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Rational Design of POSS-Based Janus Particles into Supramolecular Structures: Symmetry Breaking and Shape Commensuration ZHAO WANG, YIWEN LI, WEN-BIN ZHANG, STEPHEN Z.D. CHENG, Department of Polymer Science, The University of Akron — The synthesis, self-assembly and applications of structured nanoparticles have significantly intensified over the past decade. In the recent year, a series of precisely-defined polyhedral oligomeric silsesquioxane (POSS)-based molecular dumbbell-like Janus particles has been prepared. It was found that those non-spherical POSS Janus nanoparticles processing equally sized blocks could self-organize into a bi-layered structure with a head-to-head, tail-to-tail type of packing in its bulk state. The driving force of this hierarchical structure formation was attributed to the symmetry breakings of both geometrical sense (molecular shape) and chemical sense (selective amphiphilic interactions) of dumbbell-like Janus particles. Based on this modal system, we further developed a family of POSS-based structured nanoparticles for supramolecular structure formation in the solid state. It was found that the snowman-like Janus particle with two POSS cages in different sizes (a Janus particle with long alkyl chains on one POSS and carboxylic groups on the other) could self-assemble into frustrated lamellar structure (1.5 layered structure). Meanwhile, the supramolecular structure of corresponding mickeymouse-like Janus particle (long alkyl chains on one POSS and carboxylic groups on the other two POSS cages) could recover into normal lamellar structure (bi-layered structure). The self-assembly behaviors of those shape-persistent nanoparticles are absolutely different from those of di-block copolymers.

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