

Manifestation of Structural Differences of Atomically Precise Cluster-Assembled Solids in Their Mechanical Properties

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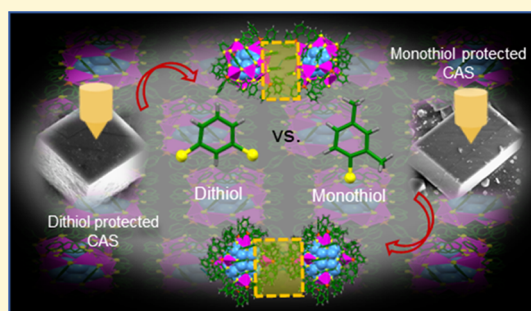


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ABSTRACT: Cluster-assembled solids (CASs) formed by the self-assembly of monodispersed atomically precise monolayer-protected noble metal clusters are attractive due to their collective properties. The physical stability and mechanical response of these materials remain largely unexplored. We have investigated the mechanical response of single crystals of atomically precise dithiol-protected Ag_{29} polymorphs, monothiol-protected Ag_{46} , and a cocrystal of the latter with Ag_{40} (formulas of the clusters have been simplified merely with the number of metal atoms). The Ag_{29} polymorphs crystallize in cubic and trigonal lattices (Ag_{29} C and Ag_{29} T, respectively), and Ag_{46} and its cocrystal with Ag_{40} crystallize in trigonal and monoclinic lattices (Ag_{46} T and $\text{Ag}_{40/46}$ M, respectively). The time and loading-rate-dependent mechanical properties of the CASs are elucidated by measuring nanoindentation creep and stress relaxation. The obtained Young's modulus (E_r) values of the CASs were similar to those of zeolitic imidazolate frameworks (ZIFs) and show the trend Ag_{29} T > Ag_{29} C > $\text{Ag}_{40/46}$ M > Ag_{46} T. We have also studied the viscoelastic properties of all of the four CASs and found that the value of $\tan \delta$ /damping factor of monothiol-protected Ag_{46} T was higher than that of other CASs. The unusual mechanical response of CASs was attributed to the supramolecular interactions at the surface of nanoclusters. This observation implies that the stiffness and damping characteristics of the materials can be modulated by ligand and surface engineering. These studies suggest the possibility of distinguishing between the crystal structures using mechanical properties. This work provides an understanding that is critical for designing nanocluster devices capable of withstanding mechanical deformations.



INTRODUCTION

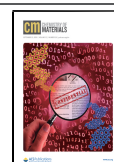
Monolayer-protected atomically precise clusters^{1,2} of noble metals are some of the most intensely studied materials of recent times. Molecular properties of these systems, such as distinct photoabsorption,^{3–5} molecular chirality,^{6,7} photoluminescence,⁸ and nonlinear optical properties,⁹ have been of interest from diverse perspectives such as sensing,¹⁰ catalysis,¹¹ and biolabeling.¹² Such molecular clusters can act as building blocks in creating self-assembled cluster materials, which are atomically precise, varied in composition, and diverse in structure. Their self-assembly can be tailored by tuning the underlying molecular or nanoscale interactions such as dipolar, van der Waals, electrostatic, and hydrogen-bonding.¹³ The archives of molecular clusters are rich with exciting properties, and therefore, the resulting cluster-assembled solids (CASs) hold the promise of high tunability in a range of material properties. The combination of atomic precision and intercluster interactions in CASs can result in novel collective properties, including tunable electrical transport,¹⁴ mechanical properties,^{15,16} magnetism,^{17,18} and luminescence,^{19,20} which have been explored only to a limited extent.

Metals, alloys, and ceramics are typically stiff and hard due to their underlying strong metallic, covalent, and ionic bonds, while the molecular crystals with weaker noncovalent interactions are softer.^{16,21–23} Such soft molecular crystals show ferroelectric^{24,25} and piezoelectric²⁶ properties that find applications in fields such as flexible electronics. The physical, chemical, and mechanical properties of materials depend on their crystal structures as well as the structural arrangements and intermolecular interactions. The mechanical properties of molecular crystals can be modulated through crystal engineering.²¹ It is known that depth-sensing techniques, such as nanoindentation (NI), can be used to study the mechanical properties of single crystals with high precision. The mechanical properties of different types of molecular materials such as active pharmaceutical ingredients (APIs),^{27–29} metal-organic frameworks (MOFs),^{30–32} hybrid organic–inorganic

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perovskites (HOIPs),^{33–35} and bio-organic peptide-based materials³⁶ have been investigated in detail using nano-indentation. These lend insights into the crystal structure–mechanical property correlations in them. Recent investigations on the three single crystals of naphthalene diimide derivatives having similar molecular structures showed different mechanical responses,³⁷ which were correlated to the weak interactions in crystal packing. The studies of Dey et al., on elastically bendable organic cocrystals of caffeine (CAF) and 4-chloro-3-nitrobenzoic acid (CNB), suggested that the exceptional mechanical stiffness and high hardness are due to the mechanically interlocked weak hydrogen-bonding networks and supramolecular interactions.³⁸ The exceptional elasticity of 2-hydroxy-5-methyl benzylidene amino phenyl-3-phenylacrylonitrile crystals in liquid nitrogen was attributed to the supramolecular interactions in the crystal.³⁹ In addition, acicular crystals of bis(acetylacetonato)copper(II) ([Cu(acac)₂]), a classic coordination compound, also displayed significant elastic flexibility without losing crystallinity.⁴⁰ Through synchrotron X-ray measurements, it was observed that under strain, the molecules in the [Cu(acac)₂] crystal rotate reversibly and thus reorganize to allow the mechanical compression and expansion required for elasticity and still maintain the integrity of the crystal structure. Theoretical studies of atomically precise Ag₄₄ CASs suggest the existence of similar ligand-flexure-induced softness.¹⁶ The mechanical response of Ag₂₉ CAS had been probed by nanoindentation, and the softness of the material was attributed to the protecting ligands.¹⁵ This implies that a correlation between mechanical properties and structures could exist in CASs as well. An investigation of these becomes possible today as several cluster systems with varying structures are now available. Miniaturization of various devices requires such materials that can be controlled and self-assembled into the form desirable. To successfully incorporate these materials into flexible electronic devices, knowledge of their mechanical deformation is necessary. The design principles to modulate the response of CASs to mechanical stress need further inputs.

In this paper, we report distinct differences in the mechanical properties of diverse mixed-ligand-protected clusters, mainly the two polymorphic Ag₂₉⁴¹ clusters. The already known cubic (Ag₂₉ C)⁴¹ and the newly discovered trigonal (Ag₂₉ T)⁴² systems have been studied. Variations in the properties are directly related to the structural differences and intermolecular interactions in their crystal packing. Similar studies have been extended to Ag₄₆⁴³ (Ag₄₆ T) and its cocrystal with Ag₄₀ (Ag_{40/46} M) to reaffirm the importance of the structure and supramolecular interactions in determining mechanical properties. Hence, the study has broad implications in crystal engineering of various flexible, ordered molecular materials.

■ EXPERIMENTAL METHODS

Chemicals. All chemicals, including sodium borohydride (NaBH₄, 99.99% metal basis), triphenylphosphine (TPP), benzene-1,3-dithiol (BDT), 2,4-dimethylbenzenethiol (2,4-DMBT), and 2,5-dimethylbenzenethiol (2,5-DMBT) were purchased from Sigma-Aldrich. Silver nitrate (AgNO₃, 99%) was purchased from Rankem. Solvents including methanol, dichloromethane (DCM), and dimethylformamide (DMF) were of high-performance liquid chromatography (HPLC) grade.

Synthesis of Ag₂₉ Nanoclusters (NCs). Synthesis of Ag₂₉ nanoclusters (NCs) was performed by following a previously reported procedure.⁴¹ Briefly, Ag₂₉(BDT)₁₂ NCs were prepared by dissolving

25 mg of silver nitrate in 5 mL of methanol. To this, 10 mL of DCM and 15 μ L of BDT were added. The color of the solution changed to turbid yellow after the addition of BDT. It became colorless by the addition of 200 mg of TPP (in 1 mL of DCM). After 15 min, 10.5 mg of NaBH₄ in 500 μ L of cold deionized (DI) water was added. The reaction was stopped after 3 h continuous stirring. The resulting orange solution was centrifuged, and the supernatant was discarded. The residue was washed several times with methanol to remove excess thiols and thiolates, and it was dispersed in DMF.

Synthesis of Ag₄₆ Nanoclusters. The synthesis and purification procedures were almost the same as those described for the mixture (see below). Here, 2,5-dimethylbenzenethiol was used in place of 2,4-dimethylbenzenethiol.

Synthesis of a Mixture of Ag₄₀ and Ag₄₆ Nanoclusters. It was synthesized by a ligand exchange-induced structure transformation (LEIST) process. [Ag₁₈(TPP)₁₀H₁₆]²⁺ was taken as the precursor in this reported procedure.⁴³ About 5 mg of the clean Ag₁₈ cluster was taken in MeOH. To this, 0.75 μ L of 2,4-dimethylbenzenethiol (DMBT) was added under stirring conditions. The reaction was allowed to continue for 12 h. After 12 h, the initial greenish reaction mixture changed to reddish-brown, which indicated the formation of the product. Then, the reaction mixture was centrifuged at 5000 rpm for 5 min to remove all of the insoluble precipitates, and the solvent was removed under reduced pressure. Around 1 mL of MeOH was added to precipitate the material, and it was centrifuged. The precipitate was dried and washed several times with hexane to remove excess TPP. This cleaned material was dried and dissolved in DCM, which was used for characterization.

Crystallization of Ag₂₉C Nanoclusters. The purified clusters (15 mg) were dispersed in DMF and filtered using a syringe filter. The concentrated cluster solution was drop-casted on a microscope slide and kept undisturbed at room temperature. After 3–4 days, luminescent red crystals were observed.

Crystallization of Ag₂₉T Nanoclusters. The purified clusters (20 mg) were dispersed in DMF and filtered using a syringe filter. The concentrated cluster solution was kept for vapor diffusion with methanol. After 10 days, luminescent red crystals were observed. The vapor diffusion method resulted in trigonal Ag₂₉ crystals alone. This observation was further confirmed by monitoring the birefringence of obtained trigonal crystals using a polarization microscope. We have not observed any Ag₂₉ C crystals by the vapor diffusion method.

Crystallization Ag₄₆T Nanoclusters. Around 40 mg of the purified cluster was dissolved in 1.5 mL of distilled DCM and 0.5 mL of MeOH, filtered by a syringe filter of pore size 0.22 μ m, layered by distilled hexane at 1:1 (by volume) ratio, and kept at 4 °C. After approximately 1 week, black hexagonal crystals were observed.

Crystallization of Ag_{40/46} M Nanoclusters. A 40 mg of the solid cluster mixture was dissolved in 2 mL of distilled DCM, filtered by a syringe filter of pore size 0.22 μ m, layered by distilled hexane at 1:1 (by volume) ratio, and kept at 4 °C. After approximately 1 week, black crystals were observed. Several batches of crystallization were carried out to obtain crystals in quantity as well as quality.

Characterization. UV–Vis Spectroscopy. Optical absorption spectra of samples were obtained using a PerkinElmer Lambda 25 spectrometer.

Electrospray Ionization Mass Spectrometry (ESI MS). The mass spectra of samples were measured using a Waters Synapt G2-Si high-resolution mass spectrometer.

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDAX) Measurements. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDAX) analyses were done using an FEI Quanta-200 SEM.

Single-Crystal X-ray Diffraction (SCXRD). Face indexing was measured using a Bruker Kappa APEX III CMOS diffractometer using Cu K α (λ = 1.54178 Å) radiation.

Nanoindentation Measurements. Nanoindentation (NI) experiments were conducted using a Hysitron TI Premier nanomechanical testing instrument. We have used a Berkovich indenter of 150 nm radius in our experiments. The indentation loads of 200, 500, and 10 000 μ N were used with a trapezoidal load function. In situ

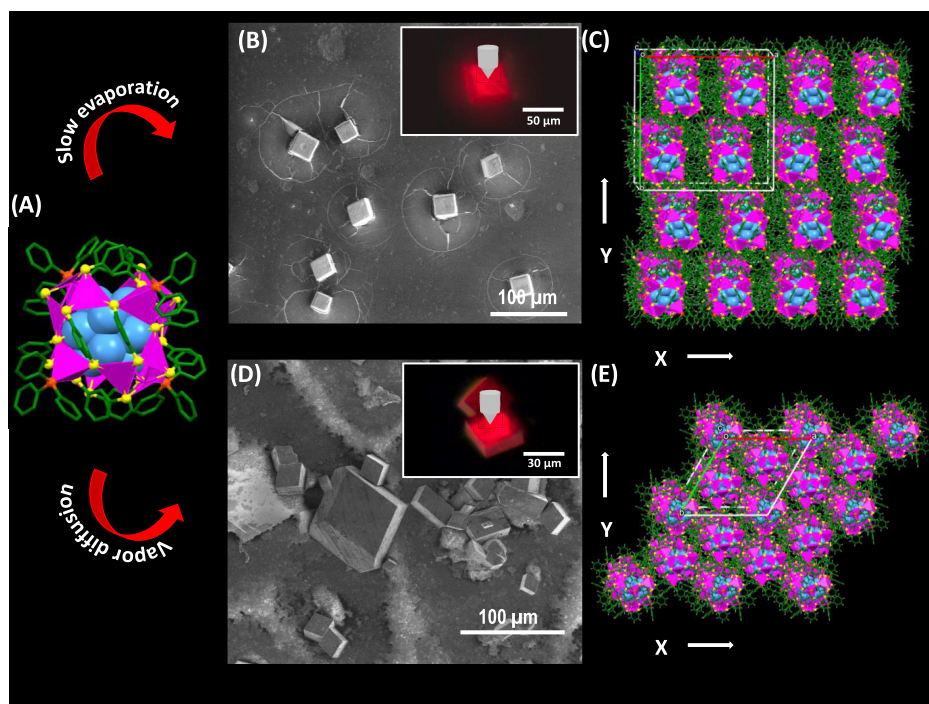


Figure 1. (A) View of the crystal structure of the Ag_{29} cluster. Images (B) and (D) are the SEM images of the three-dimensional (3D) crystals of Ag_{29} C and Ag_{29} T. Insets of (B) and (D) show a schematic representation of the nanoindentation experiments. Images (C) and (E) are the 2×2 unit cells of Ag_{29} C and Ag_{29} T CASs viewed along their Z axes. Color codes: cerulean/magenta, Ag; yellow, S; orange, P; and green, C.

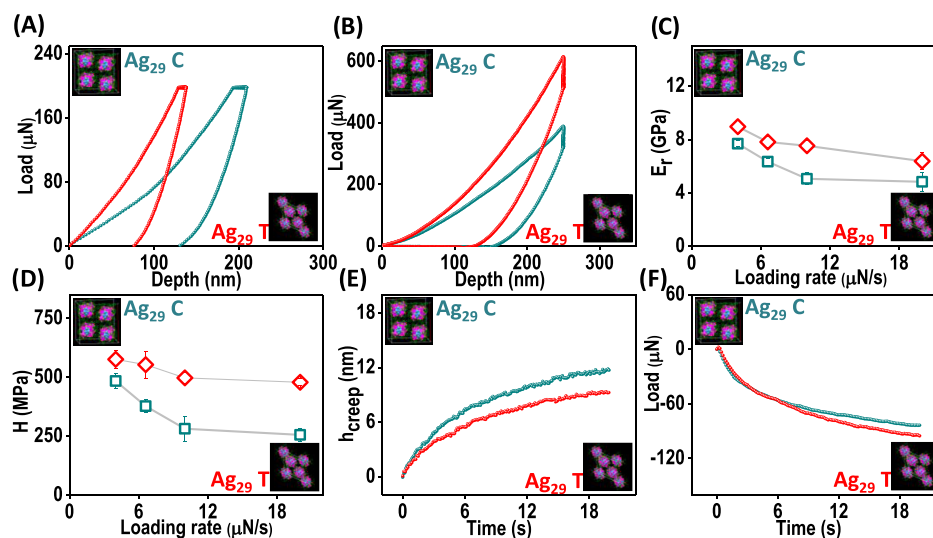


Figure 2. (A, B) Representative load- and displacement-controlled load–displacement plots of Ag_{29} C (cyan trace) and Ag_{29} T (red trace) with $200 \mu\text{N}$ load and a loading/unloading time of 20 s. (C, D) Loading-rate-dependent variation of E_r and H values of Ag_{29} C and Ag_{29} T crystal systems. (E, F) Creep and stress relaxation of Ag_{29} C and Ag_{29} T cluster crystals. Color codes: cerulean/magenta, Ag; yellow, S; orange, P; and green, C.

scanning probe microscopy (SPM) was used to examine the surface topographies prior to and after indentation. The E_r and H were calculated by applying the Oliver and Pharr method,⁴⁴ which used the initial part of the unloading segment of the load–displacement curve. Nanoindentation experiments were performed on 10 different crystals of each silver CASs. On each single-cluster crystal, three repetitive experiments were performed. The CASs of all of the four silver NCs used had a length in the range of 20–60 μm with a thickness of 10–20 μm . To reduce the possible solvent effects, the nanoindentation studies were performed on evacuated/aged crystals.

Nano Dynamic Mechanical Analysis (Nano DMA) Measurements. DMA was performed using load-controlled frequency sweep mode. In this mode, the oscillating dynamic load of 10 μN was

superimposed on a static load of $200 \mu\text{N}$ over a frequency range of 10–200 Hz. By applying a sinusoidal force signal and capturing the displacement response, the magnitudes of storage modulus, loss modulus, and damping factors were calculated.

RESULTS AND DISCUSSION

Ag_{29} CASs and Their Crystal Structures. The CASs of atomically precise mixed-ligand-protected Ag_{29} and Ag_{46} nanoclusters (NCs) with different crystal packings and densities were used in this work (Table S1). As these cluster systems are known already, we present only essential information here. Both cluster systems are co-protected by

primary thiol ligands and secondary phosphine ligands. The well-established polymorphs of bidentate ligand-protected $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]$ NCs (1,3 benzenedithiol, BDT; triphenylphosphine, TPP), labeled as Ag_{29} C and Ag_{29} T, were obtained by varying the crystallization strategy (Figure 1A).^{41,42} In our study, the $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]$ cluster was synthesized following a reported protocol⁴¹ as described in the experimental section and characterized using optical absorption and electrospray ionization mass spectrometry (ESI MS) (Figures S1 and S2). We have followed the same reported procedure^{41,42} to obtain crystals of acceptable quality and dimensions (Figure 1B,D). The total structure of individual clusters was determined by single-crystal X-ray crystallography. The structural anatomy of the Ag_{29} cluster reveals the existence of the Ag_{13} icosahedral core in it (Figure S3A), which is further capped by $\text{Ag}_{16}\text{S}_{24}\text{P}_4$ motifs (Figure S3B) to form the $\text{Ag}_{29}(\text{BDT})_{12}\text{TPP}_4$ architecture (Figure S3E). The supra-molecular arrangements in cubic and trigonal systems are quite different (Figure S3F,G).

Mechanical Response of Ag_{29} C and Ag_{29} T. The difference in the crystal packing (Figure 1C,E) and density (Table S1) of Ag_{29} polymorphs can result in distinct changes in mechanical properties. This prompted us to probe the mechanical response of CASs using the nanoindentation technique. The indented plane is $(\bar{1}01)$ in the case of Ag_{29} T (Figure S4), whereas the indentation tests were performed on the major face, preferentially oriented in the direction normal to the loading direction in the case of other systems. The load-controlled and displacement-controlled modes were used to study creep and stress relaxation. To study the creep behavior, a fixed load was held for some time and the displacement in the sample was recorded. Similarly, in the stress relaxation study, a fixed displacement was maintained and the reduction in the stress value was monitored. These experiments revealed new insights into the time-dependent mechanical behavior of cluster materials. The load–displacement plots of load-controlled and displacement-controlled nanoindentation tests on Ag_{29} C and Ag_{29} T are shown in Figure 2A,B, respectively. The corresponding piezo images of residual indentation imprints on both Ag_{29} CASs are shown in Figure S5. The absence of pop-ins on the load–displacement curves of both Ag_{29} CASs during loading is an indication of smooth penetration of the indenter and no local plasticity or phase change in response to the applied mechanical stress, unlike in most anisotropic molecular crystals with low symmetry.^{28,45} The load-controlled load–displacement plot shows a significant residual displacement in crystals of Ag_{29} C compared to Ag_{29} T, suggesting it to be less hard. The hardness (H) values of Ag_{29} C and T crystals are 282.19 ± 53.33 and 498.15 ± 23.61 MPa, respectively, which corroborated well with this observation. The observed reduced Young's modulus (E_r) values of Ag_{29} C and T systems are 5.66 ± 0.44 and 7.53 ± 0.41 GPa, respectively, indicating that density is not the dominant factor in controlling the modulus of the crystals (Table 1). The measurement of ν is complicated (due to the

sample size and other factors) for such cluster-assembled solids. In view of this, the experimentally determined Young's Modulus (E_r) is reported here rather than the bulk modulus. Both the crystals show creep during holding time, which implies a significant viscoelastic deformation in the crystals. For viscous materials, the stress is proportional to the strain rate, unlike purely elastic materials. To investigate the rate-dependent deformation behavior, we have performed indentation experiments at different loading rates (Figures S6 and S7). The values of E_r and H for both the crystals at different loading rates are plotted in Figure 2C,D, respectively. It is evident from the plot that the magnitudes of E_r and H reduce significantly with an increase in the loading rate until $10 \mu\text{N/s}$. Figure 2E shows the result of the creep study performed on both C and T Ag_{29} crystals applying quasi-static nano-indentation. The constant load was maintained at approximately $200 \mu\text{N}$. Instead of creep strain, the absolute value of the displacement of the indenter is reported here. The creep plots of both the Ag_{29} crystals indicate a two-stage creep response: primary and secondary. Creep plots at higher loads such as 500 and $10\,000 \mu\text{N}$ (Figure S8) reveal that unlike some metals and polymers, the tertiary creep region is not observed in the case of Ag_{29} CASs, which usually originates due to the rapid growth and coalescence of voids in the crystals. Here, we have observed only the secondary stage of creep for both the CASs. The upward slope (not totally flat) in the creep plots suggests the possibility of reduced coalescence of voids at this stage. In such CASs, the observed displacement/strain at the primary stage of creep (Figure 2E) could typically originate from the ligand-flexure- or stress-induced buckling of the ligands. The relatively steady secondary stage indicates the nucleation of voids under the sustained load. Strain hardening is the increased resistance to plastic deformation, and such effects dominate during the transient period of the initial creep test.⁴⁶ We have performed four consecutive creep experiments on the same area of Ag_{29} C and T crystals to probe the strain hardening effects (Figure S9). A comparison of first and fourth creep plots shows a significant reduction of displacement. The reduced displacement offers a shred of evidence for higher resistance to plastic deformation, quantified by an increase in hardness. This observation implies the existence of strain hardening in the Ag_{29} polymorphs. This is a crucial information when these crystals are used at a load range beyond the elastic limit in real-life applications. They also undergo stress relaxation, when held at certain displacement, as indicated in Figure 2F. This further validates the time-dependent behavior of these cluster crystals and complements the observed creep response. Both the crystals show a pronounced increase in creep and stress relaxation as a function of loading rate (Figure S10). To depict the viscoelastic properties of the tested materials, the stress relaxation curves were fitted to an analytical expression extracted from a rheological model composed of springs and dashpots^{47,48} (Figures S11 and S12). The fit of our model captures the behavior of both Ag_{29} crystals tested in stress relaxation experiments, allowing us to extract relaxation modulus ($G^\circ(t)$) values in addition to relaxation times (τ) (Table S2), which substantiate well with the observed E_r values.

Structural Basis for Exceptional Mechanical Response of Ag_{29} Polymorphs. In our studies of Ag_{29} polymorphs, we have observed that apart from density, there are other factors that control the mechanical response of CASs.

Table 1. Measured Young's Modulus (E_r) and Hardness (H) Values of the Ag_{29} CASs, Compared with Their Density (ρ)

CASs	ρ (g/cm^3)	E_r (GPa)	H (MPa)
Ag_{29} C	2.11	5.66 ± 0.44	282.19 ± 53.33
Ag_{29} T	2.04	7.53 ± 0.41	498.15 ± 23.61

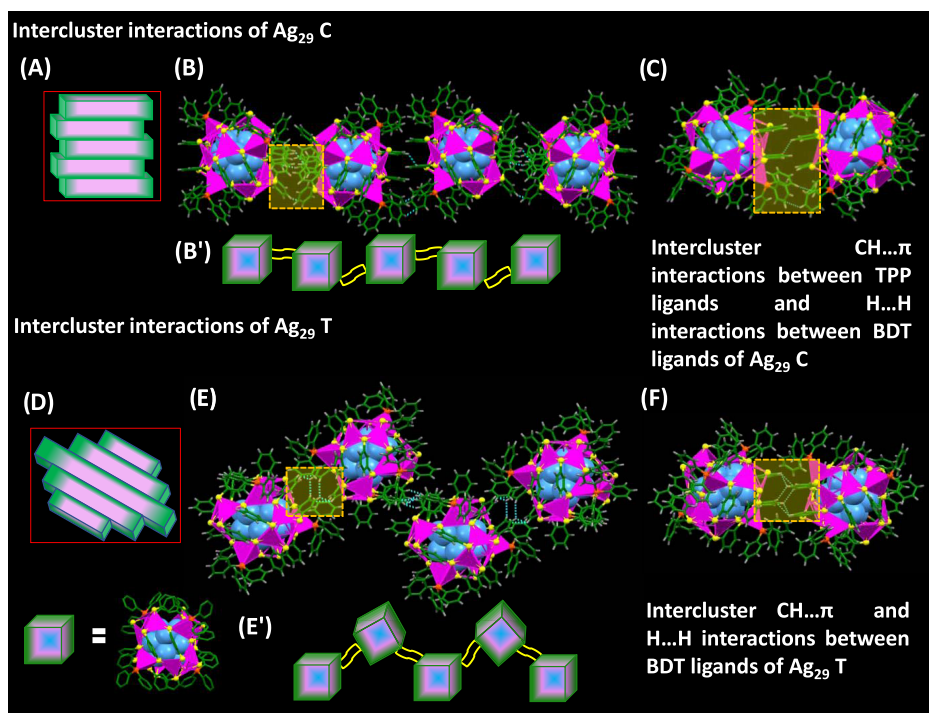


Figure 3. Anatomy of intercluster interactions of Ag_{29} C and Ag_{29} T. (A, D) Schematic representations of packing in Ag_{29} C and T crystals. (B, E) Illustrations of intercluster interactions in one-dimensional (1D) assembly of Ag_{29} C and T clusters. (B', E') Schematic representations of intercluster interactions in 1D assembly of Ag_{29} C and T systems. (C, F) Illustration of intercluster interactions between two Ag_{29} C and Ag_{29} T clusters. Color codes: cerulean/magenta, Ag; yellow, S; orange, P; green, C; and gray, H.

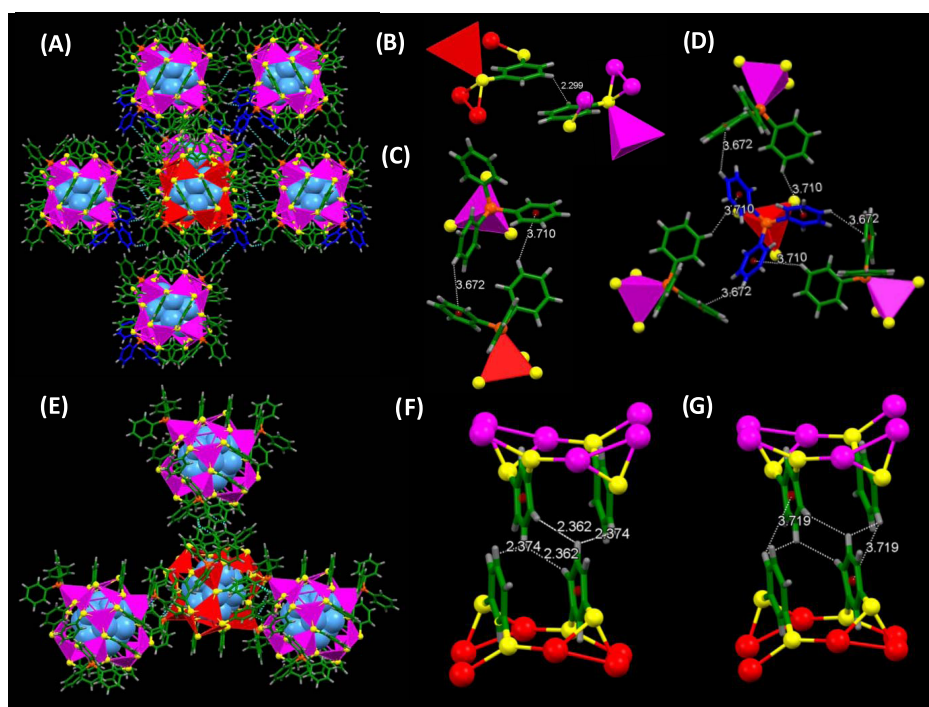


Figure 4. Supramolecular interactions in Ag_{29} C and T systems. (A, E) Interaction of the Ag_{29} cluster with neighboring clusters in cubic and trigonal lattices. Specific intercluster interactions are shown in (B)–(G). (B) $\text{H}\cdots\text{H}$ interaction between BDT ligands in the Ag_{29} C lattice. (C, D) $\text{CH}\cdots\pi$ interactions between TPP ligands in the Ag_{29} C lattice. (F, G) $\text{H}\cdots\text{H}$ and $\text{CH}\cdots\pi$ interactions between BDT ligands of Ag_{29} T. Color codes: cerulean/magenta/red, Ag; yellow, S; orange, P; green/blue, C; and gray, H.

Here, we are considering only the intercluster ligand interactions that are preserved well in the solid state.⁴⁹ Interestingly, taking a closer look at the arrangement of NCs, one can find that both the Ag_{29} polymorphs assemble linearly

to form 3D crystals (Figure S13). A schematic of such a linear assembly of Ag_{29} polymorphs is shown in Figure 3A,D. The neighboring NCs interact through specific intercluster interactions induced by BDT and TPP ligands (Figure

3B,E), which control the crystal packing of the cluster molecules (Figure 3B',E'). The surface structures of both the crystals in the solid state are mainly stabilized by intermolecular CH $\cdots\pi$ interactions, in which the C–H bonds interact with the π electrons of phenyl rings (Figure 3C,F). Such surface structures of NCs are reminiscent of biomolecules such as proteins.^{50,51} The strength of the CH $\cdots\pi$ interactions is ca. 1.5–2.5 kcal/mol.⁵¹ Apart from this, several other van der Waals interactions such as H $\cdots$ H and $\pi\cdots\pi$ stacking were also observed. In the case of Ag₂₉ C, we have found that the TPP ligands bundle in two ways: double bundles (L₁, having a pair of CH $\cdots\pi$ interactions) and triple bundles (L₃, having three pairs of CH $\cdots\pi$ interactions) (Figure S14). The high connectivity in such molecular networks enables direct interactions with six nearest neighboring clusters via H $\cdots$ H, $\pi\cdots\pi$, and CH $\cdots\pi$ interactions (Figure 4A). The relevant intercluster interactions of both Ag₂₉ polymorphs are assessed and listed in Table 2. There are six H $\cdots$ H and parallel-

Table 2. Intercluster Intermolecular Interactions of Ag₂₉ C and T Crystals^a

crystal system	H $\cdots$ H interactions	$\pi\cdots\pi$ interactions	CH $\cdots\pi$ interactions	
	between BDT ligands	between BDT ligands	between TPP ligands	between BDT ligands
Ag ₂₉ C	6 (6 $\times$ 1)	6 (6 $\times$ 1)	12 (6 $\times$ 2)	
Ag ₂₉ T	12 (3 $\times$ 4)	6 (3 $\times$ 2)		6 (3 $\times$ 2)

^aTotal no. of interactions = no. of clusters having direct interactions $\times$ no. of interactions by each cluster.

displaced $\pi\cdots\pi$ contacts between the BDT ligands of an Ag₂₉ cluster and its six neighboring clusters in the cubic lattice. The bond distances of the H $\cdots$ H and $\pi\cdots\pi$ contacts are 2.29 Å

(Figure 4B) and 5.87 Å (Figure S15A), respectively. Twelve CH $\cdots\pi$ interactions were also observed between the four secondary TPP ligands of the Ag₂₉ cluster and its six neighboring clusters. Among the four TPP ligands, three will have a pair of edge-to-face or T-shaped CH $\cdots\pi$ interactions (L₁) with the TPP ligands of the adjacent three clusters (Figure S15B). The remaining one TPP (highlighted in blue in Figure S14) will act as a soft base π -system leading to the formation of three pairs of T-shaped CH $\cdots\pi$ interactions (L₃) with three neighboring clusters (Figure S15C,D). The L₁ and L₃ bundles together constitute a total of 12 CH $\cdots\pi$ contacts between TPP ligands of adjacent clusters. The bond lengths and bond angles of such CH $\cdots\pi$ contacts range from 3.67 to 3.71 Å (Figure 4C,D) and 118–140° (Figure S16A,B), respectively. The observed CH $\cdots\pi$ bond lengths of Ag₂₉ polymorphs were similar to those of meso-tetrakis[4-(benzyloxy)phenyl] porphyrins.⁵²

The interactions that direct the 3D crystal assembly are quite different in Ag₂₉ T in comparison to Ag₂₉ C (Figure 4E). These nanoscale building blocks were found to hold together by two pairs of H $\cdots$ H (Figure 4F) and $\pi\cdots\pi$ (Figure S17A), and a pair of parallelly displaced CH $\cdots\pi$ (Figure 4G) interactions that act as structure-directing units promoting crystallization. The intercluster interactions between the TPP ligands are not observed in the case of the Ag₂₉ T system. The interactions between BDT ligands of adjacent clusters (Figure S15B) were reminiscent of the chair conformer of cyclohexane. The three pairs of BDT ligands of each cluster will interact with BDT ligands of three adjacent clusters via 12 H $\cdots$ H (Figure 4F), 6 $\pi\cdots\pi$ (Figure S15A), and 6 parallelly displaced CH $\cdots\pi$ (Figure 4G) interactions (Table 2). The bond length of intermolecular weak H $\cdots$ H interactions was 2.36 Å, which is slightly higher than in Ag₂₉ C crystals (2.29 Å). The average

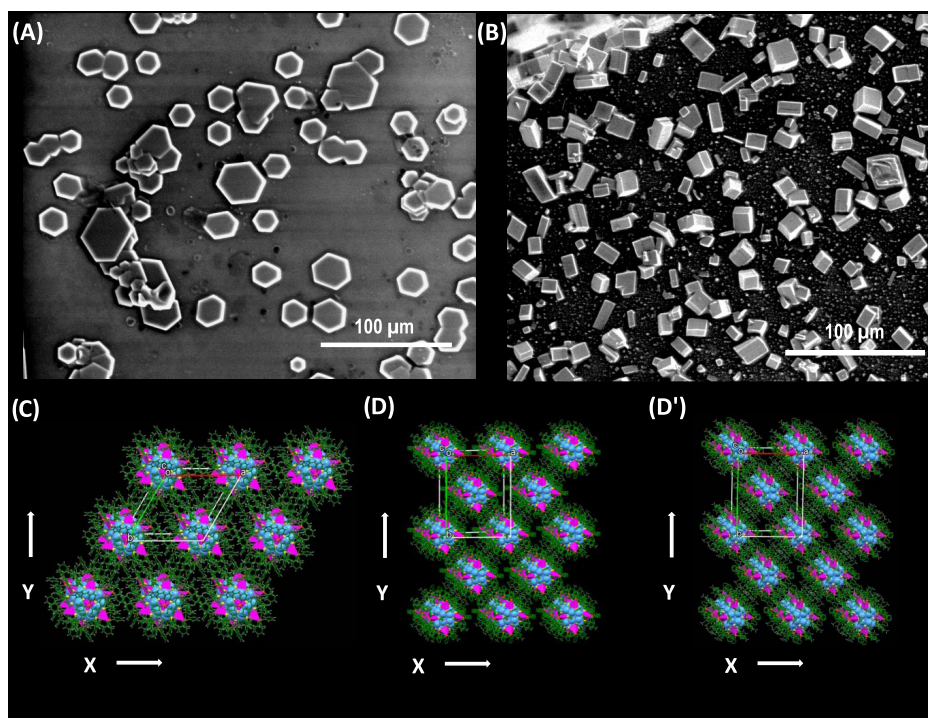


Figure 5. (A, B) SEM images of the 3D crystals of Ag₄₆ T and Ag_{40/46} M. (C, D, D') The 2 $\times$ 2 $\times$ 2 unit cells of Ag₄₆ T, Ag₄₀ M, and Ag₄₆ M clusters viewed along the Z axis. (D) and (D') refer to the structures of Ag₄₀ and Ag₄₆, respectively, in the Ag_{40/46} M cocrystal. Color codes: cerulean/magenta, Ag; yellow, S; orange, P; and green, C.

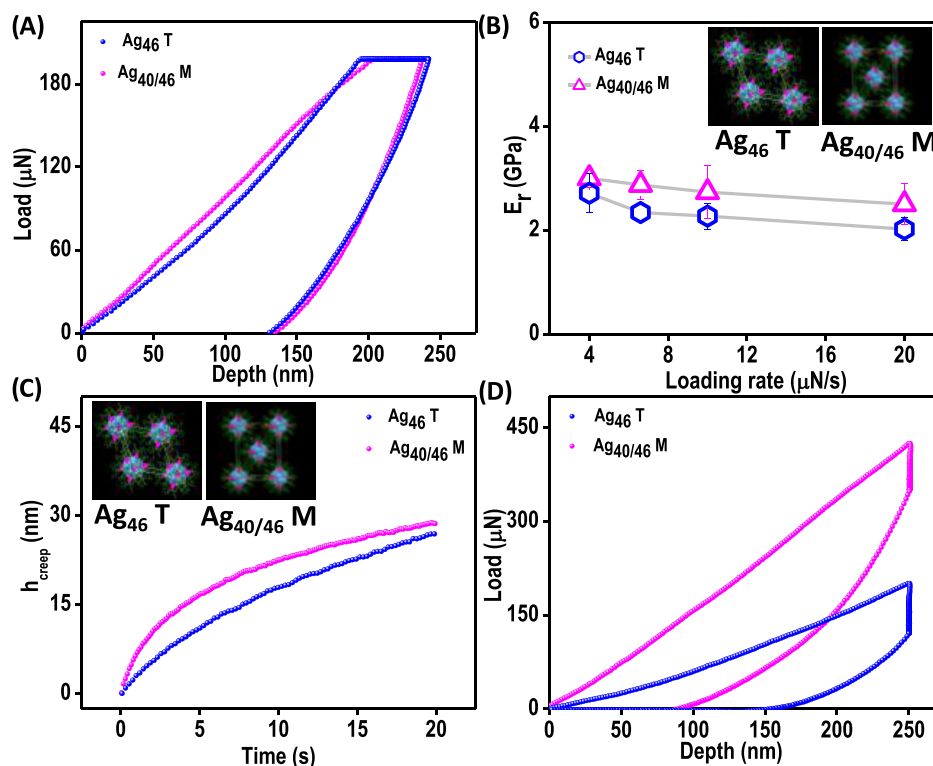


Figure 6. (A) Representative load-controlled load–displacement plots of Ag_{46} T (blue trace) and $\text{Ag}_{40/46}$ M (pink trace) with 200 μN load with a loading/unloading time of 20 s. (B) Variation of E_r values with the loading rate. (C) Creep response of Ag_{46} T (blue trace) and $\text{Ag}_{40/46}$ M (pink trace) crystal systems. Inset images are the unit cells of Ag_{46} T and $\text{Ag}_{40/46}$ M crystals. (D) Representative displacement-controlled load–displacement plots of Ag_{46} T (blue trace) and $\text{Ag}_{40/46}$ M (pink trace) with 250 nm displacement. Color codes: cerulean/magenta, Ag; yellow, S; orange, P; and green, C.

bond length of the $\text{CH}\cdots\pi$ interaction is 3.71 ± 0.2 Å, with a bond angle of 144° (Figure S17C). The strength of $\text{CH}\cdots\pi$ interactions depends on the bond distances between the hydrogen atom (in C–H) and the plane of the aromatic ring [less than 2.9 Å] as well as $\text{CH}\cdots\pi$ access angles (varied from 140 to 180°).⁵³ Here, both cubic and trigonal systems are having slightly larger intercluster $\text{CH}\cdots\pi$ bond distances and thus they are weaker in nature. The $\text{CH}\cdots\pi$ contacts of Ag_{29} C crystals involve the secondary TPP ligands, whereas, these are between primary BDT ligands in Ag_{29} T. Also, a study of the molecular arrangement of benzene at 0.15 and 0.91 GPa reveals a significant shift in the $\text{CH}\cdots\pi$ -bonded networks and substantial collapse of the voids between the molecules.⁵⁴ The observed higher E_r and H in the Ag_{29} T crystal compared to Ag_{29} C might be due to the following factors: (i) The intercluster interactions are between the primary BDT ligands rather than the secondary TPP ligands. (ii) The presence of two pairs of $\text{H}\cdots\text{H}$ interactions between BDT ligands that extend as a zig-zag chain connecting adjacent molecules, as well as a pair of $\text{CH}\cdots\pi$ interactions between the BDT ligands. The disruption of internal molecular rotations can influence the mechanical deformation of the crystals.⁵⁵ Such restrictions in the flexibility might not be there in the case of Ag_{29} C as the $\text{CH}\cdots\pi$ interactions are mainly between the TPP ligands. The absence of clear slip planes in the above crystal systems is due to their interconnected network-like structures.⁵⁶

Crystal Structures of Ag_{46} and Its Cocrystal with Ag_{40} .

In the preceding sections, we understood that the structures could be distinguished by their distinctive mechanical properties. The surface and core structures of Ag_{46} systems are completely different from those of Ag_{29} polymorphs. Also,

the structural differences in Ag_{46} and its cocrystal can reveal new insights into the mechanical response of CASs. This prompted us to perform nanoindentation studies on monothiol-protected $[\text{Ag}_{46}(\text{2,5-DMBT})_{24}(\text{TPP})_8]$ NCs (2,5-dimethylbenzenethiol, 2,5-DMBT; triphenylphosphine, TPP) crystallized in a trigonal lattice (Ag_{46} T) and a cocrystal of Ag_{46} and Ag_{40} in a monoclinic lattice ($\text{Ag}_{40/46}$ M). Ligands for both the clusters in $\text{Ag}_{40/46}$ are 2,4-dimethylbenzenethiol (2,4-DMBT) along with TPP. The clusters were synthesized following the protocol⁴³ as described in the **Experimental Methods** and characterized using optical absorption and ESI MS studies (Figures S18 and S19). Figure 5A,B shows the SEM images of Ag_{46} T and $\text{Ag}_{40/46}$ M single crystals. Figure 5C, D, D' represents the packing of Ag_{46} clusters and $\text{Ag}_{40/46}$ cocrystals in a trigonal lattice with the space group P-3 and monoclinic lattice with the space group $C2/m$, respectively. Successive jobs of least-squares refinement followed by the Fourier difference map could finally yield the structure of Ag_{40} and Ag_{46} from the cocrystal. The occupancy of each cluster was 50% in the $\text{Ag}_{40/46}$ M crystal system.⁴³ The structure of Ag_{46} is similar in Ag_{46} T (Figure S20) and $\text{Ag}_{40/46}$ M (Figure S21). The Ag_{46} cluster consists of a Ag_{14} inner core (Figures S20A and S21A) protected by a Ag_{24} outer core (Figures S20B and S21B). This Ag_{38} motif is further protected by eight Ag_3P units (Figures S20C,D and S21C,D), resulting in a $\text{Ag}_{46}\text{S}_{24}\text{P}_8$ architecture. The Ag_{40} cluster in the cocrystal consists of a Ag_8 inner core (Figure S21F) with the rest of the structure the same as that of Ag_{46} (Figure S21G–I).

Mechanical Response of Ag_{46} and Its Cocrystal with Ag_{40} . The nanoindentation studies were performed by keeping all conditions the same except that in the case of Ag_{46} T, the

holding time of 50 s was used for the dissipation of creep. The load-controlled load–displacement plots are depicted in Figure 6A. The residual indentation imprint on the Ag₄₆ T system is represented in Figure S22. We could not observe such an indentation imprint in the case of Ag_{40/46} M crystal with 200 μ N load. The obtained E_r values from the load-controlled load–displacement plots reveal the compliant nature of the Ag₄₆ T system compared to Ag_{40/46} M (Table S3). The loading-rate-dependent experiments were performed on Ag₄₆ T and Ag_{40/46} M systems (Figures S23 and S24). An increase in the values of E_r (Figure 6B) and H (Figure S25) was observed as a function of the loading rate of both the crystal systems. The Ag_{40/46} M system showed larger creep behavior (Figure 6C) compared to the Ag₄₆ T system. Similar to Ag₂₉ systems, the creep behavior of Ag₄₆ T and Ag_{40/46} M systems consists of primary and secondary stages. The tertiary creep region was not observed even at loads of 500 and 10 000 μ N (Figure S26A,B). The strain hardening behavior of Ag₄₆ systems is shown in Figure S27. We have also performed displacement-controlled experiments (Figure 6D) and evaluated the stress relaxation behavior of Ag₄₆ systems (Figure S28). The Ag₄₆ systems also show a pronounced increase in creep (Figure S29A,B) and stress relaxation (Figure S29C,D) as a function of loading rate, similar to the Ag₂₉ polymorphs. The experimental stress–relaxation curves were fitted to an analytical expression extracted from a rheological model used previously (Figure S30A,B), and the $G^0(t)$ and τ were extracted (Table S4). The extracted relaxation modulus values corroborated well with the E_r values of the Ag₄₆ systems.

Structural Basis for the Mechanical Response of Ag₄₆ and Its Cocrystal with Ag₄₀. The structural basis for the differences in mechanical responses of Ag₄₆ systems was analyzed through the examination of crystal packing (Figure S31A,B). The intercluster supramolecular interactions of Ag₄₆ T and Ag_{40/46} M crystal systems are summarized in Table 3,

Table 3. Intercluster Intermolecular Interactions of Ag₄₆ T and Ag_{40/46} M Crystals^a

crystal system	H...H interactions		CH... π interactions	
	between TPP and 2,5-DMBT ligands	between TPP ligands	between TPP and 2,5-DMBT ligands	between 2,5-DMBT ligands
Ag ₄₆ T	12 (6 $\times$ 2)	12 (2 $\times$ 6)		
crystal system	H...H interactions		CH... π interactions	
	between 2,4-DMBT ligands	between TPP ligands	between TPP and 2,4-DMBT ligands	between 2,4-DMBT ligands
Ag _{40/46} M	6 (2 $\times$ 3)		8 (4 $\times$ 2)	4 (2 $\times$ 2)

^aTotal no. of interactions = no. of clusters having direct interactions $\times$ no. of interactions by each cluster.

which reveal the complex interactions of the Ag₄₆ CASs. Each cluster in the molecular network of the Ag₄₆ T system has direct interactions with eight neighboring clusters via H...H and CH... π interactions (Figure S32A,B). The TPP and 2,5-DMBT ligands of six adjacent clusters will interact via a pair of H...H interactions, leading to hexagonal close packing of Ag₄₆ clusters (Figure S33A,B). The average bond length of such a H...H interaction is 2.36 Å (Figure 7A). Apart from this, the two pole site TPP ligands of the Ag₄₆ clusters interact with the pole site TPP ligands of other two neighboring clusters via six CH... π interactions (Figure S34A,B). The bond length and

bond angle of the CH... π interactions are 3.21 Å (Figure 7B) and 120°, respectively (Figure S34C). Such weak supramolecular interactions would allow the clusters to undergo intercluster rotations, leading to compliant behavior. In the Ag_{40/46} M cocrystal system, each cluster interacts with six neighboring clusters via CH... π and H...H interactions (Figure S35A,B). There are two types of CH... π interactions that direct the packing of Ag_{40/46} clusters in the monoclinic lattice. Type I interaction (CH... π (I)) is between TPP and 2,4-DMBT (Figures 7C and S36A), whereas type II interaction (CH... π (II)) is between the 2,4-DMBT ligands (Figure 7D). Among the six neighboring clusters, four of them are connected by type I, CH... π contacts having bond length and bond angle of 3.11 Å (Figure 7C) and 131° (Figure S36B), respectively. The remaining two clusters are connected by a pair of type II, CH... π contacts formed between the primary 2,4-DMBT ligands, having a bond length and a bond angle of 3.74 Å (Figure 7D) and 155° (Figure S36C), respectively. The types I and II together constitute twelve CH... π interactions. Besides that, three H...H interactions with a bond length of 2.06 $\pm$ 1 Å were observed between the 2,4-DMBT ligands (Figure 7E). Unlike the Ag₄₆ T system, the Ag_{40/46} M system contains supramolecular interactions between the primary 2,4-DMBT ligands, similar to Ag₂₉ T systems. Such interlocked and corrugated molecular packing of clusters imparts rigidity to the molecular crystal, which in turn manifests the E_r and H values.

Dynamic Mechanical Analysis (DMA) of CASs. To have a deeper understanding of the material properties, we have performed dynamical mechanical analysis (DMA) to understand the frequency sensitivity of different viscoelastic properties. Generally, such measurements are not performed in the case of molecular crystals; nevertheless, the creep behavior of the CASs prompted us to investigate the viscoelastic properties. The storage modulus depicts the energy stored in a system. The storage modulus values of all of the four crystal systems do not show significant frequency sensitivity (Figure 8A). The observed loss modulus value was higher for Ag₄₆ T compared to the other three crystal systems (Figure S37). The loss modulus of Ag₂₉ polymorphs shows significant frequency sensitivity compared to that of the Ag₄₆ crystal systems. Interestingly, we have observed that the damping or loss factor of Ag₄₆ T is higher than that of other cluster systems (Figure 8B) and is similar to that of natural rubber⁵⁷ irrespective of low storage modulus values. This observation points out a new possibility of using CASs as dampening materials. Studies of acoustic vibrations in nanometer-scale particles can provide fundamental insights into the mechanical properties of materials.⁵⁸ The stimulus-induced flexible metal-organic frameworks (MOFs) are highly attractive to absorb/store energy with promising prospects as nanodampers or nanosprings.^{59,60} The two factors that vary the breathing modes of a structure are the deformation of the bond angle and the distance between ligands.⁶¹ The energy of the crystal increases when bonds are deformed and decreases when the distance between the aromatic rings decreases. In the case of atomically precise clusters, the intrinsic damping has contributions due to the ligand-flexure-induced changes occurring in the metal cores and the surface layer of ligands. Recently, Maioli et al. studied the elastic properties of ligand-protected clusters, experimentally and theoretically, and two periods, corresponding to fundamental breathing and quadrupolar-like acoustic modes, were detected.⁶² They have observed a stagnation in acoustic response and attributed it

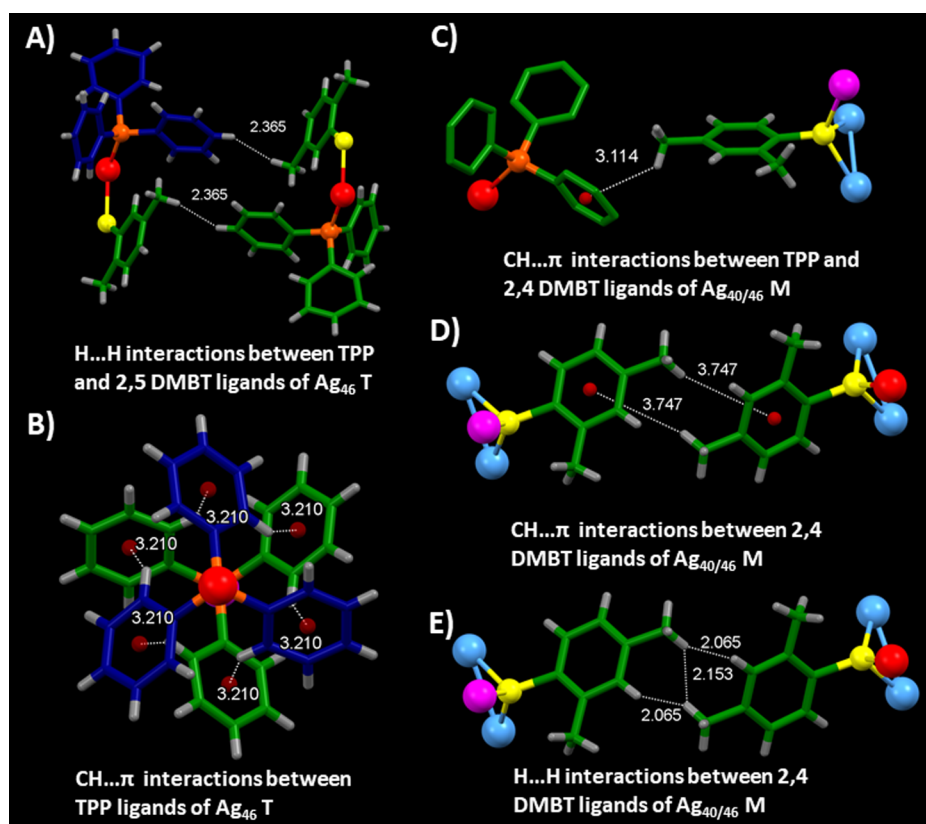


Figure 7. Supramolecular interactions in Ag_{46} T and $\text{Ag}_{40/46}$ M systems. (A) Intercluster H...H interactions between TPP and 2,5-DMBT ligands of Ag_{46} clusters in a trigonal lattice. Specific intercluster interactions are shown in (B)–(E). (B) CH... π interactions between TPP ligands in the Ag_{46} trigonal lattice. (C) CH... π interactions between TPP and 2,4-DMBT ligands in the $\text{Ag}_{40/46}$ monoclinic lattice. (D, E) CH... π and H...H interactions between 2,4-DMBT ligands in the $\text{Ag}_{40/46}$ monoclinic lattice. Color codes: cerulean/magenta/red, Ag; yellow, S; orange, P; green/blue, C; and gray, H.

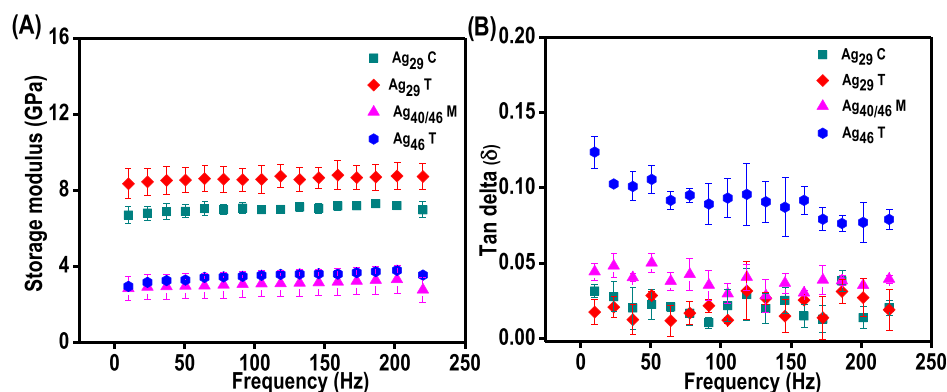


Figure 8. (A, B) Variation of storage modulus and $\tan \delta$ as a function of frequency of Ag_{29} C (cyan trace), Ag_{29} T (red trace), Ag_{46} T (blue trace), and $\text{Ag}_{40/46}$ M (pink trace).

to the mechanical mass loading effects of protecting ligands. The observed damping behavior of Ag_{46} T crystals opens up the prospects that by tailoring the nature of the metal cores and protecting ligands, different materials such as dampers and molecular springs can be obtained.

Investigation of the mechanical response of Ag_{29} polymorphs and Ag_{46} systems having different surface and core structures revealed a few fascinating insights. The compliant nature of the interconnected molecular cluster frameworks is largely driven by the protecting ligands. The cluster surface structures with dithiol ligands show higher E_r and H values than monothiol-protected clusters due to the structural rigidity⁶³ offered by

dithiol ligands. Also, the interrogation of crystal packing reveals that the cluster crystals stabilized by CH... π contacts involving the primary thiol ligands show higher E_r and H values (Ag_{29} T and $\text{Ag}_{40/46}$ M) than those directed by secondary phosphine ligands. In CAs, the cluster molecules are assembled in such a way that sufficient reorientation (rotation) of the molecules is possible without breaking the overall continuity of crystal packing. The cluster crystals assembled with weak supramolecular interactions may allow some elastic flexibility. Interlocked packing of the cluster molecules facilitates the elastic deformation. However, the absence of mechanical resistance to slip may eventually assist plastic deformation

(irreversible);⁴⁰ hence, only limited elasticity is expected. The flexure of NCs in the crystals could allow this material to serve as an energy-absorbing structure, which can convert stress to mechanical motion and can be used as molecular-scale sensors and switches. In view of our study, we postulate that it is possible to control the mechanical properties of CAs by tuning the strength and type of supramolecular interactions present between clusters. The stiffness of the CAs is enormously dependent on the rigidity and intermolecular interactions of the primary thiol ligands. We believe that there will be anisotropy in such cluster-assembled solids. Attempts to probe different faces of the crystal were not successful.

CONCLUSIONS

In summary, we demonstrated the mechanical response of CAs protected by monolayers. The atomically precise CAs of silver show large creep deformation, stress relaxation, and a pronounced rate-dependent mechanical behavior. This unusual behavior is attributed to the weak supramolecular interactions of the protecting ligands on the surface of the nanoclusters. The CAs protected by dithiols show superior E_r and H compared to the monothiol-protected CAs. CAs having supramolecular interactions between the primary ligands are stiffer than their counterparts. We have also observed that the $\tan \delta$ value of the Ag_{46} T system is comparable to that of natural rubber. By modeling the creep and relaxation behavior using rheological components, we determined both the elastic and viscous characteristics of the CAs. The present study has implications in creating flexible materials from atomically precise clusters. The results obtained will help in the effective design of flexible nanocluster devices since the low hardness and the viscoelastic properties demonstrated are not conducive to flexible applications. It is also essential to look into other CAs having supramolecular interactions or mechanically interlocked structures, which can be used as solids in materials engineering. With growing interest in engineering of materials with desired functions responding to external stimuli, the insights gained in this work will help future investigations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02905>.

ESI MS data, optical images, structural anatomy of crystal structures, face index analysis, piezo images, load–displacement plots, and Maxwell–Weichert model (PDF)

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Author Contributions

The problem was suggested by T.P. K.S.S. prepared the CAs and conducted most of the studies. P.B., K.S.S., and P.G. performed and analyzed the mechanical measurements. M.B., A.N., M.H., and W.A.D. helped in the characterization of clusters. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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