The programmed assembly of nanoscale building blocks offers exciting new avenues to creating electronic devices and materials in which structure and functions can be chemically designed and tuned. In this context, the synthesis of inorganic molecular clusters with atomically-defined structures, compositions and surface chemistry provides a rich family of functional building elements. This presentation will describe our efforts to assemble such “designer atoms” into a variety of hierarchical structures and devices, and study the resulting collective properties. In one design, single clusters are wired into electrical junctions that can be operated as molecular-scale transistors. The single cluster devices exhibit room-temperature current blockade below a threshold voltage, and they can be “turned on” by applying an electrochemical potential across the junction, enabling the temporary occupation of the cluster core states by sequential transiting carriers. A second area of exploration is in creating solid state materials in which preformed clusters emulate the role of atoms in traditional “atomic” solids. These materials offer a unique opportunity to combine programmable building blocks and atomic precision. As such, they bridge traditional crystalline semiconductors, molecular solids, and nanocrystal arrays by synergizing some of their most attractive features. Recent synthetic advances to develop this concept into a “modular” platform for materials design will be presented. It will be shown that novel, tunable, collective properties (magnetic, optical, electrical and thermal transport) emerge from specific interactions between the building blocks within these assemblies.