D. Mermin, Rev. Mod. Phys. **61** (1989) 385.

[4] J.P. Sethna, D.C. Wright, and N.D. Mermin, Phys. Rev. Lett. **51** (1983) 467.

[5] M.A. Horsch, Z. Zhang, and S.C. Glotzer, J. Chem. Phys. **125** (2006) 184903.