We demonstrate a straightforward nonbiomolecular approach for self-assembly of binary NP planet–satellite superstructures, which enables control of interparticle gaps. We have achieved using alginate-coated, self-assembled bead-like AuNPs and then redispersed AuNP building blocks with smaller variations in temperature, pH, ionic strength and solvent. The readily scalable process produces highly homogeneous samples and is tolerant to a structurally diverse range of robust binary NP assemblies. A range of well-defined colloidally stable structures have been achieved, using alginate-coated, self-assembled bead-like AuNPs and then redispersed AuNP building blocks. This strategy has proven challenging to produce uniform structures, without compromising the desired aggregate architecture. We present an operationally simple and rapid nonbiomolecular approach for fabrication of binary planet–satellite superstructures that are tolerant to a structurally diverse range of robust binary NP assemblies.
immediate colour change from red to purple (compare Fig. 2a–c). UV-vis spectroscopy confirmed a red shift in the surface plasmon resonance (SPR) band relative to the component NPs, consistent with formation of NP aggregates (Fig. 3a). On increasing the stoichiometric ratio of AuNP-1: citrate-NP, the SPR red shift was found to increase sharply, reaching a maximum shift at a ratio of 280:1, before exhibiting a gradual decrease in red shift at higher ratios (Fig. S17, ESI†). We reasoned that the maximum shift in SPR wavelength corresponds to the optimum stoichiometric ratio for achieving isotropic planet–satellite assemblies, with incomplete planet NP coverage below this value and an increasing excess of unbound satellite NPs dominating the optical response at higher ratios. Without requiring any additional stabilizers, TEM images consistent with this interpretation were readily obtained. Images of the 280:1 mixture revealed that all large NPs were fully covered with a shell of smaller AuNP-1, together with a relatively small number of unbound AuNP-1 (Fig. 2c and Fig. S18, ESI†).

At higher ratios, the planet–satellite assemblies remained unchanged, simply accompanied by an increasing excess of isolated AuNP-1 on the grid. On the other hand, at ratios below 280:1, most citrate-NPs were associated with an incomplete shell of satellites, and isolated AuNP-1 were rarely observed (Fig. S18, ESI†).

The observation of unbound AuNP-1, even at the optimized mixing ratio, prompted us to develop a purification procedure that would allow isolation of complete planet–satellite assemblies. A simple and rapid protocol was arrived at, involving centrifugation at 5900 rcf for 4 minutes, leading to partial precipitation. The lightly coloured supernatant was decanted and the precipitate redispersed in the same volume of water. TEM imaging at this stage revealed that a small number of free AuNP-1 remained (Fig. S19, ESI†). The sample was therefore subjected to a second round of centrifugation at 2900 rcf for 4 minutes. Following removal of the supernatant and redispersion of the precipitate, TEM at both low and high magnifications now revealed no persisting unbound AuNP-1, and the sample now consisted exclusively of planet–satellite superstructures (Fig. 2d and Fig. S19, ESI†). The purification process proved to be reproducible and scalable; routinely carried out on batches of up to 10 mL, limited only by centrifuge tube size. TEM images of the supernatant solution (Fig. S20, ESI†) showed only a small number of unbound satellites, representing very small losses and, correspondingly, an efficient purification process.

Consistent with the removal of excess AuNP-1, purification resulted in a further red shift in SPR maximum wavelength to 564 nm, a quite significant total shift of ~40 nm from either of the isolated component NP building blocks (Fig. 3a). The strong plasmon coupling responsible for such a large shift results from the complete isotropic coverage of the large planet NPs with satellites held at short interparticle distances (Fig. 2d, inset). From TEM images of the purified samples, an average of 70 satellites surrounding every planet can be estimated (Fig. S21, ESI†). With the purified samples in hand, the integrity of the assemblies in solution could be corroborated by dynamic light scattering (DLS) measurements, which revealed a monomodal distribution (Fig. 3b). The mean hydrodynamic diameter of 54 nm is in good agreement with the expected size of planet–satellite assemblies.

The planet–satellite NP assemblies exhibit remarkable structural and colloidal stability under a variety of conditions. No evidence of
disassembly or aggregation was observed either by eye or by UV-vis analysis upon heating the sample to 80 °C for three hours (Fig. S24, ESI†). Similarly, the assemblies remained stable in high ionic strength solutions, showing no change in the surface plasmon resonance upon addition of either NaCl or MgCl₂ (up to 3 M), in-line with the behaviour of AuNP-1 alone. By comparison, the citrate-stabilized planet NPs aggregate at electrolyte concentrations ≤50 mM (Fig. 4 and Fig. S28–S30, ESI†). The planet–satellite assemblies are also stable under a wide range of pH values. Again mirroring the behaviour of AuNP-1, no aggregation, precipitation or disassembly was observed over the range 1 ≤ pH ≤ 14, in stark contrast to the precursor citrate-stabilized NPs, which readily precipitate under moderately acidic conditions (Fig. 4 and Fig. S31, ESI†). It appears that the NP building blocks are strongly associated and that the robust colloidal stability of AuNP-1 is conferred on the entire assembly, without the need for any additional stabilizing or capping agents.

The facile purification process involving precipitation and redispersion suggested that the assemblies might be isolable as a solid for storage prior to redispersion in a range of suitable solvents. Aqueous solutions of purified planet–satellites were centrifuged to induce precipitation. Removal of the colourless supernatant left a film-like residue, which could subsequently be redispersed in water with no loss of material apparent by UV-vis analysis (Fig. S25a, ESI†). Redispersion could also be achieved after drying in vacuo, although in this case a slight decrease in absorbance was observed (Fig. S25b, ESI†), attributable to irreversible adsorption to the walls of the glass vial. However, no change in the shape or position of the SPR band was apparent, indicating the fidelity of the self-assembled structure. By contrast, solvent evaporation from a dispersion of citrate-stabilized NPs leads to irreversible aggregation, rendering redispersion impossible. The precipitation–redispersion protocol also allowed transfer from aqueous to organic environments; the planet–satellites were readily redispersible in MeCN, with no change to the assembly structure apparent by either UV-vis or TEM imaging (Fig. S26 and S27, ESI†).

Having established a protocol for assembly of these robust binary NP superstructures, we next sought to explore the generality of this approach for different planet NPs. With minimal modification to the protocol, planet–satellite assemblies were successfully obtained from spherical citrate-stabilized NPs spanning a remarkably wide size range (and from both home-made or commercial sources, Fig. 5a and b and Fig. S32, ESI†). The ability to assemble NP building blocks with different shapes substantially increases the range and complexity of possible structures and opportunities for property tuning.† We therefore prepared a sample of citrate-stabilized NPs with a variety of sizes and shapes, including large numbers of rods and prisms. Planet–satellite assembly around non-spherical NPs proceeded efficiently, and purification from unbound AuNP-1 was readily achieved in the same manner as before (Fig. 5c and d and Fig. S33, ESI†). As a preliminary attempt to expand the range of satellite NPs, we prepared 10 nm NPs stabilized with the dihydroxy-terminated ligand 1 via ligand exchange from citrate-stabilized NPs. On combination with 40 nm citrate-stabilized NPs, assembly was again observed. However, in this case the process was significantly slower and failed to produce well-defined planet–satellite structures (see Fig. S34, ESI†). Most likely, repulsive electrostatic interactions resulting from residual citrate species on the satellite NPs create a more complex set of forces governing assembly and stability. We are currently investigating alternative methods for expanding the scope of satellite NPs.

The self-assembly process appears to be governed by a highly specific interaction between the 1,2-dihydroxy functionality on AuNP-1 and citrate-stabilized NPs of virtually any sort. On replacing the dihydroxy-functionalized NPs with monohydroxy-functionalized AuNP-2 (Fig. S22, ESI†), no NP aggregation was observed, either in solution (UV-vis and DLS) or by TEM (Fig. S23, ESI†). It has recently been proposed that citrate binds to AuNP surfaces through two carboxylate–Au interactions, with the non-surface-bound carboxylate involved in hydrogen bonding to a weakly associated citric acid adlayer.11 Despite the inherently limited stabilization provided by hydroxyl-based hydrogen bonds in aqueous environments,14 a cooperative multi-point interaction between the 1,2-dihydroxy motif on AuNP-1 and a NP-bound...
carboxylate may be sufficient to displace the secondary citric acid layer; the cumulative multivalent effect of several such interactions between the two densely functionalized NP surfaces could then explain the robust planet–satellite NP association. Aside from biomolecule-based systems, 

valent hydrogen bonding under aqueous conditions has previously been invoked in only a handful cases to explain NP aggregation. Each of these involves only a single NP building block and achieves limited structural control and stability. In the current case, an alternative explanation could involve direct interaction between the 1,2-diols and the Au surface. Studies under ultrahigh vacuum conditions suggest that alcohols can adsorb weakly on noble metal surfaces at low temperatures, but it is clear from the results with monohydroxy-functionalized AuNP-2 that such a process alone is not sufficient to achieve NP self-assembly. A chelate interaction between the diols of AuNP-1 and metal surface atoms may of course enhance this interaction, yet would still require penetration and displacement of the surface-bound citrate monolayer and a significant Au–diol binding energy. Efforts are currently under way to elucidate the molecular details of the interactions involved.

In conclusion, we have developed a versatile and operationally simple protocol for the self-assembly and purification of 3D binary NP planet–satellite structures. The rapid, one-step assembly procedure does not require careful control of environmental conditions, eliminates the need for complex biological, supramolecular or macromolecular NP ligands, and is readily scalable. Isotropic coverage of the planet NPs can be achieved, irrespective of surface area, through optimization of building block stoichiometry using simple spectroscopic measurements. The highly stable characteristics of the satellite NPs are conferred on the binary assemblies, which is dispersible in either aqueous or organic media. This allows rapid and efficient preservation on the binary assemblies, which are dispersible in either aqueous or organic media. This allows rapid and efficient preservation.

Notes and references


2. N. J. Halas, S. Lal, W. S. Chang, S. Link and P. Nordlander, Chem. Rev., 2011, 111, 3913.


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