

A Two-Dimensional Crystal of Strongly Interacting Superatoms

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A Two-Dimensional Crystal of Strongly Interacting Superatoms

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Abstract

Superatoms are discrete molecular clusters exhibiting collective electronic states resembling elemental atoms. To date, most two-dimensional (2D) crystals assembled from superatoms are weakly interacting, meaning building blocks rely on surfactants or van der Waals interactions to avoid decomposition into collections of elemental atoms. Here we demonstrate that superatoms can bond in a covalent fashion in two dimensions, forming a strongly interacting superatomic crystal, thereby extending the effective periodic table. The superatoms, identified as Pd₆Se₂₀ and Pd₆Se₂₁ distorted cubes, are shown to bond strongly in a lattice and host electronic band structures with discrete energy levels, like atoms. Due to their large effective masses of 2218 and 2297 amu, their motion during 2D crystal assembly can be directly observed by electron microscopy. The resulting superatomic crystal exhibits the full hierarchy of crystalline defects—including vacancies, dislocations, and grain boundaries—analogueous to those found in conventional atomic solids. We propose that the superatoms are useful for studying the early stages of nucleation and growth of atomic crystals by analogizing the superatoms to elemental atoms.

Keywords: superatoms, two-dimensional materials, crystallization dynamics, scanning transmission electron microscopy

1 Introduction

Laplace imagined an intelligence able to comprehend every force and the position of every constituent, such that “nothing would be uncertain and the future, as the past, would be present to its eyes” [1]. While the practical and conceptual limits of predicting many-body systems are well appreciated, slowing their elementary dynamics can render otherwise inaccessible processes directly observable. Here we report a 2D system whose fundamental building blocks are atomically precise clusters, or superatoms, that retain their identity and electronic structure while forming a strongly interacting crystal lattice. The large mass of these clusters (> 2000 amu) substantially slows lattice-scale processes relative to atomic crystals, placing defect migration, interaction, and crystallization on experimentally accessible timescales.

The properties of atomic clusters are highly sensitive to their size, shape, and composition [2]. Superatoms are a class of cluster exhibiting collective, atom-like properties which emerge from their precise atomic arrangement [3, 4]. By mimicking the physical, electronic, and chemical properties of atoms, superatoms have long been envisioned as designer building blocks for crystal lattices with properties inaccessible to conventional solids [5]. However, constructing a crystal from superatoms remains a challenge.

In conventional crystals, bonding, symmetry, and emergent properties are governed predominantly by electronic degrees of freedom, while the atomic nucleus primarily serves as a confining potential for valence states. From the perspective of the crystal, the detailed nuclear composition is therefore secondary to the electronic structure it supports. Extending this principle to the superatomic regime suggests that clusters can function as effective nucleus-like cores, provided they host well-defined, delocalized electronic states capable of mediating inter-cluster bonding on energy scales comparable to covalent interactions.

Historically, superatoms fall short of this analogy in two ways. Early studies identified isolated sodium clusters with magic numbers of atoms predicted by the jellium model, whose filled valence shells mimic noble gases [4], as well as aluminum clusters exhibiting behavior analogous to noble gases [6, 7], alkali metals [8], and multivalent elements [9]. While these metallic systems established that atom-like electronic structure can emerge in isolated clusters, their extension to condensed phases revealed an intrinsic instability: metallic clusters with delocalized electronic states tend to undergo strong inter-cluster interactions, leading to agglomeration or transformation into conventional atomic solids [10–12]. In contrast, strategies designed to preserve structural identity, such as ligand-stabilized clusters [13] and fullerene-based assemblies [14–17], suppress direct inter-cluster bonding by spatially confining the electronic states. This confinement reduces overlap between tightly bound valence orbitals, yielding solids held together primarily by van der Waals interactions [18] and thus limiting the formation of electronically coherent bands. Although these van der Waals-based systems may still permit electronic coupling through diffuse superatomic molecular orbitals [19], the physical structure is still a van der Waals solid [18, 20] and weakly bound, ultimately decomposing through inter-unit covalent bonding and coalescence [21, 22].

These results define two opposing limits: structural instability driven by strong coupling, and electronic isolation enforced by weak coupling. Consequently, achieving

a dense, strongly interacting, ligand-free superatomic crystal remains experimentally elusive. To date, only a couple ligand-free superatomic solids—distorted-cube transition-metal chalcogenides such as $\text{Pd}_6\text{Se}_{20}$ [23, 24] and $\text{Au}_6\text{Te}_{12}\text{Se}_8$ [25, 26]—have been realized, and only in bulk form, leaving the realization of a two-dimensional system that simultaneously preserves identity, electronic structure, and strong inter-unit bonding an open challenge.

Here we demonstrate that certain Pd–Se clusters in the 2D limit satisfy the defining criteria of superatoms and assemble into an extended crystal lattice. We show that $\text{Pd}_6\text{Se}_{20}$ and a previously unreported $\text{Pd}_6\text{Se}_{21}$ species retain discrete, atom-like electronic states when isolated, maintain structural identity as individual units, and form strong inter-superatom bonds that stabilize a 2D crystal. We establish these clusters as superatomic building blocks in a regime of strong inter-unit coupling, realizing a two-dimensional superatomic crystal with electronically coherent bonding between units.

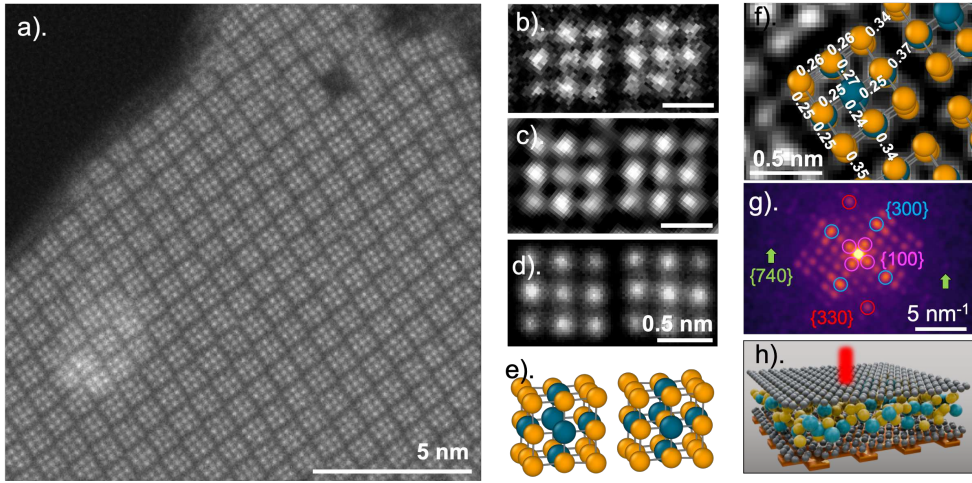


Fig. 1 Superatom structure is displayed across length scales. **a**, Image of a superatomic crystal, averaged over 10 HAADF-STEM image frames, with the black-level adjusted to increase contrast. **b**, Selected region of **a**, showing contrast-enhanced image of $\text{Pd}_6\text{Se}_{20}$ (left) and $\text{Pd}_6\text{Se}_{21}$ (right) superatoms next to each other. **c**, Filtered image corresponding to **b**. **d**, Simulated HAADF-STEM image contrast agrees with the real image. **e**, Crystal structures of $\text{Pd}_6\text{Se}_{20}$ (left) and $\text{Pd}_6\text{Se}_{21}$ (right) used for image simulation in **d**. **f**, Filtered HAADF-STEM image overlaid with the $\text{Pd}_6\text{Se}_{20}$ atomic structure, showing distances between atomic columns in Å (with spacing between superatoms exceeding 3 Å). **g**, FFT of **a** shows the {100} peaks corresponding to long-range (8.64 Å) superlattice ordering and brighter {300} peaks corresponding to the atomic periodicity. The {740} peaks define the resolution limit of the image (1.15 Å). **h**, Schematic of the a-PdSe precursor, encapsulated in graphene on a TEM grid, and ablated with a low power laser.

2 Superatom structure

To begin, we investigate the physical structure of the superatoms. A high-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) image of the superatoms is shown in Fig. 1a, processed only by adjusting the black level to enhance contrast. The HAADF intensity scales approximately with the square of the projected atomic number; thus the individual bright spots are projected atomic columns and the 3×3 structures are the superatoms. Notably, a missing superatom is directly resolved within the lattice (a vacancy), indicating that these crystals may support well-defined classical point-defect structures like those found in conventional atomic solids.

In addition to these types of superlattice defects, there are structural variations within the superatoms themselves. For example, in Fig. 1b, a contrast-enhanced selected area shows adjacent superatoms with different intensity in the central atomic site. The superatom on the right has an extra selenium atom in the center of the distorted cube ($\text{Pd}_6\text{Se}_{21}$) while the one on the left has an unoccupied site in the middle ($\text{Pd}_6\text{Se}_{20}$). This is made easier to see by cleaning the image (Fig. 1c) and comparing with a simulated image (Fig. 1d) of the two structures (Fig. 1e). A magnified image (Fig. 1f) shows the distorted cube geometry [24] of the $\text{Pd}_6\text{Se}_{20}$ superatom, taking a rhombohedral structure with a γ of 88° . Selenium atoms occupy the edges and corners of each $3 \times 3 \times 3$ cube, while palladium atoms sit at the face centers; notably, the central site remains vacant in the $\text{Pd}_6\text{Se}_{20}$ structure while being filled with a selenium in the $\text{Pd}_6\text{Se}_{21}$ structure. Although bond lengths within the distorted cube vary (with a standard deviation of $0.15 \text{ \AA}$), the superatomic lattice retains long-range order, as evidenced by the strong $\{100\}$ reciprocal lattice peaks in the fast Fourier transform (FFT) (Fig. 1g). The brightest features in the FFT, the $\{300\}$ peaks, arise from atom-atom distances within each superatom, while the intensity modulation among the $\{330\}$ peaks is a result of the rhombohedral distortion of the cube diagonals. The $\{740\}$ peaks define the resolution of the image ($1.15 \text{ \AA}$).

Stoichiometric control is critical for the formation of these extended two-dimensional superatomic crystals. During thermal processing, selenium readily sublimates, driving the system toward Pd-rich equilibrium phases such as PdSe_2 . Bilayer graphene encapsulation suppresses this loss by confining selenium, preserving local composition during laser-induced crystallization of the amorphous precursor (Fig. 1h). Beyond stabilizing stoichiometry, the graphene itself seems to have little influence on the structure of the superatomic crystal. According to DFT calculations, rotating and translating a single $\text{Pd}_6\text{Se}_{20}$ superatom between two graphene sheets results in energy changes of $\approx 10 \text{ meV}$, well below its thermal energy of 650 meV at 300 K . Thus, the graphene sheets should not determine the structure of the 2D film.

3 Electronic structure

Next, we investigate the interactions between superatoms. The mean separation between neighboring superatoms is $3.50 \text{ \AA}$ edge-to-edge, pointing to an unconventional binding mode. This is shorter than the van der Waals radii reported between selenium atoms in systems like layered PdSe_2 ($4.1 \text{ \AA}$) [27], but longer than expected

from traditional atom-to-atom covalent bonds. In other chalcogen-containing superatom systems, this type of behavior is called chalcogen quasibonding, or covalent-like quasibonding (CLQB) [25, 26, 28, 29]. To further investigate the nature of the bonding in the Pd–Se system, the binding energy per superatom is calculated as a function of distance. This reveals a deep energy well of $\sim 3\text{--}4.5$ eV, indicative of chemical bonding beyond van der Waals interactions between superatoms and comparable to CLQB in other chalcogen systems (Fig. 2a).

By comparing PBE calculations with and without Grimme’s dispersion correction, we find that 37% of the binding energy originates from chemical bonding, while the remaining 63% arises from van der Waals interactions. Upon relaxation of a 2×2 supercell, the structure develops a low-energy symmetry-breaking distortion in which two inequivalently distorted Pd–Se superatom variants form an antiferrodistortive checkerboard pattern. This instability lowers the energy by approximately 0.64 eV per cube relative to the ideal square phase. Here, we present the band structure of the high-symmetry square structure because it provides the simplest description of the system and closely represents its time-averaged structure. The distorted phase differs only by small local tilts and may be viewed as a low-energy modulation of the same underlying lattice.

The corresponding band structure shows that the superatoms are metallic in 2D crystals (Fig. 2b). This is in contrast to the bulk phase of $\text{Pd}_6\text{Se}_{20}$, which is reported as an indirect semiconductor with a 1.18 eV band gap [24]. Despite the metallic nature of the 2D film, the redistribution of electrons, calculated as the difference between the 2D charge density and the charge density of isolated molecules, shows inter-cluster bond charges between the Pd atoms at the face centers and the corner Se atoms (Fig. 2f), a standard signature of covalent bonding [30] that has also been observed in metallic materials [31]. Addition of the extra Se atom in $\text{Pd}_6\text{Se}_{21}$ essentially eliminates the Pd–Pd bond but leaves the corner bonds intact, which explains the weaker bonding of $\text{Pd}_6\text{Se}_{21}$ superatoms. At large superatom–superatom separations, the electronic bands become essentially flat (Fig. 2c–e), indicating that the $\text{Pd}_6\text{Se}_{20}$ and $\text{Pd}_6\text{Se}_{21}$ clusters are electronically isolated molecules. While the formation of bonding and antibonding states from the molecular levels can be observed as the distance decreases, the complexity of the electronic structure requires further investigation before superatomic orbitals can be sensibly defined.

4 Defects and superatom dynamics

With the electronic structure established, we explore the behavior of these superatoms within a lattice to determine the extent to which they replicate the behavior of atomic solids. If these clusters function as discrete, atom-like building blocks with well-defined bonding, then their assemblies should exhibit the same defect structures that arise in conventional atomic crystals. As famously noted by Burton, Cabrera, and Frank, “the crystals which we grow are not perfect” [32], but instead contain a hierarchy of defects governed by classical nucleation and growth processes. The superatomic crystals grown here exhibit this same set of defect structures, including vacancies, dislocations, and grain boundaries. This correspondence indicates that the superatoms

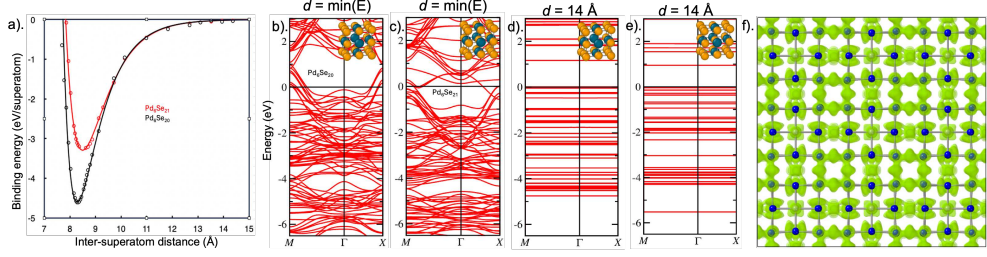


Fig. 2 Bonding of superatoms. **a**, Calculated binding energy versus distance between like-superatoms, for $\text{Pd}_6\text{Se}_{20}$ and $\text{Pd}_6\text{Se}_{21}$ exhibiting 4.7 eV and 3.2 eV binding energy, respectively, strongly indicating covalent-like quasibonding (CLQB). **b–e**, Superatoms bond metallicity when close, but show complex molecular energy levels when well separated. **f**, Electronic difference charge density between the bulk film and isolated superatoms for $\text{Pd}_6\text{Se}_{20}$, shown at an isosurface of +10% maximal difference, indicating areas of bond formation between superatoms.

not only resemble atoms in isolation but also reproduce their collective behavior in a lattice.

At the level of point defects, vacancies are directly observed (Fig. 3a) and remain stable over extended imaging at low beam currents (60 pA). At higher beam currents (90 pA), the lattice becomes dynamic and vacancies can diffuse, providing direct access to studying defect mobility. The lattice also hosts in-plane edge dislocations (Fig. 3b), characterized by well-defined Burgers vectors consistent with crystallographic conventions in atomic solids. Controlled generation of these point defects with the electron beam seems possible but is not yet reproducible under the conditions explored here.

Beyond static defects, the slowed dynamics of the superatomic lattice enable direct observation of few-body processes. In Fig. 3c–e, three superatoms within a void detach, reconfigure, and reattach over three frames. The transient blurring observed in the intermediate frame (Fig. 3d) suggests either rotational motion or internal restructuring prior to realignment with the beam.

At larger length scales, extended defects such as mirror planes (Fig. 3f) and grain boundaries (Fig. 3g) are observed, further mirroring the structural motifs of atomic crystals. Under sustained electron-beam exposure (≈ 15 min), adjacent crystallites rotate and merge into a single grain (Fig. 3g–h), directly visualizing recrystallization dynamics. Residual features of the original boundary such as edge structures and defect inclusions persist after coalescence, reflecting incomplete structural relaxation. The movie of the grain boundary healing is attached as supporting information.

In addition to collective lattice motion, dynamics of individual superatoms and small superatom clusters are directly observed. In Fig. 4a, a single superatom detaches from a three-unit cluster and remains isolated on the substrate for over one minute, demonstrating the stability of individual superatomic units outside the lattice. While the cause of this detachment is unclear—potentially arising from interactions with substrate defects or residual amorphous material—the observation supports the interpretation of superatoms as discrete, stable, and mobile building blocks. The remaining two-unit cluster subsequently interacts with the larger crystalline domain. In a separate sequence (Fig. 4b), a seven-superatom cluster approaches an extended crystal. After gaining a superatom from outside the field of view, the cluster contacts the

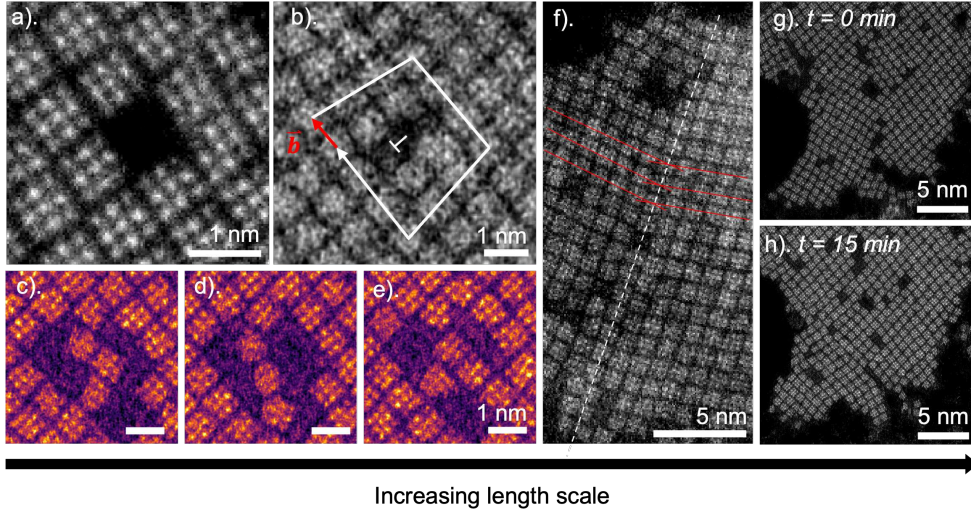


Fig. 3 Superatomic defect structures mimic those in atomic crystals. **a**, Superatomic vacancy from Fig. 1a. **b**, In-plane edge dislocation described by the Burgers vector. **c–e**, Three superatoms move inside a void, reconfiguring under electron beam irradiation. **f**, Mirror plane indicated by the dashed line. **g**, High-angle grain boundary between two crystallites. **h**, After 15 minutes of electron beam exposure, the two grains coalesce into one, although remnants of the original structure remain.

larger crystal and undergoes a structural rearrangement to match registry with the large crystal in frame three, as the point of attachment shifts from one superatom to another. In the next two frames, we see attachment of the cluster of superatoms, and finally, recrystallization into a contiguous crystal (green arrow). Such crystallization dynamics have never been directly observed before.

These observations provide direct, time-resolved evidence of crystal growth via superatom attachment and cluster-mediated incorporation, processes long inferred but rarely observed explicitly in atomic systems [33]. In this regime, superatomic crystals function as a model platform in which the kinetics and topology of crystallization can be directly interrogated: their large effective mass slows defect migration, interaction, and grain evolution into experimentally accessible timescales. As a result, microscopic pathways governing nucleation and growth—typically too rapid to resolve in conventional atomic materials—can be directly visualized in real time, as demonstrated here.

5 Discussion

This work identifies a ligand-free two-dimensional Pd–Se superatomic crystal composed of distorted-cube $\text{Pd}_6\text{Se}_{20}$ and $\text{Pd}_6\text{Se}_{21}$ superatoms. The structural model provides a strong local assignment of the repeating superatomic units and establishes the material as a true two-dimensional superatomic crystal. Observed deviations from the ideal structure, including some cases of missing selenium atoms at corner sites, indicate areas of future work focused on inducing internal structural changes to tune superatom properties.

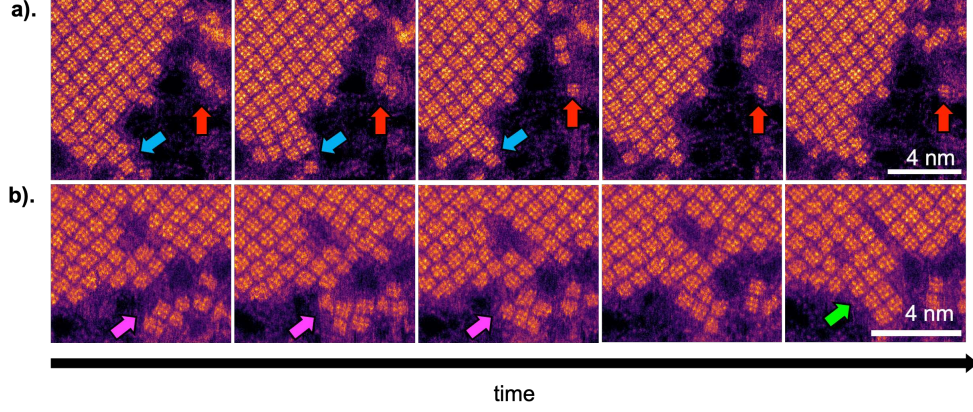


Fig. 4 Movies show superatoms are the building blocks of 2D superatomic crystals. **a**, Series of selected HAADF image frames showing a single superatom breaking off from a small cluster and residing alone on the substrate for over one minute (red arrow). A superatom detaches from the lattice and reattaches one frame later (blue arrow). **b**, Series of selected HAADF image frames showing a small cluster of superatoms reconfiguring at a distance, to align with the large crystal before attachment (purple arrow). After attachment, the small cluster recrystallizes into the larger crystal (green arrow).

The electronic-structure calculations support the interpretation of this material as more than a weakly bound molecular assembly. Binding energies and difference-charge-density maps indicate bonding stronger than van der Waals interactions, while the band structures suggest metallic behavior in the two-dimensional crystal. Future work should connect these calculations to experimental probes of electronic structure and determine how central-site occupancy, vacancies, dislocations, and grain boundaries modify the superatomic orbitals.

The movies in this study then extend the structural and electronic picture into dynamics, showing that individual superatoms, small clusters, vacancies, dislocations, and grain boundaries can be observed directly as they evolve. A central consideration in these experiments is the dual role of the electron probe as both the interrogation probe and the energy pump, two functions which are often in tension.

The most compelling future direction is to connect synthesis, structure, and dynamics into a quantitative model of superatom crystallization. Combined with automated tracking, simulation, and controlled electron-probe activation, this system could become a test bed for crystallization mechanisms in which the fundamental building block is not a single atom, but an atomically precise cluster.

6 Conclusions

In summary, $\text{Pd}_6\text{Se}_{20}$ and $\text{Pd}_6\text{Se}_{21}$ clusters form a ligand-free, 2D superatomic crystal in which discrete, atom-like building blocks retain their identity, while participating in strong, electronically coherent inter-unit bonding within an extended lattice. By operating in a regime where crystallization dynamics are both atomic in character and

experimentally accessible in time, this system enables direct visualization of nucleation, growth, and defect evolution at the level of individual building units. These results establish superatomic crystals as a platform for interrogating the fundamental mechanisms of crystallization and extend the concept of the periodic 2D solid into a regime defined by engineered, cluster-based constituents.

7 Methods

7.1 Pulsed laser deposition

An amorphous precursor film with nominal stoichiometry Pd_3Se_8 and thickness of 8 nm was deposited onto a graphene-covered TEM grid via pulsed laser deposition (PLD) at room temperature. A KrF excimer laser (248 nm, pulse duration 25 ns) was used to sequentially ablate PdSe_2 and Se targets in cycles of five pulses of PdSe_2 and one pulse of Se at 1.1 Hz, until reaching a total of 140 pulses of PdSe_2 and 28 pulses of Se. This ratio was chosen to achieve the desired precursor composition, calculated by deposition rate of each target. For PdSe_2 target ablation, the laser spot size was 0.015 cm^2 with laser energy of 30 mJ for a fluence of 2 J/cm^2 , which gave a deposition rate of 0.654 Å/pulse . For Se target ablation, laser spot size was 0.027 cm^2 , with laser energy of 55 mJ, for a fluence of 2 J/cm^2 , which gave a deposition rate of 0.414 Å/pulse . The PdSe_2 target-substrate distance was 5 cm, and the Se target-substrate distance was 10 cm. Depositions were conducted in 100 mTorr Ar, in a soft-landing regime which preserved the amorphous nature of the deposited precursor. Pre-ablation of targets was critical for consistent precursor production and was carried out for 2000 pulses at 20 Hz on each target with the substrate shielded. The final 8 nm thickness was determined via AFM performed with a Bruker Dimension Icon AFM in tapping mode with a Si probe (TESPA-V2, 7 nm tip radius, 37 N m^{-1} spring constant).

7.2 *In situ* laser synthesis

The superatoms are synthesized by encapsulating an amorphous, Se-rich PdSe precursor (a-PdSe) between two graphene layers. This encapsulation preserves stoichiometry during processing and stabilizes the material under ambient conditions for at least one year. Local laser irradiation of the graphene-encapsulated precursor (20 mJ, $200\text{ }\mu\text{s}$) induces crystallization into the superatomic phase. Superatom formation is robust across a wide range of processing conditions and can also be achieved by thermal annealing on a hot plate at temperatures as low as 70°C . While the superatoms themselves remain stable across these conditions, the influence of processing parameters on long-range crystal morphology is still under active investigation.

7.3 Graphene transfers

Graphene was transferred onto the TEM grid following a standard procedure [34]. After deposition of the amorphous precursor another graphene layer was transferred via the same procedure, excepting any heating. This is crucial in preserving the amorphous state of the precursor.

7.4 Scanning transmission electron microscopy

HAADF-STEM images and image series were captured with a probe-corrected Thermo Scientific Spectra 300 operating at 60 kV accelerating voltage with a convergence angle of 30 mrad and collection angle of 80–200 mrad. The nominal screen current varied over the experiments, using 30–60 pA for still images and 90 pA for image series designed to induce superatom motion. Samples were cleaned prior to imaging according to this procedure [35].

7.5 Density functional theory

Density functional theory calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [36, 37] with projector augmented-wave potentials [38] and Perdew–Burke–Ernzerhof exchange-correlation functionals [39]. The B88 nonlocal van der Waals density functional was used to automatically include van der Waals interactions [40], except for one calculation with the Grimme DFT-D2 functional [41] to estimate the explicit van der Waals contribution. For Brillouin-zone integration, an in-space KSPACING of $0.25 \text{ \AA}^{-1}$ was used, along with a cutoff energy of 300 eV. After finding the approximate ground-state in-plane lattice constants with fixed-lattice-parameter calculations, which were used to establish the binding-energy curves in Fig. 2a, and an out-of-plane lattice parameter of 25 Å, final relaxation of the structure was performed with fixed-volume relaxation. The relaxed lattice parameters for $\text{Pd}_6\text{Se}_{20}$ and $\text{Pd}_6\text{Se}_{21}$ are 8.33 Å and 8.44 Å, respectively, with mixed structures following a rule of mixtures. Band-structure paths in the Brillouin zone were determined with SeeK-path [42].

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Declarations

Author contributions

ACH: Conceptualization (equal); writing—original draft (lead); writing—review and editing (equal); data curation (lead); methodology (lead); visualization (lead); investigation (lead). SBH: Conceptualization (equal); writing—original draft (supporting); writing—review and editing (equal); data curation (supporting); methodology (supporting); investigation (supporting). WW: Data curation (equal); investigation (supporting); writing—review and editing (supporting). DY: Investigation (supporting). IV: Investigation (supporting). DBG: Writing—review and editing (supporting).

KX: Funding acquisition (lead); resources (equal); writing—review and editing (supporting). GD: Resources (equal); conceptualization (equal); writing—original draft (supporting); writing—review and editing (equal).

Competing interests

The authors declare no competing interests.

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