We describe a solid-state material formed from binary assembly of atomically precise molecular clusters. \([\text{Co}_6\text{Se}_8(\text{PET}_3)_6][\text{C}_6\text{O}_2]\) and \([\text{Cr}_6\text{Te}_8(\text{PET}_3)_6][\text{C}_6\text{O}_2]\) assembled into a superatomic relative of the CdI\textsubscript{2} structure type. These solid-state materials showed activated electronic transport with activation energies of 100 to 150 millielectron volts. The more reducing cluster Ni\textsubscript{10}Te\textsubscript{6}(PET\textsubscript{3})\textsubscript{8} transferred more charge to the fullerene and formed a rock-salt related structure. In this material, the constituent clusters are able to interact electronically to produce a magnetically ordered phase at low temperature, akin to atoms in a solid-state compound.

Conventional binary solid-state compounds, A\textsubscript{x}B\textsubscript{y}, are infinite, crystalline arrays of atoms A and B. Here we describe analogous binary solids in which the "atomic" building blocks are pseudo-spherical molecular clusters rather than simply atoms [for reviews on molecular clusters, see (1–3)]. We prepare these new solids by simply combining independently synthesized molecular clusters (4–6). The internal structures of the constituent clusters remain unchanged, but charge is transferred between them, forming solids analogous to NaCl. We report three new solids: \([\text{Co}_6\text{Se}_8(\text{PET}_3)_6][\text{C}_6\text{O}_2]\), \([\text{Cr}_6\text{Te}_8(\text{PET}_3)_6][\text{C}_6\text{O}_2]\), and \([\text{Ni}_{10}\text{Te}_6(\text{PET}_3)_8][\text{C}_6\text{O}_2]\). The former two assemble into a superatomic relative of the CdI\textsubscript{2} structure type, and the latter forms a simple rock-salt crystal.

Despite their ready availability, molecular clusters have been used infrequently as electronic materials. Noteworthy examples of success in this area are the organic-inorganic hybrid materials reported by Batail and Mitzi (7–11). Nanocrystals have been assembled into striking superlattices (12–14), but they do not have discrete structural, electronic and magnetic properties and cannot be regarded as genuine artificial atoms. Here, we combine independently prepared electronically and structurally complementary molecular cluster building blocks into form atomically precise binary solid-state compounds. When the building blocks are atoms (ions), binary solids assemble into simple crystalline arrays such as the rock-salt and CdI\textsubscript{2} lattices [for an authoritative text on solid-state inorganic chemistry, see (15)]. We show that when similarly-sized clusters combine the same lattice results, albeit at the dramatically increased length scale of nanometers rather than Angstroms. The constituent clusters interact to produce collective properties such as electrically conducting networks and magnetic ordering.

Our strategy was to use constituent molecular clusters that have the same, roughly spherical, shape but very different electronic properties in order to encourage reaction and subsequent structural association. By analogy to "atomic" solid-state chemistry, we reasoned that the in situ transfer of charge would produce ions (or the equivalent) that could then form an ordered solid. Thus, we sought cluster pairs in which one cluster is relatively electron-poor and the other is relatively electron-rich. C\textsubscript{60} carbon clusters are good electron acceptors (16). The electronically neutral metal chalcogenide clusters Co\textsubscript{6}Se\textsubscript{8}(PET\textsubscript{3})\textsubscript{6} (1), Cr\textsubscript{6}Te\textsubscript{8}(PET\textsubscript{3})\textsubscript{6} (2), and Ni\textsubscript{10}Te\textsubscript{6}(PET\textsubscript{3})\textsubscript{8} (3) are all electron-rich. Importantly, these clusters (Fig. 1) are similar in size and shape to the fullerene.

We combined 1 and two equivalents of C\textsubscript{60} in toluene and obtained black crystals after ~12 hours. Single-crystal x-ray diffraction (SCXRD) revealed that this solid is a 1:2 stoichiometric combination of 1 and C\textsubscript{60} (1:2C\textsubscript{60}) (Fig. 2; A and B) composed of hexagonal arrays of C\textsubscript{60}s in a chair–like arrangement separated by layers of the clusters. The C\textsubscript{60} layers are 12.5 Å apart. The centroid-to-centroid distance and the shortest non-bonded C–C spacing between two adjacent C\textsubscript{60}s is 9.9 Å and 3.4 Å, respectively. These distances are comparable to crystalline C\textsubscript{60} (17). We obtain the exact same structure when we combine the Cr\textsubscript{6}Te\textsubscript{8}(PET\textsubscript{3})\textsubscript{6} cluster 2 and two equivalents of C\textsubscript{60} in toluene (figs. S2 and S3) (18).

We measured how much charge was transferred between the components in the solid-state material using Raman spectroscopy. The A\textsubscript{1g} pentagonal pinch mode of C\textsubscript{60} (1468 cm\textsuperscript{-1} for pristine C\textsubscript{60}) shifts to lower energy by 6 cm\textsuperscript{-1} per electron transferred to C\textsubscript{60} independent of the dopant or the crystal structure [see, for example, (19); for a review on discrete fulleride anions, see (20)]. The solid-state Raman spectra of 1:2C\textsubscript{60} and 2:2C\textsubscript{60} (fig. S4) (18) were taken using a 514.5 nm excitation laser at 4.6–7.8 kW/cm\textsuperscript{2} power densities. The A\textsubscript{1g} modes of C\textsubscript{60} were centered at 1463 cm\textsuperscript{-1} and 1462 cm\textsuperscript{-1} in 1:2C\textsubscript{60} and 2:2C\textsubscript{60}, respectively. The difference between the A\textsubscript{1g} peak position of 1:2C\textsubscript{60} and 2:2C\textsubscript{60} is small and within experimental error. We estimate that clusters 1 and 2 transfer two electrons, and each C\textsubscript{60} receives one electron.

The solid-state electronic absorption spectra of 1:2C\textsubscript{60} and 2:2C\textsubscript{60} provide additional confirmation for the formation of charge transfer complexes in the materials. The electronic spectra of both materials dispersed in KBr pellets show a series of transitions between 900 and 1150 nm with the strongest band centered at 1100 nm (figs. S6 and S7) (18). These features are transitions for the radical anion of fullerene, C\textsubscript{60}− (20). Cluster 1 has four weak transitions between 350 and 700 nm that were observed in 1:2C\textsubscript{60} but not in 2:2C\textsubscript{60}.

We can compare these solids to traditional simple M\textsuperscript{2+}X\textsuperscript{2−} solids. The CdI\textsubscript{2} structure type (21) is formed by a hexagonally close-packed array of monoanions with half of the octahedral interstitial sites occupied by dications. The cations are ordered such that along the crystallographic c-direction the cation layers are alternatively empty and fully occupied, and the layers are held together by van der Waals bonding between anions of neighboring layers. The structures of compounds 1:2C\textsubscript{60} and 2:2C\textsubscript{60} can be appreciated in these same terms. Wireframe representation of 1:2C\textsubscript{60} are shown in Fig. 3; in Fig. 3A we compare one C\textsubscript{60}-cluster-C\textsubscript{60} layer to the corresponding layer in CdI\textsubscript{2}. In panels (B), (C) and (D) we show edge-on and packing views of these same layers; the similarity between our cluster-solid and the “atomic” solid is evident. Although atomic solid CdI\textsubscript{2} appears in many different polytypes, which are related
by different patterns of stacking of ab planes, we have observed only one stacking polytype in our cluster solids.

The cluster Ni₉Te₁₈(PEt₃)₁₂ (3) is rich in metal, and we expect this compound to have a greater reducing power than 1 or 2. Interdiffusion of cluster 3 and C₆₀ solutions for two weeks at ~30°C gives a black solid that is composed of micron-sized cubic crystals. Rietveld refinement of the synchrotron powder x-ray diffraction data (fig. S1) (18) reveals a 1:1 combination of 3 and C₆₀ (3•C₆₀) (Fig. 2C) in a face-centered cubic structure analogous to rock salt with a lattice parameter of 21.7 Å. We observed a broad peak centered at 1454 cm⁻¹ in the solid-state Raman spectrum of 3•C₆₀ (fig. S5) (18). We assign this peak to the A₁g mode of C₆₀, and these data strongly suggest that the fullerene in 3•C₆₀ is more reduced than in 1•2C₆₀ or 2•2C₆₀. These results show that we can prepare binary cluster materials with diverse structural and ionic properties by changing the composition of the molecular cluster building block.

These materials behave less like molecular co-crystals and more like three-dimensional solid-state compounds. For example, 1•2C₆₀ and 2•2C₆₀ exhibit activated electronic transport. Figure 4A displays the electrical transport properties of the co-crystals 1•2C₆₀ (fig. S9 shows the transport properties of 2•2C₆₀) (18) We performed two and four probe measurements on single crystals and pressed pellets of 1•2C₆₀ and two probe measurements on pressed pellets of 2•2C₆₀. Both compounds are good electrical conductors with resistivities on the order of 10 ohm-cm at room temperature. We observe an exponential decrease of the conductance (G) with decreasing temperature. This thermally activated semiconducting behavior displayed Arrhenius behavior with activation energies E₀ of ~150 meV and ~100 meV for 1•2C₆₀ and 2•2C₆₀, respectively, and indicates that 1•2C₆₀ and 2•2C₆₀ are both gapped semiconductors.

An additional feature of these superatom-assembled solids is that the magnetic properties vary as the inorganic cores are changed because of the vastly different spin states accessible with the molecular clusters. Figure 4B shows the temperature dependence of the inverse molar magnetic susceptibility (1/χₐ) and the effective magnetic moment (μₑff) of 1•2C₆₀ from SQUID magnetometry. We corrected the data for diamagnetic and temperature-dependent contributions and modeled the results using a modified Curie-Weiss law

\[ χₐ(T) = \frac{C}{T - θ} + χ₀ + χ₂F \]

where C is the Curie constant, θ is the Weiss constant, and χ₀ and χ₂F are the diamagnetic and temperature independent paramagnetic contributions, respectively. A good fit is obtained with C = 0.9 emu K Oe⁻¹ mol⁻¹ (f.u.)⁻¹ (f.u. = formula unit), θ = -0.3 K and χ₂F = 0.001 emu Oe⁻¹ mol⁻¹ (f.u.)⁻¹. The small negative Weiss constant indicates weak antiferromagnetic interactions. Above 10 K, 1•2C₆₀ showed a temperature-independent effective magnetic moment, μₑff = 2.7 μ₀ per f.u. This result agreed well with the spin-only value of 2.8 μ₀ for two non-interacting unpaired electrons and is consistent with the Raman spectroscopy data that show one electron in each of the two C₆₀ per formula unit, with the cobalt ions in the cluster not contributing to the overall moment.

Figure 4B also displays the temperature dependence of the inverse molar magnetic susceptibility (1/χₐ) of 2•2C₆₀. The important result is that 2•2C₆₀ exhibits a more complex magnetic behavior with a change in the slope of this plot around 60 K. We presume the difference in the materials is caused by the large magnetic difference between compound (1)²⁺, which contains six Co³⁺, and compound (2)²⁺, which is composed of six Cr³⁺.

The magnetism of the rock-salt 3•C₆₀ material is remarkably different from that of 1•2C₆₀ and 2•2C₆₀ both in magnitude and as a function of temperature. Figure 4C shows the temperature dependence of the magnetization (M) of 3•C₆₀. When we applied a field of 200 Oe and cooled the sample to 2 K, we measured no appreciable magnetic response until the temperature reached about 4 K, at which point we observed a sudden transition to a magnetically ordered phase with \( M \) reaching 2300 emu mol f.u.⁻¹ at 2 K. The difference between the zero-field cooled (ZFC) and field-cooled (FC) magnetizations indicates some irreversibility in the magnetically ordered phase. The magnetic response of 3•C₆₀ to an external field differs dramatically when the sample is examined at temperatures above \( T_c \) and below \( T_c \) (fig. 4D). At \( T = 10 K \), M scales linearly with H. The sigmoidal magnetization curve measured at 2 K is characteristic of ferromagnetism. Compound 1•C₆₀ exhibits a small hysteresis with a coercivity \( H_c \sim 400 \) Oe. This indicates that the spins freeze in a ferromagnetic state for \( T < T_c \). This result demonstrates that the constituent clusters are able to communicate magnetically at low temperature in the same way that atoms are able to in solid-state compounds.

By using clusters that are similar in size and shape to each other, we have created binary assemblies whose infinite crystalline structures are determined not only by the shapes of the clusters but also by the degree of charge transfer between the constituents. The intercluster charge transfer, along with the intermolecular van der Waals interactions that are typical in conventional molecular solids, hold these solid-state compounds together in much the same way that interatomic charge transfer from Cd to I holds CdI₂ together and from Na to Cl holds rock-salt together. These results chart a clear path to creating whole families of multifunctional solid-state materials whose electronic and magnetic properties can be tuned by varying the constitution of the superatom building blocks.

References and Notes


18. Materials and methods are available as supplementary materials on Science Online.


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Supplementary Materials
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Materials and Methods
Figs. S1 to S9
Table S1
References (22–25)

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Fig. 1. Structures of the $C_{60}$, $Co_6Se_8(PEt_3)_6$, $Cr_6Te_8(PEt_3)_6$, and $Ni_9Te_6(PEt_3)_8$ molecular building blocks as measured by single crystal x-ray diffraction. In the figure, the clusters are depicted on the same size scale. The diameter of the cluster is determined as the long diagonal P-P distance. The ethyl groups on the phosphines of 1, 2 and 3 were removed to clarify the view.
Fig. 2. Space filling molecular structure of 1•2C₆₀ showing the crystal packing looking down (A) the ab plane and (B) the c-axis. (C) Space filling molecular structure of 3•C₆₀. Carbon, black; nickel, red; cobalt, blue; phosphorus, orange; tellurium, teal; selenium, green. The ethyl groups on the phosphines were removed to clarify the view.
Fig. 3. Comparison of the packing structures of 1•2C₆₀ and CdI₂. (A) View of a single hexagonal layer looking down the c-axis. (B) and (C) Edge-on views of the same layer looking down the ab-plane. (D) Stacking of the ab hexagonal layers along the c-axis direction. Cluster 1 and Cd are shown in blue; C₆₀ and I are shown in grey. The ethyl groups on the phosphines were removed to clarify the view.
Fig. 4. (A) Plot of the conductance versus $1/T$ for $1\cdot2C_{60}$. The four probes conductance measurements were done on a single crystal (black) and a pressed pellet (red). The Arrhenius fits are shown as solid lines. (B) Inverse magnetic susceptibility (black) as a function of temperature for $1\cdot2C_{60}$ (circles) and $2\cdot2C_{60}$ (open circles) in an applied external field $H = 1$ T. The Curie-Weiss fit for $1\cdot2C_{60}$ is shown in red. The effective magnetic moment of $1\cdot2C_{60}$ as a function of temperature is shown in the inset. (C) Temperature dependence of the ZFC and FC magnetization ($M$ of $3\cdot C_{60}$) in an applied external field $H = 200$ Oe. In the ZFC experiment, the sample was cooled from room temperature to 2 K in zero-field prior to the measurement of $M$ from 2 K to 10 K. (D) Magnetization as a function of applied field at 10 K and 2 K for $3\cdot C_{60}$. The inset shows the enlarged magnetic hysteresis at 2 K.