Hierarchical structural complexity in atomically precise nanocluster frameworks

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ABSTRACT

The supramolecular chemistry of nanoclusters is a flourishing area of nano-research; however, the controllable assembly of cluster nano-building blocks in different arrays remains challenging. In this work, we report the hierarchical structural complexity of atomically precise nanoclusters in micrometric linear chains (1D array), grid networks (2D array) and superstructures (3D array). In the crystal lattice, the Ag²⁹(SSR)₁₂(PPh₃)₄ nanoclusters can be viewed as unassembled cluster dots (Ag²⁹–0D). In the presence of Cs⁺ cations, the Ag²⁹(SSR)₁₂ nano-building blocks are selectively assembled into distinct arrays with different oxygen-carrying solvent molecules—Cs@Ag²⁹(SSR)₁₂(DMF)ₓ as 1D linear chains (Ag²⁹–1D), Cs@Ag²⁹(SSR)₁₂(NMP)ₓ as 2D grid networks (Ag²⁹–2D), and Cs@Ag²⁹(SSR)₁₂(TMS)ₓ as 3D superstructures (Ag²⁹–3D). Such self-assemblies of these Ag²⁹(SSR)₁₂ units have only not been observed in their crystalline state, but also in their amorphous state. Due to the diverse surface structures and crystalline packing modes, these Ag²⁹-based assemblies manifest distinguishable optical absorptions and emissions in both solutions and crystallized films. Furthermore, the surface areas of the nanocluster crystals are evaluated, the maximum value of which occurs when the cluster nano-building blocks are assembled into 2D arrays (i.e. Ag²⁹–2D). Overall, this work presents an exciting example of the hierarchical assembly of atomically precise nanoclusters by simply controlling the adsorbed molecules on the cluster surface.

Keywords: hierarchical structural complexity, atomically precise nanocluster, 1D linear chain, 2D grid network, 3D superstructure

INTRODUCTION

The past two decades have witnessed significant research efforts on atomically precise metal nanoclusters [1–26]. Amongst the nanocluster science, the self-assembly of cluster building blocks has been the subject of an intense investigation to achieve a wide range of multi-dimensional nanomaterials with ordered architectures [27–39]. Such assemblies originate in different types of inter-cluster interactions such as chemical bonding, hydrogen bonding, electrostatic, van der Waals, π⋯π and C-H⋯π interactions [27,28]. On one hand, these cluster-based aggregates typically display enhanced performance (e.g. stability and fluorescence) relative to their constituent cluster building blocks owing to the synergy from the cluster—linker—cluster assembly system [27–39]. On the other hand, the precise structures of nanoclusters allow for the atomic-level understanding of inter-cluster interaction modes, and such knowledge further guides us to controllably constitute assembled cluster-based nanomaterials [27–39].

In general, nanocluster building blocks are assembled via the introduction of inter-cluster linkers (e.g. sulfur/nitrogen-carrying, multi-dentate molecules)—the covalent interactions between sulfur/nitrogen terminals of linkers and the Au/Ag surface atoms of nanoclusters are exploited to motivate the inter-cluster assembly [40–47]. For instance, by altering the bidentate nitrogenous linkers, Zang and co-workers constructed a series of 1D-to-3D Ag₁₄ cluster-assembled nanomaterials [40]. Lei et al. presented the self-assembly of Ag₆Au₆ clusters by forming both inward and outward Ag-N interactions [45]. In both cases, the
assembled modes can be dictated by the control over the nitrogen-carrying linkers [40–45].

Most recently, we have proposed a novel cluster-assembly pattern, namely, capturing Cs\(^+\) cations and dimethylformamide (DMF) molecules onto the nanocluster surface [48]. Specifically, in the crystal lattice, the Cs\(^+\)–DMF–cluster interactions assemble the Ag\(_{29}\)(SSR)\(_{12}\) nano-building blocks into 1D linear chains (SSR = 1,3-benzenedithiol) [48]. Considering that such an assembly largely relies on the Cs\(^+\)–O interactions (the O junction site comes from the DMF), we perceive a good opportunity to control the assembly modes of Ag\(_{29}\)(SSR)\(_{12}\)—simply altering the oxygen-carrying solvents in the crystallization.

Herein, the Ag\(_{29}\)(SSR)\(_{12}\) nanocluster building blocks are selectively assembled into micrometric linear chains (1D array), grid networks (2D array) and superstructures (3D array), and such hierarchical constructions are determined by the single crystal X-ray diffraction (SC-XRD). Specifically, the presence of PPh\(_3\) (or the absence of Cs\(^+\)) yields unassembled cluster dots (Ag\(_{29}\)(SSR)\(_{12}\)(PPh\(_3\))\(_4\), Ag\(_{29}\)–0D). By comparison, when the Cs\(^+\) cations are captured on the nanocluster surface with different oxygen-carrying solvent molecules, the Ag\(_{29}\)(SSR)\(_{12}\) nano-building blocks are selectively assembled into distinct arrays (Scheme 1)—the capture of Cs\(^+\)-DMF on Ag\(_{29}\)(SSR)\(_{12}\) producing 1D linear chains (Cs@Ag\(_{29}\)(SSR)\(_{12}\)(DMF))\(_x\), Ag\(_{29}\)–1D), the capture of Cs\(^+\)-NMP on Ag\(_{29}\)(SSR)\(_{12}\) making up 2D grid networks (Cs@Ag\(_{29}\)(SSR)\(_{12}\)(NMP))\(_x\), Ag\(_{29}\)–2D; NMP = N-methyl-2-pyrrolidone), and the capture of Cs\(^+\)-TMS giving rise to 3D superstructures (Cs@Ag\(_{29}\)(SSR)\(_{12}\)(TMS))\(_x\), Ag\(_{29}\)–3D; TMS = tetramethylene sulfone). Besides, the 1D–3D assemblies of these Ag\(_{29}\)(SSR)\(_{12}\) nano-building blocks have not only been observed in their crystalline state, but also in their amorphous state, with the help of the aberration-corrected high angle annular dark field scanning transmission electron microscope (HAADF-STEM). Furthermore, the optional assembly modes result from different cluster–Cs–solvent interactions. Because of the different surface structures and crystalline packing modes, these Ag\(_{29}\)-based assemblies manifest distinguishable optical absorptions and emissions in both solutions and crystallized films. Moreover, the surface areas and pore size distributions of the crystals of these nanoclusters are evaluated, and the maximum value of the surface area is reached when the cluster nano-building blocks are assembled into 2D arrays (i.e. Ag\(_{29}\)–2D).
RESULTS AND DISCUSSION

Ag_{29}–0D cluster dot and Ag_{29}–1D linear chain

The Ag_{29}(SSR)_{12} framework is composed of an icosahedral Ag_{13} kernel that is stabilized by an Ag_{12}(SSR)_{12} shell, and the obtained Ag_{29}(SSR)_{12} structure is further capped by four bare Ag atoms with a tetrahedral pattern (Fig. S1) [49,50]. Although the Ag_{29}(SSR)_{12} compound could exist in isolation, its four Ag terminals have a strong disposition to be sealed by the introduced PPh_{3} ligand, giving rise to the Ag_{29}(SSR)_{12}(PPh_{3})_{4} (Ag_{29}–0D) nanocluster (Figs 1A and S2A). In the crystal lattice, all Ag_{29}–0D entities are independent without any direct inter-cluster interactions in either direction (Fig. 1B–D). Accordingly, the presence of PPh_{3} with Ag_{29}(SSR)_{12} yields the unassembled cluster dots, representing the zero-dimensional arrangement of the Ag_{29} cluster entities in the crystalline cell.

The capture of Cs\(^{+}\) cations with Ag_{29}–0D dissociates the PPh_{3} ligands from the nanocluster surface, giving rise to Cs\(_{5}\)Ag_{29}(SSR)_{12}(DMF)\(_{x}\) (Ag_{29}–1D) nano-building block (Fig. 1E). In the crystal lattice, all Ag_{29}–0D entities are independent without any direct inter-cluster interactions in either direction (Fig. 1B–D). This openness, together with the presence of PPh_{3} with Ag_{29}(SSR)_{12} yields the unassembled cluster dots, representing the zero-dimensional arrangement of the Ag_{29} cluster entities in the crystalline cell.

Besides, the interactions among the cluster framework, the Cs\(^{+}\) cations, and the DMF molecules assemble the Ag_{29}(SSR)_{12} nano-building blocks into cluster-based linear chains (Fig. 1F and G). As shown in Figs 1G and S3, the Ag_{29}–1D linear chains extend along the y axis, and the inter-chain distance between two adjacent cluster lines along the z direction is 17.291 Å [48]. Collectively, the introduction of Cs\(^{+}\) cations and DMF molecules onto the Ag_{29} nanocluster surface assembles the cluster dots into linear arrays, representing the 1D arrangement of the Ag_{29} cluster entities in the crystalline cell.

Ag_{29}–2D grid networks

Considering that the aforementioned 1D assembly largely relies upon the Cs\(^{+}\)–O interactions where the oxygen junction site comes from the DMF, we perceive a good opportunity to tailor the assembled modes of Ag_{29}(SSR)_{12} nano-building blocks—altering the oxygen-carrying solvents in the crystallization. We first replaced DMF molecules in Ag_{29}–1D into NMP to produce the Cs\(_{5}\)Ag_{29}(SSR)_{12}(NMP)\(_{x}\) (Ag_{29}–2D; see the Methods Section for the detailed preparation). Significantly, the 2D-array assembly of Ag_{29} cluster entities was accomplished in the crystal lattice (Fig. 2). Structurally, the nano-building block of Ag_{29}–2D contains two Ag_{29}(SSR)_{12} compounds, six Cs\(^{+}\) cations, and several NMP molecules (Figs 2A, B and S2C). The two Ag_{29}(SSR)_{12} compounds...
Figure 2. Crystal structure and crystalline packing mode of Ag$_{29}$–2D. (A, B) Crystal structure (nano-building block) of Ag$_{29}$–2D. The two adjacent Ag$_{29}$ cluster units are in differently twisting angles. (B) is the enlargement of the circled section in (C). (C) Packing of Ag$_{29}$–2D grid network in the crystal lattice, viewed from the plane (001). (D–F) Packing of Ag$_{29}$–2D in the crystal lattice: view from the $x$ axis (D), $y$ axis (E) and $z$ axis (F). (G) Packing of Ag$_{29}$–2D in the crystal lattice from the $x$ axis with a certain rotation, for observing the assembled grid networks more intuitively. As depicted in (D, G), the inter-layer distance is 14.622 Å. Color codes: light blue/orange/blue sphere/stick, Ag; yellow/red sphere/stick, S; grey sphere/stick, C; green sphere/stick, O; dark purple sphere/stick, Cs. For clarity, all H, N atoms, some C, Cs$^+$ atoms and NMP molecules are omitted. Each green atom (O) represents an NMP molecule.

are in different twisting angles, and are mutually connected by two Cs$^+$ cations (Cs1 and Cs1’) through Cs–C and Cs–π interactions (Fig. 2A and B). In addition, the inter-cluster assembly is induced by the outward interactions from four Cs$^+$ conjunction sites—Cs2, Cs2’, Cs4 and Cs4’. The Cs4 is bonded on the nanocluster surface through Cs4-NMP-Cs3-cluster interactions (the same to Cs4’), whereas the Cs2 is directly anchored onto the nanocluster surface by Cs–C interactions (the same to Cs2’). Of note, the Cs4 (or Cs4’) on one cluster nano-building block also acts as the Cs2 (or Cs2’) of the adjacent block. In this context, the number of Cs$^+$ cations in each nano-building block is six, and the ratio between [Ag$_{29}$(SSR)$_{12}$]$^{3-}$ and Cs$^+$ is exactly 1:3, for achieving the charge balance (Fig. 2A and B).

For the 2D-array assembly, each [Cs$_6$@Ag$_{29}$(SSR)$_{12}$(NMP)$_x$]$_2$ unit is adjacent to four identical units through the four Cs$^+$ conjunction sites, making up an Ag$_{29}$-based, two-dimensional grid network (Fig. 3B and C). The grid network extends along the (001) plane, or both $x$ and $y$ axes (Fig. 3C–G). Along the $z$ direction, the two neighboring networks display no interaction, but are in a face-symmetric relationship (the two types of layers are labeled in blue and orange of Ag atoms in Fig. 3D–G). In this context, the assembly of Ag$_{29}$–2D in the crystal lattice follows an ABAB layer-by-layer packing mode. The inter-layer distance (from kernel Ag to kernel Ag, as shown in Fig. 2D and G) between two adjacent networks is 14.622 Å. Overall, the capture of Cs$^+$ and NMP of the Ag$_{29}$(SSR)$_{12}$ framework enables the self-assembly of cluster dots into grid networks, representing the two-dimensional arrangement of the Ag$_{29}$ nano-building blocks in the crystalline cell.

Ag$_{29}$–3D superstructure

The further substitution of oxygen-carrying solvent molecules (DMF of Ag$_{29}$–1D, or NMP of Ag$_{29}$–2D) into TMS yields Cs@Ag$_{29}$(SSR)$_{12}$(TMS)$_x$ (Ag$_{29}$–3D; see the Methods Section for the detailed preparation), which follows a 3D-array assembly in the crystal lattice (Figs 3 and S2D). To the nano-building block of Ag$_{29}$–3D, all Cs$^+$ cations are directly anchored onto the nanocluster surface through Cs–C interactions (Fig. 3A). For each Ag$_{29}$–3D nano-building block, there are six Cs$^+$ conjunction sites that are subordinate to two categories: inward Cs1, Cs1’ and Cs1” that are simply bonded on the nanocluster surface, and outward Cs2, Cs2’ and Cs2” that induce the inter-cluster assembly (Fig. 3A and B).

For the 3D-array assembly (Fig. 3C), each Ag$_{29}$–3D nano-building block is surrounded by six adjacent nanoclusters including three cluster1 (labeled

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Figure 3. Crystal structure and crystalline packing mode of Ag29–3D. (A, B) Crystal structure (nano-building block) of Ag29–3D. (B) is the enlargement of the circled section in (C). Each Ag29–3D cluster is surrounded by six adjacent Ag29–3D nanoclusters including three cluster1 and three cluster2, giving rise to the 3D superstructure of Ag29 nano-building blocks. (D) Packing of the Ag29–3D superstructure in the crystal lattice, viewed from the plane (001). (E–G) Packing of Ag29–3D in the crystal lattice: view from the x axis (E), y axis (F) and z axis (G). (H) Packing of Ag29–3D in the crystal lattice from the x axis with a certain rotation, for observing the assembled superstructure more intuitively. Color codes: light blue/blue/orange/magenta sphere/stick, Ag; yellow/red sphere/stick, S; grey sphere/stick, C; dark purple sphere/stick, Cs. For clarity, all H, O, N atoms, some C, Cs+ atoms and TMS molecules are omitted. Each green atom (O) represents a TMS molecule.

Comparison of crystal structures and packing modes

Due to the different surfaces, these Ag29 nanoclusters (Ag29–0D, Ag29–1D, Ag29–2D, and Ag29–3D) exhibited distinct crystal structures and crystalline packing modes (Figs S4 and S5, and Tables S1 and S2). Although the overall Ag29(SSR)12 configuration retained from Ag29–0D to Ag29–1D, Ag29–2D and Ag29–3D, obvious changes have been observed by comparing the corresponding bond lengths. Specifically, all of the three types of Ag–Ag interactions (Ag(core)–Ag(icosahedral shell), Ag(icosahedral shell)–Ag(icosahedral shell), and prism-like Ag(icosahedral shell)–Ag(motif) bonds) in Cs@Ag29 nanoclusters (Ag29–1D, Ag29–2D, and Ag29–3D) were much longer than those in the PPh3@Ag29 nanocluster (Ag29–0D), demonstrating an expanding trend of the overall framework along with the PPh3 dissociated process (Fig. S4A–C and Table S1). For the pyramid-like interactions between the vertex Ag and the icosahedral Ag, the bond lengths were all close to 3.04 Å for Cs@Ag29 nanoclusters. However, no analogous interaction was observed in the PPh3@Ag29 nanocluster since the corresponding distances ranged from 3.493 to 3.643 Å (Fig. S4D and Table S1). In this context, the vertex Ag atoms became closer to the icosahedral kernel when the Ag29–0D nanocluster was transformed into Ag29–1D, Ag29–2D and Ag29–3D, and the newly generated Ag4 pyramids were anticipated to make the Ag29(SSR)12 framework more robust.

The chemical environments of Cs+ ions in different Ag29-based assemblies have been compared. For Ag29–1D, three Cs+ ions (Cs1, Cs2 and Cs3) stabilize the cluster surface and the other
three Cs\(^+\) ions (Cs4, Cs5 and Cs6) assemble Ag29 nano-building blocks into 1D linear chains (Fig. 1). For Ag29–2D, all Cs\(^+\) ions are used to activate the assembly of cluster nano-building blocks into 2D grid networks (Fig. 2). For Ag29–3D, the inward Cs\(^+\) ions (Cs1, Cs1’ and Cs1”\(^+\)) stabilize the cluster surface, and the outward Cs\(^+\) ions (Cs2, Cs2’ and Cs2”\(^+\)) induce the inter-cluster assembly of cluster nano-building blocks into 3D superstructures (Fig. 3). Of note, only the presence of Cs\(^+\) can induce the assembly of Ag29 nano-building blocks; by comparison, the Ag29–0D nanocluster maintains its structure in the presence of Li\(^+\), Na\(^+\) or K\(^+\) cations [48].

The crystalline packing modes of these Ag29-based assemblies were further compared (Fig. S5 and Table S2). Of note, two types of crystallization patterns of Ag29–0D have been reported—Ag29–0D-cubic and Ag29–0D-trigonal—due to their different crystallization processes [49,50]. Because of the distinct interactions among Ag29 clusters, Cs\(^+\) cations and solvent molecules, Ag29–1D, Ag29–2D and Ag29–3D were also crystallized in different systems. Specifically, although both Ag29–1D and Ag29–2D follow an orthorhombic packing mode, their unit cell parameters (i.e. values of a, b, c) were totally different (Table S2). The Ag29–3D displayed a cubic packing mode, the same as that of Ag29–0D-cubic, whereas the unit size of Ag29–3D was remarkably smaller than the Ag29–0D-cubic (14375 Å\(^3\) versus 40006 Å\(^3\); see details in Table S2). Such differences reflected both the molecular effects of the Cs\(^+\) capture and the solvent effects in affecting nanocluster geometric structures and crystalline packing patterns.

Notably, the hierarchically 1D-, 2D- and 3D-array assemblies of Ag29 building blocks have not only been observed in their crystalline state, but also in their amorphous state. Specifically, the aberration-corrected HAADF-STEM images of Ag29–0D, Ag29–1D, Ag29–2D and Ag29–3D nanoclusters were obtained by recording the drying solutions of these nanoclusters on carbon films. The Ag29–0D cluster entities were still discrete under the microscope vision (Fig. S6A), whereas some linear assembled Ag29–1D clusters were discovered (Fig. S6B). Given that Ag29–0D and Ag29–1D were controlled to the same concentration in the aberration-corrected HAADF-STEM detection, the 1D-array assembly of Ag29–1D indeed existed in its non-crystalline state. Figure S6C and D exhibited the HAADF-STEM images of Ag29–2D and Ag29–3D. Of note, for promoting the 2D-array and 3D-array assemblies of these two nanoclusters, the concentrations of them were much higher than in Ag29–0D and Ag29–1D. Compared with Ag29–1D, which displayed the linear assembly, the Ag29–2D nano-building blocks were more inclined to be aggregated with a 2D-array reticular pattern (Fig. S6C). Furthermore, although most cluster entities were discrete in the HAADF-STEM image of Ag29–3D, several cluster-based, 3D aggregates have been observed (Fig. S6D), which unambiguously demonstrated the 3D-array assembly of some Ag29(SSR)\(_{12}\) cluster entities. To sum up, the introduction of Cs\(^+\) cations and oxygen-carrying solvents was also able to induce the self-assembly of Ag29(SSR)\(_{12}\) nano-building blocks in the non-crystalline state.

**Characterization of Ag29-based assemblies**

The electrospray ionization mass spectrometry (ESI-MS) measurement was firstly performed to verify the specific composition of each nanocluster (Fig. S7). Mass spectra of Ag29–0D showed five peaks that corresponded to [Ag29(SSR)\(_{12}\)(PPh3)\(_3\)]\(^-\), [Ag29(SSR)\(_{12}\)(PPh3)\(_2\)]\(^-\), [Ag29(SSR)\(_{12}\)(PPh3)\(_1\)]\(^-\), [Ag29(SSR)\(_{12}\)(PPh3)]\(^+\) and [Ag29(SSR)\(_{12}\)]\(^+\), respectively, in good agreement with the reported ‘dissociation-aggregation pattern’ of the PPh3 ligands on the Ag29–0D surface (Fig. S7A) [51]. These PPh3-containing signals were absent in the spectra of Cs@Ag29 nanoclusters because the PPh3 ligands had been dissociated from the nanocluster surface induced by the Cs\(^+\) capture. Two intense peaks, matching with the [Ag29(SSR)\(_{12}\)]\(^+\) and [CsAg29(SSR)\(_{12}\)]\(^+\) compounds, were observed for each mass spectrum of Ag29–1D, Ag29–2D or Ag29–3D (Fig. S7B–D), which verified the Cs\(^+\) capture in these nanoclusters. However, as to the mass spectra of each Cs@Ag29 nanocluster, only the single Cs\(^+\)-adhered Ag29 compound (i.e. CsAg29(SSR)\(_{12}\)) could be detected. The unattained mass signals of the complete Cs@Ag29 molecules resulted from the weak interactions among the Ag29(SSR)\(_{12}\) frameworks, the Cs\(^+\) cations, and the solvent molecules when the nanoclusters were in solutions.

\(^{133}\)Cs and \(^{31}\)P nuclear magnetic resonance (NMR) were then recorded to validate the capture of PPh3 ligands or Cs\(^+\) ions on the Ag29 nanocluster surface. As depicted in Fig. S8A, the \(^{133}\)Cs NMR of CH\(_3\)COOCs showed an intense signal at 72.74 ppm, and this signal shifted to high fields (69.35 ppm for Ag29–1D, 70.11 ppm for Ag29–2D and 70.30 ppm for Ag29–3D) when the Cs\(^+\) cations were captured by the Ag29(SSR)\(_{12}\) framework. The different \(^{133}\)Cs NMR signals of Cs@Ag29 nanoclusters originated in the distinct cluster–Cs–solvents interactions of these Ag29-based assemblies. Besides, the
intense $^{31}$P NMR signal of Ag$_{29}$–0D at 26.20 ppm disappeared after the PPh$_3$ ligands were dissociated from the nanocluster surface (Fig. S8B); that is, no phosphine signal was observed in the $^{31}$P NMR of Cs$_8$@Ag$_{29}$ nanoclusters.

The structures of nanoclusters are determinant of their physical-chemical properties. Due to their distinct surface structures and crystalline packing modes, these Ag$_{29}$–based assemblies manifested distinguishable optical absorptions and emissions in both solutions and crystallized films. Of note, the solution-state UV-vis and photoluminescence (PL) spectra of Ag$_{29}$–0D and Ag$_{29}$–1D were monitored in DMF, whereas Ag$_{29}$–2D was in NMP and Ag$_{29}$–3D was in TMS. The optical absorptions of these Ag$_{29}$ nanoclusters in the solution state were very similar (Fig. 4A, solid lines)—an intense peak at 445 nm and a shoulder band at 365 nm. Such a similarity might result from the fact that the molecularly electronic transitions of these nanoclusters mainly originated in their almost identically inner Ag$_{29}$(SSR)$_{12}$ framework. For the PL, all nanocluster solutions emitted when illuminated at 445 nm (Fig. 4A, dotted lines); however, remarkable differences took place. The DMF solutions of both Ag$_{29}$–0D and Ag$_{29}$–1D emitted at 640 nm, whereas the emission wavelengths of Ag$_{29}$–2D (in NMP) and Ag$_{29}$–3D (in TMS) exhibited obvious blue-shifts, of which Ag$_{29}$–2D emitted at 625 nm and Ag$_{29}$–3D luminesced at 622 nm. Furthermore, the PL intensities of Ag$_{29}$–0D, Ag$_{29}$–1D and Ag$_{29}$–3D showed 1.7-, 2.1- and 2.3-fold enhancement, respectively, relative to that of Ag$_{29}$–2D with the lowest PL intensity. These differences reflected both the structural effect and the solvent effect on nanocluster emissions.

The nanocluster crystallized films exhibited apparent differences in both optical absorptions and emissions (Fig. 4B). The UV-vis spectrum of each nanocluster presented an intense absorption at 455 nm; however, the features of these spectra varied greatly—the 455 nm signal of Ag$_{29}$–2D was much more intense than those of other nanoclusters, and the UV-vis spectrum of Ag$_{29}$–1D showed a broad shoulder band at 550 nm that was absent for other nanoclusters (Fig. 4B, solid lines). The normalized emissions of these Ag$_{29}$ nanoclusters in crystallized films were further compared. Both Ag$_{29}$–0D and Ag$_{29}$–1D films were singly emissive: the former emitted at 700 nm and the latter emitted at 670 nm. Of note, the Ag$_{29}$–0D film emitted at 700 nm when crystallized in the cubic unit cell, or at 670 nm when crystallized in the trigonal unit cell [50]. By comparison, both Ag$_{29}$–2D and Ag$_{29}$–3D films were dual-emissive: although the two of them luminesced at 680 and 725 nm, the shoulder emission (725 nm) of Ag$_{29}$–3D was more distinguishable than that of the Ag$_{29}$–2D (Fig. 4B, dotted lines). The conspicuous differences in emissions of these Ag$_{29}$–based assemblies in different forms (crystal film and solution)
arose from distinct combinations of the electronic coupling and the lattice-origin, non-radiative decay pathways occurring through electron-phonon interactions [49,52,53]. Besides, these differences can also be explained in terms of the diverse surface chemistry of these nanoclusters: the PPh3 ligand surface of Ag_{29}-0D, and the distinct cluster-Cs-solvents surfaces of Ag_{29}-1D, Ag_{29}-2D and Ag_{29}-3D.

Because of their different crystalline packing modes, these Ag_{29}-based assemblies should exhibit distinctive surface areas. Herein, the nitrogen adsorption–desorption tests were performed on the crystals of these Ag_{29} nanoclusters for evaluating their specific surface area and pore size distribution (Figs 4C–F and S9). The values of the specific surface areas of Ag_{29}-0D, Ag_{29}-1D and Ag_{29}-3D were all below 10 m²/g (about 6, 4 and 8 m²/g for Ag_{29}-0D, Ag_{29}-1D and Ag_{29}-3D, respectively). By comparison, the Ag_{29}-2D crystal generated a much bigger specific surface area of about 19 m²/g. In this context, as to this Ag_{29} system, the nanocluster crystals would expose the maximum surface areas when the cluster nano-building blocks were assembled into 2D arrays. Indeed, compared with other cluster crystals, the Ag_{29}-2D crystal presented larger pore sizes (Fig. 4C–F, insets).

CONCLUSION

The cluster-based 1D linear chains, 2D grid networks and 3D superstructures were selectively constructed by the self-assembly of Ag_{29}(SSR)_{12} nano-building blocks with different solvent-conjoining Cs⁺ cations. In the absence of Cs⁺ cations, the bare Ag atoms on Ag_{29}(SSR)_{12} were prone to be stabilized by PPh₃ ligands, producing the unassembled cluster dots in the crystal lattice. In the presence of Cs⁺ cations, the Ag_{29}(SSR)_{12} units could be selectively assembled into different arrays with different oxygen-carrying solvents: Cs@Ag_{29}(SSR)_{12}(DMF)ₓ as 1D linear chains with the DMF solvent, Cs@Ag_{29}(SSR)_{12}(NMP)ₓ as 2D grid networks with the NMP solvent, and Cs@Ag_{29}(SSR)_{12}(TMS)ₓ as 3D superstructures with the TMS solvent. Besides, the 1D–3D self-assemblies of these Ag_{29}(SSR)₁₂ nano-building blocks have not only been observed in their crystalline state, but also in their amorphous state, with the help of the aberration-corrected HAADF-STEM. Such Ag_{29}-based assemblies manifested distinguishable optical absorptions and emissions in both solutions and crystallized films, and these differences originated from their different surface structures and crystalline packing modes. The surface areas of these Ag_{29} crystals were evaluated, and the 2D-array assembled nanocluster (i.e. Ag_{29}-based grid networks) displayed the maximum value of the surface area. Overall, this work presents the hierarchical assembly of atomically precise nanoclusters by simply controlling the adsorbed molecules on the cluster surface, which hopefully sheds light on more future works touching upon the supramolecular chemistry of metal nanoclusters.

METHODS

Materials

All reagents were purchased from Sigma-Aldrich and used without further purification: silver nitrate (AgNO₃, 99%, metal basis), triphenylphosphine (PPh₃, 99%), 1,3-benzene dithiol (SSR, 99%), sodium borohydride (NaBH₄, 99.9%), cesium acetate (CH₃COO Cs, 99%), methylene chloride (CH₂Cl₂, HPLC, Sigma-Aldrich), methanol (CH₃OH, HPLC, Sigma-Aldrich), N,N-dimethylformamide (DMF, HPLC, Sigma-Aldrich), N-methyl-2-pyrrolidone (NMP, HPLC, Sigma-Aldrich), tetramethylene sulfone (TMS, HPLC, Sigma-Aldrich), and ethyl ether ((C₂H₅)₂O, HPLC, Sigma-Aldrich).

Syntheses and crystallization

Synthesis of [Ag_{29}(SSR)₁₂(PPh₃)₄]³⁻ (Ag_{29}-0D) The preparation of Ag_{29}-0D was based on the reported method of the Bakrgroup [49,50].

Synthesis of Cs@Ag_{29}(SSR)₁₂(DMF)ₓ (Ag_{29}-1D) The preparation of Ag_{29}-1D was based on the reported method of the Zhu group [48].

Synthesis of Cs@Ag_{29}(SSR)₁₂(NMP)ₓ (Ag_{29}-2D) The 50-mg Ag_{29}-1D crystal was dissolved in 5 mL of NMP under vigorous stirring. This NMP solution was poured into 200 mL of CH₂Cl₂, and the precipitate was collected and further dissolved in 5 mL of NMP, producing the Ag_{29}-2D nanocluster. The yield was 95% based on the Ag element (calculated from Ag_{29}-1D). This NMP solution of Ag_{29}-2D was directly used for the crystallization and the characterization.

Synthesis of Cs@Ag_{29}(SSR)₁₂(TMS)ₓ (Ag_{29}-3D) The 50-mg Ag_{29}-1D crystal was dissolved in 5 mL of TMS under vigorous stirring. This TMS solution was poured into 200 mL of CH₂Cl₂, and the precipitate was collected and further dissolved in 5 mL of
TMS, producing the $\text{Ag}_{29}–3\text{D}$ nanocluster. The yield was 95% based on the Ag element (calculated from $\text{Ag}_{29}–1\text{D}$). This TMS solution of $\text{Ag}_{29}–3\text{D}$ was directly used for the crystallization and the characterization.

Crystallization of $\text{Ag}_{29}–2\text{D}$ and $\text{Ag}_{29}–3\text{D}$

Single crystals of $\text{Ag}_{29}–0\text{D}$ and $\text{Ag}_{29}–1\text{D}$ were cultivated based on the reported methods [48, 49]. Single crystals of $\text{Ag}_{29}–2\text{D}$ and $\text{Ag}_{29}–3\text{D}$ were cultivated at room temperature by diffusing methanol into the NMP solution of $\text{Ag}_{29}–2\text{D}$, or the TMS solution of $\text{Ag}_{29}–3\text{D}$. After two weeks, red crystals were collected, and the structure of $\text{Ag}_{29}–2\text{D}$ or $\text{Ag}_{29}–3\text{D}$ was determined. The CCDC numbers of $\text{Ag}_{29}–2\text{D}$ and $\text{Ag}_{29}–3\text{D}$ are 1961389 and 1941329, respectively.

Characterization

All UV-vis absorption spectra of nanoclusters were recorded using an Agilent 8453 diode array spectrometer. PL spectra were measured on a FL-4500 spectrofluorometer with the same optical density of 0.1. ESI-MS measurements were performed by MicrOTOF-QIII high-resolution mass spectrometer. The sample was directly infused into the chamber at 5 μL/min. For preparing the ESI samples, nanoclusters were dissolved in DMF/NMP/TMS (1 mg/mL) and diluted ($\nu/\nu = 1:2$) by methanol. $^{133}\text{Cs}$ and $^{31}\text{P}$ NMR spectra were acquired using a Bruker 600 Avance III spectrometer equipped with a Bruker BBO multinuclear probe (BrukerBioSpin, Rheinstetten, Germany). The $\text{Ag}_{29}$-based assemblies were imaged with an aberration-corrected HAADF-STEM technique after the solvent that contained $\text{Ag}_{29}$-based assemblies was dropped casting onto ultrathin carbon film TEM grids. The microscope employed was a FEI Themis Z. The electron beam energy was 200 kV. The collecting angle HAADF detector was used to collect signals scattered between 52 (inner angle) and 200 (outer angle) mrad (camera length of 146 mm). The aberration-corrected HAADF-STEM image was obtained by Thermo Scientific Velox software using 1024\times 1024 pixels and dwell time was set to 10 us.

Nitrogen adsorption–desorption test

The specific surface area and pore size distribution were calculated from each corresponding nitrogen adsorption–desorption isotherm by applying the Brunauer-Emmett-Teller (BET) equation on ASAP2020 M plus Physisorption. By using the quenched solid density functional theory (QSDFT), the pore size distributions were derived from the sorption data. The BET surface areas of $\text{Ag}_{29}–0\text{D}$, $\text{Ag}_{29}–1\text{D}$, $\text{Ag}_{29}–2\text{D}$ and $\text{Ag}_{29}–3\text{D}$ samples are about 6, 4, 19 and 8 m²/g, respectively. Of note, the experimental errors of the nitrogen adsorption–desorption data might be 5%–10%; however, these errors have no effect on the conclusion that $\text{Ag}_{29}–2\text{D}$ displays the maximum value of the surface area because the BET surface area of $\text{Ag}_{29}–2\text{D}$ (19 m²/g) is remarkably higher than those of the $\text{Ag}_{29}–0\text{D}$, $\text{Ag}_{29}–1\text{D}$ and $\text{Ag}_{29}–3\text{D}$ samples.

SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

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AUTHOR CONTRIBUTIONS

S.W. and M.Z. proposed and supervised the project. S.W. and M.Z. conceived and designed the experiments. X.W. and X.K. carried out the syntheses, the structural characterizations and the optical characterizations. Z.Z. and F.S. performed the HAADF-STEM characterizations. All authors discussed the results and participated in analysing the experimental results.

Conflict of interest statement. None declared.

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