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# Unexpected Elasticity in Assemblies of Glassy Supra-Nanoparticle Clusters

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Abstract: Granular materials, composed of densely packed particles, are known to possess unique mechanical properties that are highly dependent on the surface structure of the particles. A microscopic understanding of the structure-property relationship in these systems remains unclear. Here, supra-nanoparticle clusters (SNPCs) with precise structures are developed as model systems to elucidate the unexpected elastic behaviors. SNPCs are prepared by coordinationdriven assembly of polyhedral oligomeric silsesquioxane (POSS) with metal-organic polyhedron (MOP). Due to the disparity in sizes, the POSS-MOP assemblies, like their classic nanoparticles counterparts, ordering is suppressed, and the POSS-MOP mixtures will vitrify or jam as a function of decreasing temperature. An unexpected elasticity is observed for the SNPC assemblies with a high modulus that is maintained at temperatures far beyond the glass transition temperature. From studies on the dynamics of the hierarchical structures of SNPCs and molecular dynamic simulation, the elasticity has its origins in the interpenetration of POSS-ended arms. The physical molecular interpenetration and inter-locking phenomenon favors the convenient solution or pressing processing of the novel cluster-based elastomers.

#### Introduction

Complex inter-particle interactions in 2D and 3D colloidal assemblies give rise to unexpected and often exceptional mechanical properties.<sup>[1]</sup> Soft colloids, represented by star polymers and microgels, can deform and overpack, eliminating

interstitial vacancies, and have elastic plateau moduli that are tunable.<sup>[2]</sup> Monolayer assemblies of alkyl-ligand coated nanoparticles (NPs) exhibit unexpected elasticity, robustness and resilience at high temperatures, enabling their use in sensors and device fabrications.<sup>[3]</sup> Van der Waals interactions can not account for the strong interactions between the NPs, leaving the interpenetration and entanglement of the ligands anchored to the surface of the NPs as the source of this behavior.<sup>[4]</sup> The size distribution, shape, deformability, and surface functionalization of the NPs will influence the packing and interactions between them<sup>[2b, 5]</sup> and, therefore, their resultant mechanical properties. Perhaps the most ill-defined of these is the surface functionalization, where the number of chains grafted to the NP surface is, at best, an average over all the NPs in the system based on, for example, gravimetric methods to determine the relative masses of the NP cores and ligands attached to the surface. Consequently, developing NPs with precisely defined surface geometries, surface functionalization, and mechanical properties is important in quantitatively understanding the packing of and interactions between NPs, and the roles of shape, including roughness, and deformability, and the influence of each of these on the global properties of the assemblies.

Nano-scale molecular clusters (MCs) with precise structures can be used to generate hierarchical architectures by typical physical and/or chemical bonding between their surface functional groups.<sup>[6]</sup> The MCs can be considered as superatoms, since they are well-defined geometrically with precisely-defined functionalities that dictate their interactions with the same or different MCs, and they constitute primary building blocks in the

# **RESEARCH ARTICLE**



**Figure 1. Design strategy for SNPCs derived from the coordination between giant ligands and copper ions to afford materials with different elasticity.** (a) Model structure of copper (II) based cuboctahedral MOP core (IPA<sub>24</sub>-Cu<sup>2+</sup><sub>24</sub>). (b) General strategy for the preparation of VPOSS-MOP, OPOSS-MOP and OPOSS-MOP-R. (c) Digital photographs of OPOSS-MOP sample which can be processed into thin membrane with certain elasticity and high light transmission. (d) Schematic illustration of the higher degree of interpenetration between OPOSS-MOP to afford homogenous and elastic membrane under high pressure.

assemblies.<sup>[7]</sup> By covalently linking MCs with a diverse range of other NPs, an even larger class of building blocks comprised of such clusters can be generated.<sup>[8]</sup> Coordination driven selfassembly has been widely used to produce complex, well-defined clusters (e.g. metal-organic polyhedron, MOPs).<sup>[9]</sup> We used this approach to construct precise NP clusters based on the coordination between MC-derived 'giant-ligands' (GLs) and metal ions. A simple self-assembly pathway is proposed to fabricate supra-NP clusters (SNPCs), where one cuboctahedron core is surrounded by 24 POSS by the precise coordination of POSSbased GLs with copper (II) ions (Figure 1). The terminal groups of GLs are varied to regulate the softness of the coronae of the clusters, the ability of coronae of different SNPCs to intermix or entangle, the softness of coronae, i.e. the deformability of the SNPCs, and, ultimately, the mechanical properties of the SNPC assemblies. The precise definition of the chemistries and physical architecture of each SNPC afford the opportunity to provide a quantitative interpretation of the unique elasticity of the bulk assemblies that serves as a guide for design of next-generation cluster-based materials.

### **Results and Discussion**

Synthesis and structural characterization of SNPCs

The construction of SNPCs is based on the cuboctahedron MOP assemblies<sup>[10]</sup> from the coordination between isophthalic acid (IPA) and Cu2+. IPA groups are attached to POSS (vinylfunctionalized POSS, VPOSS; isooctyl-functionalized POSS, OPOSS) to afford the target GLs and the further coordination with Cu<sup>2+</sup> leads to the generation of MOP-templated SNPCs (VPOSS-MOP, OPOSS-MOP and OPOSS-MOP-R; Figure 1; Supporting Information, Figure S1a, 1b). Due to the coverage of POSS components onto the surface of MOP, the obtained SNPCs have similar solubilities as but markedly different sizes than the POSS precursors, as evidenced by gel permeation chromatography (GPC) (Figure 2a) and dynamic light scattering (DLS) (Supporting Information, Figure S1c). The structure of a single SNPCs in solution was determined by small angle X-ray and neutron scattering (SAXS and SANS). To analyze the scattering data, the layers of GLs are divided into two shells adhered to the MOP cores: the POSS and linker shells (Figure 2b and 2c). The thicknesses of the shells, determined from fits to the scattering data, are comparable to the theoretical dimensions of the linker fragments and POSS. Consequently, OPOSS-MOP (ca. 3.4 nm) has a larger hydrodynamic radius than VPOSS-MOP (ca. 3.0 nm) because of the bulky, branched alkyl groups on the POSS (Supporting Information, Figure S1c). The core-shell character of the SNPCs is evidenced directly in real space by transmission electron microscopy (TEM). Contrast in the sphere-like structure

## **RESEARCH ARTICLE**

with a grey shell and dark core arises from the electronic density difference between the MOP cores and the outer chain segments (**Figure 2d**). However, the high mobility of the arm chains leads to the random distributions of them in the outer space of MOP core, thus contrast is mixed for some SNPCs in the TEM images. Core-shell structures can be further accessed from the scattering length density (SLD) distribution and atomic force microscope (AFM) data (Supporting information, **Figure S2**).



Figure 2. Structural information of the as-prepared SNPCs (VPOSS-MOP, OPOSS-MOP and OPOSS-MOP-R). (a) GPC traces of the giant precursors and corresponding SNPCs. (b) and (c) One-dimensional SAXS and SANS patterns of VPOSS-MOP and OPOSS-MOP in solution and the fitting profiles based on the core-shell model. (d) TEM image of VPOSS-MOP with a concentration of 2 mg/L in THF (the core and shell are outlined in red for two SNPCs); inset is the corresponding structural model of VPOSS-MOP.

#### The packing of SNPCs for glassy materials

The packing of SNPCs in the bulk, as prepared by a solution precipitation process, was investigated by small and wide angle X-ray scattering (SAXS and WAXS) to assess the interpenetration and deformation of the SNPCs (Figure 3a). Both SNPCs were amorphous, absent any long-range order even though the chemical constitution of the each SNPC is exactly the same. However, the sizes of different SNPCs are not the same, as seen in the TEM images (Figure 2d) and, also, as indicated by the scattering data, where the minima in the data are not very sharp, as would be expected from a sphere scattering function for monodisperse spheres of the SNPCs. Consequently, the packing of a polydisperse ensemble of soft particles that could, potentially, interpenetrate would not be expected to exhibit any long-range order. The nearest neighbor distance, indicative of a very shortrange order, is evidenced by the intense reflections at  $q_{MAX} = 0.13$ Å-1, corresponding to a SNPC-SNPC center-to-center distance of 4.8 nm. This is much smaller than the size of a single SNPCs in solution and indicates an interpenetration of the GLs of SNPCs. Maxima are also seen at  $q_{MAX} = 0.69 \text{ Å}^{-1}$ , corresponding to a VPOSS-VPOSS center-to-center distance of 0.9 nm, and at q<sub>MAX</sub> = 0.52 Å<sup>-1</sup>, corresponding to an OPOSS-OPOSS center-to-center distance of 1.2 nm (Figure 3a). The inter-OPOSS reflection is broader and less-resolved, due to the bulky, branched alkyl groups that hinder the close packing of OPOSS. One consequence of this is an enhanced mobility of the OPOSS, as indicated by the lower glass transition temperature of pure OPOSS ( $T_g = -10$  °C) in comparison to that of VPOSS, with a  $T_g$  above its decomposition temperature.<sup>[11]</sup> Suggested from its resolved inter-SNPC correlation peak, the high mobility of OPOSS facilitates the annealing of hierarchical structures in bulk OPOSS-MOP for homogeneous packing of SNPCs (Supporting Information, **Figure S3**).<sup>[12]</sup>

The deformability and softness of the SNPCs impart a disordered, glass-like nature to the assemblies. Different from previous work on crystalline MOPs, the soft GL linkers enable a deformation of the SNPCs.<sup>[13]</sup> To quantify the deformability of the SNPCs, the space occupying ratio (k) of the terminal POSS groups in the outer shell is determined by:  $k = (24 \times V_{POSS})/(V_{total})$  $V_{\rm Lf}$ ), where  $V_{\rm POSS}$  is the volume of a single POSS,  $V_{\rm total}$  denotes the volume of SNPC sphere, and  $V_{Lf}$  represents the space occupied by the MOP core and linker layer. The larger k of OPOSS-MOP (0.39) in comparison to VPOSS-MOP (0.17) can be attributed to the bulky isooctyl groups of the OPOSS (Figure 3b; Supporting Information, Scheme S4 and Table S1). The mobility of the POSS laver increases with decreasing k and increasing flexibility of the linker segments, which is also manifest in the shape and size variations of the SNPCs, as seen in the TEM image (Figure 2d) and evidenced by the disordered nature of the bulk materials.



Figure 3. Investigation of the glassy nature and mechanical properties of SNPCs. (a) SAXS and WAXS patterns of bulk VPOSS-MOP and OPOSS-MOP. (b) Schematic illustration of the space occupying ratios (k) for different SNPCs. (c) Stress-strain data for OPOSS-MOP with a strain rate of 1 mm/min. (d) The packing model we proposed for the bulk OPOSS-MOP, the outer arm chains are interpenetrated to generate interlocked structures.

#### Unique mechanical properties of SNPCs

VPOSS-MOP has a high  $T_g$  and is a brittle solid (Supporting Information, **Figure S1d**), while OPOSS-MOP has a low  $T_g$  (-10 °C) from the surface grafted OPOSS clusters (Supporting Information, **Figure S4**). Interestingly, an elastic-like membrane is formed when a powder of OPOSS-MOP, without

# **RESEARCH ARTICLE**

covalent/supramolecular cross-linking, is extruded at a pressure of ~ 20 MPa (Figure 1c). The pressed OPOSS-MOP pellet has a high light transmission, indicative of an optically homogenous system, indicating an interpenetration of the SNPCs (Supporting information, Figure S5). The pellet can be elastically bent multiple times without fracture. Tensile testing shows a linear stress-strain curve up to 8% strain with a high Young's modulus (~ 17.42 MPa), comparable to that of nature rubber<sup>[14]</sup> and recently developed stiff elastomers<sup>[15]</sup> (Figure 3c). After reaching a maximum point (15% strain), the stress abruptly decreases, characteristic of a brittle fracture. Supramolecular interactions are absent for the SNPCs and van der Waals forces cannot account for the elasticity with such a high Young's modulus. The strain cycling behaviors of OPOSS-MOP membrane are also assessed, which reveals the shape recovery during the cycle tests (Supporting information, Figure S6). Based on above structural analysis, due to the high mobility of OPOSS, pressure can facilitate a high degree of interpenetration of the GLs of different SNPCs, which could maximally double k to over 50%. Consequently, the kinetic trapping of the interpenetrated OPOSS in the outer shell of the SNPCs appears to significantly enhance the mechanical performance upon deformation and, at a specific strain, the interpenetration is abruptly released and the material fails (Figure 3d). The pressure effect is evidenced by the decrease in inter-SNPC distances at higher pressures (Supporting Information, Figure S7). Due to the physical nature of the molecular interpenetration of OPOSS and SNPCs, the SNPC-based elastomers can be regenerated by solution or pressure processing routes. The mechanical properties of OPOSS-MOP-R, which has short, rigid linker components, were also investigated. OPOSS-MOP-R behaves like a fragile solid with negligible elasticity after extrusion at high pressure (Supporting Information, Figure S8). The markedly different behavior of OPOSS-MOP-R clearly demonstrates the inability of the short, rigid linkers with a high spacing occupying ratio to interpenetrate, even under high pressure, leaving the materials brittle.



Figure 4. Molecular dynamics investigation of OPOSS-MOP with different linker lengths. (a) Molecular structure of OPOSS-MOPs (hydrogen atoms are omitted here for clarity). (b) and (C) Structure evolution of OPOSS-MOPs with  $C_{10}$  linker and  $C_{16}$  linker during the elongation process, which demonstrates the disparity of their mechanical properties.

To further investigate this unexpected phenomenon, all-atom non-equilibrium molecular dynamics simulations are performed on OPOSS-MOP with shorter and longer linker chains systems, respectively, and elongation flow field is applied for the two systems. Detailed simulation information has been provided in the attached SI file. The stress-strain responses of two system are consistent with our experimental observations, OPOSS-MOP with shorter linker chains is brittle and OPOSS-MOP with longer linker chains is in high elastic state (**Figure 4**; Supporting Information, **Figure S14**). The evolution of interface structure also demonstrates the interpenetrated and inter-locked OPOSS in the outer shell of the SNPCs is the main cause of the significant enhancement of the viscoelasticity upon deformation (Supporting Information, **Supplementary movie files**).

#### **Dynamics of glassy SNPCs**

The unexpected elasticity of the OPOSS-MOP in the bulk state is correlated with the dynamics of the SNPCs. Three relaxation processes,  $\alpha$ ,  $\beta$  and  $\gamma$ , can be observed in the dielectric loss spectra of OPOSS-MOP (Figure 5a, 5b; Supporting Information, Figure S10), arising from motions of the SNPCs and within the SNPCs. Pure OPOSS shows fast relaxation with nearly constant permittivity ( $\epsilon$ ' and  $\epsilon$ '') independent of temperature and frequency (Supporting Information, Figure S9a, S9b). The OPOSS segments are expected to be under strong confinement in the OPOSS-MOP, restraining their intrinsic relaxations (Supporting Information, Figure S9c, S9d), which could arise from the interpenetration of the OPOSS-containing arms (Figure 3d). The correlation between the relaxation time and temperature for the  $\beta$ -relaxation (Supporting Information, Figure S10, green peaks) of OPOSS-MOP was established through a Vogel-Fulcher-Tammann (VFT) fitting (Supporting Information, Figure S11, green plot). Dynamic fragility<sup>[16]</sup> (m), calculated as 83, reflects the temperature dependence of the relaxation time near  $T_g$ . In comparison to conventional polymers, OPOSS-MOP shares the same fragility value with poly(ethyl acrylate), but much lower than polystyrene and polycarbonate with bulky side groups and polar functional moieties.<sup>[17]</sup> The moderate fragility value may be associated with the symmetric shape and soft structural units. It should be noted that the value of  $T_g$  from VFT fitting is 266 K, which is consistent with that measured from DSC ( $T_g = 263$  K, Supporting Information, Figure S4b).



Figure 5. Dynamic analysis of the structural relaxation for OPOSS-MOP via different research methods. (a) Temperature dependence of dielectric loss for OPOSS-MOP at seven selected testing frequency. (b) Broadband dielectric loss spectra for OPOSS-MOP under different temperatures. (c) Temperature sweep of OPOSS-MOP with an angle frequency of 10 rad/s. (d) Master curves for OPOSS-MOP with reference temperature at 30 °C from SAOS experiments.

# RESEARCH ARTICLE



Figure 6. Comprehensive analysis of hierarchical relaxation processes inside SNPCs. (a) Integrated diagram of shifting factors ( $\alpha_T$ ) for different samples and relaxation time (r) for multiple relaxation processes. (b) Molecular structures of OPOSS-Vinyl, OPOSS-MOP, OPOSS<sub>16</sub> and OPOSS<sub>24</sub>, the yellow circle represents individual OPOSS unit. (c) A picture of the hierarchical structure dynamics inside OPOSS-MOP.

Temperature sweep and time-temperature superposition of small-amplitude oscillatory shear (SAOS) experiments yielded the dynamic behaviors over a wide temperature and frequency range (Figure 5c, 5d; Supporting Information, Figure S12a). OPOSS-MOP exhibits a relaxation scaling exponent of 0.6 in the high frequency region (Figure 5d), indicating segmental dynamics resulting, more than likely, from the OPOSS.<sup>[18]</sup> Normally, due to the weak inter-particle attraction, SNPCs are supposed to gain mobility to reach the viscous state at the appropriate conditions, e.g. MOP-templated star polymers of PEG<sup>[19]</sup> behave as viscous melts above 40 °C. However, both temperature and frequency sweeps of OPOSS-MOP indicate that the storage modulus (G') is higher than the loss modulus (G'), suggesting that the SNPC assembly remains elastic, confirming the interpenetration of the crowded OPOSS GLs due to the weak temperature and frequency dependence (Figure 3d). The absence of a rubbery plateau in the dynamics of OPOSS-MOP indicates that the contribution of the interpenetration of the SNPCs to the mechanical performance may be not as strong as other systems with entanglements<sup>[20]</sup>, and that the disengagement of the SNPC at a particular level of applied external force is guite sharp (as evidenced by the mechanical behavior in Figure 3c). The stability of the OPOSS-MOP after all the mechanical characterizations was confirmed by GPC (Supporting Information, Figure S13), where no significant change in the molecular weight was observed.

The temperature dependences of the characteristic relaxation time ( $\tau$ ) and the time-temperature superposition shift factor ( $\alpha_{T}$ ) were used to unify the dynamic behaviors resulting from different measurements and different samples containing OPOSS, so as to develop a clear picture of SNPCs' hierarchical dynamics (**Figure 6a**, **6b**, **6c**).<sup>[21]</sup> Interestingly, the  $\gamma$ -relaxation of OPOSS-MOP, with an apparent activation energy ( $E_a$ ) of ~ 37.3 kJ/mol, exhibits similar *T* dependent dynamics as the rheological behavior of OPOSS (OPOSS-Vinyl), suggesting that the  $\gamma$ -relaxation of OPOSS-MOP is correlated with the dynamics of subunits (e.g. surface alkyl groups) of a single OPOSS. The  $\beta$ -relaxation and  $\alpha_{T}$  of OPOSS-MOP show similar trends at high *T* and the relaxation can be attributed to the dynamics of GLs

(OPOSS+Linker) that are thermally-activated to achieve a more homogeneous state at higher temperatures. The discrepancy at low temperature is generated from the existence of defects/heterogeneities in the interpenetrated region. As the slowest observable dynamics mode of OPOSS-MOP, the  $\alpha$ relaxation ( $E_a = 182.5 \text{ kJ/mol}$ ) is expected to be associated with the higher order structures of POSS, most likely a cooperative relaxation of multiple OPOSSs. The  $\alpha$ -relaxation shows a T dependence similar to the rheological dynamics of previously reported dendrimers of OPOSS, OPOSS<sub>16</sub> and OPOSS<sub>24</sub>, whose structural units are branching points composed of 2 or 3 OPOSS clusters that are closely connected (replotted in Figure 6b).[11] Therefore, we argue that the  $\alpha$ -relaxation of OPOSS-MOP is the cooperative relaxation of multi-OPOSS units arising from the interpenetration and inter-locking of the OPOSS-GLs of neighboring SNPCs.

#### Conclusion

The cluster-based supramolecular hierarchical structures define a transition regime between small molecules and colloids, introducing a new class of materials-by-design. The loose packing of OPOSS resulting from the branched surface alkyl groups and the low space occupying ratio of GLs on the MOP surface promotes deformability of SNPCs and the interpenetration of OPOSS-GLs. This increases the apparent space occupancy of OPOSS around the MOPs and locks in the interpenetrated structures between SNPCs, which contributes to the high elastic modulus. Moreover, the interpenetrated OPOSSs, though interlocked, have mobility in the linker zone, providing the origin of materials' elasticity. The unique physical interaction renders the materials with both high processability and high temperature robustness.

In summary, a new type of well-defined core-shell shaped molecular NPs were prepared by convergence of precise GLs with traditional MOPs. Scattering in bulk for SNPCs shows a glassy structures, absent long-range order, arising from the deformability of outer shell structures. By fine-tuning the surface

# **RESEARCH ARTICLE**

functionality, the dynamics and mechanical properties can be effectively regulated to obtain significantly different SNPC Among them, OPOSS-ended SNPCs materials. show unexpected elasticity and high modulus, absent entanglements or strong supramolecular interactions between SNPCs. The rational explanation is a comprehensive result of the inheritance of high mobility from the OPOSS and the so-facilitated interpenetration between GLs. The elastomers can be conveniently reprocessed via solution or pressure processing. Our work uncovers a new class of materials and opens a new pathway to the design of novel cluster materials for sensors and device applications with a specific elasticity, high temperature robustness and facile regeneration. The protocol can be generally extended to conventional NPs and colloid systems for improving their mechanical performances by applying cluster-bearing capping ligands.

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6

# **RESEARCH ARTICLE**

### **Table of Contents**



**Unexpected elasticity of SNPCs**: Novel supra-nanoparticle clusters (SNPCs) were synthesized by convergence of the metal organic polyhedron scaffolds with precise giant building blocks. The mechanical properties and structural dynamics can be effectively regulated by fine-tuning the surface functionalization of the terminal POSS moieties. Unexpected elasticity with high Young's modulus of the OPOSS-ended SNPCs was found to be highly correlated with the interpenetration of the neighboring GLs. Our work uncovers a new class of materials and opens a new pathway to the design of novel cluster materials for sensors and device applications with a specific elasticity, high temperature robustness and facile regeneration