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**Combining Small Molecule with Block Copolymer: a Facile Approach to Direct Hierarchical Assembly of Nanoparticles**

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Precise control over the spatial organization of nanoscopic building blocks over multiple length scales is a bottleneck in the "bottom-up" approach to generate technologically important materials. We demonstrate a new paradigm to control the hierarchical assembly of nanoparticles through the synergistic co-assembly of block copolymers (BCP), small molecules and readily available nanoparticles. Organizations of nanoparticles into one, two and three-dimensional arrays with controlled inter-particle separation and ordering were achieved without any chemical modification of either the nanoparticles or BCPs. The ordering and distribution of small molecules between different BCP blocks are temperature dependent, leading to responsive materials where the spatial distribution of the nanoparticles can be varied, changing the local environment and the areal density of the nanoparticles. The approach described is versatile; compatible with existing fabrication processes and enables a nondisruptive approach for the generation of functional devices.