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Using Aggregation to Chaperone Nanoparticles Across Fluid Interfaces

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Capitalizing on the aggregation of NPs induces an unusual "single particle-aggregation-single particle" transfer process, which can be established through either ligand-exchange processes or electrostatic interactions. By introducing a jammed NP-polymer assembled layer at the liquid/liquid interface (LLI), the transfer process can be suppressed, opening a new strategy to manipulate the dispersion of nanoparticles in various liquid media.

Nanoparticles (NPs) transfer is usually induced by adding ligands to modify NP surfaces, but aggregation of NPs oftentimes hampers the transfer. Here, we show that aggregation during NP phase transfer does not necessarily result in transfer failure. Using a model system comprising gold NPs and amphiphilic polymers, we demonstrate an unusual mechanism by which NPs can undergo phase transfer from the aqueous phase to the organic phase via a single-aggregation-single pathway. Our discovery challenges the conventional idea that aggregation inhibits NP transfer and provides an unexpected pathway for transferring larger-sized NPs ($>20^{^}$nm). The charged amphiphilic polymers effectively act as chaperons for the NP transfer and offer a unique way to manipulate the dispersion and distribution of NPs in two immiscible liquids. Moreover, by intentionally jamming the NP-polymer assembly at the liquid/liquid interface, the transfer process can be inhibited.

Aggregation
Assembly
Gold Nanoparticles

Interfaces

Transfer

Introduction

Stable nanoparticle (NP) dispersions in a liquid can be achieved by the favorable interactions of the ligands attached to the NPs with the liquid.[1] The transfer of NPs across the interface between two immiscible liquids is crucial for the synthesis, processing, and modification of NPs in various fields such as fine chemicals, cosmetics, food industries, and biomedicine.[2] Usually, the transfer process is induced by adding ligands to modify the surface chemistry of NPs in situ.[2b] Taking citrate-functionalized AuNPs (cit-AuNPs) as an example, the negative surface charges prevent aggregation due to strong Van der Waals attractions.[3] The addition of oppositely charged surfactants or phase transfer agents will modify the surface chemistry,[4] leading to the transfer of cit-AuNPs from the aqueous phase to the oil phase. During this process, NPs aggregation can easily occur owing to neutralization of surface charges,[5] causing the failure of the transfer (Figure^^1<figr1> a-c). To avoid this, previous studies have focused on either the surface modification of AuNPs with polymer ligands (alkanethiols, alkylamines, etc.) in the aqueous phase[6] or the addition of surfactants or phase transfer agents to a second immiscible phase via ligand exchange or electrostatic interactions, by vigorous blending[5a,7] (Figure^^1<xfigr1>b). For example, Li et^^al. utilized different HS- and NH$_2$-terminated polymer ligands to transfer the AuNPs from the aqueous solution to *n*-hexane by shaking the biphasic system.[5b] Hassinen and co-workers synthesized cationic AuNPs (8--20^^nm) by a rapid two-step phase transfer protocol using amine and thiol ligands as phase transfer agents.[4] After transferring into the toluene with the assistance of octadecylamine, AuNPs redispersed in the aqueous phase via the ligand exchange process. Karg et^^al. realized the phase transfer of

AuNPs by using amphiphilic alkylamine ligands and found that the alkyl chain lengths of the ligands would affect the transfer efficiency.[6b] Despite some success, the aggregation is oftentimes believed to be indication of the failure of the transfer. In addition, most of the current methods show that there are challenges in transferring large AuNPs (>20 nm) from water to organic phases due to the poorly protected surface caused by the lower curvature of the larger NPs[2b,5a,6a,7--8] (Figure 1<xfigr1>c).

Here, we demonstrate that aggregation of NPs during the phase transfer does not necessarily result in transfer failure. In contrast to the conventional idea of modifying surfaces and transferring individual NPs, we demonstrate an unconventional mechanism wherein NPs can undergo phase transfer from the aqueous phase to the organic phase through a single-aggregation-single pathway. To gain a molecular understanding of this unique phase transfer pathway, we used gold NPs (AuNPs) as model particles, as the surface-plasmonic effect of AuNPs enables direct characterization of their dispersion state, whether as isolated individual NPs or as aggregated NPs.

Results and Discussion

An unusual mechanism for transferring NPs between two immiscible phases

To avert aggregation of NPs and efficiently transfer NPs, the mechanism discovered in this work follows an unusual "single particle-aggregation-single particle" strategy, as schematized in Figures 1<xfigr1>a, d--f. Without any external additives, cit-AuNPs,~30 nm in diameter, are well-dispersed in an aqueous medium, showing a wine-red color. By introducing an organic phase, specifically dichloromethane (DCM), which has a higher density than water, dissolving ligands such as aminopropyl-terminated polydimethylsiloxane (H_2N-PDMS-NH_2) or mono-aminopropyl-terminated polydimethyl-

siloxane (PDMS-NH$_2$), an interface is created between the water and oil phases.The ligands diffuse to and assemble at the interface but also diffuse into the aqueous phase where they electrostatically bind to citrate groups of NPs, forming a corona of PDMS around cit-AuNPs. This screens repulsive electrostatic interactions between AuNPs and leads to aggregation of the NPs (Figure 1<xfigr1>d). Due to gravity, the aggregated AuNPs settle at the water/oil interface (Figure 1<xfigr1>e). The augmented presence of polymer ligands anchored to the NP surface enhances the hydrophobicity of the particles, facilitating their dispersion into the organic phase. The solubility of the hydrophobic PDMS chains bound to the particles causes a disruption of the aggregates into single PDMS chain-covered particles (Figure 1<xfigr1>f). Insets in Figures 1<xfigr1>d--f are snapshots of aqueous cit-AuNPs dispersions in contact with DCM containing 5 wt% H$_2$N-PDMS-NH$_2$, corresponding to each state of the transfer process, respectively.

Experimentally, we tested the mechanism by using the cit-AuNPs dispersion in contact with DCM having 0.1 wt% to 5 wt% concentrations of H$_2$N-PDMS-NH$_2$ (M_n~27 kg mol^{-1}) (Figure 2<figr2>a). The observed change in the color of the AuNP dispersions from wine-red to dark blue with increasing H$_2$N-PDMS-NH$_2$ concentration indicates the aggregation of AuNPs. These aggregates settle at the water/oil interface due to gravity, forming a dark film composed of the aggregated AuNPs. Within one day, the aqueous phase becomes colorless, indicating the nearly complete removal of AuNPs from the aqueous phase. This demonstrates that H$_2$N-PDMS-NH$_2$ molecules can cross the interface, potentially by forming micelles or other structures that freely diffuse into the aqueous phase. Once in the aqueous phase, the H$_2$N-PDMS-NH$_2$ interacts with cit-AuNPs, reducing the charge density and promoting their aggregation.

These aggregates are unstable due to low electronegativity (Figure S1b), and sufficiently dense to sediment under gravity and form a layer at the water/oil interface.

Normally, the aggregation of NPs is irreversible, with a precipitate forming at the base of the container. Here, the water/DCM interface serves as the bottom of the container, where a film composed of amphiphilic-polymer-modified AuNPs aggregates is formed. This arrangement facilitates favorable interactions between DCM and the PDMS present in the aggregates. Due to DCM being a good solvent for H_2N-PDMS-NH_2, the polymer chains attached to the citrate ligands of the AuNPs become swollen by DCM. This swelling causes the aggregates to break up, resulting in the formation of individual cit-AuNPs with a PDMS corona. As a result, the organic phase, which has a high concentration of H_2N-PDMS-NH_2, changes from colorless to wine-red over a period of 30^^days in contact with the AuNP dispersion. Specifically, the organic phase with 5^^wt% or 3^^wt% H_2N-PDMS-NH_2 gradually turned pink after a few days and eventually wine-red after 30^^days. Meanwhile, the film of AuNP aggregates at the water/DCM interface disappeared. In addition, there was no sediment of AuNPs on the bottom of the vial, indicating the single NPs remained well dispersed. Ultraviolet-visible (UV/Vis) absorption spectrum of the initial aqueous phase dispersing individual AuNPs is identical to that of the DCM phase after the transfer process was complete, indicating that individual AuNPs are now dispersed in the organic phase (Figure^^S1a).

To gain further insight into the aggregation of AuNPs in the aqueous phase, we measured time-dependent UV/Vis spectra of the AuNP dispersions after contact with DCM containing 5^^wt% H_2N-PDMS-NH_2 (Figure^^2<xfigr2>b, c). In the pristine solution, the AuNP dispersion exhibited a prominent absorption peak at 529^^nm, which is consistent with the surface plasmonic resonance of AuNPs reported in previous studies.[9] However, upon immediate contact, the absorption peak at 529^^nm diminished, and a broad peak at 710^^nm emerged, indicating the initiation of AuNP aggregation. Over time, the absorption peak at 710^^nm red-shifted to higher wavelengths, and the entire absorption spectrum became more flattened, indicating a gradual enlargement of the AuNP aggregates within the aqueous phase. After 12^^hours, no absorption peaks were observed, as a sign of sedimentation of AuNP

aggregates at the water/DCM interface. The transfer and dispersion of AuNPs into DCM were characterized using in situ UV/Vis spectroscopy (Figure 2b, d). During the first 24 hours, no absorption was observed, indicating no transfer to the organic phase. After 1 day, no characteristic absorption band was detected, but instead, a broad, non-linear absorption was observed, suggesting that the decrease in transmitted light was attributed to scattering rather than absorption. The exact origin of this scattering is unknown but, more than likely arises from the presence of water droplets within DCM (Figure S2). After ~20 days of quiescent and isothermal contact between the aqueous dispersion of cit-AuNPs and the DCM solution of H_2N-PDMS-NH_2, an absorption peak at~529 nm was seen in the organic phase, demonstrating the presence of individual AuNPs in the DCM phase.

We conducted additional studies to examine the influence of ligands concentration on the transfer and redispersion process. Figure 2e illustrates the absorption spectra of resulting DCM solutions with different H_2N-PDMS-NH_2 concentrations after 30 days in quiescent contact with aqueous dispersions of cit-AuNPs. It is evident that most of the samples show a similar absorption spectrum with a characteristic peak at~529 nm, implying that this transfer and redispersion process is independent of the concentration of polymer ligands. To quantify the transfer process, we used the transfer efficiency, $E_T = A_o/A_w$, where A_o and A_w represent the absorbances of AuNPs at 529 nm in the organic and original aqueous phases, respectively.

To establish a correlation between the absorbance of AuNPs at 529 nm and their concentration, we initially measured the absorption spectra of aqueous solutions with varying AuNP concentrations. This calibration process enabled us to determine the linear relationship between the absorbance and the concentration of AuNPs, as depicted in Figure S3a. Additionally, we conducted absorption spectra measurements of AuNPs in both water and

DCM at the same concentration to further validate the aforementioned relationship (Figure$^{\wedge\wedge}$S3b), demonstrating the applicability of the derived equation.

As shown in the inset of Figure$^{\wedge\wedge}$2<xfigr2>e, higher ligand concentrations lead to a more efficient transfer of AuNPs from the aqueous phase to the organic phase, where the highest value of transfer efficiency is 47$^{\wedge}$% for 5$^{\wedge\wedge}$wt% H_2N-PDMS-NH_2 in DCM. Furthermore, we tested the transfer process using external forces. As shown in Figure$^{\wedge\wedge}$S4, after shaking 30$^{\wedge\wedge}$s by hand, the mixture of cit-AuNP dispersion and DCM containing 5$^{\wedge\wedge}$wt% H_2N-PDMS-NH_2 turned emulsion-like, and the colorless DCM phase was gradually separated. Different from the instant phase transfer by shaking in the previous studies, it still took~3$^{\wedge\wedge}$days to transfer NPs into DCM. Therefore, external forces can accelerate the transfer process, but not that much, due to the amphiphilicity of H_2N-PDMS-NH_2 ligands.

The aggregation of AuNPs in aqueous solutions could be attributed to a change in pH[10] rather than the interaction of the ligands. To examine this, we prepared cit-AuNP dispersions having pH values from 1.8 to 12. The UV/Vis absorption spectra of these dispersions are presented in Figure$^{\wedge\wedge}$S5a. Aggregation was observed in dispersions with pH values below 4 or above 11, as indicated by the broad absorption peaks at wavelengths longer than 529$^{\wedge\wedge}$nm. In the pH range from 4 to 11, the absorbance at 529$^{\wedge\wedge}$nm (Figure$^{\wedge\wedge}$S5b) remained unchanged, demonstrating the stability of the dispersions. Therefore, it can be concluded that pH is not the underlying cause of the observed aggregation behavior in this study.

In addition to the impact of pH on NP aggregation, the influence of pH on the transfer process was also examined. Figure$^{\wedge\wedge}$S6 shows snapshots of cit-AuNP dispersions in contact with a 5$^{\wedge\wedge}$wt% H_2N-PDMS-NH_2 (M_n~27$^{\wedge\wedge}$kg$^{\wedge}$mol$^{<M->1}$) solution in DCM for up to one week. Notably, the cit-AuNP dispersions with pH values between 4 and 10 show distinct color changes upon contact with the organic phase. This indicates that the diffusion of polymer

ligands from the DCM phase is enhanced with decreasing pH. After 3-day contact, all the cit-AuNP dispersions appear colorless except for that at pH~11. With prolonged contact time (7~days), the organic phase turns red for the cit-AuNP dispersions with pH<5. For other pH values, no obvious change is observed in the organic phase. Interestingly, the aggregates formed in the aqueous phase do not transfer into the organic phase for cit-AuNP dispersions with pH~1.8 and pH~12. In the former case, the transferred polymer ligands in the aqueous phase tend to react with excess dissociated citrate, rather than the surface-bound citrate on AuNPs. In the latter, the strong base environment hinders H_2N-PDMS-NH_2 from transferring into the aqueous phase (as also verified by the fact that no aggregation of cit-AuNPs was observed with pH~11), causing a significant reduction in the interactions between the H_2N-PDMS-NH_2 and the citrate anchored to the AuNPs.

Transport of NPs across fluid interfaces induced by ligands transfer

If aggregation of cit-AuNPs is induced by the transferred polymer ligands from the organic phase, the amphiphilic nature of these polymer ligands should lead to a reduction in the surface tension of AuNP dispersions. Hence, we measured the time-dependent surface tension for droplets of pure water and the cit-AuNP dispersion in a 5~wt% H_2N-PDMS-NH_2 solution in DCM as a function of time. As shown in Figure~3<figr3>a, the surface tension (ST) (against air) of pure water and the cit-AuNP dispersion remains constant at~73~$mN\cdot m^{-1}$ over time. However, for pure water that has been contacted with the organic phase, a continuous reduction in the ST is observed, indicating that H_2N-PDMS-NH_2, as expected, could easily transfer to the aqueous phase due to its finite solubility in water. Increasing contact time leads to a further reduction in the ST, suggesting a continuous migration of H_2N-PDMS-NH_2 from DCM to water. With cit-AuNPs in the aqueous phase, a more pronounced reduction in the ST of the aqueous phase is seen. After 1-minute contact, the ST decreases to~50~$mN\cdot m^{-1}$ and then to 43~$mN\cdot m^{-1}$ after 1200 seconds. These

data suggest that electrostatic interactions between negatively charged cit-AuNPs

(Figure^^S1b) and positively charged H_2N-PDMS-NH_2 enhance the migration of polymer

ligands from the organic phase to the aqueous phase. To demonstrate the effect of the binding

between cit-AuNPs and polymer ligands, the interfacial tension (IFT) was measured between

water and DCM with and without cit-AuNPs and polymer ligands. The IFT between pure

water and pure DCM is measured to be~30^^mN^m^{-1}. In the presence of H_2N-PDMS-

NH_2, the IFT gradually decreases to~23^^mN^m^{-1} after 1200 seconds due to the

amphiphilic nature of the polymer ligands. The dispersion of cit-AuNPs in the aqueous phase

leads to a more rapid and pronounced reduction in IFT (Figure^^3<xfigr3>b), indicating the

interfacial assembly of the polymer ligands and their interactions with cit-AuNPs.

To get a more direct view of aggregation, sedimentation, and transfer of AuNPs across

the liquid/liquid interface, AuNPs were collected from the aqueous phase (before and after

being contacted with the organic phase) and the organic phase for measurements.

Figure^^3<xfigr3>c shows a Transmission Electron Microscopy (TEM) image of AuNPs

collected from the original AuNP dispersion, where the diameter of AuNPs is determined to

be 32.0±2.1^^nm by Image J analysis, consistent with the value of 32.4^^nm obtained from

Dynamic Light Scattering (DLS) (Figure^^3<xfigr3>f). However, when AuNPs collected

from the aqueous phase that had been in contact with DCM containing 5^^wt% H_2N-PDMS-

NH_2 for only 1 minute, they were found in the form of 3-dimensional aggregates, as shown in

Figure^^3<xfigr3>d. This demonstrates the polymer-induced aggregation of AuNPs in the

aqueous phase. After transferring from the aqueous phase to the organic phase, AuNPs

become single particles again with a calculated diameter of 31.6±2.6 (Figure^^3<xfigr3>e),

also supported by the result of an average size of 30.4^^nm from DLS (Figure^^3<xfigr3>g).

To further compare the size distribution obtained from DLS and TEM, fitted curves

were plotted, as shown in Figure^^S7. The average sizes of particles before and after transfer

are consistent, indicating a similar polydispersity index (PDI) using both techniques. However, it is worth noting that the PDI of AuNPs in both water and DCM measured by DLS is higher than that measured by TEM. This difference is evident in the narrower peak of the size distribution given by TEM, indicating a more precise measurement of particle sizes.

Chemical structures of the surface of AuNPs in each state were characterized by Fourier transform infrared (FT-IR) spectrometer (Figure S8a). A peak at $\sim$1600 cm^{-1} in the spectrum of cit-AuNPs is attributed to the carboxylate group (COO^{-}), the characteristic group of sodium citrate. A broad peak at 1000--1100 cm^{-1} is assigned to the Si–O stretch, while the signal at 800 cm^{-1} is ascribed to the Si–C stretch, both of which are found in the spectra of aggregated AuNPs and transferred AuNPs, indicating that their outer surface is covered by H$_2$N-PDMS-NH$_2$ ligands. Accordingly, we also conducted energy dispersive X-ray (EDX) of AuNPs before and after phase transfer (Figure S8b). The characteristic elements Na and N for citrate and amino ligands are in consistent shape with Au, showing the success of surface functionalization of NPs. Since functional groups can alter surface charges, zeta potential (ζ) of AuNPs in each state was measured (Figure S1b). Transition in ζ from $-$51 mV to nearly 0 mV indicates PDMS-chain-covered AuNPs in DCM after transfer. These again support the proposed transfer mechanism.

The investigation of H$_2$N-PDMS-NH$_2$ polymer ligands with different molecular weights confirms the generality of the observed phenomena. H$_2$N-PDMS-NH$_2$ with a wide range of molecular weights ranging from 0.95 to 30 kg mol^{-1} also leads to the aggregation and sedimentation of AuNPs. Figure S9 shows that longer-chain polymer ligands have a higher likelihood of facilitating the transfer of AuNPs to the organic phase. However, it is worth noting that no significant transfer of AuNPs is observed in DCM containing 0.95 kg mol^{-1} H$_2$N-PDMS-NH$_2$ even after 50 days. This suggests that the molecular weight of the polymer ligands plays a crucial role in the NP transfer process.

When using less-dense organic phases such as toluene, the transfer of AuNPs does not occur as the aggregates are unable to contact the upper organic phase, as shown in Figure^^S10. This indicates that the density of the organic phase is an important factor influencing the transfer of AuNPs. Additionally, we used cetyltrimethylammonium bromide (CTAB) as an alternative surfactant. Surprisingly, no aggregation is observed in the aqueous dispersion after contacting DCM containing $10\ mg\ mL^{-1}$ CTAB, and no phase transfer occurs even after 30^^days. This suggests that the CTAB molecules form stable micelles in DCM, preventing their diffusion to the aqueous phase. Figure^^S10 provides further support for this observation.

Furthermore, we explored the use of mono-amino-terminated PDMS ligands (PDMS-NH$_2$ with M_n~$2\ kg\ mol^{-1}$) instead of amino-terminated PDMS ligands. Similarly, when DCM is replaced by other organic solvents denser than water, such as chloroform (CHCl$_3$) and CCl$_4$, the cit-AuNPs undergo the same "single particle-aggregation-single particle" process, demonstrating the versatility of the proposed pathway. These results are shown in Figure^^S11, Figure^^S12, and Figure^^S13.

The transfer process triggered by electrostatic interactions only

Given the weak binding affinity of the citrate molecules to AuNPs,[5a,11] amino-terminated PDMS may simply strip off the attached citrate molecules through a ligand-exchange process rather than electrostatic interactions. To test this hypothesis, we studied the transfer of 11-mercaptoundecanoic acid (MUA)-functionalized AuNPs (MUA-AuNPs), which cannot be replaced by amine groups. MUA-AuNPs were synthesized by a ligand-exchange reaction with cit-AuNPs (donated as pre-AuNPs to distinguish from cit-AuNPs). TEM images show that the NPs are well dispersed in water without noticeable aggregation (Figure^^4a), with a narrow particle size distribution and a mean size of 12.5^^nm (Figure^^4b). The maximum in the plasmon peak of pre-AuNPs is at the wavelength

of 522 nm, while that for the MUA-AuNPs is slightly red-shifted to 526 nm (Figure 4c), confirming the success of the ligand exchange on the surface of AuNPs. More distinct evidence provided by FT-IR shows the change of functional groups on the surface of NPs (Figure S14). For cit-AuNPs, the surface is covered with citrate, making the signatures of COO^- (~ 1600 cm^{-1}) and $O{-}H$ (~ 3400 cm^{-1}) well-marked in the spectrum. Compared to the spectrum of MUA, the $S{-}H$ stretching peak (1550--1600 cm^{-1}) disappears with the intensity of the COO^- signal increasing in the MUA-AuNPs spectrum, indicating a full replacement of the citrate molecules with MUA molecules on the surface of particles. Differences shown in the results of the zeta potential measurement also confirm this (Figure S15a).

To validate the proposed pathway solely based on electrostatic interactions between NPs and ligands, similar experiments were conducted (Figure 4d). MUA-AuNPs aggregate after being in contact with the organic phase containing $PDMS\text{-}NH_2$ ligands ($Mn \sim 2$ $kg\,mol^{-1}$) or $H_2N\text{-}PDMS\text{-}NH_2$ ligands ($M_n \sim 3$ $kg\,mol^{-1}$) within 1 hour. However, only those in contact with $PDMS\text{-}NH_2$ ligands transfer to the organic phase within one month (second and third rows in Figure 4d). Molecular-level investigations were given by in situ UV/Vis spectroscopy (Figure 4e). Both spectra of MUA-AuNP dispersions contacting with $PDMS\text{-}NH_2$ and $H_2N\text{-}PDMS\text{-}NH_2$ generate a broad peak at the wavelength of 700--800 nm after 30 min, with a decreased absorbance of the sharp peak at 526 nm (cyan lines and blue lines in Figure 4e), proving the ligand-transfer induced aggregation of NPs. However, for CTAB, the dispersion of MUA-AuNPs shows no change but settles within 30 days (first row in Figure 4d), consistent with that of cit-AuNPs, with the evidence of the spectra remaining almost the same in a day (red lines in Figure 4e). Interestingly, no obvious sign of NP-aggregation is observed in the dispersion of MUA-AuNPs in contact with $H_2N\text{-}PDMS\text{-}NH_2$ ($M_n \sim 27$ $kg\,mol^{-1}$) ligands on the first day, followed by the subsequent sedimentation at

the interface (bottom row in Figure^^4<xfigr4>d), with absorbance-reduced red-shift spectra within one day (purple lines in Figure^^4<xfigr4>e). To investigate the interplay of MUA-AuNPs and H_2N-PDMS-NH_2 ($M_n\sim27$^^kg^mol^{-1}) ligands at the interface, we measured the IFT (Figure^^S15b). Unlike the slightly fluctuated IFT at 21^^mN^m^{-1} between pre-AuNPs and the ligands, an evident reduction in IFT can be observed when MUA-AuNPs contact with the ligands and equilibrate at 16^^mN^m^{-1} after~300^^s. Further reduction in IFT is found when increasing the concentration of MUA-AuNPs by 10-fold.

Figure^^4<xfigr4>f presents the spectra of the AuNPs successfully transferred into DCM. For MUA-AuNPs (dotted lines), the presence of electrostatically absorbed PDMS-NH_2 on the surface causes a slight red shift in the spectrum. In the case of cit-AuNPs (solid lines), both amino-terminated PDMS and mono-amino-terminated PDMS efficiently trigger the transfer of NPs. NPs coated with low-M_n ligands exhibit a more pronounced red shift compared to those with high-Mn ligands, which can be attributed to the difference in the dielectric constant of the ligand layer.[5a]

The entire transfer process with a focus on a single particle was illustrated in Figure^^4<xfigr4>g. In Stage I, cit-AuNPs disperse well in the aqueous phase due to the presence of charged citrate layer. Upon encountering amino-terminated polymeric ligands, the cit-AuNPs attract these ligands through electrostatic interactions, resulting in surface charge neutralization and aggregation (Stage II). Over time, the polymer chain-covered NPs redisperse in the organic phase (Stage III). In contrast, MUA molecules attached to AuNPs remain unaffected by amino-terminated polymeric ligands, indicating that the transfer process is solely driven by electrostatic interactions.

Manipulation of NPs transfer across fluid interfaces

The aggregation, sedimentation, and transfer of AuNPs are triggered by the diffusion of polymer ligands from the organic phase into the aqueous phase. Therefore, in principle, the

entire process can be terminated if the diffusion of polymer ligands across the liquid/liquid interface is arrested. Consequently, we co-assembled carboxylic acid-functionalized polystyrene nanoparticles (PSNPs) and H_2N-PDMS-NH_2 at the liquid/liquid interface. Unlike AuNPs, the partial modification of PSNPs by H_2N-PDMS-NH_2 results in an amphiphilic character of the NPs, allowing them to form a stable layer at the interface. Figure^^5<figr5>a provides a schematic diagram illustrating the jamming of PSNPs at the liquid/liquid interface, effectively blocking the diffusion of H_2N-PDMS-NH_2 from the organic phase to the aqueous phase.

To demonstrate this, we used a 3D printed plastic mold (Figure^^S16) to create liquid/liquid interfaces with different shapes. The middle row in Figure^^5<xfigr5>b shows the plastic mold filled with various aqueous phases: the letters "C″ and "I″ were filled with a mixed dispersion of cit-AuNPs and PSNPs, "T″ and "Y″ were filled with a dispersion of cit-AuNPs, and "U″ was filled with pure water. When toluene containing $5^{\wedge\wedge}wt\%$ H_2N-PDMS-NH_2 ($3^{\wedge\wedge}kg^{\wedge}mol^{<M->1}$) was added to cover the bottom aqueous phases, the liquid in the letters "T″ and "Y″ immediately turned blue, while the other solutions retained their original color. This color change indicates the rapid diffusion of H_2N-PDMS-NH_2 across the liquid/liquid interface from toluene to water in the absence of an interfacial layer. The bottom row in Figure^^5<xfigr5>b shows the snapshot of liquids trapped in different letters, covered by the organic phase for 30^^minutes (Video^^S1). It is evident from the image that the self-assembled interfacial layer formed by PSNPs successfully prevents the diffusion of H_2N-PDMS-NH_2 across the liquid/liquid interface, thereby preventing the initiation of the aggregation, sedimentation, and transfer process of cit-AuNPs in the aqueous phase. This observation is further supported by the blank experiments (Figure^^S17, Video^^S2).

To probe the interfacial layer formation and the effect of adding PSNPs to the aqueous phase, we conducted time-dependent IFT measurements. As shown in Figure^^5<xfigr5>c, in

the absence of polymer ligands, the IFT of water against toluene is ~34$^{^}$mN$^{^}$m$^{<M->1}$ and

does not vary over time. Adding polymer ligands into toluene causes a decrease in the IFT of

water against toluene as a function of time for all samples, including that with cit-AuNPs

only, and with both cit-AuNPs and PSNPs. The results indicate the strong interactions

between negatively charged nanoparticles and oppositely charged polymer ligands, as well as

the co-assembly at the liquid/liquid interface. The IFT reduction is most pronounced in the

aqueous phase containing both AuNPs and PSNPs, indicating the enhanced binding of

polymer ligand-decorated NPs to the water/toluene interface. This effect is attributed to the

large number of PSNPs occupying the interface with the strong binding of H_2N-PDMS-NH_2.

Such robust binding interactions not only significantly decrease the IFT but also cause PSNPs

to jam at the liquid/liquid interface, hindering the diffusion of H_2N-PDMS-NH_2 across the

interface.

After time-dependent IFT measurements, we reduced the liquid/liquid interfacial area

by withdrawing solutions from pendant drops (Video$^{^}$S3--S4). As shown in

Figure$^{^}$5<xfigr5>c inset, wrinkles are observed for the sample with both AuNPs and PSNPs

but not for that with AuNPs only when the same amount of liquid was withdrawn from the

pendant drops. In addition, it is believed that the excess PSNPs could also serve as H_2N-

PDMS-NH_2 collectors to capture those diffused into the aqueous phase through the interfacial

jammed layer, further reducing the possibility of initiating the aggregation and phase transfer

process of AuNPs in the aqueous phase.

Conclusion

In summary, we capitalize on the aggregation behavior commonly observed in the

transfer of NPs across a fluid interface to realize a "single particle-aggregation-single particle"

transfer process. This new pathway could be established through either a ligand-exchange

process or solely electrostatic interactions. Additionally, introducing a jammed interfacial NP

layer at the liquid/liquid interface could effectively arrest the diffusion of charged amphiphilic polymers across the interface, preventing aggregation and transfer. These charged amphiphilic polymers act as molecular chaperons for transferring NPs. Our study opens a pioneering strategy to transport NPs across immiscible interfaces and for manipulating the dispersion of NPs in diverse liquid environments.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figure^^1   The difference between the conventional methods (a--c) and the method in this work (d--f) for phase transfer of AuNPs. (a) The cit-AuNPs are well dispersed in the aqueous phase. (b) The addition of surfactants or phase transfer agents containing functional groups such as sulfydryl and amidogen into the aqueous phase or the organic phase may cause the surface functionalization of the single NP, or aggregation of NPs. (c) Under external forces (such as vigorous stirring), the single functionalized NP will transfer into the organic phase, while the aggregated NPs are considered to fail to transfer into another phase. (d) The addition of amino-terminated polymers into the organic phase will lead to aggregation of NPs in the aqueous phase when two phases contact. (e) The aggregated AuNPs settle at the water/oil interface in a short time. (f) Without external forces, the aggregates will transfer to the organic phase and redisperse as single particles over a period of time. Inset of (d to f): Snapshots of the cit-AuNP dispersions and DCM with 5^^wt% of H_2N-PDMS-NH_2 (M_n~27^^kg^mol^{-1}) after their immediate contact (d), after being in contact for 1^^day (e), and after being in contact for 30^^days (f).

Figure^^2   Macroscopic and optical observations of NPs transfer across the liquid interface. (a) Snapshots of the cit-AuNP dispersions and DCM with different concentrations (0.1^^wt%, 0.5^^wt%, 1^^wt%, 3^^wt%, and 5^^wt% from top to bottom) of H_2N-PDMS-NH_2 (M_n~27^^kg^mol^{-1}) after their immediate contact (first column), after being in contact for 1^^day (second column), 14^^days (third column), and 30^^days (fourth column) with a top view of the phases (right column), respectively. Scale bar: 1^^cm. (b) Schematic representations of the experimental setup for the in situ UV/Vis spectroscopy measuring the aqueous phase and organic phase. (c) Time-dependent UV/Vis absorption spectra of AuNP dispersions after being in contact with DCM dissolving 5^^wt% of H_2N-PDMS-NH_2 ligands (M_n~27^^kg^mol^{-1}) for different periods of time. The color bar represents the contact time between the aqueous phase (2^^mL) and the organic phase (1^^mL). (d) Time-dependent

UV/Vis absorption spectra of DCM dissolving $5\,$wt% of H_2N-PDMS-NH_2 ligands ($M_n\sim27\,kg\,mol^{-1}$) after being in contact with AuNP dispersions for different periods of time. The color bar represents the contact time between the aqueous phase ($1\,$mL) and the organic phase ($3\,$mL). (e) UV/Vis spectra of DCM with different concentrations of H_2N-PDMS-NH_2 ($M_n\sim27\,kg\,mol^{-1}$, $0.1\,$wt%–$5\,$wt%) after being in contact with AuNP dispersions for $30\,$days (dashed lines), where the solid line presents the UV/Vis absorption spectrum of the aqueous AuNP dispersion as a reference. All samples were diluted to one-fourth of their original concentrations.

Figure$\,$3   The surface and interfacial activities of amphiphilic polymer ligands, and morphologies of AuNPs before and after transfer. (a) Time-dependent surface tension of pure water and AuNP dispersions that were or were not previously in contact with DCM dissolving $5\,$wt% H_2N-PDMS-NH_2 ($M_n\sim27\,kg\,mol^{-1}$). (b) Time-dependent interfacial tension of the water/DCM interface with or without AuNPs or H_2N-PDMS-NH_2 ($M_n\sim27\,kg\,mol^{-1}$). (c-e) TEM Images of the AuNPs that were collected from the aqueous phase before (c) and after being in contact with DCM dissolving $5\,$wt% H_2N-PDMS-NH_2 ($M_n\sim27\,kg\,mol^{-1}$) for $1\,$min (d) and those transferred to DCM (e), respectively. Size distribution of AuNPs before and after phase transfer obtained by Image J analysis was inserted in (c) and (e), respectively. Scale bar: $50\,$nm. (f-g) Size distributions of AuNPs in the original AuNP dispersion (f) and those transferred to DCM containing $5\,$wt% of H_2N-PDMS-NH_2 ligands ($M_n\sim27\,kg\,mol^{-1}$) after contact $30\,$days (g) measured by DLS, respectively.

Figure$\,$4   Transfer of MUA-AuNPs across the liquid/liquid interface. (a) Nanoparticles observed by TEM. Scar bar: $50\,$nm. (b) Size distribution of MUA-AuNPs with a mean value at $12.5\,$nm and standard deviation of $1.1\,$nm, derived from ImageJ analysis of (a). (c) Absorbance spectrum of the aqueous dispersion. (d-e) Snapshots (d) and in situ UV/Vis spectra (e) of MUA-AuNP dispersion in contact with DCM dissolving $10\,mg\,mL^{-1}$ CTAB (first row; red lines), $5\,$wt% PDMS-NH_2 ligands ($M_n\sim2\,kg\,mol^{-1}$) (second row; cyan lines), H_2N-PDMS-NH_2 ligands ($M_n\sim3\,kg\,mol^{-1}$) (third row; blue lines), and H_2N-PDMS-NH_2 ligands ($M_n\sim27\,kg\,mol^{-1}$) (fourth row; purple lines) for a certain time, respectively. Scale bar: $1\,$cm. (f) UV/Vis spectra of the AuNP dispersion (solid line) and the transferred AuNPs after contact with DCM containing $5\,$wt% PDMS-NH_2 ligands ($M_n\sim2\,kg\,mol^{-1}$), H_2N-PDMS-NH_2 ligands ($M_n\sim3\,kg\,mol^{-1}$), and H_2N-PDMS-NH_2 ligands ($M_n\sim27\,kg\,mol^{-1}$), together with the MUA-AuNP dispersion (dotted line) and the transferred MUA-AuNPs after contact DCM containing $5\,$wt% PDMS-NH_2 ligands

(M_n~2$\,$kg$\,$mol^{-1}) for 30$\,$days. Digit "0″ means AuNP dispersions do not contact the ligands. All samples were diluted to half of their original concentrations, except one for 3$\,$kg$\,$mol^{-1} ligand (no attenuation). (g) Hypothetical mechanisms of the phase transfer for AuNPs and MUA-AuNPs, respectively.

Figure$\,$5   Blocking the diffusion of polymer ligands across the liquid/liquid interface through the interfacial jamming of nanoparticles. (a) The schematic diagram shows the interfacial jamming of PSNPs, which blocks the diffusion of polymer ligands across the liquid/liquid interface. (b) Top row: Schematic illustrations of the letter mold and how to use it for liquid/liquid self-assembly; Middle row: All aqueous dispersions are injected into the letter trenches, where "CI″, "TY″, "U″ are separately filled with mixed dispersion of AuNPs and PSNPs (4$\,$mg$\,$mL^{-1}, 50$\,$nm) with a volume ratio of 2$:$3, AuNP dispersion, and DI water; Bottom row: Color changes occur in "TY″ trenches owing to the failure of forming a jammed interface after spreading toluene dissolving 5$\,$wt% H_2N-PDMS-NH_2 (3$\,$kg$\,$mol^{-1}) on top of trenches for 30$\,$min. (c) Time-dependent interfacial tension of water against toluene, where the aqueous phase has different nanoparticles and toluene containing H_2N-PDMS-NH_2 (3$\,$kg$\,$mol^{-1}). Scale bar: 1$\,$mm.