Two-Dimensional Nanosheets from Redox-Active Superatoms

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INTRODUCTION

In this manuscript we connect transition metal chalcogenide molecular clusters into three-dimensional (3D) and two-dimensional (2D) solids, as well as free-floating nanosheets. Monolayer 2D materials such as graphene and transition metal dichalcogenides show promise for next-generation electronics, yet are plagued by the occurrence of defects, and it is not easy to modify them synthetically. The type of nanosheet we disclose here, due to the redox activity and multinuclearity of its superatom components, provides a new level of complexity and synthetic sophistication to 2D materials. Our building blocks disclose here, due to the redox activity and multinuclearity of its superatom components, provides a new level of complexity and synthetic sophistication to 2D materials. Our building blocks, superatom components, provides a new level of complexity and synthetic sophistication to 2D materials. Our building blocks, directed-layer fullerene assemblies, and covalent assemblies through directed ligand exchange. Redox-active $M_{6}E_{8}$ clusters ($M = Re, W; E = S, Se$) have previously been functionalized with reactive ligands to generate frameworks of these preformed entities through cyanide and bipyridine coordination with transition metal ions. Others have employed a variety of techniques to direct clusters and nanocrystals into extended lattices.

The key to unlocking both the structural utility and the functional solid-state infrastructure of the superatoms is the ability to manipulate their surface properties at will. In this study, we demonstrate a method to do so by converting the $Co_{6}Se_{8}[PET_{2}(4-C_{6}H_{4}Br)]_{6}$ superatom into one that presents six carboxylic acids. We then introduce zinc carboxylate bonds via a solvothermal reaction to produce two types of crystalline solids, a trigonal 3D solid ($Trig_{3D}$) and a tetragonal 2D solid ($Tet_{2D}$) (Figure 1). Single crystal X-ray diffraction (SCXRD) reveals that $Trig_{3D}$ is a 3D network of superatoms held together with zinc carboxylate bonds, but $Tet_{2D}$ forms 2D sheets that then stack through noncovalent forces into a 3D solid. We find it remarkable that the two-dimensionality of $Tet_{2D}$ is robust: individual 2D sheets can be exfoliated intact from the solid, and these exfoliated sheets can be subsequently redeposited on arbitrary substrates. When we cast them on electrode surfaces they retain the redox activity of the superatom building blocks.

RESULTS AND DISCUSSION

We previously organized these superatoms into extended van der Waals solids; our new objective was to connect the superatoms to make extended solids through bonds. Our simple, phosphine-terminated superatoms, however, are inert in the...
sense that the phosphines (by design) chemically passivate the cluster surfaces and do not participate in the reaction chemistry. Thus, our first challenge was to create appropriately reactive superatom building blocks. To do so we first treated Co2(CO)8 and Se with EtP(4-C6H4Br) to give Co6Se8[PEt2(4-C6H4Br)]6 (SCXRD in Figure S1) in high yield. Other than the obvious differences in the size, shape, and arrangement of the organic components, the inorganic core of Co6Se8[PEt2(4-C6H4Br)]6 is identical to the parent cluster, Co6Se8[PEt2(4-C6H4COOH)]6. The structure is a network in which carboxylate nodes. SCXRD of both solids reveals that while they have the same Zn[Co6Se8] stoichiometric ratio of 3:1, both the dimensionality of their extended structure and orientation of the cluster within the solids differ significantly. 

We then sought to create solids from building block 1 through metal–carboxylate bonds. For example, would the simple replacement of the two protons with a divalent metal ion result in a structurally familiar family of new solids? Thus, we treated our hexatopic superatom with Zn(NO3)2 to determine the extent to which the carboxylate–carboxylate bonds, which constitute the adhesive that stabilizes this solid, can be modified and improved. Co6Se8 superatoms are useful building blocks in this regard because they have tunable ligands, multiple accessible redox states, significant magnetic moments, and charge transport capabilities. Our building block 1 is preformed and atomically defined, and thus programmable.

Using the same building blocks, 1 and Zn(NO3)2, we can selectively synthesize two different solids, Trig3D and Tet2D, by varying the growth conditions. It is remarkable that the only significant difference between the two reactions is the use of methanol versus ethanol as solvents. We obtained structures for both solids using SCXRD (details of the refinement can be found in the Supporting Information). In both solids, all the carboxylic acid hydrogen bonds of 1-H are replaced by carboxylate–zinc–carboxylate nodes. SCXRD of both solids shows that three point up and three point down (Figure 2d). This symmetry mirrors that of 1-H, replacing hydrogen bonds with carboxylate bonds, which constitute the adhesive that stabilizes this solid. SCXRD of both solids reveals that while they have the same Zn[Co6Se8] stoichiometric ratio of 3:1, both the dimensionality of their extended structure and orientation of the cluster within the solids differs significantly. Trig3D is a 3D network while Tet2D is a 2D structure with strong in-plane bonding and comparatively weak noncovalent interlayer interactions.

We combined 1 and Zn(NO3)2 in a DMF/MeOH solvent mixture under solvothermal conditions at 65 °C, and obtained black hexagonal crystals after 24 h. Figure 2 displays the crystal structure of Trig3D. The structure is a network in which 1 is coordinated to unusual trinuclear zinc nodes in three dimensions (Figure 2a). Looking down the b-axis we clearly see the distinct pseudotrigonal layers of the solid (Figure 2b). Within each layer, the superatoms are bound to six zinc-nodes (Figure 2c). These layers are then cross-linked by a single Zn−O bond. The approximate 3-fold symmetry of the pseudotrigonal lattice of Trig3D arises because the Co6 octahedron is tilted on its face in the layer, which orients the phosphines such that three point up and three point down (Figure 2d). This symmetry mirrors that of 1-H, replacing hydrogen bonds with carboxylate bonds, which constitute the adhesive that stabilizes this solid. SCXRD of both solids shows that while they have the same Zn[Co6Se8] stoichiometric ratio of 3:1, both the dimensionality of their extended structure and orientation of the cluster within the solids differs significantly. Trig3D is a 3D network while Tet2D is a 2D structure with strong in-plane bonding and comparatively weak noncovalent interlayer interactions.

Each zinc atom in Trig3D exhibits a different coordination environment. Zn1 and Zn2 display distorted tetrahedral geometry and together form a three-bladed trigonal paddlewheel with three bridging μ2-carboxylates. A solvent molecule (likely MeOH) coordinates Zn1 axially, and Zn2 is axially coordinated by a μ2-carboxylate, whose second oxygen coordinates Zn2. Zn3 exhibits a distorted square pyramidal geometry. Each superatom 1 within the solid contains three types of carboxylates, labeled a, b, and c in Figure 2e,f. For a, three μ2-carboxylates coordinate the Zn1−Zn1 paddlewheel; for b, two carboxylates coordinate Zn3 in an η1 fashion; for c, a μ2-carboxylate coordinates both Zn2 and Zn3. The latter ligand c also serves to cross-link the layers through its carboxylate–Zn2 bond. This bond has a length of 2.22 Å, which is a long Zn−O contact, and suggests we refer to the latter solid as 1-H. If we represent each cluster as a sphere, we see that this solid forms such that there is hydrogen-bonding between nearest neighbors (Figure 1c). The formation of this solid-state compound is reversible: 1-H dissolves in tetrahydrofuran to regenerate 1.

We then sought to create solids from building block 1 through metal–carboxylate bonds. For example, would the simple replacement of the two protons with a divalent metal ion result in a structurally familiar family of new solids? Thus, we treated our hexatopic superatom with Zn(NO3)2 to determine the extent to which the carboxylate–carboxylate bonds, which constitute the adhesive that stabilizes this solid, can be modified and improved. Co6Se8 superatoms are useful building blocks in this regard because they have tunable ligands, multiple accessible redox states, significant magnetic moments, and charge transport capabilities. Our building block 1 is preformed and atomically defined, and thus programmable.

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the interlayer carboxylate–Zn bond is a weaker, dative bond compared to intralayer carboxylate–Zn bonds.

The presence of weak interlayer zinc bonds in Trig3D prompted us to modify reaction conditions to eliminate interlayer bonding and synthesize 2D layers. Thus, we reacted 1 and Zn(NO₃)₂ at 65 °C in a DMF/EtOH solvent mixture and obtained black cubic crystals after 24 h. We note that a small fraction of Trig3D forms under these conditions but can eliminated with the addition of “extra” protons in the form of HCl in the reaction. Under these conditions, we form exclusively the new solid-state compound, Tet2D (Figure 3). Tet2D also contains complete replacement of proton-nodes with metal nodes, although the types of metal nodes and dimensionality differ from Trig3D. Distinct layers of superatoms are held together only by noncovalent forces.

Tet2D is a layered 2D material in which each layer is a square arrangement of Co₆Se₈ superatoms with four phosphine ligands residing in the 2D plane and bonding to four-bladed Zn-carboxylate paddlewheels (Figure 3a). In the direction normal to the sheet, the axial carboxylate ligands coordinate an additional Zn²⁺ ion that is positioned above or below the square sheet (Figure 3b). Figure 3c,d displays the binding interaction of each ligand of 1 within the solid. The zinc subunit within the square plane of this solid is a dinuclear four-bladed Zn-carboxylate paddlewheel (Figure 3e). The combination of two Zn²⁺ ions and four bridging μ₂-carboxylate groups yields this Zn₂ cluster with a Zn–Zn distance of 2.867(7) Å that is consistent with other such “four-bladed” paddlewheels in zinc-based metal–organic frameworks.⁴⁷ Pairs of apical phosphines on adjacent clusters that are not involved in dinuclear Zn paddlewheels within a single layer are linked via a single Zn atom (in addition to their bonding via the intralayer Zn₂ node) to form a mononuclear zinc complex. This complex features Zn–O distances of 2.20 (3) and 2.36(3) Å and a carboxylate–Zn-carboxylate angle of approximately 119°. This geometry is
typical of pseudotetrahedral Zn(O₂R)₂L₂ complexes, but in this case we note that the two L-type ligands (presumably ethanol or water) are disordered and could not be located. The layers are self-contained and stack through noncovalent interlayer interactions in an eclipsed arrangement.

The crystal packing arrangements of Tet₂D and Trig₃D are propagated in their macroscopic crystal morphologies. Figure 4a,b shows SEM micrographs of the crystals that form after 24 h growth. The black cubes (Tet₂D; Figure 4a) and hexagonal plates (Trig₃D; Figure 4b) reflect the tetragonal and trigonal lattices of their crystalline arrangements. In Trig₃D, the cluster is tilted on its side such that the symmetry is defined by a C₃ axis through the offset triangular stacks of Co₆, whereas in Tet₂D a C₄ axis through the axial cobalt atoms of the Co₆ octahedron generates a square lattice. EDX spectra of both samples (Figure S3) display zinc, cobalt, and selenium as compared to the EDX spectrum of 1 that lacks Zn peaks. Powder XRD of each sample shows homogeneous crystalline phases (Figures S4 and S5).

The 2D Tet₂D crystals behave like traditional “atomic” layered compounds such as transition metal dichalcogenides in that we can exfoliate these materials without having the layers disintegrate. We reasoned that since the multicoordinate Zn²⁺ ions in some fashion hold the layers together, a solution of a weak acid would chemically dissociate the layers of Tet₂D and that they would be stable to these conditions (having been originally formed in acidic conditions). We first immersed the cubic crystals of Tet₂D in a 1 mM solution of benzoic acid in DMF. SEM micrographs of immersed cubes show visible layered striations within the crystals (Figure 4c). Next, we immersed the Tet₂D crystals in 40 mM benzoic acid overnight and followed the transformation with powder X-ray diffraction (Figure S6). The reflections that are due to Tet₂D disappear, with only low intensity peaks corresponding to trace impurities of Trig₃D still visible. During this process, we observe a color change in the solution from clear to light brown upon suspension in the benzoic acid solution. We drop-casted this solution on a silicon substrate (SiO₂ on Si) and characterized the films with optical microscopy and atomic force microscopy (AFM). Figures 4d and S7 clearly show layered 2D sheets. Thin sheets with a thickness of 7.5 nm are present throughout the samples (Figure 4e), with step sizes between the layers corresponding to this thickness. From the SCXRD structure of Tet₂D, the expected thickness of a single sheet is 1.5 nm, corresponding to the Zn—Zn distance between stacked mononuclear Zn atoms in adjacent layers. Thus, 7.5 nm corresponds to five distinct superatom layers. In other images we also observe smaller step sizes of 3.8 and 5.3 nm (Figure S8), corresponding by SCXRD to three layers and four layers, respectively. These chemically exfoliated sheets of Tet₂D once deposited onto a substrate are clean and flat (Figure S9, roughness of 0.3 nm).

We can use these thin layers of Tet₂D from solution to coat the surface of electrodes and probe their redox activity. For comparison, 1 displays three reversible oxidations relative to Fc/Fc⁺ (Figure S10), and the bulk crystals deposited on the electrode show two broad, quasi-reversible oxidations (Figure S11). When we drop-cast the exfoliated sheets onto a glassy carbon electrode, the cyclic voltammogram of the exfoliated Tet₂D sheets (Figure 4f) reveals that the redox properties of the superatom building block 1 persist within the sheets as they display three reversible oxidations. No material is released into the electrolyte solution during the cyclic voltammetry. The redox potentials of these exfoliated materials in solution are shifted toward slightly more negative values (−0.2 V difference) relative to those of 1 in solution. We thus assign the oxidation states of the cluster within the sheets (labeled a through d in Figure 4f) as {Co₆Se₈}²⁺ through {Co₆Se₈}³⁺, using the CV of 1 as a reference point. Another interesting feature of the CV of the electrodes that are covered with the 2D layers of Tet₂D is that these are permeable to the electrolyte. Analysis of bulk Tet₂D crystals revealed that the structure contains 43% solvent-accessible void space, predominantly in open channels oriented along [101]. The porosity of the bulk crystal is thus preserved upon exfoliation. The important finding is that Tet₂D sheets are solution processable, porous, and redox-active.

Figure 4. SEM images of (a) Tet₂D cubic crystals and (b) Trig₃D hexagonal crystals as synthesized. (c) SEM images of cubic crystals of Tet₂D immersed in a benzoic acid solution in DMF. Striations in the crystals are apparent. (d) AFM height sensor and peak force error images of multilayered Tet₂D films after immersion in benzoic acid solution in DMF. The scale bar in an inset is 3 μm. (e) AFM topographic image of exfoliated sheets. Sheets remain that are about 7.5 nm in thickness, with distinct step sizes apparent. (f) Solid-state cyclic voltammogram of exfoliated Tet₂D sheets in 0.1 M TBAPF₆ in tetrahydrofuran with a 50 mV/s scan rate. The solution of exfoliated sheets was dropcast onto a glassy carbon electrode.

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CONCLUSIONS

In summary, we have developed the reaction chemistry to create the hexatomic Co₅Se₆[(PEt₃)₄(C₆H₄COOH)]₄ superatom 1. This superatom assembles into a 3D solid that is held together by a hydrogen bond adhesive. We can change this adhesive from 2H⁺ to Na⁺ and create extended crystalline solids Trig₃D and Tet₂D. A seemingly small change in the solvent system from DME/methanol to DME/ethanol yields remarkable changes in crystal morphology and structure, from a 3D to a 2D extended solid. Both solids are held together via zinc carboxylate bonds. Two-dimensional Tet₂D extends into a superatom assembles into a 3D solid that is held together by a hydrogen bond adhesive. We can change this adhesive from 2H⁺ to Na⁺ and create extended crystalline solids Trig₃D and Tet₂D. Both solids are held together via zinc carboxylate bonds. Two-dimensional Tet₂D can be chemically exfoliated to yield ultrathin yet soluble layers. These layers can be deposited from solution onto substrates. The sheets are redox-active, preserving the redox activity of their component superatoms. These types of porous, ultrathin, and redox-active sheets will find utility in a number of other applications such as modified electrodes for catalysis, batteries, and nanoscale electronic sieves.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssciencet.7b00328.

All synthetic methods, characterization, X-ray diffraction (PDF)
Crystallographic files (CIF1), (CIF2), (CIF3), (CIF4), (CIF5)

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Notes

The authors declare no competing financial interest.

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