Supporting Online Material for

Plastic and Moldable Metals by Self-Assembly of Sticky Nanoparticle Aggregates

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This PDF file includes:

SOM Text
Figs. S1 to S6
References
SUPPLEMENTAL INFORMATION

Contents:
Section 1. Experimental and synthetic details.
Section 2. Competitive Adsorption Equilibrium.
Section 3. NP-NP Interactions.
Section 4. Plasticity of supraspheres and suprasphere aggregates.
Section 5. Conductance Data.
Section 6. TEM images of supraspheres.
Section 7. Supplemental references.
Section 1. Experimental and synthetic details.

(1.1) Synthesis of 4,4’-bis(11-mercaptoundecanoyl)azobenzene [ADT]

11-Thioacetoxyundecanol

\[
\text{HO(CH}_2\text{)}_{11}\text{SCH}_2\text{CH}_2 + \text{CH}_2\text{CO}_2\text{H} \xrightarrow{\text{hv, AIBN}} \text{HO(CH}_2\text{)}_{11}\text{SCH}_2\text{CH}_3
\]

A mixture of undec-10-enol (12.00 g), thioacetic acid (20 mL) and AIBN (80 mg) was dissolved in methanol (50 mL) and irradiated with a 450 W Hg arc lamp in a quartz reactor under nitrogen atmosphere for 16 h. The reaction mixture was then concentrated \textit{in vacuo}. The residue was purified by column chromatography (chloroform:petroleum ether 3:1). Yield: 5.39 g (31%). \(^1\)H NMR: (DMSO-\textit{d}_6, 300 MHz) \(\delta\) 4.29 (br, 1H), 3.36 (t, 2H, \(J = 6.3\) Hz), 2.81 (t, 2H, \(J = 7.2\) Hz), 2.30 (s, 3H), 1.51-1.23 (m, 18H).

11-Thioacetoxy-1-bromoundecane

\[
\text{HO(CH}_2\text{)}_{11}\text{SCH}_2\text{CH}_3 \xrightarrow{\text{CBr}_4, \text{PPh}_3} \text{Br(CH}_2\text{)}_{11}\text{SCH}_2\text{CH}_3
\]

To a cooled solution of 11-thioacetoxyundecanol (2.0 g) and triphenylphosphine (5.3 g) in anhydrous (distilled over P4O10) dichloromethane (30 mL) was added a solution of tetrabromomethane (4.2 g) in anhydrous dichloromethane (15 mL). Stirring was continued for 24 h at room temperature. The solvent was evaporated \textit{in vacuo} and the residue extracted (five times) with petroleum ether. The crude product was purified by column chromatography (1:50 ethyl acetate:hexanes). Yield: 1.81 g (72%). \(^1\)H NMR: (acetone-\textit{d}_6, 300 MHz) \(\delta\) 3.51 (t, 2 H, \(J = 6.6\) Hz), 2.87 (t, 2 H, \(J = 7.2\) Hz), 2.31 (s, 3 H), 1.87 (t, 2H, \(J = 7.2\) Hz), 1.65-1.15 (m, 18H).
4,4'-Dihydroxyazobenzene

4-Hydroxyaniline was dissolved in 170mL of 1 M HCl and cooled to 0°C. A solution of KNO₂ (11.27g in 34mL H₂O) was added dropwise under constant stirring. The mixture was diluted by adding 340 mL pre-cooled methanol. In a separate batch, phenol (9.24 g) and KOH (10.42 g) were dissolved in 48 mL methanol and cooled to 0°C. This phenolate solution was added dropwise under constant stirring. The resulting red solution was stirred for additional 24 h. 1 M HCl was added to precipitate the crude product, which was collected by filtration. The crude product was then recrystallized from glacial acetic acid. Yield: 5.515 g (53%). ¹H NMR: (DMSO-d₆, 300 MHz) δ 10.10 (s, 2H), 7.75 (d, 4H, J = 8.4 Hz), 6.90 (d, 4H, J = 8.4 Hz).

4,4'-Bis(11-thioacetoxyundecanoxy)azobenzene

On the basis of (SII). 4,4'-dihydroxyazobenzene (150 mg; 1 eq) and 11-thioacetoxy-1-bromoundecane (465 mg; 2.14 eq) were dissolved in distilled DMF (11 mL). K₂CO₃ (386 mg) and KI (catalytic amount) were added and the mixture was stirred under nitrogen atmosphere at
80°C for 4 h. Solvent was removed in vacuo and the residue was dissolved in dichloromethane and washed (three times) with water. The solution was dried (MgSO₄) and the solvent was evaporated. The crude product was purified by column chromatography (1:10 ethyl acetate:hexanes). Yield: 390 mg (83%). ¹H NMR: (CDCl₃, 300 MHz) δ 7.81 (d, 4H, J = 8.7 Hz), 6.99 (d, 4H, J = 8.7 Hz), 4.04 (t, 4H, J = 6.6 Hz), 2.87 (t, 4H, J = 7.2 Hz), 2.33 (s, 6H), 1.95-1.05 (m, 36H).

4,4’-Bis(11-mercaptoundecanoxy)azobenzene

4,4’-Bis(11-thioacetoxyundecanoxy)azobenzene (400 mg) was dissolved in chloroform-methanol mixture (5 mL : 15 mL) and 2.5 M HCl solution in methanol (20 mL) was added. The mixture was refluxed in nitrogen atmosphere for 4h. After that time, the reaction mixture was concentrated in vacuo and the crude product was purified by column chromatography (1:5 dichloromethane:hexanes). Yield: 311 mg (89%). ¹H NMR: (CDCl₃, 300 MHz) δ 7.94 (d, 4H, J = 9.0 Hz), 7.00 (d, 4H, J = 9.0 Hz), 4.06 (t, 4H, J = 6.3 Hz), 2.54 (q, 4H, J = 7.4 Hz), 2.05-0.90 (m, 36H). ESI-MS: 587.4 (M+H⁺).

(1.2) Preparation of Nanoparticles.

Materials. Silver acetate AgOAc, palladium bis(acetylacetonate) Pd(acac)₂, tetrabutylammonium borohydride (TBAB), dodecylamine (DDA), decanoic acid (DA) and toluene were purchased from Sigma-Aldrich. Platinum (IV) chloride PtCl₄ and DMSO were purchased from Alfa Aesar. Didodecyldimethylammonium bromide (DDAB) was purchased from TCI America. Hydrogen tetrachloroaurate trihydrate HAuCl₄·3H₂O was purchased from DF
Goldsmith. Hydrazine monohydrate $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was purchased from Fluka. All reagents and solvents were used without further purification.

*Synthesis of Nanoparticles.* Au, Ag, Pt, Pd and Ag NPs were prepared according to a modified literature procedures ($S2$). For AgNPs, 9.6 $\mu$L hydrazine was sonicated in a solution of 516 mg decanoic acid (DA) in 30 mL toluene until dissolved, followed by the addition of 300 $\mu$L TBAB solution in toluene (9.7 mM). In a separate vial, 51 mg AgOAc and 111 mg DDA were added to 5 mL toluene and the solution was sonicated until dissolved. Thus prepared Ag$^+$ solution was then added dropwise to the hydrazine solution under vigorous stirring to yield a yellow solution of AgNPs (5.3 ± 0.3 nm). Au, Pt and PdNPs were synthesized by a seeded-growth method. For AuNPs, DDAB stock solution was first prepared by dissolving 925 mg DDAB in 20 mL toluene. 50 mg HAuCl$_4 \cdot 3\text{H}_2\text{O}$ and 450 mg DDA were added to 12.5 mL of the stock solution and sonicated until dissolved. Gold (III) was then reduced by dropwise addition of 125 mg TBAB in 5 mL of the DDAB stock solution under vigorous stirring. Thus prepared seed (4 nm NPs) solution was aged for 24 hours. The growth solution was prepared by adding 7 mL of the aged seed solution to 50 mL of toluene containing 200 mg HAuCl$_4 \cdot 3\text{H}_2\text{O}$, 1.00 g DDAB and 1.85 g DDA. Finally, 131 $\mu$L hydrazine dissolved in 20 mL of the stock solution was added dropwise to the growth solution under vigorous stirring. Thus prepared AuNPs had a diameter of 5.6 ± 0.6 nm.

For PtNPs, seed solution (2 nm NPs) was first prepared according to a literature procedure. 3.5 mL of seed solution was then added to a growth solution of 25 mL toluene, 84 mg PtCl$_4$, 500 mg DDAB and 925 mg DDA. PtNPs with an average diameter of 6.1 ± 0.6 nm were finally grown by a dropwise addition of 64 $\mu$L hydrazine dissolved in 10 mL of DDAB stock solution.

PdNPs (4.3 ± 0.5 nm) were synthesized in a manner analogous to AuNPs. Briefly, Pd seeds were prepared by a dropwise addition of 25 mg TBAB in 1 mL of stock solution to a mixture of 6 mg Pd(acac)$_2$, 90 mg DDA and 2.5 mL of stock solution. The seed solution was then aged for 24 hours. Growth solution was prepared by the addition of 3.5 mL of the aged solution to 56 mg Pd(acac)$_2$, 500mg DDAB, and 925 mg DDA dissolved in 25 mL toluene. Finally, 20 mM hydrazine in 10 mL of stock solution was added dropwise under vigorous stirring.
Fig. S1. Transmission electron microscope (TEM) images of as-prepared (a) Au NPs, (b) Ag NPs, (c) Pd NPs, and (d) Pt NPs.

(1.3) Characterization of Supraspheres.

Suprasphere sizes were measured by Dynamic Light Scattering (Brookhaven Instruments BI-9000; operating wavelength 514 nm; scattering angle 90°) and by transmission electron microscopy (Hitachi H-8100; accelerating voltage 200 kV). Mechanical properties of supraspheres were probed with TriboIndenter (Hysitron, Inc.) device. Suprasphere assemblies (wires and foams) was characterized by scanning electron microscopy (SEM, LEO 1525, 3-12 kV) and their purity was verified using energy dispersive analysis by X-rays (EDX, Hitachi S3500) and X-ray photoelectron spectroscopy (Omicron XPS). Various regions of the same sample were analyzed by focusing the beam at an appropriate region. Surface area was estimated using the Brunauer-Emmett-Teller (BET) technique.
Section 2. Competitive Adsorption Equilibrium.

In experiments, \textit{trans}-azobenzene dithiol (ADT) was mixed with gold nanoparticles (AuNP), dodecylamine (DDA) capping agent, and didodecylmethylammonium bromide (DDAB) surfactant. After equilibration, the AuNPs were covered by a mixture of ADT and DDA (cf. Fig. 1B in the text; the adsorption of DDAB was negligible in comparison) whose composition depended on the relative amounts of DDA, ADT, and AuNP in solution. Because direct instrumental techniques were not feasible to determine the amounts of NP-bound ADT (e.g., relaxation times were too long for NMR, NPs were too small for Raman), we used thermodynamic reasoning to estimate the number of surface bound ADT ligands per NP. Specifically, we estimated the fractional coverage of ADT by solving the equilibrium adsorption problem accounting for the \textit{finite} number of ADT molecules and gold adsorption sites in solution. The equilibrium constants for the adsorption of ADT and DDA onto gold – \( K_T \) and \( K_D \), respectively – are related to the equilibrium concentrations as follows.

\[
K_D = \frac{[DS]}{[S][D]} \quad \text{and} \quad K_T = \frac{[TS]}{[S][T]}
\]

Where \( [DS] \) and \( [TS] \) represent, respectively, the concentrations of DDA and ADT adsorbed onto a gold site \( S \), and \( [D] \) and \( [T] \) represent the concentrations of DDA and ADT in solution. Furthermore, the total number of gold sites and ADT molecules must be constant:

\[
[S]_{total} = [S] + [DS] + [TS] \quad \text{and} \quad [T]_{total} = [TS] + [T].
\]

Due the excess of DDA in solution (\([D] \gg [S]_{total}\), its concentration in solution remains unchanged to good approximation.

For the experiments discussed in the text, \([D] = 35 \text{ mM}, \) [Au atoms] = 2 mM, and \([T] \) varied from zero to 2.4 mM. From the AuNP diameter (5.6 nm), we estimate that each particle contained \(~5400\) gold atoms and \(~460\) binding sites (assuming a binding area of 21.4 \( \text{Å}^2 \)) (S3). Therefore, the concentration of binding sites can be estimated as \([S]_{total} = 0.17 \text{ mM}.\) Equilibrium adsorption constants for alkyl thiols on gold surfaces have been measured experimentally to be \( K_T \sim 10^4 \text{ M}^{-1} \) (S4). While there exist no experimental data for the adsorption of alkyl amines onto gold surfaces, we estimate [using data from digestive ripening experiments (S4-S5)] that \( K_D \sim 10^2 \text{ M}^{-1} \) – i.e., about two orders of magnitude less than that of thiols. From these estimates, one can calculate the fractional surface coverage of ADT on the surface of the AuNPs.
\[ \theta = \frac{1}{2} \left( \frac{K_D[D]}{K_T[S]_{total}} - \sqrt{\left( \frac{K_T^2[T]_{total}^2 - 2K_T^2[D][S]_{total} + 2K_TK_D[D][S]_{total} + \ldots}{K_T^2[S]_{total}^2 + 2K_TK_D[S][S]_{total} + 2K_T[S]_{total} + K_D^2[D]^2 + 2K_D[D] + 1} \right) + K_T[S]_{total} + K_T[T]_{Total} + 1} \right) \]

Where \( \theta \) is the fractional coverage of ADT (i.e., \([TS]/[S]_{total}\)). The plots below give the fractional coverage, \( \theta \) (Fig. S2, left) and the numbers of ADT adsorbed onto one AuNP (Fig. S2a) and the numbers of ADT adsorbed onto one AuNP (Fig. S2b). The minimum ADT concentration necessary for forming aggregates was determined experimentally to be \( \sim 0.02 \) mM (Fig. 1C), at which there were \( \sim 18 \) ADT molecules adsorbed onto each AuNP (cf. dashed lines in plots).

**Fig. S2.** (a) Fractional surface coverage of ADT as a function of ADT solution concentration, calculated for \([DDA] = 35 \text{ mM}, [\text{Au atoms}] = 2 \text{ mM}, K_T \sim 10^4 \text{ M}^{-1}, K_D \sim 10^2 \text{ M}^{-1} \). (b) Number of ADT adsorbed per NP as a function of ADT solution concentration.
Section 3. NP-NP Interactions

The interaction energy between two cis-ADT-coated NPs can be estimated as the dipole-dipole energy gained by bringing the NPs into close contact. This energy may be expressed as the product of the number of dipole-dipole pairs and the energy per pair – i.e., \( E_{\text{NP}} = N_{\text{dd}}E_{\text{dd}} \). To estimate \( N_{\text{dd}} \), we consider the NP surface to be covered with a given number \( N_{\text{azo}} \) of randomly distributed cis-azobenzene dipoles. At contact, the effective area between the spheres can be approximated as \( A_{\text{eff}} \approx 2\pi Ra \) (S6), where \( R \approx 4.2 \text{ nm} \) is the NP radius (including the SAM: \( R_c \approx 2.8 \text{ nm} \) and SAM is \( \sim 1.4 \text{ nm} \) thick), and \( a \) is a characteristic molecular scale \( a \) (here, \( a \sim 5\text{Å} \), corresponding to closest dipole-dipole spacing). Thus the number of dipole-dipole pairs can be estimated as \( N_{\text{dd}} \approx (N_{\text{azo}}A_{\text{eff}}/4\pi R^2)^2 \). The pairwise dipole-dipole energy is given by

\[
E_{\text{dd}} = \frac{[(\mu \cdot \mu)/|\vec{r}|^3 - 3(\mu \cdot \vec{r})(\mu \cdot \vec{r})/|\vec{r}|^5] / (4\pi\varepsilon_0\varepsilon)}{4\pi \varepsilon_0 \varepsilon} \]

and for the most favorable configuration of “stacked”, antiparallel dipoles (cf. Fig. S3 below) simplifies to \( E_{\text{dd}}(r) = -\frac{\mu^2}{4\pi\varepsilon_0\varepsilon r^4} \), where \( \mu \) is the dipole moment (here, \( \mu = 4.4 \text{ D} \)), \( \varepsilon_0 \) is the dielectric permittivity of vacuum, \( \varepsilon \) is the dielectric constant of the medium (e.g., \( \varepsilon_{\text{toluene}} = 2.379 \)), \( k \) is Boltzmann’s constant, \( T \) is temperature, and \( r \) is the distance between dipoles (here, \( r = a \sim 5\text{Å} \)). Because the magnitude of this interaction for dipoles in close contact is greater than \( kT \) (i.e., \( E_{\text{dd}}(a) \sim 3.9 \text{ kJ/mol} \) and \( kT \sim 2.5 \text{ kJ/mol} \), such that \( E_{\text{dd}}(a)/kT \sim 2 \)), we make the approximation that the dipoles are immobilized in some configuration close to the minimal dipole-dipole energy \( E_{\text{dd}}(a) \). Therefore, the NP-NP interaction energy is given by \( E_{\text{NP}} \approx N_{\text{azo}}^2\mu^2/16\pi\varepsilon_0\varepsilon R^2a \).

Substituting numerical values for the relevant parameters, this expression becomes: \( E_{\text{NP}} = -(0.014 \text{ kJ/mol})N_{\text{azo}}^2 \). Therefore, the interaction energy is comparable to the thermal energy of an NP \((3/2kT)\) when \( N_{\text{azo}} \sim 16 \), which is close to our experimental estimate of \( \sim 18 \) ADT molecules per NP necessary for forming aggregates (cf. Fig. 1C in the main text).

**Fig. S3.** Two cis-ADT ligands with their azobenzene units stacked on “on-top” of one another. The energy of the structure was minimized using CHARMM force-field and with the conformations of the side-chains constrained.
Section 4. Plasticity of supraspheres and suprasphere aggregates.

**Plasticity of individual supraspheres.** Once placed on a substrate, a suprasphere undergoes deformation that is driven by the adhesive (VdW) forces with the substrate. In this process, gravity is negligible since gravitational energy is several orders of magnitude smaller than adhesive energy (e.g., $E_g = 2\pi R^4 \rho / 3 \approx 10^{-23}$ J vs. $E_{adh} \sim \pi R^2 \gamma \approx 10^{-15}$ J for SS radius $R \sim 100$ nm, adhesion radius $r \sim 10$ nm, density $\rho \sim 1$ g/cm$^3$, and typical value of $\gamma \sim 10$ J/m$^2$; also cf. Fig. S4.1). The adhesive forces tend to increase the interfacial area of contact and, as a result, the SS flattens and eventually assumes a shape that is well approximated by a truncated sphere (Fig. S4.2). Importantly, the observation that contact angles of the spheres change with sphere size (cf. main text and Fig. 1D,E therein), indicates clearly that they behave like a deformable solid (and not like, for example, a droplet of “liquid” for which contact angles would be independent of size).

![Fig. S4.1.](image) Side-view of a group of supraspheres on a silicon surface. Some of the supraspheres are “glued” together and stand up from the surface indicating that at this scale gravity is negligible compared to adhesive forces.

![Fig. S4.2.](image) (left) An SEM image of a typical suprasphere with its contour highlighted in red. (right) The contour and the least-square fit of an approximating circle (blue). Fitting to this and other contours was done using Matlab.
The so-called Ramberg-Osgood (RO) (S7) model of hardening provides a general framework for the analytical description of the spheres’ mechanical properties. In brief, the RO model assumes that the deformation of a body preserves its volume and proceeds in two steps – initially, it is reversible and elastic (until stress reaches the yield threshold, $\sigma_y$) and then irreversible and plastic. According to this scenario, the strain, $\varepsilon$, is a sum of elastic, $\varepsilon_e$, and plastic, $\varepsilon_p$, components. In the elastic regime, the stress, $\sigma$, is related to the elastic deformation by $\varepsilon_e = \sigma/E$, where $E$ is the Young's modulus. The plastic deformation is related to the applied stress, $\sigma$, by the following formula: $\varepsilon_p = (\sigma - \sigma_y)/K$, where $K$ is the plastic resistance, and the exponent $M$ determines the stress-strain dependence in the yield region.

For the supraspheres, the experiments suggest that the elastic strain contribution is small (cf. images of the glued spheres), and the so-called “rigid-elastic solid” approximation can be used. Within this approximation, $\sigma = \sigma_y + K\varepsilon_p^{1/M} \approx K\varepsilon_p^{1/M}$. In addition, the initial radius of the SS, $R_0$, and the radius of the deformed sphere, $R$, can be related by $R_0 = 4R(1 - 4x/\pi + \sin^2 x \cos x)^{1/3}$, where $x = \alpha/2$, and $\alpha$ is defined in Fig. S4.3 and measures the degree of deformation (and strain, $\varepsilon \sim \alpha$) of the SS.

![Fig. S4.3. Quantities used to describe deformation of the suprasphere. Forces driving the deformation and acting around the perimeter of the contact surface are indicated schematically by blue arrows.](image)

The characteristic stress, $\sigma$, in the SS resulting from the plastic deformation can be then estimated by first noting that the atomic forces act at typical distances of the order of a few Å, which are small compared to the size of the SS. Thus, the SS-surface force, $F$, responsible for the deformation is localized at the line of contact between the SS and the substrate (blue lines in Fig. S4.3). One has: $F \sim 2\pi r$, where $r$ is the radius of the contact area between the SS and the substrate. One the other hand, the characteristic area, $A = \pi r^2$, of the yield surface is equal to the contact area. Thus, one has $\sigma \sim F/A \sim r^{-1}$. One can write the scaling relation for the plastic
deformation as \( \alpha^M \sim r^{-1} \sim \left( R \sin \alpha / 2 \right)^{-1} \). It then follows that \( \alpha \) is a decreasing function of the (apparent) radius, \( R \), in agreement with experiment.

In Fig. 1D of the main text, we quantified this trend in terms of the aspect ratios, \( h/w \), for spheres of various sizes (these ratios were a more accurate measure of deformation than contact angles obtained from SEM images). The curve in the figure was obtained by numerical fitting the relation \( \alpha^M \sim r^{-1} \sim \left( R \sin \alpha / 2 \right)^{-1} \) to experimental data.

**Section 5. Conductance Data.**

**Fig. S5.** The SEM images illustrate the evolution of a freestanding wire made of \( <D> \sim 150 \text{ nm} \) Au supraspheres (overall wire dimensions are \( \sim 500 \mu\text{m} \) by \( 150 \mu\text{m} \) by \( 30 \mu\text{m} \); scale bare = 200 nm) under gentle heating at 50 °C. During the entire transformation from a plastic (left) to a microcrystalline (right) material, the wire maintains Ohmic current-voltage characteristics, but with decreasing resistance. The I-V curves were recorded at 5, 720, and 1800 min. from the beginning of heating. Standard deviations of all measurements are commensurate with the sizes of the solid markers except for voltages below \( \sim 0.1-0.2 \text{ V} \) where they are up to 10%-30% of the value of the current (below the lowest measured voltages, instrument noise was too large to determine the currents reliably). Note that the scales on the graphs are logarithmic to emphasize Ohmic conductance all the way down to low voltages and sub-picoampere currents. As heating progresses, conductance increases (i.e., lines shift upwards).
Section 6. TEM images of supraspheres.

Fig. S6. TEM images of SS obtained from NPs with low (a) and high (b) ADT surface coverages. The images demonstrate that the metal cores of the NPs within SS are separated by the SAMs coating these cores.

Section 7. Supplemental References.